DEPARTMENT OF THE INTERIOR

UNITED STATES GEOLOGICAL SURVEY

Informal Notes:

WORKSHOP ON THE APPLICATION OF ISOTOPE SYSTEMS TO GEOLOGICAL PROBLEMS

Robert Ayuso and Klaus Schulz
Convenors

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Auditorium
National Center
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INTRODUCTION

About the Workshop:

The intended audience of this workshop is the general geological community at the Survey and interested faculty and graduate students from nearby universities. The main objective of the discussions is to provide a broad introduction for a non-isotope geologist audience into modern methods of geochronology and isotope tracer studies and to give examples of their application to solve complex problems in stratigraphy, petrology, ore petrogenesis, and tectonics. The participants will be, for the most part, from the Geologic Division at the Survey, and consequently they have varying levels of understanding about isotope systems and their uses. The sessions will start with general talks on the general systematics of the isotope techniques to be illustrated that day. Note that the oral presentations are scheduled for 45 minutes and that 15 minutes are reserved for discussion after each talk.

During the first day, we will discuss modern applications of precise U-Pb geochronology and common Pb isotope studies. The contributors will illustrate how these techniques have been applied to solve stratigraphic problems in the northern Appalachians, date high grade metamorphism and stromatolites, tracing sand dunes, study the hydrothermal stability of zircon, and to establish the crustal evolution of the central and southern Appalachians.

The second day will start with an introduction into the Rb-Sr, Nd-Sm, and Re-Os dating techniques. Practical illustrations of the use of these systems will also be given, including examples of dating ductile deformation fabrics in New England, the application of Re-Os systematics for dating ultramafic rocks and to study the petrogenesis of these and associated ore deposits, and the use of Nd isotopes as tracers of continental lithosphere evolution. This session will end with a presentation on the isotopic provinciality in the mantle, on-craton and off-craton volcanism and implications for lithospheric growth in the western USA.

The third day will begin with an introduction to Ar thermochronology and applications to stratigraphy, tectonics, and mineralization. Recent results of Ar studies on fluid inclusions from Battle Mountain (Nevada) will be reported, as well as dating of multiple events in the Bayan Obo deposit (China) and examples of Ar dating of ore deposits from the western United States, England, and Portugal. The rest of the day will be devoted to an introduction to U-Th disequilibria and dating of young rocks, a discussion of radiogenic isotopes in seawater and sedimentary systems, and to recent developments in dating ancient crustal fluid flow.
Due to the number of non-USGS speakers and the length of the workshop, USGS contributors from Reston have prepared posters instead of oral presentations. The posters will be shown in the Exhibit Hall (just outside of the Auditorium) and will be available for viewing Monday afternoon through Wednesday afternoon. The posters will illustrate some of the current projects in progress in Reston, including: the use of Pb-Nd-O isotopic data for terrane correlation in the northern Appalachians, Pb isotopic compositions of tin deposits, the combined use of paragenetic data and Pb isotopic compositions in Ag-Au veins as exploration tools, Re-Os isotope systematics in shales, Ar geochronology in low grade rocks, Sr-Nd-Pb isotopic data and basement terranes in Alaska, Re-Os systematics in meteorites, Nd-Pb isotopic evolution and evidence for plume-lithosphere-asthenosphere interaction in the Midcontinent, a Re-Os isotopic study of a granite-molybdenum system, and a study of isotopic reference materials. Ample time during the workshop will be available to study the posters.
SCHEDULE

Monday, September 14, 1992
Morning Session

8:30-8:45 AM ROBERT AYUSO and KLAUS SCHULZ: Welcome

8:45-9:00 AM NANCY MILTON, Assistant Chief Geologist, Eastern Region: Welcome

9:00-9:45 AM GIL HANSON: Radiometric dating of events and processes that affect sedimentary and metamorphic rocks

9:45-10:00 AM Discussion

10:00-10:15 AM Break

10:15-11:00 AM TOM KROGH: Modern applications of precise U-Pb geochronology

11:00-11:15 AM Discussion

11:15-11:45 AM KLAUS MEZGER: Geochronology in granulites

11:45-12:00 AM Discussion

12:00-1:00 PM Lunch

Afternoon Session

1:00-1:45 PM JOHN ALEINIKOFF: Innovative uses of Pb isotopic measurements: Dating stromatolites and tracing sand dunes

1:45-2:00 PM Discussion

2:00-2:45 PM KRISHNA SINHA: The hydrothermal stability of zircon: Preliminary experimental and isotopic studies
KRISHNA SINHA: Crustal evolution of Grenville terranes in the central and southern Appalachians: The Pb isotope perspective for Grenville tectonics

2:45-3:00 PM Discussion

3:00-3:15 PM Break

3:15-5:00 PM Posters: To be displayed through Wednesday

ROBERT AYUSO, SANDRA BARR, FRED LONGSTAFFE, and ERNST HEGNER: Pb-Nd-O isotopic compositions of igneous rocks: Implications for petrogenesis and terrane correlation, Cape Breton Island, Nova Scotia, Canada

BRUCE DOE: Lead isotopic composition of galena from Malaysia, an S-type granite terrane
NORA FOLEY and ROBERT AYUSO: Paragenetic constraints on the Pb isotopic and trace element character of Au-Ag mineralized rocks of the North Amethyst vein, Mineral County, Colorado

MARY HORAN: Re and Os isotopic study of Ni-Mo-PGE-rich sulfide layers and black shales, Yukon territory, Canada and south China

EIRIK KROGSTADT: Pb isotopic composition of Paleozoic sediments derived from the Appalachian orogen

MICK KUNK: Alleghanian cleavage and acadian diagenesis in the Martinsburg Formation, eastern Pennsylvania: $^{40}$Ar/$^{39}$Ar whole-rock data and geological constraints

ELIZABETH MOLL-STALCUP: The nature of the crust in western Alaska as inferred from the chemical and isotopic composition of Late Cretaceous to early Tertiary magmatic rocks in western Alaska

JOHN MORGAN: Rhenium and osmium isotope systematics in meteorites

SUZANNE NICHOLSON and STEVE SHIREY: Nd and Pb isotopic evolution of basalts of the 1.1 Ga Midcontinent rift: Evidence for a region-wide model for plume-lithosphere-asthenosphere interaction

HOLLY STEIN, JOHN MORGAN, RICHARD WALKER, and MARY HORAN: Rhenium-osmium data for sulfides and oxides from climax-type granite-molybdenum systems: Mt. Emmons, Colorado

ROBERT VOCKE: Isotopic reference materials - absolute or otherwise
Tuesday, September 15, 1992

Morning Session

8:30-9:30 AM  STEVE SHIREY: The Rb-Sr, Sm-Nd and Re-Os isotopic systems and the cosmochronology and geochronology of igneous rocks

9:30-9:45 AM  Discussion

9:45-10:30 AM  STEVE GETTY: Direct dating of ductile deformation fabrics: An integrated microstructural/geochronologic approach

10:30-10:45 AM  Discussion

10:45-11:00 AM  Break

11:00-11:45 AM  RICH WALKER: Applications of the rhenium-osmium isotope system to geologic problems

11:45-12:00 AM  Discussion

12:00-1:00 PM  Lunch

Afternoon Session

1:00-1:45 PM  LANG FARMER: Nd isotopes as tracers of the origin and evolution of the continental lithosphere

1:45-2:00 PM  Discussion

2:00-2:45 PM  ROBERT ZARTMAN: The Pb-Sr-Nd isotopic troika--Theory and applications

2:45-3:00 PM  Discussion

3:00-3:15 PM  Break

3:15-4:00 PM  MARTIN MENZIES: Isotopic provinciality in the shallow mantle, on-craton and off-craton volcanism, and implications for lithospheric growth in the western USA

4:00-4:15 PM  Discussion
Wednesday, September 16, 1992
Morning Session

8:00-8:45 AM  JOHN SUTTER:  $^{40}$Ar/$^{39}$Ar thermochronology: Applications to stratigraphy, tectonics, and mineralization

8:45-9:00 AM  Discussion

9:00-9:45 AM  TED MCKEE:  $^{40}$Ar/$^{39}$Ar studies of fluid inclusions in vein quartz from Battle Mountain, Nevada
JAMES CONRAD:  The use of K-Ar and $^{40}$Ar/$^{39}$Ar techniques to date multiple thermal events: An example from the Bayan Obo Fe-Nb-REE ore deposit, China

9:45-10:00 AM  Discussion

10:00-10:15 AM  Break

10:15-11:00 AM  LARRY SNEE:  Argon thermochronology of mineral deposits

1:00-11:15 AM  Discussion

11:15-12:00 AM  LARRY EDWARDS:  Mass spectrometric measurements of $^{234}$U/$^{238}$U and $^{230}$Th/$^{238}$U and dating late Quaternary carbonates

12:00-12:15 PM  Discussion

12:15-1:00 PM  Lunch

Afternoon Session

1:00-1:45 PM  J. MACDOUGALL:  Radiogenic isotopes in seawater and sedimentary systems

1:45-2:00 PM  Discussion

2:00-2:45 PM  ALEX HALLIDAY:  Recent developments in dating ancient crustal fluid flow

2:45-3:00 PM  Discussion
U-Pb geochronology historically has involved measuring radiogenic Pb isotopic compositions and U and Pb concentrations in minerals such as zircon, monazite, and sphene to calculate crystallization ages of igneous rocks. Over the past several decades, the technique has been greatly modified and improved (mostly by T. Krogh and colleagues) to allow dating of very tiny samples (of single grains or even parts of single grains). The application of the method has been diversified to now include dating of a wide variety of minerals for the determination of the timing of metamorphism, ore deposition, provenances of sedimentary rocks, and faulting. Another important facet of U-Pb geochronology is the measurement of the initial Pb isotopic compositions of igneous rocks, usually determined by analyzing U-deficient minerals (those in which there is very little in situ growth of radiogenic Pb) such as K-feldspar and plagioclase. Initial Pb isotopic compositions are used to calculate geochronologic data, and are also useful in discerning petrologic and tectonic origins of specific rocks and in modeling the geochemical evolution of the earth (Aleinikoff and others, 1987; Plumbotectonics models such as Zartman and Haines, 1988). Two relatively new and rarely utilized applications of Pb isotopic analyses are the direct dating of stromatolitic limestones and dolomites and determination of provenances of Holocene sand dunes.

The first study describing the dating of stromatolites by the Pb-Pb method (Moorbath and others, 1987) produced an isochron of 2839 ± 33 Ma for the Mushandike stromatolitic limestone in Zimbabwe. The method is predicated on the assumption that carbonate incorporates small amounts of uranium during deposition and over long periods of time, the uranium decays to its stable daughter product, lead. Despite the potential broad appeal of the technique for dating sedimentary sequences, a surprisingly few number of papers have been published using this method (see bibliography for references). Some of the problems of this technique include the somewhat difficult chemical procedure, possible contamination of the carbonate by detrital material, partial silicification of the dolomite, measurement of very small quantities of U, Th, and Pb (in the 10-500 ppb range), scatter in the data, small radiogenic growth of Pb because of the low concentrations of U and Th, and, perhaps most important, questions related to the interpretation of the data (i.e. does the calculated age represent a depositional (or diagenetic) age or were the isotopic systematics reset by metamorphism?). In the Hartville uplift of eastern Wyoming, we have collected preliminary data from a stromatolitic dolomite, currently at garnet metamorphic grade, that indicates an age of 1.9 ± 0.1 Ga (Fig. 1). This age is in conflict with interpretations of the regional geology (Fig. 2), based on cross-cutting relationships and lithologic correlations, that suggest an age of >2.6 Ga for the sequence (cf. Hofmann and Snyder, 1985). At this time, we are unable to establish if the regional interpretations are incorrect or if the date on the stromatolite is a metamorphic age. Two other samples of stromatolitic dolomite (Kona Dolomite, MI and Nash Formation, Medicine Bow
Mtns, WY), containing beautifully preserved algal structures, do not yield colinear data (Fig. 3). Pb concentrations and isotopic compositions suggest addition of large quantities of Pb, obliterating the subtle radiogenic signature. Thus, Pb-Pb dating of stromatolitic limestone and dolomite appears to be a method of some promise for determining the age of sedimentary sequences; however, with the wide variety of possible complications, the technique presently has limited appeal.

The identification of provenances of Holocene eolian sands of the central Great Plains is critical for developing models of regional paleoclimate changes and for understanding the origin and evolution of midlatitude sand seas. Prevailing winds have deposited vast quantities of sand-sized material in dunes (of several geomorphologic types) and sand sheets in northeastern Colorado and the Sand Hills of western Nebraska (Muhs, 1985; Swinehart, J.B., 1990). As part of a multidisciplinary effort by the U.S. Geological Survey to understand the relationships between climatic variability, development of surficial deposits, and environmental changes in arid and semiarid regions (cf. Muhs and Maat, in press), we have attempted to determine the bedrock sources of eolian sands using Pb isotopic ratios in detrital K-feldspar as a fingerprint. Interpretations of the isotopic data will be combined with existing sedimentologic, geochemical, and meteorological data to derive a model for prevailing wind directions in the recent past (up to about 5000 years BP).

The objective of this study is to identify the source of K-feldspar (and, by inference, quartz) in Holocene eolian sands of the northern Great Plains. North of the Cheyenne belt in northern Colorado and southern Wyoming, most of the crystalline rocks are Late Archean (~2.7 Ga), whereas to the south throughout Colorado most of the igneous rocks are 1.7 and 1.4 Ga; the basement rocks are intruded by small Cretaceous and Tertiary stocks. Sanidine, a significant component of the K-feldspar in the Holocene eolian sands, probably was derived from a number of Tertiary volcanic centers in the western U.S. The different provenances of the K-feldspars are easily distinguished because Archean, Proterozoic and Tertiary rocks have distinctly different Pb isotopic compositions.

In northeastern Colorado, Pb isotopic compositions from bulk fractions plot in a fairly tight array, slightly more radiogenic than Pb in 1.4-Ga plutonic rocks from the Colorado province (Fig. 4a). Analyses of individual grains (distinguished by color and clarity) suggest that the bulk fractions are composed of feldspars from 1.7- and 1.4-Ga igneous rocks, plus Tertiary sanidine, with no obvious evidence for an Archean (Wyoming) component (Fig. 4b). We conclude that materials in Holocene eolian sand dunes of northeastern Colorado were derived from Early and Middle Proterozoic crystalline rocks of the Colorado province and from Tertiary volcaniclastic rocks, were deposited along major fluvial systems, and were redeposited by prevailing northwesterly (and sometimes southeasterly) winds (Fig. 5). In contrast, Pb isotopic compositions of bulk K-feldspar fractions from the Sand Hills of northwestern Nebraska plot as a broad field with ratios that are more radiogenic than ratios from Colorado sands (Fig. 6a). Analyses of individual grains indicate that these eolian sediments had Archean, Proterozoic and Tertiary sources (Fig. 6b). Thus, as previously suggested by sedimentologic studies, the materials that comprise the Sand Hills were derived from both the Wyoming and Colorado provinces.
Selected Bibliography


Figure 1.

Stromatolitic dolomite, Hartville dump, Hartville uplift, Wyoming

age = 1919 ± 98 Ma
(MSWD = 83)

Figure 2
(From Hofmann and Snyder, 1985)

dated stromatolite
Figure 3.

The graph shows a plot of $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$.

- The data points are grouped into categories:
  - Stromatolites
  - Silicate residues
  - Carbonate

Two regions of interest are highlighted:
- A circle labeled "Kona Dolomite, Marquette, MI"
- A circle labeled "Nash Formation, Medicine Bow Mtns., WY"

A line with a label indicates a correlation:
- $1.70 \pm 0.12$ Ma
Figure 4a.

Northeastern Colorado
Bulk K-feldspar fractions

Figure 4b.

Northeastern Colorado
Bulk fractions and single grains
Figure 5.
(Compiled by D. Muhs, 1990)
Figure 6a.

Sand Hills, Western Nebraska

Figure 6b.

eige 6a.

Middle-Late Archean rocks, Granite Mountains, WY (Fischer and Stacey, 1986)

north-central Nevada, (Rye et al., 1974)

San Juan Volcanics, CO (Lipman et al., 1978)

39-mile Volcanics, CO
Workshop on the Application of Isotope Systems to Geological Problems

**Pb-Nd-O ISOTOPIC COMPOSITIONS OF IGNEOUS ROCKS: IMPLICATIONS FOR PETROGENESIS AND TERRANE CORRELATION, CAPE BRETON ISLAND, NOVA SCOTIA, CANADA**

AYUSO, R., U.S. Geological Survey, Reston, VA 22092, USA; BARR, S., Acadia University, Wolfville, Nova Scotia, Canada; BOP 1X0; LONGSTAFFE, F., University of Western Ontario, London, Ontario, Canada N6A 5B7; and HEGNER, E., Universitat Tubingen, 7400 Tubingen, Germany

The geochemical nature of the lower continental crust is difficult to determine directly because for the most part these rocks are not exposed. One important but indirect source of information regarding the type and age of unexposed crustal rocks, however, can be obtained by establishing the isotopic compositions of igneous source regions (e.g., Zartman, 1974; Farmer and DePaolo, 1983; Ayuso, 1986; Aleinikoff and others, 1987). In an effort to test whether Pb, Nd (Barr and Hegner, 1992), and O isotopic data of plutonic rocks in Cape Breton Island can be used to correlate with plutons within terranes in mainland North America (Ayuso and Bevier, 1991), the present study uses isotopic data on 20 well-characterized (petrography, major- and trace element geochemistry) felsic units ranging from Precambrian to Paleozoic, and representing the pre-Carboniferous tectonic blocks in Cape Breton Island proposed by Barr and Raeside (1989). The Pb and Nd isotopic data in general show variations in agreement with a subdivision of the Island into magmatic source regions which may be related to unique terranes; the O isotopic data do not allow for the definition of distinct terranes.

In the New England and Canadian Appalachians, use of geochemical data for characterizing crustal segments is complicated by tectonic events which resulted in superposition and juxtaposition of crustal blocks. This kind of structural
complexity has led to the recognition that magmatic rocks exposed at the surface may now be part of thrust slices or dismembered blocks which have separated the magmatic rocks from their source rocks (Ayuso and Bevier, 1991). Even in this case, however, geochemical information can be of help to identify magmas that had a common source region. In fact, the isotopic data can assist in characterizing plutonic rocks within dismembered slices which ultimately belonged to unique crustal blocks.

Pb isotope compositions in Cape Breton Island are consistent with a source in the Northwest Highlands which resulted in a relatively unradiogenic group of Grenville-age syenites and anorthosites (Blair River Complex) (feldspar measured values of 206Pb/204Pb = 17.408-17.850; 207Pb/204Pb = 15.504-15.522; 208Pb/204Pb = 36.689-37.329); this source is similar to that inferred for plutonic rocks in northern New England. Plutons from the Blair River Complex plot below the Pb evolution curve, consistent with derivation from source rocks with generally low U/Pb (and low μ) and Th/Pb ratios (Fig. 1). Syenite from the Blair River Complex has an initial εNd value of +0.4 (Fig. 2) and a depleted mantle model age (TDM) of 1.66 Ga, reflecting a major component of older crust during its evolution; initial εNd values in the Complex at 400 Ma range from -6 to -1.5.

Highly variable δ18O values are found in granitic rocks from Cape Breton Island, from about +2.3 to +10.8 permil; if all of these values are magmatic, they would be consistent with an origin from widely different source rocks (Fig. 3). The narrowest range in δ18O values is in the Blair River Complex (~ +8 permil). A few of the plutons in the terranes to the south of the Northwest Highlands—Aspy, Bras D'Or, and Mira, have exceptionally low δ18O values (as low as 2 permil), implying that these are not magmatic, or alternatively, if the values are magmatic, that the source rocks must have undergone hydrothermal alteration prior to melting.

The Pb isotopic values of plutons from terranes to the south of the Northwest Highlands are more radiogenic (206Pb/204Pb = 18.192-18.644; 207Pb/204Pb = 15.584-15.712; 208Pb/204Pb = 37.815-
In the Aspy and Bras D'Or terranes the plutons had source regions containing more evolved components (higher U/Pb) than in the Northwest Highlands, and virtually all of the results plot higher than the Pb evolution curve. Granite and rhyolite (Devonian?) associated with Grenville-age rocks in the Northwest Highlands appear to have been derived from the same type of crustal sources as Devonian plutons in the Aspy terrane which contain initial values of $\varepsilon$Nd from -1.2 to +2.8 ($\varepsilon$Nd at 400 Ma from -1.8 to +2.4). In the Bras D'Or terrane plutonic rocks (mostly 565-555 Ma) have values of $\varepsilon$Nd from -1.8 to +1.4 ($\varepsilon$Nd at 400 Ma from 0 to -3.8). The Nd isotopic data do not provide clear evidence for distinction between the Aspy and Bras D'Or terranes; the range in initial $\varepsilon$Nd values (+2.8 to -1.8) and the depleted mantle model ages (0.7 to 1.1 Ga) are similar. Granitic rocks from the Bras D'Or terrane have a wide range in $\delta^{18}$O values (~+4 to +11 permil), overlapping the range in the Aspy (~+7.5 to +9). In general, isotopic data for plutons from the Aspy and Bras D'Or terranes reflect a source region similar to that for plutons in the Central and Southern groups (Gander and Avalonian zones) in mainland North America (Ayuso and Bevier, 1991).

Pb isotopic compositions of Devonian plutons from the Mira terrane ($^{206}$Pb/$^{204}$Pb = 18.243-18.460; $^{207}$Pb/$^{204}$Pb = 15.587-15.640; $^{208}$Pb/$^{204}$Pb = 37.922-38.174) overlap that of plutons in the Aspy and Bras D'Or terranes. However, older granitic rocks (Precambrian?) in the Mira terrane are distinctly more radiogenic than in all the other units ($^{206}$Pb/$^{204}$Pb = 18.832-18.874; $^{207}$Pb/$^{204}$Pb = 15.590-15.608; $^{208}$Pb/$^{204}$Pb = 38.155-38.200). In the Mira terrane, the plutonic rocks (ca. 620 Ma and Devonian) range in initial $\varepsilon$Nd values from +0.8 to +5 ($\varepsilon$Nd at 400 Ma from -1.1 to +3.7). In the Mira terrane, the older plutons (ca. 620 Ma) previously distinguished by their relatively high $^{206}$Pb/$^{204}$Pb values, also contain unusually low $\delta^{18}$O values (<6 permil?) relative to the younger group of granites (ca. 380 Ma) (>6 permil). The isotopic data in the Mira terrane are consistent with a source region for the granitic rocks similar to that in
the Avalonian of Newfoundland and mainland North America (Ayuso and Bevier, 1991; Whalen and others, 1989; Fryer and others, 1991).

Igneous rocks from Cape Breton Island, except for those in the Blair River Complex, have relatively young Nd model ages (<1.1 Ga), in agreement with the suggestion that the magmas do not reflect merely the type of older component found in the Blair River Complex. Pb and Nd isotopic data are consistent with a source region characterized by generally unradiogenic Pb and with εNd values < 0 in the Northwest Highlands (Blair River Complex); the source region of the plutons in the terranes to the south contained increasingly more radiogenic Pb and higher values of εNd. Pb and Nd isotope data are thus in agreement with the idea that the Aspy and Bras D'Or terranes cannot be uniquely defined, and that they may represent crustal reworking of mixtures ultimately derived from unradiogenic Grenville-type sources and more radiogenic Proterozoic Avalonian basement rocks. The fact that both the Aspy and Bras D'Or terranes probably overlie the same deep crustal block as suggested by seismic reflection data (Marillier and others, 1989; Loncarevic and others, 1990) permit the suggestion that the plutons may have had a common source region.

The results imply that at least two blocks or terranes were present in Cape Breton Island by the beginning of the Paleozoic: the Grenvillian Blair River Complex, and the Avalonian Mira terrane. Moreover, the Pb isotope data are not consistent with the idea that the Blair River Complex is merely a different level of exposure of the Mira terrane because the Blair River Complex does not contain a 620 Ma granite or metamorphic event, and because the Pb isotopic compositions of the 620 Ma granites do not lie along the estimated Pb evolution from 1040 Ma to 620 Ma. The isotopic contributions could have been made by including both blocks (or sedimentary debris obtained thereof) in the source region of the Bras D'Or magmas. In this case, the results imply that by ~565 Ma the Blair River Complex and the Mira terranes had already been amalgamated or that the two blocks were
geographically close enough to have contributed sedimentary material that ultimately melted to produce the granitic magmas. Younger Devonian granitic magmas produced at ~400-360 Ma in the Aspy terrane, and at ~380 Ma in the Mira terrane are also in agreement with a process involving melting of similar source materials as those in the 565 Ma granitic magmas or remelting of the ~565 Ma rocks themselves previously derived from a combination of the Grenvillian and Avalonian blocks. Pb, Nd, and O isotopic compositions of plutonic rocks can help in delineating regional characteristics of the magmas and this information can be of assistance in more detailed terrane correlations in conjunction with geological and geophysical observations.

**REFERENCES**


Doe, B.R., Delevaux, M., and Albers, J.P., 1985, The plumbotectonics of the West Shasta mining district, Eastern


FIGURES

Figure 1. 206Pb/204Pb-207Pb/204Pb evolution plots showing isotopic compositions of feldspars from granitic rocks in Cape
Breton Island. Pb isotope data for granites from the Aspy, Bras D'O, and Mira terranes in New Brunswick (NB), equivalent to terranes in Nova Scotia, are from Ayuso and Bevier (1991) and are shown for comparison. Grenville data are from Zartman and Wasserburg (1969), and the composition of the Devonian mantle is from Doe and others (1985). Symbols are as follows: BRC, Blair River Complex (Northwest Highlands); ASP, Aspy terrane; BDO, Bras D'Or terrane; MIR, Mira terrane; S&K, Stacey and Kramers (1975) Pb evolution curve (tick marks at intervals of 250 m.y. before the present).

Figure 2. Initial $\varepsilon_{Nd}$ values plotted against age for samples from Cape Breton Island; Nd data from Barr and Hegner (1992).

Figure 3. 206Pb/204Pb-$\delta^{18}O$ plot for granitic rocks from Cape Breton Island. Symbols as in figure 1.
Cape Breton Island, Nova Scotia

Granitic Rocks at 400 Ma

Figure 1

Figure 2
Figure 3
The use of K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ techniques to date multiple thermal events: An example from the Bayan Obo Fe-Nb-REE ore deposit, China

James E. Conrad

Bayan Obo in Inner Mongolia, northern China, is the world's largest known rare-earth element ore deposit and a major iron and niobium producer as well. The Bayan Obo ore bodies are in Middle Proterozoic dolomite that is part of a 2,000 m thick sequence of quartzite, carbonate rock, and shale. These sedimentary rocks are thought to represent a platform sequence deposited in east-trending grabens along the north edge of the Archean crystalline Sino-Korean craton. They are variably metamorphosed, cut by numerous veins and dikes, and complexly deformed by a system of south vergent thrust faults. The entire sequence of faulted metasedimentary rocks and Archean basement is intruded by granite of Permian age.

K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ studies have established four significant thermal events: amphibole veining at about 1,260 and 820 Ma, 460-400 Ma regional metamorphism, and a 300-225 Ma intrusive event. In general, the 460-400 and 300-255 Ma thermal events are easily dated by K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ techniques because these rocks have relatively simple cooling histories. The 1,260 and 820 Ma thermal events, however, are largely overprinted by the younger thermal events and minerals of this age often give spurious partially or fully reset ages.

$^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating techniques are usually necessary to evaluate the degree of disturbance and help identify samples giving reliable cooling ages. For example, the 820 Ma event appears to be represented by samples giving apparently disturbed ages in the range 560-800 Ma. These include discordant K-Ar ages, variable ages by $^{40}\text{Ar}/^{39}\text{Ar}$ single-grain total-fusion techniques, and $^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating analyses that give complexly disturbed spectra. A single grain from a sample that exhibited all these characteristics yielded a plateau age of 820 Ma using laser-heated age-spectrum techniques. This indicates that samples showing considerable thermal disturbance may contain occasional grains that preserve an original cooling age. This grain-to-grain variation in apparent age within a single sample is poorly understood, however.

The 1,260 Ma thermal event is suggested by a $^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating analysis that shows significant argon loss. The age spectrum shows a steady increase in apparent age from a minimum of about 640 Ma to an apparent plateau at 1,180 Ma. This apparent plateau includes the last 4 steps and comprise about 20 percent of the total $^{39}\text{Ar}$ release. This pattern represents a disturbed spectrum indicating a loss of radiogenic argon during a subsequent heating event, so the apparent plateau age of 1,180 Ma must be considered a minimum age. To assess the degree of resetting, this spectrum was compared to model diffusion curves that suggest that the plateau age has been lowered by about 6 percent by later heating of the sample, suggesting original crystallization at about 1,260 Ma.
References on the age and origin of the Bayan Obo Fe-Nb-REE ore deposit


SUMMARY OF K-Ar AND $^{40}$Ar/$^{39}$Ar AGES FROM THE BAYAN OBO Fe-Nb-REE ORE DEPOSIT, NORTHERN CHINA

HERCYNIAN

CALEDONIAN

DISTURBED AGES

LATE PROTEROZOIC THERMAL EVENT
LEAD ISOTOPIC COMPOSITION OF GALENA FROM MALAYSIA, AN S-TYPE GRANITE TERRANE

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Abstract -- Seven new samples of galena from Malaysia have Pb isotope ratios of 18.609 to 19.057 for \(^{206}\text{Pb}/^{204}\text{Pb}\), 15.704 to 15.765 for \(^{207}\text{Pb}/^{204}\text{Pb}\), and 38.950 to 39.385 for \(^{208}\text{Pb}/^{204}\text{Pb}\). Both the tin-bearing East and West Belts of Hosking (1977) and the Au- and base-metal-bearing Central Belt are represented. The East and West Belts coincide with the East Coast (ECP) and West Coast (WCP) Provinces of batholiths of Bignell and Snelling (1977). The range in isotope ratios is surprisingly small in that the WCP plutons are Late Triassic in age, are exclusively S-type, and have a concealed basement age of 1500-1700 Ma, whereas the ECP plutons are Permo-Triassic, are both I- and S-type, and have a concealed basement age of 1100-1400 Ma (Liew and McCulloch, 1985). Although all their values of \(^{87}\text{Sr}/^{86}\text{Sr}\) are at least somewhat high for mantle ratios (>0.705), the WCP has some of the highest values known (up to 0.7512).

Probably the most distinguishing feature of the Pb isotopes is the high value of \(^{207}\text{Pb}/^{204}\text{Pb}\), which has a distinct continental upper-crust nature. Because the Stacey-Kramers model Pb ages range from ~260 Ma (close to the age of the deposits) to ~450 Ma, there is no indication of cratonized crust (values of U/Pb and Th/Pb reduced by high-grade metamorphism in the Precambrian). The high values of \(^{207}\text{Pb}/^{204}\text{Pb}\) in the galenas require an extended Precambrian history for the Malay Peninsula, as concluded by Liew and McCulloch (1985) from neodymium isotopes and U-Th-Pb isotopic dating of zircons.

Similar Pb-isotope ratios are known from tin-bearing Belitung Island of Indonesia, which is included in an extension of the Malaysian tin belt to the SE by Hosking (1970). Appropriate ratios are not known from adjacent Sumatra; however, Pb isotope ratios similar to Malaysia are also known in Java. The other major tin province, Bolivia, also has many high values of \(^{207}\text{Pb}/^{204}\text{Pb}\) (Tilton et al., 1981).

A model is presented in which a lead-isotope source was established 3700-Ma ago with values normalized to the present day of 10 - 10.3 for \(^{238}\text{U}/^{204}\text{Pb}\) and 3.79 - 4.05 for \(^{232}\text{Th}/^{204}\text{U}\). At some intermediate time, e.g. 1600-Ma ago, the values of \(^{238}\text{U}/^{204}\text{Pb}\) were altered to higher values, e.g., up to approximately 12.

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INTRODUCTION

General

Tin is an element that has become of increasing geochemical interest over the last 15 years since the classification of granites into S-type (generated by melting of sedimentary sources) and I-type (by melting of igneous sources) (Chappell and White, 1974). Tin in the largest geochemical anomalies is associated with S-type or two-mica granites, although the mined deposits are usually in placers eroded from the granites rather than in lode deposits in the granites themselves. Tin is an unusual element in that to be commercial, it must be in the form of the mineral cassiterite. Tin-bearing fluids appear to have an igneous origin with deposition of cassiterite by a number of methods, in many cases through replacement of carbonate rocks (Heinrich, 1990). Southeast Asia accounts for at least 65 percent of the Western world's tin production. Malaysia has long been the largest individual producer of tin; yet no lead-isotope data is known for this area. This paper presents new data on seven samples of galena from Malaysia.

A model is presented in which a lead-isotope source was established 3700-Ma. ago with values normalized to the present day of $^{238}\text{U}/^{204}\text{Pb}$ between 10.0 and 10.3 and $^{232}\text{Th}/^{238}\text{U}$ between 3.79 and 4.05 (Fig. 5).
At some intermediate time, e.g., 1600-Ma. ago, the values of $^{238}\text{U}/^{204}\text{Pb}$ were altered to higher values, e.g., up to approximately 12.

**Terrane classification**

Malaysia is included in the Southeast Asian Tin Belt that extends from Thailand to Sumatra, Indonesia (Fig. 1). Provincial terminology used for Malaysia is confusing but bears on interpretations in this paper. Thus a rather complete discussion follows. Hosking (1977) separates Indonesia into East, Central, and West Belts, which are mineral belts. The East and West Belts contain the tin mineralization and the Central Belt has gold, barite, and base-metal sulfides dominant. The West Belt is further subdivided into parts I (to the west) and II (to the East). Mitchell (1976, 1977) classifies Malaysia into four stratigraphic-structural zones from west to east. Zone 4 is essentially Hosking’s East Belt whereas zone 3 is largely in Hosking’s Central Belt; Mitchell’s zone 2 mainly is in Hosking’s West Belt (within part II) with zone 1 overlapping part I but extending westward from Malaysia. The mineral belt classification of Hosking (1977) mainly will be accepted in this report because galenas are analyzed from each of these mineral belts. In addition, his East and West Belts, which are mineral belts, coincide with the East Coast, Central, and West Coast Provinces for granite batholiths of Bignell and Snelling (1977) as cited in Liew and McCulloch (1985). Mitchell’s
classification is valuable, however, because of his extensive tectonic interpretations. For example zone 2 contains the "ophiolite-melange association" or medial "ophiolite line" of Hutchison (1977) that might represent a former convergent plate margin. The geologic section of Malaysia consists entirely of Phanerozoic rocks; no outcrops of Precambrian rocks are known from the entire region.

It is a matter of some interest that Belitung Island of Indonesia is placed in the Eastern Belt by Hosking, but Mitchell (1977) puts it in Hosking's West Belt. One objective of the present study was to see if lead isotopes could solve this difference in classification.

Unfortunately, a somewhat different classification also has been given by Mitchell (1977) who separated Malaysia into Eastern, Central and Western Tin-bearing Granite Belts. Although Hosking's and Mitchell's Eastern Belts are the same, Mitchell has no equivalent to Hosking's Central Belt, a gold and base-metal belt (Mitchell refers to it as tin-barren). Mitchell's Central Belt then is Hosking's West Belt (and Hosking sometimes also refers to his West Belt as a West Tin Belt). Mitchell's Western Belt, which is further west than anything considered by Hosking, has no equivalent in the Hosking classification. This second classification of Mitchell will not be referred to further because of the confusion it introduces. Where necessary, Mitchell's terminology will be converted to the Hosking system.
Tectonic hypothesis

Mitchell (1976) gives an interesting plate tectonic interpretation for Southeast Asia. He hypothesizes that his zones 3 and 4 (Hosking East and Central Belts) were emplaced above an eastward dipping subduction zone during the Carboniferous to Triassic Periods. Zone 2 of flysch-type sediments, radiolarian cherts, Devonian shales and ultrabasic bodies formed the outer arc. The tin-barren granites of zone 3 were emplaced to the ocean side and the tin-bearing granites of zone 4 were emplaced in the continental crust side of the overriding plate. As the ocean closed at the end of the Triassic, zone 1, a continental shelf covered with platform carbonate rocks, was subducted producing the tin-bearing granites of zone 1 (Hosking's West Belt).

Granite batholiths

The following discussion is an abstract of discussions of the Eastern and Western Provinces from Liew and McCulloch (1985). They did not work on the Central Province:

The batholiths in the East Coast Province intrude Carboniferous to Triassic sedimentary rocks which include volcanic rocks of the andesite stem with calcalkaline affinities. Intrusive rocks can range from gabbro to potassic granite with biotite ± hornblende
granodiorite of I-type dominant. Minor peraluminous intrusions of S-type are present. Zircon concordia intercept ages range from 227 Ma to 264 Ma for both I-type and S-type granites, ages in general agreement with K-Ar biotite and Rb-Sr ages. Samples containing inherited zircons give upper intercept ages of 800 to 1350 Ma. I-type granites have values of $^{87}\text{Sr}/^{86}\text{Sr}_1$ of 0.7054 to 0.7092 whereas S-type granites range from 0.708 to 0.714. Both I-type and S-type granites have values of $^{143}\text{Nd}/^{144}\text{Nd}$ epsilon initial values in the range of -0.7 to -6.2 (or ratios of 0.51250 to 0.51118) with the S-type granites values only near the more negative values. Model $^{143}\text{Nd}/^{144}\text{Nd}$ source ages are 900-1400 Ma, with the age range 1100-1400 Ma. interpreted to be the best value. The model source ages are interpreted to estimate the time at which the crust separated from a depleted mantle.

The batholiths of the West Coast Province are S-type granodiorites to granites of Triassic age that contain biotite, muscovite, tourmaline and, rarely, a high-Mn almandine garnet. [The batholiths are intruded into Mitchell's (1977) zones 1 and 2 which are upper Permian to Middle Triassic limestones to the west and metamorphosed Devonian to Triassic turbidites and flysch towards the east.] These granites are enriched in K, Rb, Th, U, and Pb. Concordant zircon ages are 198-215 Ma. K-Ar ages range from 40 Ma to 210 Ma and are younger than Rb-Sr whole-rock ages of 200-220 Ma. Discordant zircons give upper intersect ages on concordia of 1500-1700 Ma. Values of $^{87}\text{Sr}/^{86}\text{Sr}_1$ range broadly from 0.716 to 0.751 whereas $^{143}\text{Nd}/^{144}\text{Nd}$ is more restricted with epsilon initial values of
-6 to -10 (or ratios of 0.51128 to 0.51106). Model $^{143}$Nd/$^{144}$Nd source ages are 1300-1700 Ma including two metasedimentary rocks, in general agreement with the zircon upper intercept ages, especially when considering modeling uncertainties.

**ANALYTICAL METHODS**

The lead-isotope compositions were measured by two different but comparable mass spectrometric methods. Sample G-1, G-2, G-4, and G-6 were analyzed by the thermal ionization (triple filament) method and samples G-7 and G-9 were analyzed by the surface emission ionization method (silica gel). Both were standard methods, normalized to absolute ratios using the NBS 981 lead-isotope standard, and yielded ratios within 0.1 percent of absolute.

**LEAD-ISOTOPE DATA**

Seven new samples of galena from Malaysia have Pb isotope ratios of 18.609 to 19.057 for $^{206}$Pb/$^{204}$Pb, 15.704 to 15.765 for $^{207}$Pb/$^{204}$Pb, and 38.950 to 39.385 for $^{208}$Pb/$^{204}$Pb (Table 1, Fig. 2). Represented are both the East (two samples) and West Belts (three samples) of Hosking (1977) that are tin-bearing and the Central Belt (two samples) containing Au and base metal deposits. The data are shown on Fig. 3 with selected lead-isotope data from Indonesia. Although
the samples were collected from as much as 250 km apart and from three diverse tectonic terranes, the spread in data is small. The samples from the West Belt, however, are seen to have slightly greater values of $^{208}\text{Pb}/^{204}\text{Pb}$ than the samples from the East and Central Belt. Samples from the East Belt are seen to have slightly greater values of $^{206}\text{Pb}/^{204}\text{Pb}$ than the Central Belt.

Probably the most distinguishing feature of the Pb isotopes is the high values for $^{207}\text{Pb}/^{204}\text{Pb}$. In this regard, it is interesting that lead-isotope data on ores from Bolivia (Tilton et al., 1981), the second largest tin producing province, overlap the data from the Malaysian/Belitung area (Fig. 4). The data from the tin deposits of Belitung Island (Jones et al., 1977) some 800 km to the southeast, also have isotope ratios similar to Malaysian deposits. The best isotopic match is with the Central Belt of Malaysia, the tin-barren zone. With such sparse data, such large distances, and such a small isotopic spread, the significance of the match can be questioned.

The data on Southeast Asia deposits suggest some kind of provincial tie between Belitung and Malaysia, however, because a few galenas from adjacent Sumatra (Doe and Zartman, 1979) have lead-isotope compositions with more average values of $^{207}\text{Pb}/^{204}\text{Pb}$. One of these samples is from the Sungei Tuboh prospect near Palembang, which is near the southeast Asian Tin Belt. Lead-isotope data are known from Java (Doe and Zartman, 1979) that are isotopically similar to data from the Southeast Asian Tin Belt, although the relations
between the deposits in Java and the Tin Belt are not known.

**LEAD-ISOTOPE SYSTEMATICS**

Although the systematics of lead isotopes have been described many times, some modeling bears on the interpretations contained herein. In modeling neodymium isotopes, Liew and McCulloch (1985) form an Earth at 4500 Ma. ($T_1$) with chondritic initial neodymium-isotope ratios and values for Sm/Nd. They propose the mantle was depleted in samarium relative to neodymium, arbitrarily, at 2700 Ma ($T_2$). Their subsequent interpretations are not sensitive to this age. They then present an interpretation of neodymium isotopes and zircon U-Th-Pb isotope dating that the crust of the East Province was formed about 1100-1400 Ma. ago, and the crust of the West Province was formed about 1400-1700 Ma. ago ($T_3$) which existed to the time of formation of the granite batholiths 200-250 Ma. ago.

A somewhat parallel argument has long been proposed regarding common-lead isotopes. The most sophisticated of these is the multi-stage plumbotectonic model IV given by Zartman and Haines (1988); however, for the purposes of this paper, the two-stage model of Stacey and Kramers (1975) is a sufficient beginning point. They developed a model in which the Earth was formed at $T_1$ (4500 Ma.) with a lead-isotope composition similar to the troilite phase of iron meteorites. In the first stage of lead-isotope evolution, an average $^{238}\text{U}/^{204}\text{Pb}$ (normalized to the present day for radioactive
decay) of 7.19 existed until 3700 Ma. ago (T2). At this time, the continental crust (the orogene of Doe and Zartman, 1979) was estimated to have formed with an average $^{238}\text{U}/^{204}\text{Pb}$ of 9.74, which exists down to the present. During the past 15 years, there has been little change in these average global values. Improvements have been made by considering more complex Earth models (e.g., Doe and Zartman, 1979, separated the crust into upper and lower crust as well as the orogene; Zartman, 1984, separated the lithospheric mantle from the asthenosphere.). But for present purposes modification of the models of Stacey and Kramers (1975) will suffice.

**DISCUSSION**

The great values of $^{207}\text{Pb}/^{204}\text{Pb}$ rule out young mantle sources. For example, Doe and Zartman (1979) model the average mantle today as having values for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ of 18.08, 15.42, and 37.68, respectively, instead of the observed ratios for the Malaysian ores of 18.609 to 19.057 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15.704 to 15.765 for $^{207}\text{Pb}/^{204}\text{Pb}$, and 38.950 to 39.385 for $^{208}\text{Pb}/^{204}\text{Pb}$. Furthermore, the source of the ores also would have values of $^{207}\text{Pb}/^{204}\text{Pb}$ too great to be representative of pelagic sediments, which would average today about 18.70, 15.63, and 38.62 for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, respectively (Stacey and Kramers, 1975). The conclusion is that the sources are continental crust that includes Precambrian material, and adds to the evidence in favor of
this environment from other studies, . Indeed, the observed ratios are remarkably similar to the modeled ratios of average upper crust by Doe and Zartman (1979) of 19.0, 15.7, 38.9, adjusted to 250 Ma. ago.

Because the spread in Malaysian isotopic data is so small, the source of the lead appears to be from sediments in all cases because sedimentation is the best mixer. For example, the range in $^{206}\text{Pb}/^{204}\text{Pb}$ for volcanic rocks of Hawaii Island over a distance of only 40 km greatly exceeds what is seen in the Malaysian Tin Belt. It should be noted, however, that a small percentage of lead-rich continental sediment assimilated into a basaltic parent melt would dominate the lead-isotope ratios, but might not influence the neodymium- or strontium-isotope ratios. Liew and McCulloch (1985), however, do find convincing evidence of incorporation of sediments in the batholiths in the strontium isotope data.

The Stacey-Kramers model-lead-isotope ages range from 260 Ma (close to the age of the deposits) to -450 Ma. Thus there is little indication of cratonized crust where values of U/Pb and Th/Pb have been reduced by high-grade metamorphism in the Precambrian. Cratonization would result in non-radiogenic values of $^{206}\text{Pb}/^{204}\text{Pb}$ and great model values of Th/U (Doe and Zartman, 1979) in young melts. For example, great values of $^{207}\text{Pb}/^{204}\text{Pb}$ are known in present-day ratios of Archean rocks (Goldich et al., 1975), but the spread in ratios is greater than for Malayan samples and values of apparent Th/U are also greater. When younger Precambrian periods
are considered, cratonized crust can be harder to recognize (Doe and Delevaux, 1980), because of a lack of time for reduced values of U/Pb to take effect. However, if the source is Middle Precambrian as estimated by Liew and McCulloch (1985) and if the mineralization age is young (around 200-250 Ma.) as determined, it seems most likely that we are not dealing with cratonized Precambrian crust, although "normal" Precambrian crust is quite possible.

Liew and McCulloch (1985) present an interpretation of the neodymium isotope data in which a mantle depleted in neodymium relative to samarium formed at the time of presumed major global continent formation 2500-3000 Ma. ago. They estimate the formation of the Malaysian arcs to have occurred at 1100-1400 Ma. in the East Province and 1500-1700 Ma. in the West Province, based on both neodymium isotope modeling and inherited zircon U-Pb dating. At these times, the value of Sm/Nd increased during crust formation. Granites then formed 200-250 Ma. ago from this enriched source material.

Lead-isotope data likewise indicate pre-history for the source materials involved in ore formation related to the igneous activity. Some source enriched in uranium relative to lead must have developed a long-time ago to produce the observed ratios. The time cannot be determined by these means, but the youngest time at which any of the galena isotopic compositions could have been produced from a source that evolved with a $^{238}U/^{204}Pb = 9.74$ (The
mean orogene value of Stacey and Kramers, 1975, for a system beginning at 3700 Ma. ago.) is about 2000 Ma. ago. The average $^{238}\text{U}/^{204}\text{Pb}$ must have been greater to obtain the larger observed values of $^{207}\text{Pb}/^{204}\text{Pb}$ for many of the samples. A $^{238}\text{U}/^{204}\text{Pb} \approx 10.3$ beginning at 3700 Ma. ($T_2$), for example, would produce the greatest observed value of $^{207}\text{Pb}/^{204}\text{Pb}$ and its accompanying $^{206}\text{Pb}/^{204}\text{Pb}$ at about 250 Ma. ago, the presumed age of mineralization (sample G-6)(Fig. 5). Values of $^{207}\text{Pb}/^{204}\text{Pb}$ between 10.0 and 10.3 can satisfactorily explain the two galenas from the Central Belt.

Such an undisturbed old source, however, cannot explain the more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ values of the two samples from the East Belt and one sample from the West belt (G-1, G-5, and G-7). To generate such ratios beginning with the lead-isotope ratios at 3700 Ma. of Stacey and Kramers (1975) ($T_2$), a second stage is needed with values of $^{238}\text{U}/^{204}\text{Pb}$ between the orogene value of 9.74 and 10.3, and then a third stage beginning at time ($T_3$) with variable higher values. Adopting an age of 1600 Ma. for the time of beginning of the third stage, which is in the range estimated by Liew and McCulloch (1985) for the Precambrian source material, a $^{238}\text{U}/^{204}\text{Pb}$ of about 12 would be needed to explain the most radiogenic ratios.

A parallel argument can be developed for $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{238}\text{U}$ (Fig 5). A value of 10.3 is all right for $^{238}\text{U}/^{204}\text{Pb}$ if $^{232}\text{Th}/^{238}\text{U}$ is increased to 4.05 in order to bring the model $^{208}\text{Pb}/^{204}\text{Pb}$ age of G-2 into agreement with the uranium system. No change in $^{232}\text{Th}/^{238}\text{U}$ is needed to model the galenas with the greatest values of $^{206}\text{Pb}/^{204}\text{Pb}$ so
a $^{238}\text{U}/^{204}\text{Pb}$ of 10 in the second stage and a $^{238}\text{U}/^{204}\text{Pb}$ of 12 in the third stage beginning at 1600 Ma. is adequate.

There is a good deal of flexibility in the ages and $^{238}\text{U}/^{204}\text{Pb}$ values of the stages, but there must be a stage of high $^{238}\text{U}/^{204}\text{Pb}$ beginning before 2000 Ma. ago and another, generally higher, stage since. Adequate models can be developed beginning the third stage at 2700 Ma. to be more compatible with Liew and McCulloch (1985) or having a "mantle second stage" between 3700 and 2700 Ma., but then a fourth stage is needed to explain the observed lead-isotope data. In addition some values of $^{207}\text{Pb}/^{204}\text{Pb}$ will need to be decreased and some increased. Thus the three-stage model is attractive because it is simpler and values of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{238}\text{U}$ in the second stage are either adequate or are increased.

CONCLUSIONS

1. There is a tectonic tie between the Southeast Asian Tin Belt in Malaysia with Belitung Island in Indonesia. The best lead-isotope match is for Belitung Island is with the Central Belt of mineralization in Malaysia.

2. The values of $^{207}\text{Pb}/^{204}\text{Pb}$ for galenas of the Southeast Asian Tin Belt are unusually high, and cannot be the result of any kind of mixture of mantle and pelagic sediment lead-isotope compositions.
3. The history of the Malay Peninsula is estimated to have begun in the Precambrian, much older than the oldest observed rocks of Early Paleozoic age. This conclusion agrees with the interpretation of Liew and McCulloch (1985) based on neodymium isotopes and U-Th-Pb dating of zircons.

4. The simplest lead-isotope models begin at 3700 Ma. with the lead-isotope values of Stacey and Kramers (1975). Second stages are formed with values of $^{238}U/^{204}Pb$ between 10.0 and 10.3 to explain some of the lead-isotope data rather than the global value of 9.74 used by Stacey and Kramers (1975). Some samples require a third stage (e.g., beginning at 1600 Ma.) to explain the most radiogenic values of $^{206}Pb/^{204}Pb$.

5. The values of $^{207}Pb/^{204}Pb$ for galenas from Malaysia are overlapped by ratios found in ore samples from the other largest tin province, Bolivia. Although the sample size is small, there might be some connection between major geochemical anomalies of tin and $^{207}Pb/^{204}Pb$ found in major tin districts.

Acknowledgements The samples were obtained from Melvin Jones of the University of Adelaide, Australia, and collected by K.F.G. Hosking and Ee Beng Yeap of the University of Malaya. Sample locations and descriptions were provided by Ee Beng Yeap. M.H. Delevaux and A.A. Afifi made the excellent lead-isotope analyses. Discussions with Bruce L. Reed of the U.S. Geological Survey were most helpful.
References


APPENDIX: SAMPLE LOCATIONS AND DESCRIPTIONS

(From Ee Beng Yeap)

G1. N 4° 9'40", E 103°40'50". Bandi area, Trengganu. Replacement sulfide body of post Mid-Carboniferous age in Mid-Carboniferous (?) marble. Galena with pyrite, chalcopyrite, magnetite and other minerals.


vein of estimated post-Upper Triassic age in marble in Paleozoic(?) marble and metasediment. Coarse galena replacing sphalerite.


Table 1: $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ for galenas from Malaysia and selected data from other areas.

<table>
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<th>Sample No.</th>
<th>Deposit or Province Name</th>
<th>$^{206}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{207}\text{Pb}/^{204}\text{Pb}$</th>
<th>$^{208}\text{Pb}/^{204}\text{Pb}$</th>
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<td>G-1gn-E</td>
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**Bolivia**

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(1) This paper, (2) Jones et al. (1977), (3) Doe and Zartman, (4) Tilton et al. (1981)
Fig. 1. Map of Malaysia and part of Indonesia showing sample locations of the galenas analyzed for this study and principal tectonic zones.

Fig. 2. $^{206}\text{Pb} / ^{204}\text{Pb}$, $^{207}\text{Pb} / ^{204}\text{Pb}$, and $^{208}\text{Pb} / ^{204}\text{Pb}$ plots for galenas from Malaysia. Letters designate mineral belts: E is East Belt, C is Central Belt, and W is West Belt. (A) $^{207}\text{Pb} / ^{204}\text{Pb}$ vs. $^{206}\text{Pb} / ^{204}\text{Pb}$ plot including the Stacey-Kramers (1975) curve with $^{238}\text{U} / ^{204}\text{Pb}$ of 9.74 beginning at 3700-Ma. ago. Curve (1) has the same starting point for lead-isotope ratios as the Stacey-Kramers curve 3700-Ma. ago; however, curve (1) evolves with a $^{238}\text{U} / ^{204}\text{Pb}$ of 10.0 and curve (2) 10.3. (B) $^{208}\text{Pb} / ^{204}\text{Pb}$ vs. $^{206}\text{Pb} / ^{204}\text{Pb}$ plot including the Stacey-Kramers curve with $^{232}\text{Th} / ^{238}\text{U}$ of 3.78 and $^{238}\text{U} / ^{204}\text{Pb}$ of 9.74. Curve (1) has a $^{232}\text{Th} / ^{238}\text{U}$ of 3.78 and a $^{238}\text{U} / ^{204}\text{Pb}$ of 10.0; curve (2) has a $^{232}\text{Th} / ^{238}\text{U}$ of 4.05 and a $^{238}\text{U} / ^{204}\text{Pb}$ of 10.3. Ticks on the curved line are in Ma.

Fig. 3. $^{206}\text{Pb} / ^{204}\text{Pb}$, $^{207}\text{Pb} / ^{204}\text{Pb}$, and $^{208}\text{Pb} / ^{204}\text{Pb}$ plots comparing galenas from Malaysia (this study) with Indonesia (Doe and Zartman, 1979; Jones et al., 1977). The symbols represent: Malaysian mineral belts -- E - East Belt, C - Central Belt, W - West Belt; Indonesia -- B - Belitung, J - Java, S - Sumatra. See Fig. 2 for further explanation.
Fig. 4. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ plots for galenas from Malaysia (this study) and Bolivia (Tilton et al., 1981). See Fig. 2 for additional explanation.

Fig. 5. (A) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ evolution diagram to model lead-isotope ratios for galenas from Malaysia. The Stacey-Kramers model begins a second stage at 3700 Ma. with values of 11.152 for $^{206}\text{Pb}/^{204}\text{Pb}$ and 12.998 for $^{207}\text{Pb}/^{204}\text{Pb}$ with a value for $^{238}\text{U}/^{204}\text{Pb}$ of 9.74 (normalized to the present day) for the second stage. Curve (1) represents lead-isotope evolution for a second stage with $^{238}\text{U}/^{204}\text{Pb} = 10.0$ and curve (2) a second stage with $^{238}\text{U}/^{204}\text{Pb} = 10.3$. Curve 3 represents a change of $^{238}\text{U}/^{204}\text{Pb}$ from 10.0 to 12 ($^{206}\text{Pb}/^{204}\text{Pb} = 16.100$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.426$) at 1600-Ma. ago to show third-stage lead-isotope evolution. (B) $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ plot to model lead-isotope ratios for galenas from Malaysia. The Stacey-Kramers curve for $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ uses a value of 3.79 for $^{232}\text{Th}/^{238}\text{U}$; the curve is omitted for clarity. Curve (2) begins at the second stage ratios ($^{208}\text{Pb}/^{204}\text{Pb} = 31.23$) adopted by Stacey-Kramers at 3700 Ma. and evolves with a $^{238}\text{U}/^{204}\text{Pb}$ of 10.3 as for curve (2) in plot A but with a $^{232}\text{Th}/^{238}\text{U}$ of 4.05 to give sample G-2 a model $^{208}\text{Pb}/^{204}\text{Pb}$ age in approximate agreement with its known age. Curve (3) is parallel to curve (3) in plot A. Lead isotopes evolve with a $^{238}\text{U}/^{204}\text{Pb}$ of 10.0 and $^{232}\text{Th}/^{238}\text{U} = 3.79$ until 1600-Ma. ago. These conditions would evolve a curve (1) that is omitted for clarity here (see Fig. 2). At 1600 Ma. ago, the value of $^{238}\text{U}/^{204}\text{Pb}$ changes to 12 with no
change in $^{232}\text{Th}/^{238}\text{U}$, which gives approximate model $^{208}\text{Pb}/^{204}\text{Pb}$ ages for the samples with the greatest values of $^{206}\text{Pb}/^{204}\text{Pb}$ (e.g., East Belt galenas).
Fig. 3A
\[ \frac{^{208}\text{Pb}}{^{204}\text{Pb}} \]

\[ \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \]
Mass Spectrometric Measurements of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ and Dating Late Quaternary Carbonates

R. Lawrence Edwards, University of Minnesota

Thermal ionization mass spectrometric (TIMS) methods for measuring $^{230}\text{Th}$ (Edwards et al., 1987a) and $^{234}\text{U}$ (Chen et al., 1986) have provided improved precision and sensitivity over earlier techniques. This allows us to obtain precise $^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th}$ ages of carbonates younger than 500 ka (Edwards et al., 1987b). Two sigma precisions range from ±3 y for materials younger than 1000 y, to ±25 y at 10 ka, to ±1 ka at 130 ka. For corals younger than 8 ka, comparisons with other chronometers show that $^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th}$ ages are accurate (Edwards et al., 1988; 1992). For corals older than 100 ka, $^{234}\text{U}/^{238}\text{U}$ ratios are sometimes consistent with closed system evolution from sea water and other times indicate diagenetic shifts to higher values (even for aragonitic samples that retain their original Sr and Mg concentrations). The sensitivity of $^{234}\text{U}/^{238}\text{U}$ to diagenetic shifts makes it an important indicator of alteration, and provides a criterion for selecting materials that are likely to record accurate ages (e.g. Edwards et al. 1987b; Banner et al., 1991; Gallup et al., 1991; 1992).

The detailed timing of part of the late Quaternary sea level curve (e.g. Edwards et al., 1987b; Li et al., 1989; Gallup et al., 1991; 1992) has been determined via application of these techniques to corals and cave deposits. The results have a bearing on the causes of Quaternary climate shifts. A second application focuses on extracting regional climate records from inorganically precipitated calcite. This approach has produced some of the first continuous high resolution regional climate records longer than $10^5$ years (Winograd et al., 1990, Ludwig et al., 1990, Richards et al., 1992a, b). Such records are important, particularly within the context of the high-resolution sea level curve. By comparing regional and sea level records, one may resolve leads and lags between regional and global climate shifts. A third application involves combined $^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th}$ and $^{14}\text{C}$ analyses on the same corals. As $^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th}$ ages are at least as precise as $^{14}\text{C}$ ages, they provide the opportunity to calibrate the $^{14}\text{C}$ chronometer for times earlier than the dendrochronology calibration (Edwards et al., 1988). Results show offsets between $^{14}\text{C}$ and $^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th}$ ages (Bard et al., 1990) indicating large shifts in atmospheric $^{14}\text{C}/^{12}\text{C}$, particularly between 10,900 and 12,300 B.P., when differences between conventional $^{14}\text{C}$ and $^{238}\text{U} - ^{234}\text{U} - ^{230}\text{Th}$ ages jump from 800 to 2100 years (Edwards et al., 1992). The jump appears to result from shifts in the ocean - atmosphere carbon cycle.

Here, I discuss the TIMS measurements, as well as improvements in these measurements that have recently been made at the University of Minnesota. I then discuss data that have a bearing on the accuracy of the ages, and finally some of the applications discussed above.

References


Nd Isotopes as Tracers of the Origin and Evolution of the Continental Lithosphere

G. L. Farmer, CIRES and Dept. of Geological Sciences, Campus Box 216, Univ. of Colorado, Boulder, CO 80309

Abstract

Over the past 15 years, neodymium isotopic data have provided important constraints regarding the formation, tectonic modification, and subsequent degradation of the continental lithosphere. The technique is based on the fact that the Earth's crust and mantle have, over time, developed discretely different Nd isotopic compositions, due to the α-decay of $^{147}$Sm to $^{143}$Nd combined with the small differences in Sm/Nd that have developed in the Earth primarily as a result of magmatic processes. The Nd isotopic compositions of continental igneous, metamorphic, or sedimentary rocks can then be used to determine the sources involved in the rock formation if the isotopic compositions of the potential source rocks are known and are distinguishable. However, continental rocks often contain Nd derived from a variety of different sources and so it is often difficult to extract unambiguous information regarding the origin of a given rock from its Nd isotopic compositions alone. Instead, the Nd isotopic compositions of continental rocks are best interpreted in conjunction with other isotopic, geochemical, and geologic information.

In many continental regions, particularly in North America, extensive Nd isotope data bases exist for the Precambrian crust which can be used not only to study crustal genesis but also to study magmatic and tectonics events that subsequently modified the continental lithosphere. In the U.S., the Nd data reveal that the Precambrian crust can be divided into distinct provinces which define distinct arrays (pseudoisochrons) on conventional isochron plots. These arrays have implications for how the Precambrian crust was generated and assembled and also provide convenient templates against which to compare the isotopic compositions of younger rocks which may have been formed, at least in part, from Precambrian components. The comparison between the isotopic compositions of Mesozoic and younger peraluminous granites in the western U.S. and the Precambrian crust clearly demonstrate that these granites were derived solely from anatexis of pre-existing felsic to intermediate composition Precambrian crust. The Nd isotopic compositions of large-volume Cenozoic rhyolites in the western U.S., on the other hand, show that these rhyolites are not simple crustal melts, as commonly assumed, but instead differentiated from mafic magmas derived from the upper mantle that interacted extensively with the crust. Other studies of Cenozoic volcanic rocks in the western U.S. have shown that Nd isotopic data can distinguish between lithosphere and asthenospheric mantle derived basalts. As a result, temporal and spatial variations in the isotopic compositions of syn-extensional basalts can be used to track the physical response of the deep continental lithosphere to extension. Nd isotopic data have also proved useful in constraining the provenance of marine siliciclastic sediment shed from North America. One example is the recent demonstration that the large volumes of Cenozoic flysch accreted to the southern margin of Alaska represent detritus derived from the unroofing of the northern portions of the Coast Ranges Plutonic Complex in SE Alaska and British Columbia.
General Systematics

![Diagram showing relationships between surface, crust, mantle, and asthenospheric mantle with variables and annotations.]

- Surface: MG, PG
- Crust: 4, 3, 1
- Mantle: 1
- Asthenospheric Mantle: 1

![Graph showing variation in εNd with age (Ga).]

- DM: ΔT_{DM}
- Lines: εNd vs. Age (Ga)
- Symbols: □, △, □
- Parameters: {\( \text{D}_{\text{Nd}}, \text{C}_{\text{Nd}(\text{Nd})} \)} = {0.5, 0.1, 70; 0.5, 0.9, 130; 0.9, 0.9, 70}

![Diagram showing Nd depletion (εNd) vs. 87Sr/86Sr ratio.]

- Mantle Endmember: L
- Crustal Endmember: F = 0.1
- Symbols: □, △, □
- Parameters: C_{\text{Nd}(\text{Nd}), r\text{C}_{\text{Nd}(\text{Nd})}}
- Graph extends from 87Sr/86Sr ratio 0.70 to 0.74
Precambrian of Continental U.S.
PROTEROZOIC

PHANEROZOIC

Precambrian sedimentary rocks

Provinces 1 & 2 crust

Provinces 1 & 3 crust

Greeneville crust

Ancean crust

Greeneville province

S. margin of Wyoming/Superior provinces

Wyoming/Superior provinces

87Rb/86Sr

147Sm/144Nd

εNd(1.0 Ga)
Origin of Rhyolite

Timber Mountain Tuff
TR HSR
○ Ammonia Tanks Member
◇ Rainier Mesa Member
Paintbrush Tuff
LSR
△ △ Tiva Canyon Member
□ □ Topopah Spring member
Continental Extension

**Pure Shear**

- On-Axis
- Off-Axis

**Simple Shear**

- On-Axis
- Off-Axis

**Map**

- UTAH
- COLORADO PLATEAU
- GREAT PLAINS
- RIO GRANDE RIFT
- TRANSITION ZONE
- BASIN AND RANGE
- COLORADO PLATEAU

- Time

NEW MEXICO
COLORADO PLATEAU
TRANSITION ZONE
RIO GRANDE RIFT
REFERENCE LIST
Nd Isotopes as Tracers of the Origin and Evolution of the Continental Lithosphere- G. L. Farmer

Overview

1) General systematics:


2) Mixing Systematics:


Nd tracer studies

1) Magmatic processes/Origin of rhyolite:

Cameron, K.L., and M. Cameron, 1985, Rare earth element, $^{87}Sr/^{86}Sr$, and $^{143}Nd/^{144}Nd$ compositions of Cenozoic orogenic dacites from Baja California, northwestern Mexico, and adjacent West Texas: evidence for the predominance of a subcrustal component: Contrib. Mineral. Petrol., v. 91, p. 1-11.

2) Continental growth and tectonism:

Precambrian continental growth of continental U.S.:

Mechanisms of continental extension:


4) Sedimentary provenance


PARAGENETIC CONSTRAINTS ON THE PB ISOTOPIC AND TRACE ELEMENT CHARACTER OF Au-Ag MINERALIZED ROCKS OF THE NORTH AMETHYST VEIN, MINERAL COUNTY, COLORADO

by

Nora K. Foley and Robert A. Ayuso

U.S. Geological Survey, National Center, Reston, Virginia 22092

Chemical redistribution as a result of alteration and mineralization in the North Amethyst vein illustrates the combined effects of metasomatism, dissolution, and crystallization of new minerals. The vein is hosted by the 27.6 Ma (Lanphere, 1988) Carpenter Ridge Tuff (CRT), which consists of dacites and rhyodacites related to the evolution of the central cluster of calderas in the San Juan volcanic field (Lipman, 1976; Lipman and Sawyer, 1988). The vein is located ~7 km north of the Creede mining district (Bethke and Lipman, 1987). The vein system has an older mineral association that consists of quartz, rhodonite, Mn-carbonates, hematite, magnetite, electrum, Au-Ag-sulfides, Ag-sulfosalts, and base metal sulfides and a younger mineral association (~25 Ma, M. Lanphere, 1987) that crosscuts the Mn- and Au-bearing assemblages and consists of quartz, calcite, sericite, chlorite, hematite, adularia, fluorite, base metal sulfides, and Ag-tetrahedrite (figure 1; Foley, 1990). A stage of brecciation and deposition of sediment in veins separates the two mineral associations.

Samples of least altered wallrock, more highly altered wallrock, and early vein material have geochemical patterns that reflect the amount of vein material incorporated into the wallrock and the mobility of REE's and other elements in the hydrothermal fluid (Foley and Ayuso, 1992). In general, REE's and trace incompatible elements (e.g., Th, Ta) in the volcanic wallrock were relatively
immobile during the alteration events that preceded or were concurrent with mineralization. In contrast, the relative mobility of base and precious metal elements was an important factor controlling the evolving chemical composition of the altered wallrock.

Potassium-metasomatized CRT that constitutes the least altered and unbleached host of the vein (samples located 3-10 m from vein, and consist of wallrock >97%, vein material <3%) has ratios of incompatible element abundances (table, WR97) that match those in regionally potassium-metasomatized rocks of CRT (K-m CRT, e.g., Krause-Webber, 1988) for Th/Ta, although other ratios show large discrepancies (Th/Hf). Least altered wallrocks also have rare earth element (REE) contents and chondrite-normalized patterns (at SiO₂ =66-74%) characterized by Ce/Yb ratios that range from 8 to 12 and small negative Eu anomalies (Eu/Eu*=0.47-0.81) in the range of volcanic rocks of the central San Juan calderas (e.g., Lipman, 1987). In addition, the least altered wallrocks have values of Zn/Ta that are similar to regionally K-metasomatized rocks of CRT (table 1, K-m CRT).

With increasing alteration, primarily as a result of metasomatism produced by vein mineralization, the wallrocks are systematically bleached, silicified, and (or) chloritized (wallrock =90-95%, vein material =5-10%), with higher Na/K values proximal to the vein (figure 2; Foley and Ayuso, 1992; this study). Contents of trace elements of widely different geochemical behavior in the more bleached rocks overlap the content values of least altered wallrocks. This overlap suggests that vein mineralization and metasomatism did not significantly disturb the composition of wallrocks a few meters away from the veins (table, WR90). The most obvious effect of the vein mineralization is the increased abundance of base and precious metals relative to immobile elements for the altered rocks compared to the least altered wallrocks (table, WR97). Silicified, bleached, and chloritized wallrocks, for the most part, retained the original REE signature of the CRT volcanic
rocks. The REE pattern of the K-metasomatized volcanic rocks also is preserved in more highly altered wallrocks (wallrock =70-85%, vein material =15-30%) that have not retained their volcanic fabric and have a higher density of quartz veining. These rocks have relatively undisturbed incompatible element ratios (table, WR70), but vein effects are enhanced and so produce significantly higher base-and-precious metal to immobile-element ratios. Feldspar-stable altered wallrocks have overlapping or slightly lower REE contents and patterns that match those of the unaltered patterns. Although highly metasomatized wallrocks adjacent or within a few centimeters of vein, having a high density of veining (wallrock = 50%, vein material = 50%) and resorbed feldspars, have trace element ratios that are similar to those of the least altered hostrocks (table, WR50); these wallrocks have high abundances of base and precious metals compared to abundances in least altered wallrocks.

Initial Pb isotopic values for ~40 samples of galenas and feldspars from the North Amethyst vein system and associated host rocks have a narrow compositional range, but significant differences exist among volcanic wallrock, older vein assemblages, and younger vein assemblages (figure 3, Foley and Ayuso, in prep.). Pb isotopic compositions of paragenetically early galenas associated with Au mineralization are relatively less radiogenic (206Pb/204Pb, 18.826-18.881; 207Pb/204Pb, 15.588-15.602; and 208Pb/204Pb, 37.790-37.926) compared to compositions of galenas associated with the younger mineralization (206Pb/204Pb, 19.041-19.115; 207Pb/204Pb, 15.627-15.672; and 208Pb/204Pb, 37.829-38.057). Pb isotopic compositions of galenas from the North Amethyst vein are comparable to those of galenas from the southern part of the Creede mining district, located ~5 km to the south (Doe and others, 1979; Foley, 1990; Foley and Ayuso, in prep.). Pb isotopic compositions of the vein system are more radiogenic than the compositions of host volcanic rocks (e.g., 206Pb/204Pb, 18.501 to 18.742; 207Pb/204Pb, 15.564 to 15.607; and
$^{208}\text{Pb}/^{204}\text{Pb}$, 37.886 to 38.183; Lipman and others, 1978; Matty and others, 1987; D. Matty, written commun., 1987; this study). The older assemblage may represent the product of a hydrothermal system that interacted with a source having a slightly different Pb isotopic character than that of the younger mineralization, or it may represent an increasing and variable mixture of volcanic rock with ore-fluid lead as characterized by galena in the later mineralization. Pb isotopic compositions correlate with bulk chemical variations (e.g., Au, Ag, As, Cu contents); however, neither the Pb isotopic ratios nor the metal abundance ratios permit the ores to have been derived solely from local wallrock (Foley and Ayuso, 1992). The geochemical profile of the vein material requires the addition of Pb and other base and precious metals from mineralizing fluids that originated at depth.

Table. Geochemical data for mineralized rocks of North Amethyst Au-Ag vein.

<table>
<thead>
<tr>
<th>Rock</th>
<th>K-m CRT(^1)</th>
<th>WR97</th>
<th>WR90</th>
<th>WR70</th>
<th>WR50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th/Ta</td>
<td>14.9-8.9</td>
<td>13.1-9.4</td>
<td>13.6-11.5</td>
<td>13.3-8.9</td>
<td>12.6-10.6</td>
</tr>
<tr>
<td>Th/Hf</td>
<td>8.2-7.3</td>
<td>3.3-1.7</td>
<td>3.4-3.0</td>
<td>3.3-2.3</td>
<td>3.4-1.4</td>
</tr>
<tr>
<td>Zn/Ta</td>
<td>70</td>
<td>45-197</td>
<td>29-2102</td>
<td>45-1503</td>
<td>864-5327</td>
</tr>
<tr>
<td>Pb/Hf</td>
<td>6-34</td>
<td>3.7-214</td>
<td>5-380</td>
<td>409-902</td>
<td></td>
</tr>
<tr>
<td>Pb/Ta</td>
<td>24-136</td>
<td>15-877</td>
<td>17-1421</td>
<td>1534-6034</td>
<td></td>
</tr>
<tr>
<td>Ag/Ta</td>
<td>1.5-35</td>
<td>0-25</td>
<td>6-148</td>
<td>35-2431</td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) K-m = K-metasomatized; percentage of wallrock (WR) varies from 97 to 50%.

References Cited

Bethke and Lipman, 1989, Mineralization in silicic calderas: Questa, New Mexico and the San Juan Mountains, Colorado: American Geophysical Union, 28th International Geological Congress, Field trip guidebook T320, 75p


Lanphere, M.A., 1988, High resolution $^{40}$Ar/$^{39}$Ar chronology of Oligocene volcanic rocks, San Juan Mountains, Colorado: Geochimica cosmochimica acta, v. 52, pp. 1425-1434.


### NORTH AMETHYST VEIN SYSTEM

<table>
<thead>
<tr>
<th>Stage</th>
<th>Mineral Assemblage</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Mn-Calcite &gt;&gt; Quartz &gt;&gt; Pyrite</td>
</tr>
<tr>
<td>2</td>
<td>Quartz &gt; Mn-Calcite &gt; Rhodocrosite &gt; Adularia &gt; Fluorite &gt; Chlorite &gt; Pyrite &gt; Mn-siderite</td>
</tr>
<tr>
<td>1</td>
<td>Q &gt; Sphalerite &gt; Galena &gt; Pyrite &gt; Chalcopyrite &gt; Chalcedony &gt; Pyrite &gt; Chalcopyrite &gt; Tetrahedrite</td>
</tr>
<tr>
<td>Breccia</td>
<td>Chalcedonic Quartz cement</td>
</tr>
<tr>
<td></td>
<td>Sphalerite &gt; Galena &gt; Chalcopyrite &gt; Pyrite &gt; Tetrahedrite &gt; Ag-Au minerals &gt; Electrum (Hematite &gt; Magnetite)</td>
</tr>
<tr>
<td>α</td>
<td>Rhodocrosite &gt; Quartz &gt; Mn-Calcite &gt; Rhodonite &gt; K-feldspar &gt; Sphalerite &gt; Pyrite &gt; Galena</td>
</tr>
<tr>
<td></td>
<td>[Barite]</td>
</tr>
</tbody>
</table>

Figure 1. Paragenetic sequence for mineralized rocks of the North Amethyst vein system (Foley, 1990). Stages 2 and β are the main sulfide-bearing assemblages.
Figure 2. Samples of least altered wallrock (A), more highly altered wallrock (B, C), and early vein material (D) have geochemical patterns which reflect the amount of vein material incorporated into the wallrock and the mobility of REE's and other elements in the hydrothermal fluid. Samples are normalized to least altered Carpenter Ridge Tuff. The most obvious effect of the vein mineralization is the increased abundance of base and precious metals relative to immobile elements.
Figure 3. Lead isotope values for galenas and adularia from mineralized structures (Doe and others, 1979; Foley and Ayuso, 1992) compared to data for feldpars from volcanic rocks of the central cluster of the San Juan volcanic center (Lipman and others, 1978; Matty and others, 1987; D. Matty, written commun., 1987; this study). The data straddle but are more radiogenic than the secondary isochron at 1.78 Ga defined by the volcanic rocks from the central caldera cluster (Lipman and others, 1978; Matty and others, 1987). Dashed line (S&K) is average lead evolution line for Stacey and Kramer's (1975) two-stage Pb evolution model.
Direct Dating of Ductile Deformation Fabrics: An Integrated Microstructural/Geochronologic Approach


The ages of deformational fabrics in regionally metamorphosed rocks are typically constrained by dating bracketing events such as pre- or post-tectonic plutonism or mineral cooling. In some cases, however, ductile deformational fabrics can be dated directly with mineral isochrons by integrating structural, microstructural, and geochronologic observations. This approach is based upon experimental data indicating that extensive chemical exchange can occur among deforming minerals by the ductile deformation mechanisms of dislocation creep and grain boundary diffusion creep (i.e., pressure solution), even if metamorphic temperatures are too low to permit significant exchange by volume diffusion through the crystal lattice. In naturally deformed rocks, these two deformation mechanisms are intimately related to the development of recrystallized textures and mesoscopic deformation fabrics. Thus, detailed field and petrographic observations can be used to identify samples likely to have undergone chemical and isotopic exchange by these two deformation mechanisms.

Several criteria are used to identify samples where deformation fabrics can be directly dated with mineral isochrons. Constituent minerals should (1) define part of the mesoscopic fabric of the tectonite (e.g., foliation, lineation), (2) exhibit microstructures in thin section indicating that ductile deformation and metamorphic processes have eliminated relict grains (i.e., complete recrystallization has occurred), and (3) remain unaffected by post-tectonic diffusive exchange or retrogression. Minerals that do not satisfy these three criteria yield scatter on isotope diagrams. Coexisting minerals that do satisfy these criteria constitute a deformational mineral assemblage. By analogy with the concept of a metamorphic mineral assemblage, minerals of a deformational assemblage undergo chemical and isotopic exchange during ductile deformation under a given set of conditions (e.g., P, T, bulk composition). For a given deformational assemblage, constructing isochrons with three or more minerals in multiple radiometric systems provides a rigorous test of whether equilibration was achieved during deformation, and whether mineral isotope systems were disturbed after that time.

Two examples from the late Proterozoic crystalline rocks of the New England Appalachians (Willimantic dome) illustrate the principles described above. At one locality, mylonitic amphibolites were totally recrystallized during dynamic recrystallization and grain boundary diffusive mass transfer at 500-550°C in a major shear zone. Virtually identical Sm-Nd, Rb-Sr, and U-Pb mineral isochrons (272±7 Ma, 274±15 Ma, 258±6 Ma, respectively) plus structural and geochronologic relations within neighboring samples indicate that the minerals achieved complete equilibration by these ductile deformation processes, and underwent only very limited isotopic exchange during cooling. In a porphyroclastic gneiss (i.e., incompletely recrystallized) structurally beneath the mylonitized amphibolite, U-Pb analyses of sphene reveal rare sphene porphyroclasts with late Precambrian radiogenic signatures, and a dominant population of clear sphene euhedra that grew during gneiss formation at 304±2 Ma. Rb-Sr and Sm-Nd mineral compositions form scattered arrays due to relict, pre-300 Ma radiogenic components (within fragments of sphene, allanite, and feldspar porphyroclasts) and to partial exchange during the later, non-penetrative deformational overprint during mylonitization in the overlying amphibolite at ~270 Ma. Combined with isotopic and structural studies in the overlying sequence of metasediments, the ability to identify discrete ductile deformation events at the Willimantic dome constrains the age of tectonism along map-scale structures and the amalgamation of distinct rock groups in this region.
Selected References

Ductile deformation mechanisms:


Chemical / isotopic exchange during ductile deformation:


Radiogenic isotopes and metamorphic mineral growth:


Christensen, J.N., Rosenfeld, J., and DePaolo, D.J., 1989, Rates of tectonometamorphic processes from Rubidium and Strontium isotopes in garnet, Science, 244:1465-1469.

Selected Figures

Figures are adapted from Getty and Gromet (1992), except for table of isotope exchange mechanisms and underlying compositional profile of "recrystallized" feldspar grain (Fig. 3).


Figure 2. Schematic diagram of structural relations at the Willimantic dome, and approximate structural positions of mylonitized amphibolite (1) and augen gneiss (2) discussed in abstract. Isotopic data for two metasediment samples (3 & 4) are shown in Figure 6.

Figure 3. Profile of feldspar compositional variations across "recrystallized" matrix grain.

Figure 4. Sm-Nd, Rb-Sr, and U-Pb relations in the mylonitized amphibolite.

Figure 5. Sm-Nd and U-Pb relations in the porphyroclastic gneiss.

Figure 6. U-Pb and Sm-Nd relations from two metasediment samples (3&4) structurally overlying the mylonitized amphibolite and porphyroclastic gneiss (see fig. 2).

Figure 7. Summary diagram of structural and metamorphic events at the Willimantic dome.
AVALONIAN BASEMENT
(Esmond-Dedham)

AVALONIAN BASEMENT
(Hope Valley)

50 km NW-SE

high-angle normal shear

f/f-pinch-and-swell zone

low-angle normal shear

cross-section to stretching direction

86
Distinctions among Mechanisms of Isotopic Exchange

Volume Diffusion:
- random motion of atoms through a crystal lattice.
- in general, diffusivities are variable for different radiometric systems in a given mineral.
- isotopic exchange is strongly temperature-dependent and favored by fine grain sizes.
- no rock fabric modification.

Dynamic Recrystallization:
- strain accommodated by dislocation glide.
- driven by differences in strain energy (i.e., variable dislocation densities) either between adjacent grains or within different portions of a grain.
- affects all radiometric systems equally in recrystallizing grains.
- isotopic exchange is controlled by rate and extent of recrystallization.
- characterized by grain-size reduction, polygonal grains, highly variable dislocation densities.

Grain Boundary Diffusion Creep:
- strain accommodated by dissolution, grain boundary diffusion, and reprecipitation.
- driven by chemical potential gradients.
- affects all radiometric systems equally in dissolving grains.
- isotopic exchange is strongly favored by fine grain sizes and grain boundary fluid phase.
- characterized by evidence for grain growth and grain dissolution, low average dislocation densities.

![Graph showing X anorthite mole % against distance (µm) in Mylonitized Amphibolite](image)
lozenge interior
high-grade pelitic gneiss
sample 3

lozenge–bounding shear
mylonitic schist
sample 4

---

Pinch-and-Swell Zone

Monazite

Pelitic Gneiss (lozenge interior)
Mylonitic Schist (shear zone)

Intercepts (monazite)
392±7 Ma to 286±20 Ma
(mswd = .18)

---

143Nd/144Nd

Pelitic Gneiss (lozenge interior)

Garnet
Monazite
"Feldspar"

---

147Sm/144Nd

---
Intense Mylonitization
Formation of Avalonian Crust

Avalonian Basement Complex

Acadian Metamorphic Belt

Acadian Orogeny
Extension and Plutonism
Regional Cooling

Gneissic Deformation Metamorphism
Felsic Plutonism
Cooling / Uplift

Age (Ma)
600 500 400 300 250 200
RECENT DEVELOPMENTS IN DATING ANCIENT CRUSTAL FLUID FLOW

Alex N. Halliday, Matthias Ohr, Klaus Mezger, John T. Chesley, Shun'ichi Nakai, and Charles P. DeWolf
Department of Geological Sciences
University of Michigan, Ann Arbor

Abstract. Several isotopic techniques have recently been developed or substantially improved, allowing the accurate determination of the timing of fluid-related processes. These include K-Ar, Rb-Sr, and Sm-Nd dating of diagenetic minerals in clastic rocks, U-Pb dating of carbonates, Sm-Nd dating of fluorite and uraninite, Re-Os and Rb-Sr dating of sulfides, and Ar-39Ar and Rb-Sr dating of fluid inclusions, and U-Pb dating of ilmenite/magnetite, sphene, and rutile. While many of these techniques require further evaluation, some have already resulted in new constraints on a variety of crustal fluid flow models.

INTRODUCTION

The movement of crustal fluids in the geological past is not easily studied, because the products of such activity generally preserve only partial evidence of the scale of circulation, origins of fluid, and mechanisms responsible for migration. Such fluid movement leads to the redistribution of significant amounts of certain components in the crust, including hydrocarbons [Burst, 1969], and the formation of economic concentrations of metals (Cu, Pb, Zn, U) and other raw materials (such as barite and fluorite) [Bethke, 1986; Bethke and Marshak, 1990; Sverjensky, 1986; Oliver, 1986; Duane and DeWit, 1988]. Fluids are of more fundamental significance than this, however, since they exercise a critical control on the processes of diagenesis, metamorphism, metasomatism, and melting. As such, the timing and scale of fluid movements in the crust are of interest to a far broader range of scientists than those concerned with economic geology per se.

Our understanding of large-scale crustal fluid flow has been hampered by the paucity of constraints on the timing and magnitude of migration and interaction. Radiogenic isotope geochemistry provides tracers to quantify the interaction between fluids and various crustal reservoirs as well as methods of dating the products of fluid flow. This paper is concerned with the latter of these two applications and attempts to point out both the potential and limitations of most of the new techniques, as applied to hydrothermal mineralization, diagenesis, and low-grade metamorphism (<300°C).

The development of reliable geochronology for the growth of specific mineral phases in low-temperature environments has been slow for several reasons.

1. The number of minerals demonstrated to have suitable parent/daughter element ratios for precise geochronology was relatively small until recently.

2. Many of the processes of interest are recorded in mixtures of inherited assemblages formed at different times. As such these phases were not in isotopic or chemical equilibrium.

3. Several of the traditional techniques are subject to resetting or disturbance, particularly those involving metastable phases.

4. The development of some methods has required technical improvements in blanks and mass spectrometry.

As a direct consequence of these problems there has been a lack of tightly constrained models for the timing and ultimate cause of large-scale fluid movements. Furthermore, the complexity of the systems and ambiguity of some of the isotopic data that do exist have resulted in equivocal interpretations.

GLOSSARY

Blanks: Analytical backgrounds that must be corrected for or reduced to negligible levels in order for the data to truly represent the composition of the analyzed sample material.

Closure Temperature: Temperature below which diffusion of the radioactive and radiogenic nuclides is
effectively negligible or, more strictly, the temperature that a slowly cooling mineral had at the time defined by its age [Dodson, 1973].

Diagenesis: Chemical and mineralogical changes in a sediment that take place after deposition including those involved in lithification, for example, compaction, loss of water, low-temperature recrystalization, and later replacement. The term is used by some in the context of processes that occur within a few million years of deposition but more broadly by others. It does not include metamorphic and metasomatic reactions.

Metasomatism: Chemical and, in some instances, mineralogical modification of rocks via medium- to high-temperature fluids.

TRADITIONAL APPROACHES

The major problem with traditional chronometers of crustal-scale fluid flow is that those which are most commonly deployed reset easily with mild heating (<200°C), chemical exchange with hydrothermal fluids, or stress-activated recrystallization. For example, it has long been known that K-Ar and 40Ar<sup>-</sup>39Ar dating of hydrothermal feldspars and clays suffer from the problem of low-temperature resetting [Halliday, 1977; Halliday and Mitchell, 1976, 1984]. While it is well established that these minerals retain argon at temperatures below 100°C [Ineson and Mitchell, 1972; Bonhomme et al., 1983; Aronson and Lee, 1986], it is doubtful that such minerals completely retain Ar for long periods at higher temperatures or in hydrothermal environments. If the thermal history is not well established, as for example in many older rocks, it will be difficult to discern whether clays and feldspars have lost Ar during burial and deformation (in the case of sedimentary rocks) or repeated hydrothermal activity (in the case of vein systems) and hence yield ages that merely date the last tectonic or thermal disturbance. Such a disturbance could be of interest and may correspond to fluid flow [Macintyre, 1986], but it is difficult to be certain whether the apparent ages correspond to the growth of the mineral, to later deformation or heating, or are geologically meaningless because of partial resetting.

A major problem with feldspars and clays is that there does not exist at this time a clear understanding of the transport paths for Ar loss and why some feldspars are more retentive than others. Some early models based on the assumption that the width of alkali feldspar exsolution lamellae defines the effective grain size for diffusion [Harrison and Bé, 1983] have largely been superseded by models that consider argon loss properties to be dominated by submicroscopic pores and domain (or subgrain) boundaries [Parsons et al., 1988; Lovera et al., 1989; Kelley et al., 1989]. Certainly, evidence for fluid-related microcracks and micropores in feldspars is abundant [Montgomery and Brace, 1975; Rodgers and Holland, 1979; Worden et al., 1990; Walker, 1990] and presents a severe difficulty to those attempting to infer loss properties of feldspars in the low-temperature fluid-rich environments of diagenesis and hydrothermal activity.

Such ambiguities surround the often cited conclusion that widespread formation of K-feldspar overgrowths and illite in early Paleozoic sedimentary rocks in the Appalachians took place during the Alleghanian Orogeny at circa 300 Ma [Hearn and Sutler, 1985; Hearn et al., 1987; Elliot and Aronson, 1987]. The data can also be interpreted in terms of partial resetting during burial and deformation [Crandock and van der Pluijm, 1989].

The 40Ar<sup>-</sup>39Ar dating of feldspars and K-Ar dating of clays are clearly useful for studying thermal histories [Harrison and McDougall, 1982; Harrison and Bé, 1983], for determining minimum ages and timing of hydrothermal overprinting [Halliday and Mitchell, 1984; Jackson et al., 1982], or for dating the growth of diagenetic minerals formed during or immediately following lithification in young sedimentary rocks for which a low-temperature (<100°C) thermal history can be established with some confidence [Aronson and Hower, 1976; Aronson and Douthit, 1986; Lee et al., 1989]. The most reliable K-Ar geochronology of ore deposits utilizes 40Ar<sup>-</sup>39Ar dating of coarsely crystallized micas [Snee et al., 1988], combines the data with Rb-Sr studies of the same minerals [Jackson et al., 1982; Böhike and Kistler, 1986], or is undertaken on a variety of different minerals in a young setting [Bethke et al., 1976].

The U-Th-Pb dating of fine-grained U and Th rich minerals such as pitchblende and coffinite can suffer analogous problems of Pb loss, although it may be possible to discern the original history from the Pb isotopic compositions [Stuckless et al., 1979; Cunningham et al., 1982; Ludwig et al., 1984; Hon et al., 1985].

Model ages offer another rather limited approach in which an "age" is calculated assuming a specific source for the components (hence initial isotopic composition). Such approaches have been used for Pb, Sr, and Nd isotopic ages [Godwin and Sinclair, 1982; Ruiz et al., 1984; Kesler et al., 1988; Halliday et al., 1986, 1990]. However, in many situations the source of components is poorly constrained, and as a consequence, the results are dependent on the model chosen. Even if source reservoirs have been characterized in detail, it needs to be established that the fluids equilibrated isotopically with the bulk lithologies rather than with a select assemblage of minerals that were more susceptible to leaching and reaction with the fluids [Halliday et al., 1990].

NEW APPROACHES

The most promising new techniques generally involve small samples, necessitating low blanks and high-sensitivity mass spectrometry but utilize decay systems
that have been studied for some time including $^{87}$Rb-$^{87}$Sr, $^{147}$Sm-$^{143}$Nd, $^{40}$K-$^{39}$Ar, $^{40}$Ar, $^{238}$U-$^{206}$Pb, and $^{187}$Re-$^{187}$Os.

Of these, the $^{187}$Re-$^{187}$Os system has been least studied because of difficulties with the chemical preparation and the ionization of Os, traditionally tackled using secondary ionization or resonance ionization mass spectrometry. It has recently been shown that Os isotopic compositions can be determined relatively simply and at much higher sensitivity using negative thermal ionization mass spectrometry [Creaser et al., 1991]. This has greatly helped to pave the way for a variety of interesting new studies using Os isotope geochemistry. Reconnaissance studies of hydrothermal ores and clastic sediments [Luck and Allègre, 1982; Ravizza and Turekian, 1989; Walker et al., 1989] indicate considerable fractionation of Re/Os ratios in fluid-related crustal processes and precipitation of sulfides, offering potential as a chronometer of crustal fluid flow.

Even though the uses of the other decay schemes have been appraised more fully, the most exciting developments with respect to dating crustal fluid flow are still in their infancy and need to be evaluated carefully on a mineral-by-mineral basis, to determine the closure temperatures and general robustness to resetting. In all of these systems it is critical that the ratio of the parent element to the daughter element should be relatively high and/or display a considerable range among a cogenetic suite of minerals and that the amount of radiogenic daughter isotope should be high relative to background levels (be they "common" inherited components or analytical blank).

In many of the techniques that we now discuss the exact host of the parent and daughter elements and the factors controlling the fractionation of parent/daughter ratio are ill defined. This is because a number of the new techniques utilize host minerals into which the radioactive parent element does not readily substitute. For many of these it is far from obvious whether the parent element is hosted in defects, strained sites, or submicroscopic inclusions of some minor phase, distinct from the major host mineral. It is then even more difficult to assess what factors are controlling the parent/daughter ratios. In certain instances this may be of little consequence, but in low-temperature nonequilibrium environments it is critical to know which phase and process in the potentially complex, multistage history is being dated.

### Dating Diagenesis

K-Ar dating of illite and diagenetic K-feldspar over-growths have been used very effectively to date the diagenesis of clastic sediments and migration of hydrocarbons in young sedimentary basins [Lee et al., 1985, 1989; Liewig et al., 1987; Girard et al., 1988; Hamilton et al., 1989; Burley and Flisch, 1988]. Laser probe $^{40}$Ar-$^{39}$Ar dating of clastic diagenesis, as first illustrated by the work of York and Hall [1986], has been surprisingly slow to develop. Kelley et al. [1989] report the presence of a component of excess argon in alkali feldspars which can be degassed easily by mild heating at low temperatures but otherwise results in meaningless total degassing ages using a pulsed laser. These effects need to be carefully evaluated before further progress can be made.

Some recent studies of fluid-induced clay diagenesis in clastic sedimentary sequences have highlighted the potential usefulness of Rb-Sr dating of authigenic illite, provided great care is exercised in eliminating older mineral grains that were part of the original sedimentary detritus and removing nonradiogenic Sr by acid leaching [Clauer, 1976, 1979, 1982; Chauduri and Brookins, 1979; Ohr et al., 1991]. A more controversial approach has been to use the combined Rb-Sr data for the leachate and for the residue from leaching, to define the age of illite growth [Erwin and Long, 1989], assuming that exchangeable Sr has not reequilibrated with later pore fluids since crystallization of the illite. In certain cases it can be shown that such late reequilibration has in fact occurred and such ages would be meaningless [Ohr et al., 1991]. In contrast, the residues from leaching of fine-grained clay fractions (assumed to be pure diagenetic illite) commonly display a reasonable spread in Rb/Sr (possibly inherited from the rock-dominated pore fluid). The Rb-Sr isotopic data for such leached diagenetic clays sampled over a considerable depth range (>1,000 m) can define an apparent isochron, thought to define the age of growth of the authigenic illite. Results obtained in this manner have been interpreted in terms of simultaneous fluid movement over several thousand meters of sediment [Morton, 1985a, b; Ohr et al., 1991].

There are some critical questions to be addressed in this type of work. For example, what exactly is happening to the clay grains during the leaching procedure? Is "exchangeable Sr" absorbed in some way on the clay surfaces or does it represent submicroscopic growth of soluble low-temperature phases? Is the exchangeable Sr irrelevant or does it record an important aspect of the fluid-mineral interaction history? What controls the variations in Rb/Sr in the leached residues of fine-grained authigenic illite; is it protolith variations in Rb/Sr? If so, there must surely be some heterogeneity in initial $^{87}$Sr/$^{86}$Sr in such a rock-dominated diagenetic system. Despite considerable efforts, these important aspects remain largely unresolved.

Awwiller and Mack [1989, 1991] have argued that Sm/Nd can be fractionated during diagenesis of fine-grained clastic sediment. This has been confirmed by the findings of Ohr and Halliday [1990] who have shown that leaching of fine-grained authigenic illite fractions from clastic sediments produces a leachable component with high Sm/Nd, in apparent isotopic equilibrium with nonleachable diagenetic illite with low Sm/Nd at the time of diagenesis. In this respect, the commonly held assumption that the rare earth elements are immobile in clastic
diagenesis is clearly incorrect. Research on Paleozoic low-grade metasediments from the Appalachians and the Welsh Basin indicate that it may be possible to date fluid equilibration in older clastic rocks using such a single sample approach [Ohr and Halliday, 1990]. Again, the questions of what the leachable component represents and the mechanisms of Sm/Nd fractionation need to be addressed. In this respect, it is important to determine the chemical composition of the leaches and examine the mineral separates before and after leaching using scanning transmission electron microscopy. There is, however, a clear advantage of single sample Sm-Nd leachate-residue ages over the Rb-Sr isochron approach, namely that the effect of provenance variations can be eliminated.

In recent years the U-Pb and Pb-Pb methods have found increasing application in the dating of marine carbonates and their metamorphosed equivalents [Moorbath et al., 1987; Jahn, 1988; Smith and Farquhar, 1988; DeWolf and Halliday, 1989; Jahn et al., 1990]. The high U/Pb commonly found in such rocks is partly a reflection of the high U/Pb of seawater. However, high U/Pb has also been found in secondary dolomites [Hoff and Jameson, 1989], and U-Pb dating of secondary carbonates associated with late fluid movements in limestones and hydrothermal vein systems may be possible. U-Pb dating of limestones appears to be a relatively robust technique that may record the time of early diagenesis [DeWolf and Halliday, 1991] even when the rocks have been disturbed. For example, the Paleozoic limestones of New York State acquired a pervasive fluid flow during the Alleghanian Orogeny [Wisniewiecke, 1983; Jackson et al., 1988; Van der Voo, 1989] yet display no sign of this disturbance in the U-Pb systematics of the calcites [DeWolf and Halliday, 1989]. The mechanisms of U incorporation are not well understood, and it may be a late process [Hoff and Hanson, 1990]. Chung and Swart [1990] have suggested that variations in U concentration in carbonates may result from changes in the CO$_2$ of the fluid, together with selective exclusion of U during precipitation of calcite.

U-Pb techniques have also been applied to hydrocarbons themselves [Parnell and Swainbank, 1990], and the direct dating of oil formation or accumulation may be possible in the near future.

Dating Mineralization

The Rb-Sr method has been successfully applied to hydrothermal phases such as low-temperature K-rich alkali feldspar with high Rb/Sr, fine-grained muscovites, and sulfides [Halliday, 1980; Jackson et al., 1982; Nakai et al., 1990; Brannon et al., 1991]. In the case of sulfides it is unclear where the small amounts (<1 ppm) of Rb and Sr are located and what exact mechanism produces the range in Rb/Sr. Nonetheless, the method seems to permit the determining of ages of otherwise undateable hydrothermal assemblages such as Mississippi Valley type (MVT) mineralization. The results obtained so far are interesting since the major MVT mineralization in the eastern United States appears to have taken place at circa 380 Ma [Nakai et al., 1990] and therefore cannot be related to large-scale fluid flow during the Alleghanian Orogeny at 300 Ma [Oliver, 1986; Miller and Kent, 1988].

A potentially very promising technique is the application of Sm-Nd dating to hydrothermal assemblages that fractionate rare earth elements (REE) strongly [Möller et al., 1976; McLennan and Taylor, 1979; Alderton et al., 1980; Morgan and Wandless, 1980; Graf, 1984; Humphris, 1984]. The mechanisms of REE fractionation appear to be variable and are in some instances poorly understood. Complexing involving volatile phases such as CO$_2$, Cl, and F could potentially play a role, as well as middle REE substitutions into Ca minerals such as CaF$_2$ (fluorite). In addition, the precipitation of REE-enriched phases in hydrothermal systems can lead to marked changes in Sm/Nd in the fluid. Sm-Nd dating has been applied to heavy REE enriched uraninites [Fryer and Taylor, 1984], scheelites [Bell et al., 1989], and fluorites [Chernyshev et al., 1986; Halliday et al., 1986, 1990; Chesley et al., 1991]. Sm/Nd in fluorite can vary by as much as an order of magnitude in an individual mineral vein, permitting precise (±1%) isochron ages [Chesley et al., 1991]. This technique may be useful for determining the ages of fluorite-bearing MVT deposits.

Another powerful approach has been to study fluid inclusions in quartz with Rb-Sr, U-Pb, and 40Ar-39Ar methods. Rb-Sr dating by total dissolution of quartz, in which it is assumed that the Rb and Sr are held in fluid inclusions, has been highly successful [Powers et al., 1979; Shepherd and Darbyshire, 1981; Shepherd et al., 1982; Shepherd, 1986; Darbyshire and Shepherd, 1987]. Similar approaches have been adopted by Hemming et al. [1990] utilizing the U-Pb technique. All of these studies are useful but suffer from the uncertainty in the location of the Rb, Sr, U, or Pb (fluid inclusion, solid inclusion, or host mineral). This may not be a problem if the fluids and host are truly co-genetic, but if the fluid inclusions are wholly or in part unrelated to the growth of the quartz (as is commonly thought to be the case), the isotopic ages may date this later process. Relatively little work has been done on extracted fluids, and that which exists does not distinguish separate populations of fluid inclusions [Norman, 1978; Norman and Landis, 1983; Changkakoti et al., 1988]. It may prove possible to separate individual generations of fluid inclusions, but this is not a trivial task. For many kinds of fluid inclusions the difficulty of this extraction process is the limiting factor rather than blank or machine sensitivity.

The 40Ar-39Ar dating of fluid inclusions has developed slowly over the past few years [Kelley et al., 1986; Böhleke et al., 1987; Kirschbaum et al., 1987; Turner, 1988]. Turner [1988] shows how, using correlation plots, the different Ar components (radiogenic, atmospheric,
extraneous) can be deciphered in such materials. As with all of the fluid inclusion techniques, there is the limitation of measuring unknown mixtures of different generations of inclusion fluids, unless the inclusions are of sufficient size and age that they can be analyzed on an individual basis with laser methods.

Some of the most impressive geochronologies of hydrothermal ore deposits utilizes the power of the $^{40}$Ar$-^{39}$Ar dating technique for precise resolution of small age differences. Snee et al. [1988] report a resolution of 0.3% in $^{40}$Ar$-^{39}$Ar ages of mica populations from Panasqueira, Portugal. The use of the laser probe $^{40}$Ar$-^{39}$Ar method for dating different phases in hydrothermal mineral assemblages has so far been barely explored [York et al., 1982; Sutter et al., 1983; Hall et al., 1989] but offers exciting possibilities for future research.

Some of the chronometers that have been developed for studying high-grade metamorphism may prove ideal for the dating of other, more demonstrative products of crustal-scale fluid flow. These new chronometers include Sm-Nd, Rb-Sr, and U-Pb dating of garnet [Cohen et al., 1988; Christensen et al., 1989; Mezger et al., 1989a; Vance and O’Nions, 1990] and U-Pb dating of sphene [Tucker et al., 1987], monazite [Copeland et al., 1989], rutile [Mezger et al., 1989b], and ilmenite/magnetite [Burton and O’Nions, 1990]. Corfu and Muir [1989] showed that Precambrian gold mineralization could be dated using accessory phases that grew from the hydrothermal fluids. Similarly, Schandl et al. [1990] utilized hydrothermal rutile to date sulfide deposition and associated alteration. Finally, Zeiler et al. [1990] have been able to deduce the timing of fluid flow in the formation of quartz-graphite veins by U-Pb ion microprobe dating of zircon overgrowths.

Accessory mineral U-Pb chronometers are in some respects superior to all others, since they can give very high precision ($\pm 0.1\%$) ages, and neither reset readily nor suffer from the assumptions of isotopic equilibrium critical to the isochron approach. In addition, with the utilization of ion probe techniques they may be especially useful for placing the detailed mineral parageneses into a framework of absolute time.

CONCLUSION

The new technique developments in isotope geochemistry over the past 5 years have facilitated the accurate dating of a wide range of fluid-related assemblages and have opened up new possibilities for constraining models of geologic processes such as diagenesis, brine migration, mineralization, and hydrocarbon emplacement. The major advances have been in the application of the Rb-Sr, U-Pb, and Sm-Nd systems to new phases in which significant fractionations of the parent/daughter ratio have recently been discovered. These methods complement traditional approaches, some of which are more appropriately used to define thermal histories or date the last significant thermal or tectonic event. The major developments needed include integrated isotopic, chemical, and mineralogical studies of the same geological problem. For example, dating clastic diagenesis could involve combined Rb-Sr, Sm-Nd, and K-Ar dating studies of authigenic illite and associated phases, in which the chemical compositions of leachates are fully determined, and mineral separates and leachate residues are characterized using scanning transmission electron microscopy. More exploratory work is needed and anticipated, specifically with low-temperature applications of Re-Os, Sm-Nd dating of diagenesis, U-Pb dating of hydrocarbons, and $^{40}$Ar$-^{39}$Ar and U-Pb dating of hydrothermal and diagenetic phases. Major problems remain with our understanding of the location of radioactive parents in some of the phases of interest, the factors controlling parent/daughter ratios, and the effects of acid leaching. Finally, new techniques are needed for separating phases of interest at the microscopic and submicroscopic scale, especially fluid inclusions from their host minerals. Further applications may involve broad-scale integrated approaches using a variety of isotopic methods to study large crustal sections and determine the ages of fluid expulsion from sediments, mineral overgrowths in aquifers, hydrocarbon migration, and base metal mineralization and hence assess the relationships between these diverse products of crustal fluid flow. With such information it should be possible to formulate dynamic models of crustal fluid flow that are considerably more reliable than has hitherto been the case.

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REFERENCES


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Halliday et al.: DATING ANCIENT CRUSTAL FLUID FLOW


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Rhenium, osmium and platinum abundances and $^{187}\text{Os}/^{186}\text{Os}$ ratios were determined in six Devonian black shales and associated Ni-Mo enriched sulfide layers from the Nick Property, Yukon Territory, Canada and in seven early Cambrian black shale-hosted Ni-Mo sulfide layers from mines at Tianeshan, Guizhou province, and at Ganziping, Daping and Sansha, Hunan province, China.

Ni-Mo sulfides at the Nick mine are spectacularly enriched (up to 33,164 ppb) in Re, and enriched in Os to a lesser degree. The Ni-Mo sulfides have distinctly higher Re/$^{192}\text{Os}$ than associated black shales, but Pt/Re and Pt/common Os are similar in both black shales and sulfides. The two ore samples lie near a 375 Ma reference isochron with an initial $^{187}\text{Os}/^{186}\text{Os}$ between about 1 and 6, similar to the age of deposition of the associated shales. The ores appear to be approximately isochronous with the overlying shales (Figure 1). This suggests that the sulfide layer was enriched in Re, Os and probably the other PGE soon after deposition of the black shales. One black shale sampled immediately beneath the ore layer lies on the Re-rich side of the errorchron and, since deposition, may have gained Re (and Pt) from the overlying Re-rich sulfide.

In the Chinese Ni-Mo sulfide samples, Re ranges from 900 to 15,000 ppb. All the sulfides lie near a 530 Ma reference line with an initial ratio between 1 and 6 (Figure 2). As for the Ni-Mo sulfide layer in the Yukon, Re and Os have seen only minor redistribution since soon after the time of deposition of the host shales. Five of the sulfides group closely in $^{187}\text{Os}/^{186}\text{Os} - ^{187}\text{Re}/^{186}\text{Os}$ space, and Re, common Os and Pt ratios are constant these sample five samples, although their locations are separated by as much as 400 km. Two other Ni-Mo sulfides have higher Re/common Os and Re/Pt, and therefore have more radiogenic Os.

The Re and PGE enrichment in sulfide layers in both the Yukon and southern China probably have occurred soon after deposition of the host black shales when oxidizing fluids carrying high concentrations of Re and PGE were introduced into the reducing environment characterized by the black shales. Because the sulfide layers have a conglomeratic texture and were somewhat more permeable than the black shales, the fluids were channelled along the sulfide layers. Re and the PGE would have been easily precipitated in the anoxic environment.
Figure 1. Black shales and sulfides from Yukon, Canada.

Figure 2. Ni-Mo sulfides from southern China.
Precise U-Pb Dating

Precise U-Pb geochronology is providing essential, new information to aid in the understanding of a wide variety of geological problems. Lead background levels have been reduced by six orders of magnitude over the past two decades leading to similar reduction in sample size and increase in sample selectivity. Methods that include abrading away geologically-leached or altered surfaces have been developed so that precise, closed-system results are obtained in most cases, (Krogh 1982).

In ensimatic regimes zircon inheritance is generally absent so ages for volcanism, intrusion and ophiolite formation with geologically-meaningful errors of ± 1 or 2 Ma are routinely achieved, (Dunning and Krogh 1985, Krogh et al., 1988 Davis et al 1985, Corfu and Ayres 1991). In Davis et al. (1985), we report 6 ages for two adjacent rhyolite horizons collected over a 15 km interval that have a range in age of 1.5 m.y. at 2735.5 Ma.

Post-accretion Archean rocks, and young continental arcs can be more challenging since inherited zircons are common (Figs. 1-4). Selection of specific grain types and extremely small samples can aid in avoiding such problems but tests for inheritance must be made. Xenocrysts may be identical morphologically to cognate grains. A special case occurs when single visibly-cored grains provide an age for the granite protolith (Fig.5). In regions of rapid continental overthrusting such as the Grenville Front, where all Ar systems are reset (Haggart, et al. 1992 sub.), both the thrusting and the preceding metamorphic history can be determined by using partially to completely reset or newly-grown titanite, monazite and zircon (Figs.6-8). A special case occurs when coronitic gabbros are found to contain zircon forming at the expense of baddeleyite. These date the time of metamorphism (Fig.9, Davidson and van Breemen, 1988). In regions of more severe overthrusting and metamorphism, titanite and monazite are commonly completely reset while zircon U-Pb systems are preserved even under granulite conditions (Figs. 10, 11). Slow cooling may provide titanite ages younger than the zircon lower intercept. Results for the Kapuskasing granulite terrane indicate successive stages of horizontal laminations and post-accretion dehydration and rehydration suggestive of infra-crustal and crust-mantle delamination, (Figs. 12-16, T.Krogh submitted). Precise ages for these lower crustal processes and for gold deposits in nearby greenstone belts show that both are coeval and post-date magmatism by 20 to 95 Ma. (Fig. 17, Jemielita et al. 1990).

Precise ages for diabase dyke emplacement utilizing baddeleyite, or perovskite provide a means of dating continental rifting. (Figs.18, 19, LeCheminant and Heaman, 1989). These data demonstrate coeval dyke emplacement on 2,000 km scale. Continental plate interactions produce sediments which can be traced to their sources by using the chemically-inert, mechanically-resistant mineral zircon. For example, the Meguma zone of Nova Scotia shows affinity with North Africa, (Keppie and Krogh 1990) and the Torridonian sandstone of Scotland could be derived from Laurentia (Figs. 20-23).

An exceptional example is provided by data for single zircons from the K-T boundary layer that exhibit varying degrees of shock and provide ages for both the K-T event and the impact site at 65.5±3 and 550±10 Ma, respectively.
References

Figure Captions

Fig. 1 U-Pb isotopic results for a single zircon tip and several microgram multigrain zircon fractions for an Archean rhyolite quartz porphyry flow.

Fig. 2 U-Pb isotopic results for single and multigrain fractions for an intrusive granodiorite that cuts the volcanic pile dated in Fig.1.

Fig. 3 Data for two samples from similar volcanic units, one from New Brunswick, the other from Maine, indicate identical ages and inheritance.

Fig. 4 Data for a Nova Scotia granite that illustrate how inherited components can be avoided to provide a precise age of intrusion.

Fig. 5 Large, visibly-cored grains from two Nova Scotia 'S' type granites indicate a common circa 630 Ma protolith. Data for other grains and circa 630 Ma, grain fragments plot between 372 Ma and about 2000 Ma.

Fig. 6 Titanite U-Pb data from the Grenville Front Zone south of Sudbury, Ontario. Note that these "Grenville" gneisses are pre-Grenville.

Fig. 7 U-Pb data for variably reset monazite, new titanite, and new zircon tips (the latter with ages of 987, 987 and 986 Ma) from the Grenville Front north of North Bay, Ontario.

Fig. 8 U-Pb data for titanite, monazite and zircon from a 200 by 100 km zone in the Grenville Front of Labrador. The insert shows data for selected core-free new growth zircon from a Grenville-thrusting-induced melt pod in a 1650 Ma batholith.

Fig. 9 U-Pb data for primary skeletal zircons and new microcrystalline zircon from the Grenville Front tectonic zone in Labrador. New grains define the time of coronite formation at 995±5 Ma.

Fig. 10 U-Pb zircon results for a least-migmatized norite sample (sample 1A), and a highly-reconstituted, melted and deformed sample (sample 2). Note the correlation between degree of discordance and field appearance.

Fig. 11 U-Pb zircon data for variably-discordant grains from an Archean granodiorite in a Proterozoic granulite terrane. The most and the least discordant grains were selected on the basis of lustre and have 50 and 500 ppm uranium, respectively.

Fig. 12 Location map showing main structural elements of the Superior Province and the Kapuskasing structural zone.

Fig. 13 Geological relationships in the study area.

Fig. 14 U-Pb isotopic results for selected grains and grain fragments representing successive zircon growth stages.

Fig. 15 U-Pb isotopic duplicate results for small and large grains from 200-600 g conglomerate clasts.

Fig. 16 Schematic diagram illustrating how ages of ductile and brittle deformation young with depth.

Fig. 17 Isotopic results for titanite and rutile from the Camflo gold deposit.

Fig. 18 Map showing the extent of the MacKenzie dyke swarm.

Fig. 19 U-Pb isotopic ages for baddeleyite from dykes in the MacKenzie dyke swarm.

Fig. 20 Overview of U-Pb zircon data for detrital grains from the Goldenville
Fig. 21  Detail of Lower part of Fig. 20.
Fig. 22  Detail of Upper part of Fig. 20.
Fig. 23  Results for detrital grains from the Torridonian sandstone, Scotland.
Fig. 24  U-Pb data for zircons used to date the Ordovician time scale (Tucker, et al. 1990).
Fig. 25  Results for variably-shocked and reset zircons from the K-T boundary layer.
Pb isotopic composition of Paleozoic sediments derived from the Appalachian orogen.

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In Phanerozoic Earth history, the relatively depleted state of shorter-lived 235U relative to longer-lived 238U has resulted in a subdued growth rate of 207Pb relative to that of 206Pb. Thus, differences in 207Pb/204Pb at similar 206Pb/204Pb values must date from pre-Phanerozoic times, when the relative growth rate of 207Pb was greater. These differences in 207Pb/204Pb at similar 206Pb/204Pb are robust indicators of the earliest history of a crust or mantle reservoir, surviving later changes in U/Pb that may be due to melting, metamorphism, or sedimentary reworking. Distinct Pb isotopic compositions of discrete crustal blocks have been used as a tracer of magmas derived from those blocks. In the Appalachians, Ayuso (1986) and Ayuso and Bevier (1991) have used the 207Pb/204Pb differences between Devonian granites to trace their sources in either Laurentian ("Grenville") lithosphere, or allochthonous, docked ("Avalonian") lithosphere. If the Pb isotopic composition of Avalonian lithosphere is unique to that source, among all lithospheric reservoirs in the Appalachian orogeny, then the sediments shed off the orogen should record the first appearance of rocks with this extraneous Pb isotopic composition as they become accreted. Pb isotopic compositions of Paleozoic sediments in the Appalachians have been determined for a variety of sedimentary, metasedimentary, and basement rocks from three major areas in the orogen. These are N. Maine (collaboration with R. Hon, Boston College), W. New England (collaboration with G. N. Hanson, Stony Brook), and S. Virginia (samples from M. Norman, ANU, and K. Eriksson, VPI). Analysis of samples from Maryland has also been initiated.

The high 207Pb/204Pb at similar 206Pb/204Pb that may be indicative of all "outboard" terranes, including Avalonia, occurs in all igneous, metaigneous and -sedimentary rocks in the Waterbury-Bridgeport CT area. It also occurs in rocks younger than middle Ordovician in New York and Maine, and younger than Ordovician in Virginia. Older sediments (Hadrynian, Cambrian), as well as autochthonous basement and paraautothonous basement slices, have lower 207Pb/204Pb at similar 206Pb/204Pb. The low 207Pb/204Pb at similar 206Pb/204Pb shown by these rocks may be a locally diagnostic signature of Late Proterozoic Laurentian lithosphere. The high 207Pb/204Pb at similar 206Pb/204Pb may be a locally diagnostic signature of Late Proterozoic accreted terranes. Rocks with the "accreted terrane" Pb isotopic composition became dominant in the provenance of sediments along the strike of the Appalachian orogen by middle Ordovician time.

Because sediments tend to mix materials from various parts of their provenance, "unmixing" of grain populations would seem a logical next step to determining various isotopic sources. Such unmixing studies, stressing highly stable accessory minerals (monazite, zircon), have been made by other workers. These minerals, while preserving U-Pb age information, do not preserve Pb isotopic initial ratios. However, single grain isotopic studies of major minerals (preserved feldspars, etc.) should more accurately represent the compositions of various source components.
ALLEGHANIAN CLEAVAGE AND ACADIAN DIAGENESIS IN THE MARTINSBURG FORMATION, EASTERN PENNSYLVANIA: $^{40}\text{Ar}/^{39}\text{Ar}$ WHOLE-ROCK DATA AND GEOLOGICAL CONSTRAINTS

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$^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum analysis of whole-rock samples from the Ordovician Martinsburg Formation at Lehigh Gap, eastern Pennsylvania, and structural and stratigraphic constraints support an Alleghanian age for the regional slaty cleavage and an Acadian age for initial diagenesis in these rocks. The $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra from mudstone and slate samples from the Martinsburg climb from Tertiary to late Proterozoic ages and are sigmoidal in shape. They are interpreted to reflect simultaneous degassing of a mixture of detrital late Proterozoic muscovite, late Devonian authigenic white mica, and early Permian cleavage-forming muscovite. The 280±10 Ma age of cleavage is calculated by subtracting the total gas ages of a parent mudstone from a daughter slate sample. A similar method is used to calculate the ~360 Ma age of authigenic mica in the mudstone sample. These interpretations are supported by the calculated pressure-temperature-time path for these rocks, based on measured sections and inferred Permian tectonic loading. The calculations show that diagenetic conditions consistent with the illitization of smectite were first reached in the Middle Devonian, and that temperature >250°C were first reached in the Early Permian. No regional cleavage was produced in the Martinsburg Formation at Lehigh Gap during the Taconic orogeny--these rocks were buried by no more than 2 km of overburden prior to deposition of the unconformably overlying Silurian Shawangunk Formation.
References for "Radiogenic Isotopes in Seawater and Sedimentary Systems"


Capo, R.C. and DePaolo, D.J. (1990) Seawater strontium isotopic variations from 2.5 million years ago to the present. Science 249, 51-55.


A representation of the geochemical cycling of Sr, showing the important sources and sinks. This figure is modified after that in Palmer and Elderfield (1985). "Limestone" is used here to represent all types of marine sediment that carry Sr of seawater origin, i.e. carbonates in general, evaporites, etc.

Figure 1 from Burke et al., 1982.
Fig. 1 (left). Measured \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios and \(\Delta^{87}\text{Sr}\) values of late Eocene and Oligocene chalks and marls plotted as a function of stratigraphic position as determined by magnetic reversals (11, 20). Numbers on lower scale designate the paleomagnetic chron (6). The \(\Delta^{87}\text{Sr}\) parameter is the difference between a measured \(^{87}\text{Sr}/^{86}\text{Sr}\) value and the value for modern carbonates, multiplied by 10\(^5\).

Fig. 2 (right). Measured \(^{87}\text{Sr}/^{86}\text{Sr}\) and \(\Delta^{87}\text{Sr}\) values of Cenozoic marine carbonate samples as a function of age.

Fig. 1. Three-point running average of Sr isotopic data for the past 8 Ma. The error bars are \(\pm 14 \times 10^{-6}\) and represent 95% confidence limits. The \(^{87}\text{Sr}/^{86}\text{Sr}\) seawater curve is marked by a series of steep climbs and plateaus, with two slope changes at \(\sim 5.5\) and \(\sim 2.5\) Ma, which mark the beginning of steep rises in \(^{87}\text{Sr}/^{86}\text{Sr}\) values.

The \(^{87}\text{Sr}/^{86}\text{Sr}\) record is quite well defined for the Tertiary, but shows much more scatter for earlier times, as is obvious from the Figure from Burke et al. on the previous page. But even in the Tertiary, the record shows inflections at almost every level of resolution, as can be seen from the examples above. Figs. 1 and 2 (top) are from DePaolo and Ingram (1985); Fig. 1 (below) is from Hodell et al. (1990).
The Nd isotopic composition of present day seawater is not constant, unlike the case for $^{87}\text{Sr}/^{86}\text{Sr}$. Fig. 5a (left) shows two Atlantic Ocean profiles from Piepgras and Wasserburg, 1987.

Keto and Jacobssen (1988) have attempted to construct a "global average" Nd isotope curve for seawater over the past 800 Ma in Fig. 5 (left). Note the inter-oceanic variability. Except possibly for the high values of $\epsilon_{\text{Nd}}$ near the Permian-Triassic boundary, where the Sr isotopic ratio plummets to low values, there is little correspondence between Sr and Nd isotopic records.
O’Nions et al. (1983) showed that stratigraphic and calculated model ages for crustal sediments diverge for younger rocks (left), suggesting sedimentary recycling. At first glance, Sr isotopes do not support this hypothesis, but Goldstein (1988) proposed that the discrepancy is due to open system behavior, with possibly the addition of small amounts of high Sr content, low \(^{87}\text{Sr}/^{86}\text{Sr}\) orogenic material to the sedimentary mass. In addition, weathering removes Sr and adds Rb to the sediments. Figs. 1a, 1b and 1c below are from Goldstein (1988).
Fluid inclusions in vein quartz from the radiometrically dated Late Cretaceous Buckingham stockwork molybdenum deposit and from quartz veins associated with radiometrically dated late Eocene to early Oligocene leucogranites near Buckingham yield isochron ages corresponding to these periods of igneous activity. The younger period (late Eocene to early Oligocene) is clearly defined by three isochrons at about 38 Ma. The Late Cretaceous age is recognized by three isochrons, one well defined at 75.5 ± 1.1 Ma, one that is 55.1 ± 3.7 Ma and one that is 51.2 ± 16.3 Ma. All samples had inherited excess \(^{40}\text{Ar}\) in amounts of about 30 percent of the total argon. Because of the excess argon, individual age determinations are highly variable and cannot be interpreted—iscochrons based on several analysis are necessary to yield a meaningful age. Samples with small amounts of potassium proved unusable; sufficient potassium must be present to have produced enough radiogenic \(^{40}\text{Ar}\) to mask the excess \(^{40}\text{Ar}\).
CONCLUSIONS

$^{40}$Ar/$^{39}$Ar dating of fluid inclusions in igneous minerals has promise as a means of dating the fluid and hence the age of mineralization assuming that the two are related and nearly synchronous. Several limiting factors are apparent from the quartz samples from the Battle Mountain mining district, Nevada.

1) Excess inherited $^{40}$Ar may be present, and should be expected, in the trapped fluid. Because of this a number of analysis are needed to provide points on a $^{40}$Ar/$^{36}$Ar versus $^{39}$Ar/$^{36}$Ar diagram from which an isochron can be drawn. The slope of the isochron gives the age, the intercept on the ordinate ($^{40}$Ar/$^{36}$Ar axis) indicates the amount of excess argon if the value is above 295.5 or the $^{40}$Ar/$^{36}$Ar of air.

2) Samples with small amounts of potassium which yields proportionally small amounts of $^{39}$Ar on irradiation are difficult to analyze with good precision and produce points on a $^{40}$Ar/$^{36}$Ar versus $^{39}$Ar/$^{36}$Ar diagram that cluster near the $^{40}$Ar/$^{36}$Ar axis and are of little value in describing an isochron. Low potassium samples proved nearly unusable in this study.

3) Areas with several periods of igneous activity such as Battle Mountain (Late Cretaceous and late Eocene to early Oligocene) probably produce several populations of fluid inclusions. At Battle Mountain the youngest period of igneous activity (late Eocene to early Oligocene) proved datable with reasonable confidence. The Late Cretaceous event was evident but obscure. The mechanism for partial argon loss from fluid inclusions and of multiple periods of fluid entrapment in minerals is poorly understood but has a great effect on dating of mixed populations of fluid inclusions by the $^{40}$Ar/$^{39}$Ar technique.
K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ ages of the Buckingham stockwork system and nearby intrusive rocks. Location shown on fig. 2. From McKee 1992.

<table>
<thead>
<tr>
<th>Rock type (host rock fig. 2)</th>
<th>Mineral dated</th>
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<td><strong>Buckingham stockwork system</strong></td>
<td></td>
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<tr>
<td>Monzogranite porphyry</td>
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<td>61.3 ±1.5</td>
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<tr>
<td>&quot;</td>
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<td>61.7 ±1.5</td>
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<tr>
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</table>

| **Intrusive rocks north and southwest of Buckingham stockwork system** |               |                     |
| Rhyolite                    | Biotite       | 37.3 ±1.1           |
| Leucotonalite               | Hornblende    | 37.7 ±1.4           |
| Monzogranite                | Biotite       | 38.8 ±1.1           |
| "                           | Hornblende    | 39.0 ±1.1           |
| Rhyolite                    | Biotite       | 39.1 ±1.0           |

| **Intrusive rock northeast and cutting Buckingham stockwork system** |               |                     |
| Granodiorite porphyry       | Hornblende    | 35.4 ±1.1           |

1/ Age from the two greatest release steps from an incremental heating $^{40}\text{Ar}/^{39}\text{Ar}$ experiment
$^{40}$Ar/$^{36}$Ar versus $^{39}$Ar/$^{36}$Ar diagram with isochron plots from all samples from the Battle Mountain district.
REFERENCES


____, 1974, $^{40}\text{Ar}^{39}\text{Ar}$ age spectra of some undisturbed terrestrial samples: Geochimica et Cosmochimica Acta, v. 38, p. 715-738.


Isotopic provinciality in the shallow mantle, on-craton & off-craton volcanism, and implications for lithospheric growth in the western USA.

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University of London,
England

INTRODUCTION

Information regarding the temporal and spatial evolution of the continental lithosphere is forthcoming from the study of exposed crustal rocks and high pressure xenoliths. Basement crustal rocks [Zartman 1974] indicate that growth of the circum-cratonic lithosphere of the western USA, in post-Archaean times, occurred to the south and west of the ancient cratonic nucleus in Wyoming-Montana [Ernst, 1988; Hoffman, 1988]. Gradual accretion of oceanic/arc terranes took place in the early Proterozoic and continued into the late Proterozoic and Phanerozoic when supra-subduction processes dominated. During the late Phanerozoic crustal thickening and extension led to recrystallisation and deformation of crustal rocks. Intrusive crustal rocks (e.g. volcanic rocks) erupted in late Phanerozoic times [Armstrong 1970], provide a present-day probe of deep lithosphere composition and evolution. Pioneering studies noted lateral changes in the source region of volcanic rocks [Hedge 1966; Doe et al., 1969; Leeman 1970; Hedge and Noble 1971] and the presence of mantle heterogeneity in the deep lithosphere. Several decades later the presence can be demonstrated of unique on-craton reservoirs and “oceanic” off-craton reservoirs. Moreover the coincidence of these lithospheric domains with crustal age provinces is marked and their tectonic context similar to that of crustal rocks. High pressure xenoliths preserve a history of on-craton and off-craton isotopic provinciality that is consistent with deductions made from crustal rocks - (a) formation of a >2500 Ma cratonic nucleus in Montana-Wyoming stable to depths in excess of 150km; (b) modification of that cratonic keel by post-Archaean processes (subduction); (c) circum-cratonic accretion of oceanic lithosphere incorporating a recycled lithospheric component (eclogites), and (d) asthenospheric upwelling and the formation of young continental lithosphere in regions of Phanerozoic extension (Figure 1).

Figure 1. Peridotite stability fields beneath the continental crust. Note the predominance of garnet peridotites (GP) beneath the craton, spinel peridotite (SP) beneath mobile belts and the overall paucity of plagioclase peridotites (PP) except in regions of considerable crustal extension. Lithospheric architecture changes in a similar fashion from the Basin and Range (oceanic) to the Wyoming-Montana craton (cratonic).
Lithospheric mantle comprises a mechanical boundary layer (MBL), which provides an isolated repository for the development of aged isotopes. The thermal boundary layer, at the base of the MBL, acts as an important buffer between the rigid cold lithosphere and the hot convecting asthenosphere believed to have the characteristics of MORB (mid-ocean ridge basalt) or OIB (ocean island basalt). Heat flow and seismic data reveal that convecting asthenosphere occurs at shallow depth beneath the Basin and Range and the southern Rio Grande rift thus insuring that the TBL has the characteristics of MORB/OIB. Consequently a thick, heterogeneous MBL has not survived in parts of California, Arizona and New Mexico but seismic tomographic data [Grand 1986] and the occurrence of diamondiferous kimberlites indicate that a thick MBL exists elsewhere in Montana, Wyoming and northern Colorado.

ON-CRATON XENOLITHS

Geochemical data on xenoliths from within the cratonic part of the western USA are restricted to the Crazy Mountains [Dudas et al., 1987] and the Highwoods [Irving & Carlson, 1991]. The Crazy Mountain xenoliths have isotopic ratios similar to the Leucite Hills and Crazy Mountains magmas (EM1) and the Highwoods xenoliths much higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (EM2)(Figure 2). The approximate range of on-craton xenolith data is $^{87}\text{Sr}/^{86}\text{Sr} = 0.706-0.769$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.5120-0.5105$, in part equivalent to EM1 and EM2 domains. Recent Re-Os data for the Highwoods reveal melt extraction in the late Archaean and melt migration in the late Archaean to early Proterozoic. Ancient metasomes with extremely low $^{143}\text{Nd}/^{144}\text{Nd}$ ratios may be important in the genesis of on-craton potassic and ultrapotassic volcanic rocks.

OFF-CRATON XENOLITHS

In contrast to the on-craton xenoliths, the off-craton xenoliths of the western USA are amongst the most intensively studied in the world [Eggle et al., 1987; Wilshire et al., 1988 for comprehensive review]. Basalt-borne xenoliths are characterised by $^{87}\text{Sr}/^{86}\text{Sr} = 0.7018-0.7065$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.51345-0.51240$ (Figure 2) similar to depleted oceanic domains (DMM and OIB) with a propensity toward an enriched arc component (EM2) in some xenoliths (e.g. Sierran Province, Colorado Plateau). This isotopic range is significantly different from that of on-craton xenoliths and to a large degree this difference reflects time and not necessarily the enrichment process. Overall off-craton xenoliths indicate that several enrichment processes have affected the lithosphere in post-Archaean times. An integration of petrological, geochemical [Kempton et al., 1987] and isotopic [Menzies et al., 1985] data reveal that the depleted mantle protolith (formed in the Proterozoic) was enriched by suprasubduction and intraplate processes in the Proterozoic to Phanerozoic (Menzies, 1990). The spatial relevance of such chronological information has been investigated beneath the Colorado Plateau where the lower lithosphere is chemically stratified [Roden et al., 1990]. Immediately beneath the crust the lithosphere comprises a depleted spinel peridotite protolith ($^{87}\text{Sr}/^{86}\text{Sr} = 0.703$, most probably produced and stabilised in the Proterozoic, which has been enriched ($^{87}\text{Sr}/^{86}\text{Sr} < 0.706$) in the Proterozoic and Phanerozoic by upwelling melts from sub-lithospheric sources.

Figure 2 - Sr and Nd isotopic variability in xenoliths from the western USA. Note that the on-craton lower lithosphere is enriched (EM1/EM2) and the off-craton lower lithosphere is primarily depleted with a propensity toward enriched (arc) compositions (EM2).
Figure 3. Sr and Nd isotopic variability in volcanic rocks and xenoliths from the western USA. Off-craton volcanic rocks have mantle sources broadly similar to mid-ocean ridge basalts (Geronimo, Arizona), ocean island basalts (Lunar Crater, Nevada) or island arcs (Navajo, Sierran Province). On-craton volcanic rocks have a source component that appear to be unique to the lower lithosphere beneath the Archaean crust (after Menzies 1989).

ON-CRATON AND OFF-CRATON VOLCANIC ROCKS

In general, throughout the western United States elemental abundances and isotopic ratios in volcanic rocks (Figure 3) vary in accordance with the age of the basement and the thickness of the underlying crust [Leeman 1982, Menzies 1989].

ON-CRATON VOLCANIC ROCKS

Alkaline/potassic/ultrapotassic volcanic rocks are found within the craton in the Highwood Mountains, Elkhead Mountains, Smoky Butte, Crazy Mountains, Independence, Leucite Hills and Bearpaw Mountains [Vollmer et al., 1984; Fraser et al., 1985; Meen and Eggler, 1987; Leat et al., 1988; O'Brien et al., 1991; MacDonald et al., 1992] (Figure 3). On-craton alkaline volcanic rocks exhibit a range in $^{87}$Sr/$^{86}$Sr=0.704-0.710 and $^{143}$Nd/$^{144}$Nd=0.5126-0.5113 very different from that observed in oceanic volcanic rocks. While tholeiitic volcanic rocks from the Yellowstone Plateau Volcanic Field and the Snake River Plain [Leeman 1982; Doe et al., 1982; Menzies et al., 1983] are also erupted within the craton they have less extreme isotopic ratios similar to the Sierran Province volcanic rocks (Figure 3). Although the origin of these “flood basalts” is debated [Carlson et al., 1981; Carlson 1984] the alkaline to ultrapotassic magmas are believed to be wholly derived from within the Archaean lower lithosphere. This cratonic domain is preserved in a region of low heat flow and thick crust (50 km) similar to the Kaapvaal craton of South Africa. It is apparent from Figures 3 & 4 that the cratonic lithosphere has a unique isotopic character and location, a result of both process and, more importantly, age.

OFF-CRATON VOLCANIC ROCKS

Off-craton alkaline and tholeiitic volcanic rocks have been intensively studied within the Great Basin, Colorado Plateau and the Rio Grande Rift [e.g. Hedge 1966; Doe et al., 1969; Leeman 1970; Hedge and Noble 1971; Van Kooten 1980, 1981; Leeman 1982; Menzies et al., 1983,1985,1991; Hart 1985; Perry et al., 1987; Fitton et al., 1988; Leat et al., 1988; Ormerod et al., 1988; Farmer et al 1989; Lum et al., 1989; Fitton et al., 1991; Kempton et al., 1991]. The difference between on- and off-craton volcanic rocks is immediately apparent (Figure 3) and is similar to the differences observed between on-craton and off-craton kimberlites in South Africa [Smith 1983]. In general off-craton volcanic rocks fall into two groups (a) those derived from sources similar to the source of oceanic magmas, or (b) those derived from an “arc” source with elevated LIL/LREE ratios. It can be inferred from these data that the cratonic nucleus in Wyoming-Montana is surrounded by accreted Proterozoic lithospheric domains with some of the attributes of oceanic lithosphere formed at active margins [Ernst 1988; Ormerod et al., 1988]. These mantle domains are characterized by $^{87}$Sr/$^{86}$Sr < 0.707 and $^{143}$Nd/$^{144}$Nd > 0.51240 [Fitton et al., 1988]. “Arc” like lower lithosphere is evident in recently enriched (<200 Ma) off-craton xenoliths from the western USA [Mattey et al., 1989]. In contrast regions of thinned continental crust and high heat flow are characterised by the presence of mantle identical to the source of mid-ocean ridge or ocean island basalts (Figure 4). This presumably replaced most of the pre-existent “arc” like lithosphere in the southern Basin and Range and the Great Basin [Menzies et al., 1983]. Many Basin and Range xenoliths can be interpreted as fragments of
recently accreted (< 200 Ma) MORB or OIB mantle - the compositional antithesis of the on-craton source for potassic volcanic rocks.

Figure 4 - Mantle source character for volcanic rocks in relation to crustal thickness. While the EM1 domain (filled circles) appears to be unique to the thick crust of the Wyoming-Montana craton, the sub-lithospheric DMM sources (open circles) are dominant in the areas of thin crust in California, Nevada, Arizona, & New Mexico. Accretion of lithosphere during destructive plate processes in the Proterozoic and Phanerozoic may account for the enriched ("arc") character (EM2) (half-filled circles) of the circum-cratonic lithosphere. Accretion of young intraplate lithosphere explains the presence of depleted (DMM/OIB) shallow mantle in the Basin and Range, a region where crustal extension has permitted upwelling of asthenosphere (after Menzies 1989).

CRUSTAL EXTENSION & SOURCE HETEROGENEITIES

Localized isotopic provinciality has been recently reported in the Western Great Basin [Ormerod et al., 1988; Farmer et al., 1989] and the Rio Grande rift [Perry et al., 1987, 1988; Menzies et al., 1991]. In the Western Great Basin, elemental and isotopic data for volcanic rocks indicates participation of depleted asthenospheric and enriched lithospheric mantle sources. These two sources correlate with depleted mid-ocean ridge mantle (i.e., DMM) and enriched mantle (i.e., EM2), respectively. In contrast, systematic temporal variations in the chemistry of magmatism close to the Rio Grande rift has been interpreted as the result of involvement of two isotopically depleted mantle sources (87Sr/86Sr < 0.7045) [Perry et al., 1987, 1988]. One of these source regions is similar to MORB and is believed to be located in the asthenosphere and the other, which has a slightly higher 87Sr/86Sr and slightly lower 143Nd/144Nd ratio than MORB, is believed to be located in the lithosphere (i.e., OIB). Depleted (87Sr/86Sr < 0.7045) and enriched (87Sr/86Sr > 0.7045) sources are reported from the Zuni-Bandera volcanic field, New Mexico [Menzies et al., 1991]. As in other models the depleted component is believed to be sub-lithospheric either as part of the MORB source or a plume OIB source. The enriched source has intraplate characteristics and is unlike the enriched "arc" like lower lithosphere encountered elsewhere. It is suggested that this enriched source occurs within the lower lithosphere but may represent "plume" contaminated lithosphere [Figure 5]. In principle, the models proposed for the Rio Grande rift [Perry et al., 1987, 1988; Menzies et al., 1991] are similar to that invoked for the Big Pine Volcanic field in the western Great Basin [Ormerod et al., 1988], but in all cases the enriched lithospheric mantle reservoirs are isotopically and genetically different.
Figure 5. Stratified lithosphere proposed for the Zuni-Bandera Volcanic Field on the flanks of the Rio Grande Rift [after Menzies et al., 1991]. This is similar to that outlined for the Colorado Plateau on the basis of data from spinel (shallow) and garnet (deep) peridotite xenoliths [Roden et al., 1990]. Part of the problem in Zuni Bandera is that both the alkaline and tholeiitic magmas have an intraplate character and as such one cannot invoke extraction of one or other from “arc” like lithosphere. If one accepts that the asthenosphere beneath the Basin and Range is MORB like then it is a suitable source for the alkaline basalts. However for the tholeiitic basalts with more OIB like character one has to argue for either (a) considerable sub-crustal mantle heterogeneity at the time of eruption (MORB-OIB mix) or (b) imposition of OIB intraplate chemistry on the lithosphere in the past such that it can be recently reactivated.

SUMMARY

Over the last thirty years models for the genesis of Tertiary to Quaternary volcanic rocks erupted throughout the western USA have been refined (Figure 6) such that the identity of the enriched reservoirs (Hedge 1966; Doe et al. 1969; Leeman 1970 & Hedge and Noble 1971)) can be resolved. Careful selection of volcanic rocks unaffected by shallow crustal processes (e.g. McMillan and Dungan 1988) indicates the presence of the following reservoirs in the upper mantle.

Cratonic lithospheric sources
Aged enriched lower lithosphere ($^{87}\text{Sr}/^{86}\text{Sr} > 0.7055$ & $^{143}\text{Nd}/^{144}\text{Nd} < 0.5120$) stabilised in the Archaean (>2500Ma) and affected by early Proterozoic enrichments. This mantle source is similar to that encountered as inclusions in diamonds.

Circum-cratonic lithospheric sources
Subduction modified lower lithosphere ($^{87}\text{Sr}/^{86}\text{Sr} < 0.7080$ & $^{143}\text{Nd}/^{144}\text{Nd} < 0.5124$; Ba/La > 31) accreted in the Proterozoic and Phanerozoic. This mantle source is similar to that encountered in arc environments and occurs beneath the Sierran province and the Colorado Plateau.

Plume contaminated lower lithosphere ($^{87}\text{Sr}/^{86}\text{Sr} < 0.7060$ & $^{143}\text{Nd}/^{144}\text{Nd} < 0.5124$; Ba/La < 31) produced in Phanerozoic times. This mantle source is similar to that of enriched ocean island basalts but may reside in the lower lithosphere.

Oceanic mantle sources
Sub-lithospheric reservoirs that include an ocean island basalt/plume source ($^{87}\text{Sr}/^{86}\text{Sr} < 0.7060$ & $^{143}\text{Nd}/^{144}\text{Nd} > 0.5124$) and a mid-ocean ridge source ($^{87}\text{Sr}/^{86}\text{Sr} < 0.7034$ & $^{143}\text{Nd}/^{144}\text{Nd} > 0.5130$). The latter is important throughout the Basin and Range [Leeman, 1970; Menzies et al. 1983] and the former is important within the “sphere of influence” of any active plumes (e.g. Yellowstone)
Figure 6. Representative crust-mantle sections depicting different mantle source regions inferred from the isotopic and elemental geochemistry of volcanic rocks from the western USA. Early investigations concluded that the high \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios in continental basalts did not always indicate contamination with continental crust. Cratonic mantle sources were originally defined on the basis of volumetrically significant tholeiitic basalts from the Snake River Plain and Yellowstone National Park [Leeman, 1975; Doe et al., 1983] and more recently on the basis of volumetrically insignificant potassic-ultrapotassic magmas from Montana, Wyoming and Colorado [e.g., Vollmer et al., 1984; Fraser et al., 1985]. Circum-cratonic (arc-like) mantle sources were alluded to by Leeman (1970) and confirmed by Carlson (1984), on the basis of Sr-Nd-Pb isotopes, and Fitch et al. [1988, 1991] and Kempton et al. [1991] on the basis of elemental data (e.g., LIL/LREE ratios). Oceanic mantle sources were originally noted by Hedge (1966) and have been subdivided into asthenosphere (MORB) (Menzies et al., 1983) and plume (OIB) (Leat et al., 1988).
REFERENCE LIST


ABSTRACT. Techniques are now available to obtain high precision age information on a variety of metamorphic minerals such as zircon, garnet, monazite, sphene, rutile, hornblende, micas, apatite and feldspars. These ages provide valuable information on the timing of geologic events and duration of processes. In order to provide a valid interpretation for these mineral ages it is essential to have some knowledge of the closure temperatures. By combining the ages with the closure temperatures and the maximum temperatures reached during metamorphism it is generally possible to decide whether the ages give information on the prograde or retrograde metamorphic path. Quantitative pressure-temperature-time paths of metamorphism can be constructed when age data are combined carefully with temperature, pressure and textural data.

In some cases it has been possible to use age information deduced from minerals that are involved in mineral reactions to constrain the timing of partial melting, intrusion of synmetamorphic magmas and the duration of prograde metamorphism even in granulite terranes. More commonly rates of cooling have been determined from ages deduced from minerals with different closure temperatures for various parent/daughter systems.

1. Introduction

It is essential to understand the dynamic aspects of metamorphism in order to be able to relate metamorphism to tectonic processes (England and Thompson 1984, Thompson and England 1984). Most successful qualitative correlations of crustal dynamics and metamorphism have been made for amphibolite facies terranes. This is because in such terranes a wealth of information on the prograde metamorphism can be deduced from mineral textures and mineral zoning (Selverstone et al. 1984, Spear and Rumble 1986). In granulite terranes, all prograde mineral zoning and most of the reaction textures are obliterated by the high temperatures and deformation associated with the formation of these high-grade rocks. As a result the construction of even qualitative pressure-temperature-time (P-T-t) paths for high grade terranes is difficult. In rocks up to and including grades of the middle amphibolite facies it is possible to obtain precise age information from a large variety of minerals (Table I). However, most mineral systems have closure temperatures that are significantly lower than those achieved during granulite grade metamorphism. Therefore the determination of precise mineral ages that give reliable age information on processes that occurred prior and during high grade metamorphism is particularly challenging and requires new approaches.

This articles discusses examples where it has been possible to obtain high precision mineral ages and relate them to the sequence of mineral reactions and duration of from various geologic processes in high grade terranes. The correlation of ages with geologic events and processes is a prerequisite for the construction of quantitative P-T-t paths for metamorphism and to correlate metamorphism with tectonic processes that are responsible for orogenesis.
2. Requirements for High Precision Geochronology

In order to obtain precise information on rates of metamorphic processes and the absolute timing of certain geologic events (e.g., mineral reactions, partial melting, heating, cooling, deformation, magmatic intrusions), it is essential to have chronometers capable of high temporal resolution. This restricts one to minerals that incorporate only small amounts of the daughter isotopes during their growth or later re-equilibration. In such minerals, the uncertainties related to the corrections for these incorporated daughter isotopes can be minimized. If minerals incorporate significant amounts of daughter element, mineral-mineral or mineral-whole rock isochrons can be determined. Although it is possible to obtain very precise ages from such isochrons, it is generally difficult to interpret such ages with the same confidence as mineral ages where the correction for the daughter isotope is negligible. The precision of an isochron is a function of the analytical precision of each data point as well as the amount of data points and their scatter around the isochron. The requirements for an isochron are only strictly fulfilled, if the scatter of the data around the isochron is random and purely analytical. In slowly cooled terranes, it is likely that the individual phases cool below their respective closure temperatures at different times, and thus produce a systematic variation in the position of the data points with respect to the isochron. In this case each point may represent a different temperature and time during a prolonged cooling history (Giletti 1985). Therefore, an apparently precise mineral isochron can only be related to a specific geologic event with the same confidence as mineral ages if all phases closed to diffusion of parent and daughter elements at the same time, or have grown at the same time and the rock did not reach temperatures above the temperature of closure. In order to interpret isochrons, it is important to know the closure temperature for each phase and to evaluate with which other phase(s) the mineral under consideration was in isotopic equilibrium at the time recorded by the isochron. If whole rocks are used for construction of isochrons, it must be shown that all samples had the same initial isotopic value at the time given by the isochron and that the isochron is not the result of mixing of two or more components, for the age to have significance.

Most high precision ages, i.e., uncertainties of ±0.5% or less, have been determined on K-bearing minerals using the $^{40}$Ar/$^{39}$Ar method and on U-bearing minerals using the U-Pb method. For $^{40}$Ar/$^{39}$Ar geochronology the following minerals are commonly used: hornblende (e.g., Harrison and McDougall 1981, Harrison 1981, Easton 1986, Harrison and Fitz Gerald 1986, Onstott and Peacock 1987), biotite (e.g., Harrison et al. 1985, Easton 1986), feldspar (e.g., Harrison and McDougall 1982, Harrison and Bé 1983). The most commonly used minerals for U-Pb dating are zircon, sphene (e.g., Hanson et al. 1971, Tucker et al. 1987) and monazite (e.g., Köppel and Grünenfelder 1975, Copeland et al. 1988, Parrish 1988). Less commonly used minerals are apatite (Oosthuyzen and Burger 1973), baddeleyite (Krogh et al. 1984), garnet (Mattinson 1986, Mezger et al. 1989a), rutile (Mezger et al. 1989b), and thorite (Hansmann 1987).

3. Closure Temperatures

In order to relate the ages obtained from the different minerals to geologic processes and events it is essential to know the closure temperature ($T_c$). $T_c$ is defined as "the temperature the mineral experienced at the time given by its age" (Dodson 1973). Dodson showed that $T_c$ can be calculated from:

$$T_c = \frac{\frac{E_s}{R}}{\ln((A \cdot R \cdot T_c^2 \cdot D_0/a^2)/(E_s \cdot C))}$$

where $E_s =$ activation energy; $R =$ gas constant; $A =$ geometry factor, i.e. sphere, infinite cylinder or infinite plate; $D_0 =$ frequency factor; $a =$ effective diffusion radius; $C =$ cooling rate.
This equation takes into account that minerals gradually change over a finite temperature range from being open to diffusion to become closed (or vice versa). Thus during cooling the daughter products are not completely lost before Tc is reached, nor completely retained thereafter. A requirement of Dodson's statement is that the phase cooled from a temperature significantly higher than Tc. If a mineral grew significantly below Tc and is subsequently exposed to temperatures only slightly above Tc, it may not reset completely and record an age that does not correspond to Tc but is older. For a mineral that grew at a temperature only slightly higher than Tc, the age will be too young.

<table>
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</tr>
<tr>
<td>Biotite</td>
<td>350</td>
<td>-</td>
<td>Jäger et al. 1967, Purdy and Jäger 1976, Wagner et al. 1977,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dodson 1979, Harrison and McDougall 1982</td>
</tr>
<tr>
<td>Orthoclasite</td>
<td>320</td>
<td>1000</td>
<td>Dodson 1979</td>
</tr>
</tbody>
</table>

Table I. Approximate closure temperature for selected minerals using a cooling rate of ca. 1-10°C/Ma and common grain sizes.

By comparing Tc with the maximum temperature achieved in a given rock sample (as determined by careful thermometry), it is possible to assess whether the ages record the time of mineral growth, and give information on prograde metamorphism, or whether they record cooling ages, and thus relate to the retrograde metamorphic history.
There is insufficient knowledge to be able to predict the diffusion behavior for a given ion in a specific mineral from first-principles. Therefore, closure temperatures have to be determined empirically. This is possible through experiments (Harrison 1981, Harrison et al. 1985) or in geologic settings where the thermal history may be evaluated such as contact aureoles (Hart 1964, Hanson and Gast 1967, Hanson et al. 1971) or regional metamorphic terranes (e.g., Purdy and Jäger 1976, Mezger et al. 1989b).

Table I summarizes Tc's for minerals that can yield high precision ages using the U-Pb, $^{40}$Ar/$^{39}$Ar - K-Ar, Rb-Sr and Sm-Nd systems and a brief discussion follows below. For the discussion cooling rates of ca. 1-10°C/Ma will be assumed. Tc is strongly dependent on the effective diffusion radius. In cases, where no exsolutions or structural transformations occur, this might be approximated by the grain size (e.g., U-Pb in garnet, monazite, rutile) in other cases it is a function of the size of exsolution lamellae (e.g., $^{40}$Ar/$^{39}$Ar in hornblende, alkali-feldspar). Tc may also show a dependence on the composition of the mineral, the composition of the surrounding fluid and deformation after mineral growth. However, for most minerals there is very little known as to the importance of these parameters and in certain case they might lead to appreciable deviations from the values given in Table I. Therefore the values given in Table I should be used with the appropriate caution.

3.1. U-Pb SYSTEM

The U-Pb system has a great advantage over other systems because two isotopes of U decay to two isotopes of Pb. By analyzing for U and Pb abundances and Pb isotopic compositions it is possible to obtain three ages ($^{207}$Pb/$^{235}$U, $^{206}$Pb/$^{238}$U, $^{207}$Pb/$^{206}$Pb; see Faure (1986) for a general reference). These ages give an internal check on the possible disturbance of the system after the last complete reequilibration. By plotting the data on a U-Pb concordia diagram it is possible to obtain two additional ages in many cases. The age given by the upper intercept with concordia ideally corresponds to the time the mineral grew and the age given by the lower intercept on the concordia corresponds to the time of disturbance or partial reequilibration. However, care must be taken to interpret ages derived from such discordance patterns.

3.1.1. Zircon

The U-Pb systematics in zircon are generally considered to be the most difficult to reset completely, even by granulite grade metamorphism and partial melting (Pidgeon and Aftalion 1978, Schenk 1980, Kröner et al., 1987a, 1987b) and Tc is considered to be >900°C. It is likely that only very small zircons can be reset during metamorphism in the continental crust. Larger zircons probably must be destroyed completely and reprecipitated in order to eradicate all memory of their previous isotopic composition. Zircons typically show some disturbance in their U-Pb systematics as a result of Pb-loss at low temperature. At higher grades of metamorphism new zircon overgrowths may form and therefore give discordant ages (e.g., Kröner et al. 1987a). This problem can be overcome by analyzing different batches from the same sample and treating the zircons, preferentially by air abrasion (Krogsh 1982a, Krogh 1982b, Goldich and Fischer 1986). In some studies, zircons are leached with acids to yield more concordant ages. This method may complicate, however, the discordance patterns by superimposing an artificial discordance on already discordant populations. Therefore leaching of zircons is strongly discouraged in favor of air abrasion techniques to obtain more concordant populations. Particular care must be taken in interpreting the lower intercept ages, because they may not have any obvious geologic significance (e.g. Tilton 1960, Goldich and Mudrey, 1972). In situ spot analysis by ion microprobe (although associated with comparatively large analytical errors e.g., Kröner et al., 1987b), or conventional analysis of single zircon cores (Krogstad et al., 1986) should be able to resolve most of these ambiguities in interpreting discordant U-Pb zircon ages.
3.1.2. Garnet

Garnet is an important mineral in isogradiatic reactions, geothermometers and geobarometers (Essene 1982, Bohlen and Lindsley 1987, Essene 1989, Powell and Holland 1988) and is one of the most widely used minerals for determining metamorphic P-T paths (Spear and Selverstone 1983, Bohlen 1987, Spear and Rumble 1986). U-Pb ages for garnet are particularly useful for dating times of mineral reactions or the development of equilibrium mineral assemblages in metamorphic terranes. Such ages are essential to construct quantitative P-T-t paths.

Since Ca and U have identical ionic radii, it can be expected that U is incorporated to a limited extent in the M^2+ site in garnet. Except for andradite-rich garnets in skarns, almandine-pyrope-grossular-spessartine garnets typically have U concentrations of less than 1 ppm (Haack and Gramse 1972).

Garnet has been successfully used for fission track dating for which it has a closure temperature of about 280°C (Haack, 1976). The garnets used for fission track dating have come from a large selection of geological sites and have a broad range in compositions. Haack (1976) found that garnets show a regular distribution of the fission tracks. The fission tracks and thus U, are more evenly distributed throughout individual garnets than almost any other common mineral used for fission track dating. However, garnets may also host U-rich phases within the matrix or along grain boundaries and fractures (Haack 1976, Mezger et al. 1989a). Special care has to be taken to remove or leach these extraneous U-rich phases that could overwhelm the structurally bound U in garnet. Relatively large, and thus visible inclusions, will preserve information that might be unrelated to garnet-growth. These larger inclusions can be easily detected using a petrographic microscope or with back scattered electron imaging on the electron microprobe. Hand picking of small, clear grains under a microscope should reduce the possibility of incorporating the larger inclusions. Acid washing of the garnet before analysis should eliminate the U-rich phases along grain surfaces.

If inclusions are only micron-sized, possibly as a result of exsolution, they will have a low Tc. The rate at which the U and Pb associated with these small inclusions will diffuse into or out of the garnet, will be controlled by the garnet structure and the Tc for garnet will apply. The age obtained from garnets with such small inclusions will record the time garnet, rather than the inclusion, became closed to U-Pb diffusion.

Many garnets contain significant amounts of common Pb. Using Pb isotope ratios for the common Pb correction based on a Pb-evolution model such as that of Stacey and Kramers (1975), as is done routinely for zircons, can introduce a significant error in the U-Pb ages for garnet. In order to obtain precise ages it is therefore recommended that a common Pb correction be applied using the isotopic ratios obtained from the whole rock or from a coexisting phase with high Pb to U ratios such as K-feldspar. The accuracy of the garnet-K-feldspar age is dependent on the time elapsed between the closure for garnet and that of the K-feldspar. If this time is long, the age can be biased significantly towards younger values. Therefore, feldspar should only be used if it reequilibrated at approximately the same time as the garnet, or if 238U/204Pb for the whole rocks was low and the Pb-isotopic ratios did not evolve very much over time.

Some garnet populations show variable discordance with a lower intercept age of 0 Ma, suggesting that the discordance is a result of analytical procedures. Improvement of analytical techniques might solve this problem (Mezger et al. 1989a).

U-Pb systematics in almandine-pyrope rich garnets are not reset by granulite facies metamorphism at temperatures of at least 800°C (Mezger et al. 1989a). So far only a small number of garnets have been dated by the U-Pb method (Mattinson 1986, Mezger et al. 1989a), so it is not known whether there is a significant compositional dependence of Tc in garnet.
3.1.3. Monazite

Recent studies have shown that U-Pb systematics in monazite are only partially disturbed during partial melting at temperatures of ca. 700°C (Parrish 1988, Copeland et al. 1988), and are not disturbed by contact metamorphism at temperatures of ca. 650°C but completely reset by regional metamorphism reaching 740°C (Mezger et al., in prep.). This high Tc for monazite is in contrast to the earlier suggestion by Wagner et al. (1977) that Tc may be as low as 550°C, but is consistent with the study by Köppel and Grünenfelder (1975) who favored a Tc significantly higher than 550°C. Such high closure temperatures indicate that, in granulite grade terranes, monazites (0.04–0.2 mm grains) record information following the maximum thermal conditions. In terranes that have undergone at most upper amphibolite grade metamorphism they may record growth ages.

3.1.4. Sphene

Sphenes give concordant U-Pb ages in most terranes. However, some sphene populations show discordance patterns similar to those observed in zircons (Tucker et al. 1987). In such cases, sphenes seem to record two different events. The discordance patterns can be the result of a short thermal disturbance (Tucker 1988) but may also be a result of a second episode of sphene growth with new material overgrowing older cores. In the latter case, the discordance cannot be used to infer a short thermal disturbance, but may indicate that the terrane did not reach conditions significantly above lower amphibolite facies at any time bracketed by the two ages. To distinguish the two different discordance patterns it is necessary to evaluate the Th/U/Pb ratios as well as their concentrations, as a function of location within the sphene grains (core vs. rim). It also helps to be able to constrain the highest temperatures achieved during the period of the disturbance or new growth of the rim material.

Tc's for sphenes are commonly considered to be about 500-550°C (e.g., Mattinson 1978, Gascoyne 1986, Cliff and Cohen 1980), for typical igneous and metamorphic sphenes which are commonly smaller than 1 mm in their longest dimension. In some pegmatites and high grade marbles, sphenes can reach several cm in their longest dimension. For a sphene 30 mm in maximum dimension Tc is about 670°C at a cooling rate of ca. 2°C/Ma (Mezger et al. in prep). Thus by selecting sphenes of different sizes from the same area, it is possible to obtain information on rates of cooling following high grade metamorphism.

3.1.5. Rutile

Only a few rutiles from metamorphic rocks have been analyzed for their U-Pb systematics. Rutiles typically give concordant or only slightly discordant U-Pb ages (Schärer et al. 1986, Mezger et al. 1989b). U-Pb ages deduced from rutile are typically younger than those determined for sphene ages and are equivalent or slightly younger than ⁴⁰Ar/³⁹Ar ages obtained from metamorphic amphiboles. Tc for 0.2-0.4 mm grains is about 420°C (Mezger et al. 1989b).

3.1.6. Apatite

Tc for the U-Pb system in apatite is still poorly known. Experimental studies by Watson et al. (1985) suggest a Tc for Pb in fluorapatite (grain size of 0.2-0.1 mm) of 530-590°C at a cooling rate of 1-10°C/Ma. Mattinson (1978) found that igneous apatite and sphene give similar U-Pb ages and suggested a Tc of ca. 500°C. Cliff and Cohen (1980) found that metamorphic apatite has a Tc similar to the K-Ar system in muscovite i.e., ca. 350°C. Only a small part of this discrepancy may be the result of different cooling histories, the major part may be related to different composition (particular OH, F, Cl) of apatite or the fluid phase present in the rocks during
cooling. Apatite is isostructural with pyromorphite and thus incorporates large amounts of common Pb into its structure during growth. High precision ages can therefore be obtained only if the uncertainty in the common Pb correction can be minimized (see discussion at 3.1.2.), proper interpretation of the ages must await better knowledge of Tc.

3.2. \(^{40}\text{Ar} / ^{39}\text{Ar}\) AND K-Ar SYSTEM

3.2.1. Hornblende

The most widely used mineral dated by the \(^{40}\text{Ar} / ^{39}\text{Ar}\) method is hornblende. It seems that among the major rock forming minerals hornblende has the highest Tc for the \(^{40}\text{Ar} / ^{39}\text{Ar}\) system. Tc is typically around 500°C (Harrison 1981), but can be quite variable. Variations in Tc may be a function of the composition of the hornblendes and the cooling rate. It has not been shown conclusively whether there is a direct correlation between hornblende composition, particularly Fe/Mg ratio and Tc, but it is evident that the composition has an effect on the possible exsolution and alteration of hornblendes during cooling (Robinson et al. 1982). Exsolution and alteration reduce the effective grain size of the hornblendes and if they occur at high enough temperatures, can lead to substantially lower Tc (Harrison and Fitz Gerald 1986, Onstott and Peacock 1987). Due to these complexities it is advisable to determine the composition and structural state of hornblendes used for geochronology (e.g., Onstott and Peacock 1987). An additional problem is that some hornblendes can contain extraneous argon and thus can yield old ages of no geologic significance. However, using the \(^{40}\text{Ar} / ^{39}\text{Ar}\) technique and step-wise degassing it is possible to detect the presence of extraneous Ar and ideally make the required corrections (e.g., Harrison and McDougall 1981).

3.2.2. Micas

Micas can yield precise \(^{40}\text{Ar} / ^{39}\text{Ar}\) and K-Ar ages but biotites can also be prone to the incorporation of extraneous argon (e.g., Phillips and Onstott 1988). Tc for the K-Ar system in muscovite is about 350-400°C (Hanson and Gast 1967, Purdy and Jäger 1976, Cliff and Cohen, 1980). Experimental studies indicate that Tc for \(^{40}\text{Ar}\) in biotite is a function of composition and has a significant pressure dependence (Harrison et al. 1985). For most biotites Tc is around 300°C (Purdy and Jäger 1976, Dodson and McClelland-Brown 1985) but increases with the Mg/Fe ratio (Harrison et al. 1985) and can be as high as 450°C in phlogopite (Dodson 1979). Hart (1964) studied the K-Ar and Rb-Sr systematics of biotite flakes with a diameter of ca. 8 mm, by separating different zones from individual flakes. The result show a significant decrease in ages from core to rim. Harrison et al. (1985) suggest that biotite has an effective diffusion radius of 0.15-0.2 mm and flakes that are larger yield the same ages independently of grain size. A decrease in ages with decreasing grain size was only observed for smaller flakes. These results are consistent with the findings of Hanson and Gast (1967).

3.2.3. Feldspars

Microclines have a Tc for the \(^{40}\text{Ar} / ^{39}\text{Ar}\) system of about 150-250°C (Harrison and McDougall 1982). They give information on the very late stages of cooling, close to the time the rocks are exposed to the surface. Orthoclase has Tc's that are significantly higher than those for microcline (Heizler et al. 1988).
3.3. Rb-Sr SYSTEM

3.3.1. Micas

According to the study by Hanson and Gast (1967) the Rb-Sr system has only a slightly higher Tc than the K-Ar system for the same mica, and Tc for the Rb-Sr and K-Ar system in muscovite is significantly higher than in biotite. Tc for Rb-Sr in muscovite is ca. 450-500°C and in biotite ca. 350°C (Hanson and Gast 1967, Jäger et al. 1967, Purdy and Jäger, 1976 Dodson 1979). Compared to the $^{40}$Ar/$^{39}$Ar system, the Rb-Sr system is only rarely used for obtaining mineral ages, although it can yield very precise ages particularly for micas (see also Peterman and Sims 1988).

3.4. Sm-Nd

Sm and Nd have similar ionic radii, the same charge and therefore similar geochemical properties. As a consequence they are not fractionated sufficiently in any rock-forming mineral to allow to obtain a mineral age without significant correction for inherited Nd. The Sm-Nd system can thus be used only if an isochron is constructed. This requires that at least two components (i.e. two minerals or one mineral and the corresponding whole rock) are analyzed. If two minerals are used, ideally both of them should have the same Tc for the Sm-Nd system. In order to avoid ambiguities mineral-whole rock isochrons should be obtained rather than mineral-mineral isochrons. The precision obtainable for a two point isochron is a function of the spread in the Sm/Nd ratio of the two points. A common rock-forming mineral that discriminates strongly between Sm and Nd is garnet. Thus garnet-whole rock isochrons hold promise for dating metamorphic rocks on which age information is difficult to obtain by other methods.

Tc for the Sm-Nd system in garnets is not well established. Humphries and Cliff (1982) concluded in their study Tc is ca. 480-600°C. However, a recent study by Cohen et al. (1988) indicates that garnets preserve their Sm-Nd systematics up to temperatures of 900°C. This high temperature is consistent with the proposed Tc of ca. 850°C for the system garnet-clinopyroxene from an eclogite xenolith studied in detail by Jagoutz (1988). If these high values for Tc are correct, then Sm-Nd mineral isochrons involving garnet can yield absolute age information on processes in the upper mantle and lower crust. Since zircon is extremely rare in mafic rocks and absent in ultramafic rocks, and because these garnets may have low concentrations of U, Sm-Nd geochronology on garnet-bearing samples may be the system of choice to obtain age information on these types of rocks.

4. Dating Metamorphic Processes

The above discussion of Tc's indicates that it is comparatively easy to obtain information on the cooling history of granulite terranes, but it is more difficult to obtain reliable information on the timing of prograde metamorphic processes and events (see also summary in Cliff 1985). The only systems that seem to be able to provide precise age information on prograde events in high grade terranes are U-Pb in zircon and garnet and possibly Sm-Nd in garnets.

In the following discussion we will give examples where geochronology provides important age constraints on the evolution of high grade metamorphic terranes. The data are taken from our studies in the Pikwitonei granulite domain (Manitoba, Canada), the Adirondack Mountains (New York, USA) as well as from the literature. For a further discussion the reader is referred to references given in the text.
4.1. DURATION OF METAMORPHISM

First order questions one faces in attempting to understand the evolution of metamorphic terranes concern the duration of metamorphism and whether metamorphism was caused by a single continuous change in P and T or whether there were several distinct metamorphic episodes. In some cases structural studies combined with petrographic observations may provide clues regarding the poly-metamorphic history of a terrane. The ultimate test, however, is dating metamorphic minerals with high Tc's. The most promising systems are U-Pb in zircon and garnet. Figure 1 gives an example from the Pikwitonei granulite domain in Manitoba, where metamorphic garnets indicate four distinct episodes of garnet growth that we interpret as distinct thermal peaks in the metamorphic history. The garnet ages are similar to zircon ages from the same area and support the episodic character of metamorphism. Metamorphism lasted for about 150 Ma, but during this time, new minerals (garnet and zircon) grew only during short intervals from 2744-2734 Ma, 2700-2687 Ma, 2660-2637 Ma and 2629-2591 Ma (Mezger et al. 1989a, 1989c).

Figure 1. This diagram shows the temperature history of a small area within the Pikwitonei granulite domain. Temperatures were estimated from the location of garnet forming reactions identified by mineral textures. The temperatures are then combined with the ages obtained from such garnets. The crosses give the age and temperature uncertainties (assuming a(H_2O)=1) for the different points. This diagram indicates that high grade metamorphism lasted for at least 150 Ma within this area and there were several thermal "peaks" (modified after Mezger et al. 1989a).

4.2. MINERAL REACTIONS

The construction of truly quantitative P-T-t paths for metamorphic terranes requires precise knowledge of the time at which certain pressures and temperatures were achieved in a rock. In most granulite grade rocks, prograde zoning in garnet is obliterated by the high temperatures achieved during metamorphism. In such rocks information on P-T and time can only be inferred if the garnet-forming reaction can be observed in the sample. For example: in metapelitic gneisses from the Pikwitonei domain, it is possible to observe textures that give an indication of which reaction lead to the formation of garnet. Several samples show textures that indicate that garnet formed by the breakdown of staurolite according to the reactions given in Table II. These
Figure 2a. Sketch of migmatite sample from the Pikwitonei granulite domain. From this sample three batches of petrographically distinct garnets were extracted for dating by the U-Pb method (Mezger et al. 1989a). The three types of garnet yielded the distinct ages of 2697 Ma (a), 2659 Ma (b) and 2641 Ma (c).

Figure 2b. This photomicrograph (plane light, 3x4.2 mm) shows an area of the migmatite sample along the leucosome-melanosome interface where all three petrographically distinct garnets are present: a = corroded garnet surrounded by biotite in the melanosome; b = large garnet at the leucosome-melanosome border; and c = small garnet in the leucosome surrounded by K-feldspar.
garnets were dated by the U-Pb method and the ages are given in the same table. According to experimental studies and the assumption that $a_{H_2O}$ is ca. 1 the formation of garnet by the reactions in Table II require temperatures of 680°C and 795°C (Richardson 1968)(Fig. 4).

4.3. PARTIAL MELTING

High grade metamorphism commonly results in in-situ partial melting. In the Pikwitonei granulite domain, garnets formed by partial melting reactions such as those given in Table II. Determination of the growth ages of garnets in the leucosome yields the time of formation of the partial melts. Care must be taken to separate newly formed garnets from those accidently incorporated into the melt from the melanosome or those that formed on the melanosome/leucosome interface. The garnets in the melanosome may have formed by a completely different reaction than those in the leucosome and may give significantly older ages (Mezger et al. 1989a). Those on the melanosome leucosome interface may give an intermediate mixed age (Figure 2).

At higher crustal levels it might be possible to determine the origin and time of intrusion of S-type granites, by dating the garnets in these intrusions. One example where the garnets can give information on the time of intrusion as well as the timing of earlier metamorphic episodes in the source is a late-kinematic S-type granite from the Pikwitonei granulite domain. Four garnets from the same granitic intrusion were dated and yielded ages of 2984, 2744, 2605 and 2591 Ma (Mezger et al. 1989a). The two older ages most likely represent metamorphic episodes in the source of the granite whereas the two younger ages may date the time of intrusion of the granite (Mezger et al. 1989c). The ages indicate, that restite and melt did not separate completely and that some of the garnets formed directly from the granitic melt.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Age</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NATAWAHUNAN LAKE:</strong></td>
<td></td>
</tr>
<tr>
<td>(A) staurolite + quartz = garnet + sillimanite + vapor</td>
<td>2744 Ma</td>
</tr>
<tr>
<td>(B) staurolite = garnet + sillimanite + spinel + vapor</td>
<td>2738 Ma</td>
</tr>
<tr>
<td><strong>CAUCHON LAKE:</strong></td>
<td></td>
</tr>
<tr>
<td>(C) biotite + cordierite + quartz + vapor = garnet + melt</td>
<td>2700 Ma</td>
</tr>
<tr>
<td>(B) staurolite = garnet + sillimanite + spinel + vapor</td>
<td>2687 Ma</td>
</tr>
<tr>
<td>(D) biotite + plagioclase + sillimanite + quartz = garnet + K-feldspar + melt</td>
<td>2641 Ma</td>
</tr>
</tbody>
</table>

Table II. Ages of mineral and partial melting reactions in the Pikwitonei granulite domain (from Mezger et al. 1989a).

4.4. SYNMETAMORPHIC INTRUSIONS

Synmetamorphic intrusions play a significant role in the overall heat-budget during high grade metamorphism (e.g., Wells 1980). Table III gives two examples from the Adirondack Mountains where the intrusion of a now metamorphosed igneous body was dated by the U-Pb method on zircon. The time of the syn-regional contact metamorphism of the surrounding metapelite gneisses was determined by dating metamorphic garnets (Table III).
One of the intrusions is the Diana Complex located along the amphibolite granulite facies transition, the other, a hornblende granite from Piseco Dome within the granulite terrane (for a location map see McLelland et al. 1988). The Diana syenite shows igneous fabrics but is also strongly deformed in many places and has preserved a contact aureole as indicated by metamorphic temperatures $>850^\circ$C in a terrane that regionally experienced temperatures of ca. 650$^\circ$C (Powers and Bohlen 1985). The hornblende granite from the core of Piseco Dome has a strong gneissic fabric and has no obvious unusually high temperature mineralogy preserved adjacent to the intrusion that could indicate the presence of a syn-regional metamorphic contact aureole. Dating of zircons from metaigneous rocks (Grant et al. 1986, McLelland et al. 1988) and garnets from adjacent country rocks (Mezger et al. 1988, Mezger et al. in prep.) shows that garnet growth was contemporaneous with the intrusion. Combining ages obtained on zircon, garnet and monazite throughout the Adirondacks it can be shown that these magmatic bodies intruded during a time of regional metamorphism lasting from ca. 1170-1130 Ma (Mezger et al. 1988). Such a relationship of magmatism and metamorphism was predicted by Powers and Bohlen (1985) for the area surrounding the Diana Complex and the age information deduced from zircons and garnets corroborates this important relationship. These data support the broader conclusion that synmetamorphic intrusions can play an important role in the heat budget for a metamorphic terrane. Due to their strong deformation, some synmetamorphic intrusions may be recognized as such only with difficulty, and may be interpreted instead as pre-metamorphic. Comparison of the ages obtained for the intrusions and minerals in the immediate contact aureole with ages obtained from metamorphic minerals taken further away from the contact zone should allow determination of relative timing of igneous intrusion and metamorphism.

<table>
<thead>
<tr>
<th>Intrusion</th>
<th>Temperature</th>
<th>Age of intrusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diana Complex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Syenite</td>
<td>$&gt;1000^\circ$C</td>
<td>1154$\pm$3 Ma*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1155$\pm$4 Ma**</td>
</tr>
<tr>
<td>Piseco Dome:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hornblende Granite</td>
<td>?</td>
<td>1154$\pm$11 Ma*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1150$\pm$5 Ma***</td>
</tr>
</tbody>
</table>


4.5. RATES OF DEFORMATION

Garnets strongly prefer Sr over Rb and will record the Sr-isotope composition of the matrix at the time of mineral growth. By analyzing different garnet zones for their Sr-isotope composition and the assumption that the Rb/Sr ratio of the matrix changes only by incorporation of Sr into the garnet and no other processes, it is possible to obtain growth rates. Christensen et al. (1988)
studied large (3 cm) snowball garnets from the amphibolite facies Ottauqueche Formation (Vermont) and combined the growth rates with the amount of rotation contained in the garnet. The shear strain rate obtained is on the order of $10^{14}$ s$^{-1}$. Depending on Tc for Sr in garnet and the availability of snowball garnets this technique might have some promise to yield also valuable information on the deformation history of granulite facies rocks.

4.6. RATES OF HEATING

In order to determine rates of heating it is important to be able to determine the ages of temperature sensitive mineral reactions. In theory it should be possible to obtain values for the rate of heating form the two reactions given in Table II and the prograde parts of the temperature-time diagram shown in Figure 1. Although the ages for mineral growth are quite precise, the reconstruction of the P-T conditions of garnet growth by the dehydration reactions is hampered by the extreme difficulty to reconstruct the fluid activity for the time of garnet formation. This uncertainty introduces a large error in any estimate of the heating rates based on the reaction given in Table II. Thus in order to obtain reliable heating rates it will be necessary to select areas where the fluid activities are well constrained or where garnet forms by solid-solid reactions with a significant temperature dependence.

4.7. RATES OF COOLING

By combining various mineral ages with their closure Tc's it is possible to describe the rate of cooling of a granulite terrane following high grade metamorphism. Table IV gives the mineral ages determined on garnet, monazite and rutile from a single sample taken from the Adirondacks. If the garnet grew during peak metamorphism as given by the metamorphic temperatures (Bohlen et al. 1985) and the monazite and rutile Tc's are correct, this yields a cooling rate of $2.0\pm0.5^\circ$C/Ma. Using a single sample to determine cooling rates by dating several minerals with different Tc's avoids the ambiguities that can be introduced by comparing ages from different minerals over a large area where cooling might be quite variable.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Age</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garnet</td>
<td>1064±3 Ma</td>
<td>750±30°C</td>
</tr>
<tr>
<td>Monazite</td>
<td>1033±1 Ma</td>
<td>670±30°C</td>
</tr>
<tr>
<td>Rutile</td>
<td>911±1 Ma</td>
<td>420±30°C</td>
</tr>
</tbody>
</table>

> time integrated cooling rate $2.0\pm0.5^\circ$C/Ma

Table IV. Cooling history of sample SP-1 from the Adirondack Highlands (from Mezger et al. in prep.).

Figure 3 gives the ages from various minerals plotted as a function of their closure temperatures for the southern part of the Adirondack Highlands (Mezger et al., 1989b). The diagram yields a cooling rate of ca. 3°C/Ma immediately following high grade metamorphism and ca 1°C/Ma in the time period around 800 Ma. $^{40}$Ar/$^{39}$Ar ages in K-feldspar are consistent with a
cooling rate of 0.5°C/Ma at around 700 Ma (Heizler and Harrison 1986). The slow and gradually decreasing cooling rate may indicate that the terrane was not uplifted very fast, if at all, and cooling is mostly the result of the decay of the perturbed geotherm following high grade metamorphism.

For minerals that have a well defined \( T_c \) or where \( T_c \) can be calculated, it is possible to contour a terrane with the ages obtained for these minerals. These contours have been termed thermochrons (Harper 1967) or chrontours (Armstrong 1966). They describe the time a specific area passed below the \( T_c \) for a single mineral. In some ways, these chrontours are similar to isograds but give information of the retrograde rather than the prograde history (see examples in Easton 1986). Thermochrons can be used to describe late stage, large scale deformations and uplift histories (e.g., Peterman and Sims 1988, Harrison et al. 1989).

![Cooling History](image)

**Figure 3.** In this diagram mineral ages obtained on garnet, monazite, sphene and rutile with the U-Pb method and hornblende and biotite with the \(^{40}\)Ar\(^{39}\)Ar method are plotted against the \( T_c \) from Table I; garnet is assumed to have grown at peak temperatures. Based on this diagram the Adirondacks cooled initially at a rate of ca. 3°C/Ma and at a rate of ca. 1°C/Ma at 800 Ma.

### 4.8. CONSTRUCTION OF P-T-t PATHS FOR HIGH GRADE TERRANES

By combining mineral ages with mineral reactions for which the temperature can be estimated, it is possible to derive a temperature-time path. Figure 1 describes the possible temperature history of a small area at Cauchon Lake within the Pikwitonei granulite domain. This diagram indicates that high grade metamorphism lasted for at least 150 Ma within this area and there were several thermal "peaks". These peaks correspond to periods of abundant mineral growth (i.e., garnet and zircon growth) separated by times of no observed mineral growth. Thus it seems that the terrane was not metamorphosed by a single heating and cooling event, but there were at least three periods of increasing temperature possibly separated by times of cooling. Following the last metamorphism, the terrane cooled initially at a rate of only 2°C/Ma.

In Figure 4 all petrographic information is combined with the geochronology and thermometry.
and barometry to describe a P-T-t path for the Pikwitonei granulite domain at Cauchon Lake (Mezger et al. 1989c). Based on pseudomorphs of andalusite after sillimanite, the prograde path must have passed below the aluminosilicate triple point. The first observable reaction that can be dated is the formation of garnets around 2700 Ma by the partial melting reaction (C) (Table II). Around 2687 Ma new garnets formed by reaction (A). Between 2687 Ma and 2660 Ma no new garnets formed and it is possible that the terrane cooled somewhat before the next thermal pulse. From 2660-2637 Ma a second set of migmatises formed. In one pelitic sample garnets formed via the melt producing reaction (D) at 2641 Ma. Peak metamorphic conditions as given by thermo-barometry most likely coincide with the last formation of metamorphic garnets at 2637 Ma. Following the last metamorphic pulse, garnet- and sillimanite-bearing granites and pegmatites intruded around 2600 Ma as dated with garnet, zircon and allanite. The stable occurrence of sillimanite in the late felsic intrusives indicates that at the time of intrusion the pressure was below the sillimanite-kyanite transition. The retrograde dP/dT is also deduced from retrograde reactions and retrograde zoning in garnet (Mezger et al. 1989c).

Figure 4. The P-T-t path for the Cauchon Lake area in the Pikwitonei granulite domain is based on the combination of reaction textures, mineral zoning, geothermometry, geobarometry and U-Pb geochronology on zircon, garnet and rutile. Although it is possible to draw a continuous path, the geochronologic data indicates that mineral growth was episodic. During the intervals with no new mineral growth (dotted parts) there may have been excursions towards lower temperatures (see also Figure 1). (circles indicate ages, numbers give ages in Ma, the contoured boxes represent P-T estimates; the location of the garnet-forming dehydration reactions is approximate) (after Mezger et al. 1989c).
The youngest age is given by U-Pb ages from rutile. This age corresponds to a temperature of ca. 420°C (Mezger et al. 1989b). Thus from 2630 Ma to 2430 Ma the terrane cooled only 350°C. This corresponds to a time integrated cooling rate of 1.6°C/Ma.

5. Error Assessments

In many cases it may not possible to take full advantage of the high precision of many of the mineral ages particularly for determining heating and cooling rates. A special problem is dating of continuous reactions. By dating individual minerals, the age obtained represents an average for the growth episode. To improve on this it will be necessary to date individual zones within single crystals.

An additional uncertainty is introduced, because the mineral compositions found in the rocks now may be significantly different from the composition at the time the dated mineral grew. Although the mineral texture may be diagnostic for a specific reaction, the individual phases may have reequilibrated with respect to their major element compositions at significantly higher temperatures and pressures. The trace elements used for geochronology, particularly U-Pb and Sm-Nd, may not have reequilibrated due to their lower diffusivity as a result of their large ionic radii. In other cases one or more phases involved in the reaction are depleted or are only preserved as relic inclusions. In these situations subsequent reactions may have changed the compositions of some of the phases as well. Since almost all geothermometers and geobarometers use the major element compositions of the minerals, the temperatures and pressures may reflect conditions that were attained after the minerals formed. Many garnet-producing reactions are dehydration reactions. In granulite terranes $a_{H_2O}$ can be quite variable and is difficult to estimate its value at the time of garnet growth. These petrologic uncertainties may contribute significantly to the uncertainty in a proper geologic interpretation of the ages.

It will always be very difficult to get precise information about the rate of rapid processes. For example, consider a heating rate of 10°C/Ma. With such a heating rate, it would take 10 Ma to increase the temperature by 100°C. If it were possible to find reactions in a rock that documented this temperature increase and the reactions could be dated with a precision of ±2 Ma, the rate of heating would be uncertain by at least 35%. For a heating rate of 1°C/Ma the uncertainty would be only 3%. In many cases there is a substantial uncertainty in the temperature estimates for a specific reaction. This is the result of the uncertainty in the composition of the phases at the time of reaction and the uncertainty in the activities of the fluid species. For each case it is necessary to consider separately which factor causes the major uncertainty in the correlation of the petrologic information with geochronology, and where it is most important to improve on the precision of the data.

6. Concluding Remarks

In order to improve our understanding of metamorphic processes it will be necessary to select phases for geochronology that give information on at least one other parameter (i.e., pressure, temperature, melting, deformation) in addition to the age. Some examples for such an approach are given above and they lead to important conclusions concerning metamorphic processes.

Figures 1 and 4 show, that at least in the Pikwitonei granulite domain (Manitoba, Canada), the mineral assemblages observed are not the result of a single metamorphic pulse, but rather of prolonged metamorphism with punctuated temperature, pressure and fluid activities. This suggests that in other terranes even if a smooth, continuous P-T-t path can be drawn based on observed mineral reactions or textures, it may not reflect the actual complete metamorphic history of the terrane.
Acknowledgments

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7. References


Mezger K, Hanson GN, Bohlen SR (1989b) U-Pb ages of metamorphic rutiles: Application to the cooling history of high grade terranes. submitted to *Earth Planet Sci Lett*.


The nature of the crust in western Alaska as inferred from the chemical and isotopic composition of Late Cretaceous to early Tertiary magmatic rocks in western Alaska by Elizabeth Moll-Stalcup and Tom Frost

The remnants of an usually wide continental margin arc discontinuously cover much of western Alaska, overlapping a number of exotic basement terranes. The basement terranes are all pre-Cretaceous and the overlying arc rocks are latest Cretaceous and early Tertiary (73-56 Ma). Some of the pre-Cretaceous basement terranes have continental affinities but most are thought to be pieces of oceanic crust or island arcs that were accreted to the north American continent in mid-Cretaceous time.

We studied the chemical and isotopic composition of the 73 to 56 m.y. old arc rocks to see if there are correlations between the composition of the arc rocks and the type and age of the underlying basement. We have studied numerous volcanic fields and plutons over a 250 x 1000 km along-strike segment of the continental margin arc. Our data set for 10 volcanic fields and 6 plutons indicate that the most common rock type is andesite or its plutonic equivalent. Basalt is uncommon and rocks having less than 56% SiO₂ and more than 6% MgO are rare. Chondrite-normalized Rb, Ba, Th, and K contents are elevated and Nb and Ta contents are depleted relative to the LREE in all the andesites and dacites and in their plutonic equivalents. Almost all the rocks fall into one of three groups: (1) Moderately LREE-enriched andesites, (2) strongly LREE-enriched andesites and dacites, and (3) highly variable felsic rocks. We describe the salient features of each group below.

The first group, moderately LREE-enriched andesites and their plutonic equivalents, comprises the most common rock type in the 250 x 1000 km study area. The andesites are surprisingly uniform in major and trace-element composition over a broad region. LREEs within a given pluton or volcanic field generally increase slightly with increasing SiO₂ from a low value of 40-60 x chondrites to a high value of 90-120 x chondrites. HREE remain anchored at about 8-20 x chondrites. Andesites and intermediate composition plutonic rocks that intrude island arc terranes have Sr and Nd isotopic compositions plot between the field for MORB and bulk earth on ²⁷Sr/²⁶Sr vs. ¹⁴³Nd/¹⁴⁴Nd diagrams (Fig. 1). Andesites that were erupted through Paleozoic and Precambrian continental terranes have ¹⁴³Nd/¹⁴⁴Nd near bulk earth and ²⁷Sr/²⁶Sr from 0.704-0.708. We only have Pb isotopic data for the rock within the island arc terranes; all of these data plot within the MORB field. We believe the parent magmas of the moderately LREE-enriched intermediate rocks originated in a
subduction modified mantle-wedge and arrived at present compositions by crystal fractionation and assimilation as they rose to the surface. Their final isotopic composition is a mixture between the starting composition of the magma and the composition of the crust. Shifts in isotopic composition may occur in this group but are only apparent when the isotopic contrast between the magma and the crust is large. The only clear case of crustal contamination is found in rocks of the Nowitna and Sischu volcanic field which were erupted through the Precambrian Nixon Fork terrane and have relatively low initial $^{143}\text{Nd} / ^{144}\text{Nd}$ (0.51257-0.51244).

The second group consists of strongly LREE-enriched andesites and dacites that are much less abundant within the study area than the first group, although they are the dominant rock type within individual volcanic fields and plutons. These rocks are characterized by steep REE pattern that have LREE 80-200 and HREE 3-5 x chondrites. They generally have higher SiO$_2$ contents than the moderately LREE-enriched andesites though the two groups have considerable overlap. Sr and Nb isotopic compositions generally plot in a broad area near bulk earth on $^{87}\text{Sr} / ^{86}\text{Sr}$ vs. $^{143}\text{Nd} / ^{144}\text{Nd}$ diagrams (Fig. 1). The strongly LREE-enriched andesites and dacites originated by partial melting of garnet or hornblende-bearing lower crust in areas underlain by accreted terranes having arc affinities.

The third group consists of dacites and rhyolites within the study area. These felsic rocks have highly variable trace-element and isotopic compositions and were generated by a variety of processes (Fig. 2). Most of the rhyolites have Nd isotopic compositions that are similar to at least some of the nearby andesites and plutonic rocks, but Sr isotopic compositions that vary significantly, probably because their $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios are much more easily modified by assimilation of basement rocks than their $^{143}\text{Nd} / ^{144}\text{Nd}$ ratios due to their low Sr contents. Rhyolites and dacites with moderately LREE-enriched patterns like nearby andesites (Blackburn Hills) were generated by fractionation of the andesites. Those with extremely low HREE patterns (Sischu volcanic field) are highly evolved rocks that have fractionated at least some garnet. Others that high very high trace-element concentrations appear to have assimilated significant amounts of crust. Some of the rhyolites from areas underlain by known Paleozoic or Precambrian continental crust have anomalously high Th, Sn, W, U, and F values, whereas none of the rhyolites from areas underlain by arc or oceanic crust have anomalously high contents of these elements. In general the highly evolved felsic rocks appear to be most sensitive to crustal type but they are also most difficult to interpret because they are so
highly evolved and because their low Sr contents make them more susceptible to secondary alteration as well as more sensitive to assimilation.
FIGURE 1. Data for mafic and intermediate

Moderately LREE-enriched group
Oceanic terranes
- Kipchik-Tulip vf
- Crooked Pluton
- Plummer and Canyon plutons
- Yukon river vf
- BBH vf, group 1

Continental terranes
- Nowitna vf
- Sischu vf

Strongly LREE-enriched group
- Kanuti vf
- BBH vf, group 2

Figure 2. Data for rhyolites

BBH rhyolites
Sischu rhyolites
Kanuti rhyolite
Yukon River
Rhenium and osmium are highly siderophile elements. They are amongst the least abundant elements in the Earth's crust and mantle because most of the complement of these elements resides in the Earth's core. The low terrestrial abundances of Re and Os have been a major difficulty in the application of Re-Os isotope systematics to terrestrial systems. The Re-Os isotopic system is uniquely suited to the geochronology of iron meteorites, however. The highly siderophile nature of these elements contrasts with the largely lithophile character of other elements with useful long-lived radio-isotopes; K, Rb, Sm, Lu, Th and U.

Many iron meteorites are fragments of the cores of asteroids. These meteorites are called magmatic irons and divide into groups, each of which samples a small planetary core that has undergone fractional crystallization. The two most populous of these are the IIAB and IIIAB groups. An isochron through six IIA irons yields an intercept of 0.8007 +/- 0.0029 that is not significantly different from the carbonaceous chondrite initial of 0.802 +/- 0.049. Uncertainty in the slope (0.07824 +/- 0.00053) corresponds to an error of +/- 31 Ma for an 4500 Ga age. A closure age of 4,596 +/- 152 Ma is derived if errors in decay constant- are included. Accepting the canonical chondrite age as an upper limit, the IIA irons crystallized between 4,560 and 4,444 Ma ago. The IIB iron, Mount Joy, lies 3 per mil. above the IIA isochron. The IIB irons crystallized from a highly evolved IIA melt with 187/Re/186Os possibly as high as 20. Thus Mount Joy could have a closure age <5 Ma younger than the IIA irons.

Three IIIA meteorites plot significantly above (7 to 10 per mil) the IIA isochron. The slope of 0.0775 +/- 0.0018 is similar to that of the IIA irons but the intercept of 0.8120 +/- 0.0075 appears significantly higher. Thus, there may be isotopic heterogeneities between the IIAB and IIAB parent bodies. Alternatively, the IIIAB irons may have evolved somewhat later than the IIA irons.

Not all iron meteorites are of magmatic origin. Group IAB irons, for example, possibly originated as pockets of impact melt near the surface of their parent body. In the Canyon Diablo IA iron, the bulk metal datum lies about 5 per mil above the IIA isochron, and forms a linear array with data for "swathing" kamacite and adjacent schreibersite from the rim of a large troilite nodule. The steep slope and low intercept of this array suggest isotopic disequilibrium or recent Re distribution (perhaps due to shock on impact ?)

Chondrites are essentially collections of space junk and whole rock samples do not yield Re-Os isochrons in the same sense as the magmatic irons. An enstatite chondrite (Pillister, EL6) and an ordinary chondrite (Chainpur LL3) are almost identical in isotopic composition and plot 7 per mil below the IIA isochron. A carbonaceous chondrite (Michel CM2) is even less radiogenic and plots 11 per mil below the IIA line.
Nd and Pb isotopic evolution of basalts of the 1.1 Ga Midcontinent rift: Evidence for a region-wide model for plume-lithosphere-asthenosphere interaction

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The more than $1 \times 10^6$ km$^3$ of dominantly tholeiitic basalt erupted during the Midcontinent rifting event has been attributed to the upwelling of a mantle plume beneath North America at about 1.1 Ga (Paces and Bell, 1989; Hutchinson et al., 1990; Nicholson and Shirey, 1990). Volcanism associated with the Midcontinent rift lasted less than 25 m.y. from about 1109 Ma to 1086 Ma (Davis and Sutcliffe, 1985; Palmer and Davis, 1987). Basalts exposed around Lake Superior span the entire age range, thus providing an ideal suite in which the chemical and isotopic composition can be used to deduce the evolution of basaltic magmatism as continental rifting progressed.

In the western Lake Superior region, the basal flows are slightly alkalic to transitional tholeiites that fall into two compositional groups (Nicholson et al., 1991). One group has clinopyroxene phenocrysts, a rarity in younger high-alumina flows, and is characterized by low Al$_2$O$_3$ contents, steep REE patterns (Fig. 1A) and average La/Yb = 23, Th/Ta = 1.45, and Zr/Y = 11. For this group, model initial $\mu$ ranges from 7.7 to 8.3 and initial $\varepsilon_{Nd} = -0.7$ to +0.7. In contrast, the second group is either aphyric or contains olivine and plagioclase phenocrysts rather than clinopyroxene phenocrysts. Additionally this group has higher Al$_2$O$_3$ contents, lower light REE enrichment and average La/Yb = 11.2, Th/Ta = 2.6, and Zr/Y = 6.1. Model initial $\mu$ range from 8.2 to 8.7 and initial $\varepsilon_{Nd} = -0.3$ to -6.9.

The main stage high-alumina basalts are widespread and represent the bulk of the erupted volcanic rocks. These basalts fall into distinctly high- and low-TiO$_2$ types having different lines of descent. Incompatible trace elements in both types of tholeiites are enriched compared to depleted or primitive mantle (La/Yb=5.4-5.6; Th/Ta = 2.03-2.53; Zr/Y= 4.5-4.8) (Fig. 1B) and both types are isotopically indistinguishable. Nd and Pb isotopic compositions of the Portage Lake tholeiites (representative of the mainstage lavas) have initial $\varepsilon_{Nd} = 0\pm2$ and
model initial $\mu = 8.2$ (Brannon, 1984; Dosso, 1984; Paces and Bell, 1989; Nicholson and Shirey, 1990).

The very youngest rift basalts are exposed in the North Shore Volcanic Group and as dikes cutting older rift basalts in the Powder Mill Group. Compared to the main stage basalts, the youngest basalts are more depleted in incompatible trace elements (Figs. 1A, 1B). These basalts have $\text{La/\text{Yb}}=4.1$, $\text{Th/\text{Ta}} = 1.78$, and $\text{Zr/\text{Y}}= 4.4$. Initial $\varepsilon_{\text{Nd}}$ ranges from -2.4 to 3.6 ±2; and model initial $\mu = 8.0-8.2$.

Klewin and coworkers (Klewin and Berg, 1991; Klewin et al., 1991; Klewin and Shirey, in press) had first proposed a model of time-dependent plume-lithosphere-asthenosphere interaction based on the continuous basaltic section exposed at Mamainse Point in eastern Lake Superior. The new data presented here from widespread exposures in western Lake Superior fit this model and allow it to be extended to the entire rift that is exposed in the Lake Superior basin. In addition, basalts that erupted earlier than basal picrites at Mamainse Point allow a clear look at what appear to be first melts from the plume.

The clinopyroxene-bearing basal basalt flows were the first lavas to be erupted in the western Lake Superior region and are hypothesized to be the products of low degrees of partial melting of the plume that would have had an initial $\varepsilon_{\text{Nd}} = 0±2$ and model initial $\mu = 8.2$ (Fig. 2). If this were true, then in northwestern Lake Superior there appears to have been local crustal contamination by rocks of the Superior Province that resulted in a lowering of initial Pb isotope compositions towards model initial $\mu = 7.7$ but little change in initial $\varepsilon_{\text{Nd}}$ (Fig. 3). The non clinopyroxene-bearing early basalts are slightly younger than the clinopyroxene-bearing basalts based on stratigraphic relations at Pigeon Point, Minnesota. In some areas of northwestern, southwestern and eastern Lake Superior these rocks are the basal basalts. This magma type is widespread around Lake Superior and can be explained by mixing of melts derived by higher degrees of partial melting of the plume and melts from some other source, which may have been crust or mantle lithosphere.

The main stage basalts are remarkable for their great volume (Hutchinson et al., 1990), apparent high extrusion rate (Davis and Paces, 1990), and their apparent isotopic homogeneity (Figs. 2, 3). Although a subcontinental lithospheric source can not be ruled out on isotopic grounds, the most likely source that could account for these characteristics is an upwelling, enriched mantle plume that underwent decompression melting in a region of lithosphere thinned by extension.
The youngest basalts are more strongly depleted than the older rift basalts. As indicated by their trend towards more depleted initial $\epsilon_{Na}$ (up to +3.5) (Figs. 2, 3), they most likely resulted from mixtures of melts formed by higher degrees of partial melting of the plume and melts from a MORB-type asthenosphere.

Thus, the progression in sources through time began with localized small degree plume melts which were the first magmas to erupt, followed by widespread flood basalts derived from mixtures of small degree plume melts+lithospheric melts as the lithosphere began to thin substantially. Voluminous high-alumina tholeiitic basalts followed, most of which were deposited in the rapidly subsiding central graben. These basalts were derived from plume melts that represented large degrees of partial melting. Most of the early and mainstage lavas were erupted through fissures; thus, there was little fractionation of magmas. Towards the end of the mainstage of volcanism, crustal magma chambers were established (for example, beneath the Porcupine Mountains in Michigan and in some intrusions in the Duluth Complex) in which extensive assimilation and fractional crystallization took place. Finally the last fissure basalts to erupt occurred as the plume had begun to wane, allowing mixtures to develop of plume melts and MORB asthenosphere.
References


Fig. 1: A. Rare earth element patterns for early, main stage, and late basalts of the Midcontinent rift. B. Spidergram shows trace element abundances for average early, main stage, and late basalts normalized to primitive mantle abundances. Elemental abundances for primitive mantle are from Taylor and McClenann (1985).
FIG. 2: SOURCE RESERVOIRS FOR MRS MAGMATISM

<table>
<thead>
<tr>
<th>Western Lake Superior¹</th>
<th>Eastern Lake Superior²</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{Nd}$</td>
<td>SOURCES</td>
</tr>
<tr>
<td>0 to +3</td>
<td>Plume</td>
</tr>
<tr>
<td>-9 to -17</td>
<td>Plume + asthenosphere</td>
</tr>
<tr>
<td></td>
<td>Plume + local</td>
</tr>
<tr>
<td></td>
<td>crustal assimilation</td>
</tr>
<tr>
<td>about 0</td>
<td>Plume (main stage)</td>
</tr>
<tr>
<td>-2 to -7</td>
<td>Plume + lithosphere</td>
</tr>
<tr>
<td>about 0</td>
<td>Plume</td>
</tr>
</tbody>
</table>

¹ Data for the western Lake Superior region include published analyses for main stage basalts (Nicholson and Shirey, 1990) and the authors' unpublished data for the early (in the North Shore Volcanic Group and the Powdermill Group) and late basalts (basalt flows in the North Shore Group and a dike that intrudes the Powdermill Group).

² Data for the eastern Lake Superior region from Mamainse Point, Ontario (Klewin and Shirey, in press).
Fig. 3: Diagram of initial $\varepsilon_{\text{Nd}}$ vs. $\mu_1$ illustrating estimated reservoirs available at about 1100 Ma. Reservoir symbols as follows: CM=Central Minnesota, DM=depleted mantle, EM=enriched mantle, ALC I=Archean lower crust, low-$\mu$ composition, ALC II=Archean lower crust, high-$\mu$ composition, AUC=Archean upper crust, and WMT=Wisconsin Magmatic terrane.
Introduction

The detailed understanding of igneous systems and the role they play in the Earth's crustal and mantle evolution has been greatly advanced by the application of the naturally occurring long-lived radioactive decay schemes of Rb-Sr, Sm-Nd and Re-Os. The long half-life of these decays (40 to 100 Ga) makes these isotopic systems suited to problems in the cosmochronology of lunar rocks and meteorites and in the geochronology of terrestrial rocks ranging in age from the Archean through to the Paleozoic. Together with the U-Pb system, these decay schemes form the backbone of our understanding of the age relations of early Solar System materials and of Precambrian and younger igneous rocks. It is now quite common for data from several of these isotopic systems to be obtained on one suite of rocks. Each isotopic system has a different geochemical response to geological disturbances, therefore the independent chronometers can serve as checks on closed-system behavior -- an important part of any study of absolute age. A more involved, but equally fundamental approach has been to use these decay schemes to trace the long-term changes that occur in their parent to daughter ratios as rocks are melted or remelted. These different systems are useful because they display wide differences in sensitivity to typical igneous processes. The multiple isotope system approach is and will continue to be an important direction in isotope geoscience.

The three isotopic systems covered, the Rb-Sr, Sm-Nd and Re-Os systems, are in widely different states of maturity and degree of application in isotope laboratories around the world. The Rb-Sr system has been actively applied to geochronology for more than 35 years resulting in more than 5000 references dealing with isochron-determined ages. The Sm-Nd system has been applied only over the last 16 years in a much smaller number of laboratories and has resulted in more than 400 references dealing with isochron ages. The Re-Os system has been applied for the last 11 years, and for terrestrial geochronology really only the last 4 years in a handful of laboratories. This has resulted in less than 20 references using the Re-Os system for geochronology.

Historical development of parent-daughter isochrons

The discovery of radioactivity early in the twentieth century and the application of natural radionuclides to absolute age determination has had a profound impact on the earth sciences. Major advances such as the correct assessment of the age of the Earth and the Solar System and the theory of plate tectonics hinge on the correct analysis and application of radioactive decay schemes.

The historical development of the Rb-Sr system has been chronicled in Hamilton (1965) and Faure and Powell (1972). According to these authors, the beta decay of $^{87}$Rb to $^{87}$Sr was conclusively proven when Sr separated from an old lepidolite by Hahn and coworkers in 1937 was shown by Mattauch in the same year to be composed of 99.7% $^{87}$Sr. Goldschmidt was the first to suggest that old Rb-rich minerals could be dated by this decay and the first age of 530 Ma was obtained by Hahn and coworkers in 1943 on pollucite. Early on, only extremely Rb-rich minerals could be dated and the application of the Rb-Sr scheme in its present form had to await techniques for the efficient chemical separation of Rb and Sr from rocks and improvements in mass spectrometer precision, accuracy and sensitivity. These advances occurred through the application of cation exchange chromatography and isotope dilution to the chemical procedures and through the addition of the vibrating reed electrometer, the digital voltmeter, the magnetic field controller and the microcomputer for on-line data reduction and instrument control (e.g. Wasserburg et al. 1969).

The graphical representation of the Rb-Sr, Sm-Nd and Re-Os systems for cosmochronology and geochronology is the parent-daughter isochron diagram. In this diagram, the numerator isotope in the isotopic ratio of the abscissa (e.g. $^{87}$Rb in $^{87}$Rb/$^{86}$Sr) decays to the numerator isotope in the isotopic ratio of the ordinate (e.g. $^{87}$Sr in $^{87}$Sr/$^{86}$Sr) and the denominator isotopes are the same stable isotope (e.g. $^{86}$Sr), having no component derived from radioactive decay. All rocks and minerals that are part of the same closed system, having the same initial $^{87}$Sr/$^{86}$Sr and age, will fall on a straight line, the slope of which corresponds to the age of the system. The mechanics of this diagram can be found in numerous texts (e.g. Faure and Powell, 1972; Hamilton, 1965; Faure, 1986 and DePaolo, 1988).

According to Hamilton (1965), the use of this diagram for the graphical analysis of the age of a suite
of rocks and minerals was first applied to the Rb-Sr system by Allsopp and Nicolaysen at the Bernard Price Institute in South Africa and was referred to at the time as a "Nicolaysen" or a "B.P.I." diagram. After its utility had been clearly demonstrated for the Rb-Sr system, it was subsequently applied to the K-Ar, U-Pb, Th-Pb, Sm-Nd and Re-Os isotopic systems, among others. In general, the advantage of the isochron method is in the statistical treatment that can be applied to the analyzed rocks and minerals to evaluate the uncertainty of the age, to discover any geological basis for this uncertainty and to investigate multiple disturbances to the system. These advantages are important in studies that combine the Rb-Sr, Sm-Nd and Re-Os isotopic systems because of their differing behavior during post-crystallization processes such as metamorphism in the Earth's crust and shock metamorphism in the Solar System.

Compared to the Rb-Sr system, the historical development of the Sm-Nd system (see, O'Nions et al. 1979-for brief discussion) proceeded exceedingly rapidly primarily because the theoretical basis for such isochrons was well understood and because mass spectrometers capable of high-precision isotope ratio measurements were already being applied to Rb-Sr studies on lunar materials and the Allende carbonaceous chondrite. Also, chemical procedures for the effective separation of Sm from Nd had been fully established. In a pioneering study, Notsu et al. (1973) tried to determine whether a $^{142}$Nd/$^{144}$Nd anomaly existed in the achondrite Juvinas that would imply the existence of the extinct radionuclide $^{146}$Sm in the early Solar System and that might put age constraints on the formation interval of the Solar System. They pointed out that $^{143}$Nd, the decay product of the the long-lived radionuclide $^{147}$Sm, could be used to date the crystallization age of the meteorite at the same time the product of the extinct radionuclide was being studied. While the analytical uncertainties on the $^{142}$Nd/$^{144}$Nd and $^{143}$Nd/$^{144}$Nd ratios were too large to provide meaningful results, they showed that a sufficient range was present to answer both the age and isotopic anomaly questions if higher precision Nd isotopic determinations could be made. Shortly thereafter Lugmair et al. (1975) published the first high precision Sm-Nd isochron which was obtained on a mare basalt from Apollo 17 (sample 75075).

The development of the Re-Os isotope system (discussed briefly by Faure, 1986) has proceeded in stages since the pioneering work in the early 1960's of Herr and coworkers on meteorites and Hirt and coworkers on molybdenites. This early work provided the most accurate age estimates at the time for iron meteorites and showed that, within 800 Ma age uncertainties, they probably had early Solar System ages. The application of the Re-Os system was severely limited by the low sensitivity of the thermal-ionization mass spectrometers (TIMS) of the day and the low abundances of Re and Os (sub-ppb) in terrestrial crustal rocks. Sixteen years later, using the much more sensitive secondary ion mass spectrometry (known as SIMS or the ion-probe), Luck and Allegre (Luck et al. 1980) initiated a new era in the application of the Re-Os isotopic system to cosmochronology with a study of iron meteorites and the metallic phase from one chondrite. Their results were an order of magnitude more precise analytically than the previous studies and gave an age of 4580 ± 210 Ma. This age is in surprisingly good agreement with the early data and gave further support to the early Solar System age for iron meteorites. More importantly, this work spurred the application of the newest high-sensitivity mass spectrometric techniques to Re-Os isotopic analysis and to apply the Re-Os isotopic system to new geological problems.

**Rb-Sr system**

The Rb-Sr system is based on the beta decay of $^{87}$Rb to $^{87}$Sr (Table 1). Faure (1986), Steiger and Jäger (1977), Faure and Powell (1972) and Hamilton (1965) review the history of measurements of the $^{87}$Rb decay constant. The currently used decay constant of $1.42 \pm 0.01 \times 10^{-11}\text{yr}^{-1}$ is that adopted by the IUGS subcommission on geochronology (Steiger and Jäger, 1977) which was based on the best measurements at that time of the growth of $^{87}$Sr in a pure Rb salt (Davis et al. 1977) and samples of well known age. Up to this time, much previous work had used a $^{87}$Rb decay constant of $1.37 \times 10^{-11}\text{yr}^{-1}$. Subsequent work on lunar samples and chondrites that have been dated very precisely with the U-Th-Pb systems have shown better agreement with Rb-Sr ages if a decay constant between these two values is used (e.g. $1.402 \times 10^{-11}\text{yr}^{-1}$; Minster et al. 1982). In reading the literature, it is important to be aware of which decay constants have been used to calculate Rb-Sr ages. The accuracy of the Rb decay constant still is one of the major absolute uncertainties in employing the Rb-Sr system. All ages in this paper have been calculated with the $1.42 \times 10^{-11}\text{yr}^{-1}$ decay constant.

The potential of the Rb-Sr system for geochronology and as an isotopic tracer was recognized early because there is a large range in Rb/Sr ratios present in common rock forming minerals and in some igneous rocks and sediments (Table 2, Fig. 1). The accuracy of Rb-Sr isochrons is largely dependent on whether or not the system has remained closed since crystallization. Unfortunately, the parent radionuclide, $^{87}$Rb, is a volatile and mobile alkali element, characteristics which lead to open-system behavior and
anomalous ages. The current practice is not to rely on the Rb-Sr system to give the only absolute age information on the crystallization age of a suite of rocks but to use it in concert with other decay schemes. Summaries of the Rb-Sr system and its applications in geochronology can be found in Faure and Powell (1972), Jäger (1979), Faure (1986) and Potts (1987).

An $\varepsilon_{\text{Sr}}$ notation to represent $^{87}\text{Sr}/^{86}\text{Sr}$ in the Rb-Sr system in a manner analogous to the Sm-Nd system (see below) has been defined and is sometimes used. It has not gained widespread acceptance probably because of the difficulty in defining a bulk earth reference reservoir for Sr and because the often radiogenic initial Sr isotopic compositions found in crustal rocks leads to exceedingly large $\varepsilon_{\text{Sr}}$ values. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ compositions in this paper are given directly without the $\varepsilon_{\text{Sr}}$ notation.

In the chemistry laboratory, Rb and Sr abundances typically are analyzed by the isotope dilution method using enriched $^{85}\text{Rb}$ and $^{84}\text{Sr}$ spikes. If the $^{84}\text{Sr}$ spike is pure enough, the Sr isotopic composition can be measured on the same aliquot used for isotope dilution. Separation of Rb from Sr and from the rock is by a one-step procedure using cation-exchange chromatography. The separated Rb and Sr typically are loaded on Ta or W filaments, respectively and analyzed by positive thermal ionization mass spectrometry. Potts (1987) gives a recent summary of the chemical and mass spectrometry procedures.

Sm-Nd system

The Sm-Nd isotope system is based on the alpha decay of $^{147}\text{Sm}$ to $^{143}\text{Nd}$ (Table 1). DePaolo (1988) presents a review of the half-life determinations of $^{147}\text{Sm}$. The current decay constant value of $6.54 \times 10^{-12} \text{yr}^{-1}$ (Table 1) is based on an average of the last 4 precise measurements from 1960 to 1970, which are in good agreement.

An important use of the Sm-Nd isotopic system, in conjunction with absolute age determinations, is to trace the history of light REE enrichment or depletion that accompanies the evolution of an igneous system. This history is recorded in initial $^{143}\text{Nd}/^{144}\text{Nd}$ variations of the igneous system. Because these variations are small, generally they are expressed in $\varepsilon_{\text{Nd}}$ units which are defined as deviations in parts in $10^4$ of the Nd isotopic composition of the sample at the time of interest compared to the Nd isotopic composition of a reference reservoir at the same time. A popular reference reservoir for the Nd system is the chondritic uniform reservoir or CHUR. DePaolo (1988) and Patchett (1989) give the appropriate equations and CHUR parameters. Positive values of $\varepsilon_{\text{Nd}}$ at a given time indicate a long-term history of light REE depletion (higher Sm/Nd) of a rock or its source relative to the chondritic reference reservoir (CHUR) whereas negative $\varepsilon_{\text{Nd}}$ indicates a history of long-term light REE enrichment (lower Sm/Nd) of a rock or its source relative to the chondritic reference reservoir. In general, the Earth's upper mantle or juvenile continental crust displays positive $\varepsilon_{\text{Nd}}$ values during and subsequent to the Archean whereas older, recycled continental crust displays lower positive or negative $\varepsilon_{\text{Nd}}$ values. It is important to remember that one $\varepsilon_{\text{Nd}}$ unit corresponds to a difference in $^{143}\text{Nd}/^{144}\text{Nd}$ of only 0.000050! This is only about 2 - 3.5 times the state-of-the-art for mass spectrometer precision between different runs of the same standard.

The utility of the Sm-Nd system for dating ancient rocks is enhanced by the ability of the REE to reside in some common rock-forming minerals (e.g. clinopyroxene in komatiite and basalt) and common accessory minerals (e.g. monazite, allanite, sphene and zircon in granitoids) that are resistant to alteration. This makes the isotope system relatively unsusceptible to parent and/or daughter redistribution on the whole-rock scale during metamorphism, a feature which has been highly touted in Archean geochronology. However, as shown below, this characteristic can be a disadvantage because the system can be difficult to reset during crustal melting and it often displays only a narrow range in Sm/Nd (Table 2, Fig. 1) which limits the absolute age precision possible from a Sm-Nd isochron. Introductions to the behavior of the Sm-Nd isotopic system in geochronology are given in O'Nions et al. (1979), Faure (1986), DePaolo (1988) and Patchett (1989).

The common practises in the chemistry laboratory is to determine Sm and Nd concentrations by isotope dilution using spikes of $^{149}\text{Sm}$ and $^{150}\text{Nd}$. Typically, Sm is separated from Nd after the light rare-earth elements (REE) have been separated as a group from the rock using cation-exchange chromatography. An excellent overview of this procedure can be found in Potts (1987). An efficient time to carry out the light REE group separation is at the end of the primary column separation of Rb from Sr. Two methods to separate Sm from Nd are in widespread use with equally good results: 1) ion-exchange chromatography using 0.25 molar methyllactic acid on a cation column and 2) ion-exchange chromatography using di-(2-ethylhexyl)-orthophosphoric acid mixed with teflon powder. Typically, the purified salts of Sm and Nd are loaded separately on Ta and Re filaments (respectively) and analyzed by positive thermal ionization mass spectrometry (e.g. Potts, 1987).

Two different schemes for normalization of Sm-Nd isotopic data for instrumental fractionation com-
commonly appear in the literature. In one scheme, \(^{146}\text{Nd}/^{144}\text{Nd}\) is taken to be 0.72190 and present day \(\varepsilon_{\text{Nd}}\) of zero equals a \(^{143}\text{Nd}/^{144}\text{Nd}\) of 0.512638. In the other scheme, \(^{146}\text{Nd}/^{144}\text{Nd}\) is taken to be 0.636151 and a present day \(\varepsilon_{\text{Nd}}\) of zero equals a \(^{143}\text{Nd}/^{144}\text{Nd}\) of 0.511847. The different normalization schemes used have been discussed in detail by DePaolo (1988), Faure (1986) and Wasserburg et al. (1981). Note that in going from the latter to the former, \(^{143}\text{Nd}/^{144}\text{Nd}\) is multiplied by 1.0015. The different normalization schemes will produce slightly different atomic weights for Nd which will result in slightly different \(^{147}\text{Sm}/^{144}\text{Nd}\) depending on the normalization scheme. Note that in going from the latter to the former, \(^{147}\text{Sm}/^{144}\text{Nd}\) is multiplied by 1.0015. When working with literature data it is especially important to be aware how these normalization schemes affect \(^{143}\text{Nd}/^{144}\text{Nd}\) since the raw ratios are 30 \(\varepsilon_{\text{Nd}}\) units different. The differences in \(^{147}\text{Sm}/^{144}\text{Nd}\) have a lesser effect on the differences between age-corrected initial \(^{143}\text{Nd}/^{144}\text{Nd}\) but they are significant and will be important for example, when comparing data from each scheme on an isochron diagram. Each normalization uses reference reservoir values that are appropriate for that normalization, so initial \(\varepsilon_{\text{Nd}}\) values quoted in any paper and model ages generally are equivalent regardless of normalization used.

Re-Os system

The Re-Os isotopic system is based on the beta decay of \(^{187}\text{Re}\) to \(^{187}\text{Os}\) (Table 1). Lindner et al. (1989) have recently measured the decay constant of \(^{187}\text{Re}\) at 1.64 ± 0.05 \(\times 10^{-11}\) yr\(^{-1}\) and have reviewed previous determinations of the decay constant. Their value is higher outside of experimental uncertainties of the best geological estimate of the decay constant (1.52 ± 0.04 \(\times 10^{-11}\) yr\(^{-1}\)) from the iron meteorite isochron of Luck and Allegre (1983) and slightly higher than their earlier estimate of 1.59 ± 0.05 \(\times 10^{-11}\) yr\(^{-1}\) (Lindner et al. 1986). Re-Os isochron ages in this paper have been calculated using the earlier Lindner et al. (1986) \(^{187}\text{Re}\) decay constant because it is intermediate between the extremes of the experimental and geological determinations and gives the best agreement between the precise U-Pb zircon age for the Stillwater Complex and its Re-Os isochron age. Obviously, continued use of this geochronometer will require determining the decay constant of \(^{187}\text{Re}\) to higher accuracy and precision.

The Re-Os system has great potential as a tracer of geological processes and for geochronology in igneous systems because initial \(^{187}\text{Os}/^{186}\text{Os}\) can vary by more than several tens of percent and \(^{187}\text{Re}/^{186}\text{Os}\) can vary by more than several orders of magnitude (Table 2, Fig. 1). Because it is uncertain just how susceptible the Re-Os system is to alteration during metamorphism, it is not clear yet whether the Re-Os system will be routinely useful in Proterozoic and Archean rocks.

Re and Os abundances are analyzed by isotope dilution using spikes of \(^{185}\text{Re}\) and \(^{190}\text{Os}\). Since Re and Os occur at such low concentrations in igneous rocks, large samples (1 to 50 g) are used. Typically, these have typically been dissolved by silicate digestion or by flux-fusion. Os can be separated from silicate digests by distillation into HCl, from peroxide fusions by distillation into HBr or from Na\(_2\)CO\(_3\)-borax fusions by concentration into an immiscible sulfide liquid (nickel-sulfide fire-assay). After Os distillation, Re can be separated from the rock by solvent extraction or by anion-exchange chromatography.

Until recently all of the modern Re-Os isotopic analyses were determined by secondary-ion mass spectrometry (SIMS). Currently, four techniques other than SIMS can produce Re-Os isotopic data: resonant ionization mass spectrometry (RIMS), inductively-coupled plasma mass spectrometry (ICP-MS), accelerator mass spectrometry (AMS) and negative thermal ionization mass spectrometry (NTIMS). At present, NTIMS has superseded all other techniques because of its superior sensitivity which leads to an order of magnitude more precise data.

Geochronology and cosmochronology with the Rb-Sr, Sm-Nd and the Re-Os systems

The concerted co-application of the Rb-Sr and Sm-Nd systems to terrestrial and extraterrestrial chronology has been extremely valuable in spite of the fact that the most precise ages are derived from the U-Th-Pb system. The Sm-Nd system has made the major contribution to the chronology of the moon by providing a reliable time-scale for lunar highlands formation, mare basalt eruption and KREEP evolution. It also has been a major source of reliable ages for differentiated and cumulate meteorites (Patchett, 1989). The Rb-Sr system has only been useful as a cosmochronometer in lunar basalts, chondrites and some achondrites. However, it has been valuable as an indicator of disturbance and as a tracer of planetary evolution.

In studies of Archean and Proterozoic crust on Earth, the Rb-Sr and the Sm-Nd systems have been pivotal in highlighting the differences among cratons. One endmember of craton formation, typified by the Superior Province, that formed by the relatively rapid extraction of crust from the mantle and its stabilization on 50 to 200 Ma timescale. If significant reprocessing of existing crust occurred, it often happened within the uncertainties of Sm-Nd and Rb-Sr isochrons. Therefore these systems themselves can not be
used to quantify the reprocessing except to put an upper limit on it and petrogenetic constraints derived from trace and major elements must be used. The other endmember of craton formation, typified by the North Atlantic Craton, the Yilgarn Block or the Antarctic Craton, is protracted tectonothermal evolution and significant crustal reprocessing which may be coincident with crustal extraction from the mantle. This may have occurred over the 1000 Ma timescale. In this case, Rb-Sr and Sm-Nd isochrons and their initial Sr and Nd isotopic compositions provide vital information on the protoliths, allow an evaluation of the relative proportion of juvenile crust to reprocessed crust and help unravel the deformational and metamorphic history of the craton.

The application of the Sm-Nd isotopic system to cosmo- and geochronology can be divided conveniently into five major groups of igneous rocks: lunar samples and meteorites, volcanic rocks (ultramafic and mafic to felsic), gabbros and anorthosites, lower crustal granulites, and ophiolites. For the purposes of these short course notes, the discussion of the combined application of the Rb-Sr Sm-Nd and the Re-Os isotopic systems will follow these basic groups. Space limitations here prohibit most of the discussion of the geochronologic application of these isotopic systems which is found in Shirey (1991). The entire list of these isochron studies has been included as Table 3 for completeness.

Except for felsic volcanic rocks, feldspathic granulites, and sialic gneisses, these five groups of igneous rocks are largely basic in bulk composition. For the Sm-Nd system in particular, rocks of basaltic chemistry are the chief ones to have sufficient variation in $^{147}\text{Sm}/^{144}\text{Nd}$ for a geochronologic study, either using mineral separates, different lava flows, or layers of contrasting mineralogy in layered intrusions. However, the generally limited spread in $^{147}\text{Sm}/^{144}\text{Nd}$ and the current analytical precision on $^{143}\text{Nd}/^{144}\text{Nd}$ determinations of 0.003% translates to an optimum age uncertainty of ± 20 Ma regardless of the age of the rock under study (e.g. DePaolo, 1988). It is only in older rocks where a 20 Ma absolute age uncertainty will produce an acceptably low uncertainty as a percentage of the absolute age. This has limited the practical application of the Sm-Nd system for geochronology to extraterrestrial samples and Precambrian to Phanerozoic rocks older than several hundred million years. Since there are large variations the parent daughter ratios in the Rb-Sr and the Re-Os systems this severe a limitation for them does not exist. The Rb-Sr system has other features which limit its utility in basic systems, namely the mobility of Rb and to a lesser extent Sr during alteration and metamorphism under a wide variety of conditions. One example of the mobility of Re and Os during alteration and metamorphism under a wide variety of conditions. One example of the mobility of Re and Os during amphibolite grade metamorphism of ultramafic-mafic, Archean schists has been discovered; it remains to be seen whether the Re-Os system will show more widespread open-system behavior.

The Sm-Nd system is less useful for internal and whole-rock isochrons on granitic rocks because granitic magmas usually have a rather restricted and low Sm/Nd which imparts a low Sm/Nd to all their crystallizing major and trace phases. Indeed, apart from the applications of the Sm-Nd system to the dating of Archean trondhjemite-tonalite-granodiorite gneisses, there have been fewer applications to granitic systems than there have been to mafic-ultramafic systems. Because of this low Sm/Nd, the main use of the Sm-Nd isotopic system in granitoids is to obtain model ages for the time at which the granitoid or its precursor was extracted from the depleted mantle.

The Rb-Sr system can yield good isochron systematics in granitic systems when the constituent minerals are fresh. However, in a granite, the phases with the most radiogenic Sr isotopic compositions which will control the isochron age (e.g. biotite, K-feldspar), commonly reflect the last hydrothermal, metamorphic or uplift event to which the granite was subjected. Since nearly all granites contain zircon, the U-Pb system is often the most successful technique for determining the emplacement age of granites. The Re-Os isotopic system has yet to be used to obtain isochrons on granites.

In many igneous suites, the Rb-Sr system has fallen into disfavor for providing absolute crystallization ages because it is too easily reset. This is not true for all igneous suites, especially those that are young, involve large fractionations between Rb and Sr and have high abundances of Rb and Sr. Some notable examples are the following: carbonatites, kimberlites, and evolved rhyolites. The ability of the Rb-Sr system to be reset has created a valuable niche for its use in the study of post-crystallization processes such as hydrothermal circulation, regional metamorphism, crustal uplift and brittle deformation.

**Lunar samples and meteorites**

The Rb-Sr and Sm-Nd isotopic systems have formed an invaluable pair of decay schemes for investigation of the age, pre-Solar System history and shock metamorphism of extraterrestrial samples. The most precise Sm-Nd cosmo-chronology on extraterrestrial materials has been carried out on single samples using internal Sm-Nd isochrons between mineral separates and their whole rock. Wherever possible, the use of these internal isochrons has been preferred because differences in the individual isochron age of meteorites in the same class can exist as can differences in age between different meteorite classes. In
addition, since the exact relationship between the sources of extraterrestrial samples is unknown, there is the possibility of radiogenic isotopic source heterogeneity even though work to date has shown it to be small and difficult to demonstrate. Chondrites and some achondrites show significant variations in $^{87}\text{Rb}/^{86}\text{Sr}$ and for these meteorite classes good ages can be obtained with the Rb-Sr system. Since many stony meteorites have low $^{87}\text{Rb}/^{86}\text{Sr}$ or contain phases with low $^{87}\text{Rb}/^{86}\text{Sr}$, the Rb-Sr system has been very useful for examining initial $^{87}\text{Sr}/^{86}\text{Sr}$ in the early Solar System. This has been facilitated by the volatility of Rb which has resulted in a large range in $^{87}\text{Rb}/^{86}\text{Sr}$ between the solar nebula, basaltic meteorites, the moon and the earth and hence a large degree of isotopic divergence in Sr in a rather short time. The Re-Os system is just beginning to be applied to iron meteorites and metals in stony meteorites. At present, the analytical precision on $^{187}\text{Os}/^{186}\text{Os}$ has improved so substantially that the isotopic system is showing great promise as a cosmochronometer. Some research groups have found systematic differences in initial $^{187}\text{Os}/^{186}\text{Os}$ between iron meteorites and chondrites. An example of Rb-Sr and Sm-Nd isochrons on the achondrite Angra dos Reis are shown in Fig. 2.

In Lunar rocks, the Sm-Nd system gives the most reliable ages because of favorable partitioning into the major silicate phases which produces a large variation in $^{147}\text{Sm}/^{144}\text{Nd}$. Some of the Lunar Sm-Nd isochrons are among the most precise yet produced. The Rb-Sr system is less reliable for lunar chronology. Rb was volatilized during lunar impacts, many Lunar rocks have low $^{87}\text{Rb}/^{86}\text{Sr}$ and much of the variation in $^{87}\text{Rb}/^{86}\text{Sr}$ in Rb-Sr mineral isochrons is evident in individual olivine splits perhaps due to the presence of small amounts of an exotic, high $^{87}\text{Rb}/^{86}\text{Sr}$ component. Rb-Sr and Sm-Nd isochrons on lunar troctolite 76535 are shown in Fig. 3.

### Ultramafic to felsic volcanic rocks

The initial applications of the Sm-Nd system to terrestrial geochronology were for absolute age determinations in Archean mafic to ultramafic volcanic rocks. Historically, these initial Sm-Nd results for each terrane were quite exciting for geochronology because they demonstrated that on the scale of individual whole-rocks and relative to the Rb-Sr and Pb-Pb systems, the Sm-Nd system is resistant to being reset by metamorphism.

By the time that the Sm/Nd system was first being applied to terrestrial rocks it was recognized widely from the general disagreement between whole-rock and internal Rb-Sr isochrons and U-Pb zircon ages, that Rb-Sr isochron ages accurately reflecting crystallization were difficult to obtain in mafic to ultramafic Archean rocks. This is a consequence of the limited range in $^{87}\text{Rb}/^{86}\text{Sr}$ in these rocks, the low Rb and Sr content of primary minerals such as olivine, orthopyroxene and clinopyroxene and the susceptibility of these primary minerals to alteration. In current studies of Archean mafic to ultramafic rocks, there are relatively few researchers that combine Sm-Nd with Rb-Sr data for primary crystallization ages. Rb-Sr is sometimes included for completeness in a study or to show the degree to which subsequent metamorphism may have affected the rocks.

The Sm-Nd isotopic system now has been applied successfully to the geochronology of Archean supracrustal rocks on every Archean craton. The main limitation to getting good Sm-Nd isochron systematics is the limited spread in parent-daughter ratio that is displayed by rocks related to the same source. This spread can be maximized by careful collecting of geologically related flows in the field to sample their natural variations in modal mineralogy or by carrying out mineral separations on well preserved samples. The best Sm-Nd ages are obtained with internal isochrons on fresh mafic to ultramafic rocks. Such fresh samples are exceedingly rare in the Archean, however. The next best alternative is to analyze related volcanic rocks that, because of field relations, are suspected to have a common source. In the push to maximize the Sm-Nd isochron systematics, caution must be exercised in putting rocks that, because of major or trace element compositional differences, are clearly petrogenetically unrelated on the same isochron. They may have had isotopically distinct sources which can lead to large scatter about the isochron or worse yet can give anomalously old or young ages A good example of this can be seen in Fig. 4. In general, the limited spread in $^{147}\text{Sm}/^{144}\text{Nd}$ for whole rocks prevents the Sm-Nd isotopic system from being able to reach practical precisions of less than ± 50 Ma on average. Although this age uncertainty is not small enough to permit stratigraphic correlations such as those possible with the U-Pb system in zircon, it is sufficient to resolve major age discrepancies in the ages of the supracrustal rocks. Further, initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, determined from isochrons, accurately reflect the time-averaged light REE patterns of the mantle sources for the supracrustal rocks. This is important in understanding the geochemical evolution of the mantle, especially as the ultimate source of continental crust, throughout the Precambrian. It also can lead to an understanding of Precambrian tectonic and petrogenetic processes.

The Re-Os system shows great promise for geochronology in mafic-ultramafic rocks because of the large range in $^{187}\text{Re}/^{186}\text{Os}$ that occurs in whole-rocks. Under greenschist-grade, burial metamorphism the
Re-Os isotopic system has remained closed even when the Rb-Sr system has been severely disturbed (Fig. 5). It can be, however, severely disturbed under the tectonic conditions that might involve shear in the amphibolite facies, high degrees of fluid flow and the remobilization of other platinum group elements.

**High-grade gneisses and granulites**

Sm-Nd geochronology indirectly has been a boon to the unravelling of the complex tectono-thermal history to which most gneiss terranes have been subjected. In high-grade gneisses, the Sm-Nd isotopic system applied as a geochronometer commonly has not been able to achieve a satisfactorily low age uncertainty because sialic crustal rocks have 147Sm/144Nd that is too low and too limited in range. The resistance of the Sm-Nd system to disturbance, though, has allowed the calculation of initial ɛ_{ Nd}'s that are accurate enough for petrogenetic purposes when the Rb-Sr, U-Pb and/or Pb-Pb isotopic systems have been used in conjunction with the Sm-Nd system. Comparison to these other systems and use of field relations between the rocks on an isochron are necessary to discern geological significance of the Sm-Nd isochron. It is not always clear whether it is the absolute age of the protolith, the age of high grade metamorphism or the age when two distinctly different rocks were interleaved into a single mixed rock.

The Rb-Sr system in such rocks typically yields substantially younger ages than the Sm-Nd system, demonstrating that the Rb-Sr system is usually strongly disturbed. For the study of such rocks it is best to rely on U-Pb system in zircon for ages, to use the Sm-Nd system for initial ɛ_{Nd} information and to employ the Rb-Sr system for information on post-crystallization metamorphism and hydrothermal circulation. One of the rare examples where the Rb-Sr system and the Sm-Nd system give comparable results in high-grade gneiss terranes is shown in Fig. 6. The Re-Os isochron method is yet to be attempted on such rocks.

**Gabbros, anorthosites and layered intrusions**

Gabbros and mafic layered intrusions have proven amenable to dating with Sm-Nd internal isochrons if typical magmatic mineral assemblages such as plagioclase + clinopyroxene ± orthopyroxene are freshly preserved. Internal isochrons have been successful in establishing the crystallization ages to within several tens of Ma. Whole rock samples alone from any one mafic layered intrusion, however, rarely have large enough variations in Sm/Nd ratio to form precise isochrons because the layered sequences all crystallize from the same magma that is being mixed by convection. The Rb-Sr system in such rocks commonly has been disturbed and has recorded younger ages that are post-crystallization. The few studies to date with the Re-Os system suggest it will have widespread application in producing precise ages because of the large magmatic variations in 187Re/186Os that exist in magma chambers (e.g. Fig. 7).

In general, anorthosites have been quite troublesome to date with the Sm-Nd isotopic system because their mineral-whole rock Sm-Nd systematics apparently have not survived the amphibolite to granulite grade conditions to which many anorthosites have been subjected and the whole-rock variations in Rb/Sr and Sm/Nd are limited. The Fiskenaesset Anorthosite Complex, in the North Atlantic Craton, is one of the anorthosite complexes that has been most successfully dated with the Sm-Nd system (Ashwal et al.; 1989). Small-scale open system behavior, which is minimal for the Fiskenaesset data, plagues the Sm-Nd isochron work for other anorthosites. Therefore, getting good precision on the isochrons has required judiciously removing certain data from the age regressions. Proterozoic massif anorthosites also typically have problems with open system behavior, as well.

**Ophiolites**

Ophiolite complexes, samples of obducted oceanic crust, are the focus of Sm-Nd isotopic studies because of their important role in defining the Nd isotopic composition of the depleted mantle from a period predating the formation of the present oceanic crust. It is still not known, however, just how the oceanic crust that becomes obducted is generated, e.g. whether it forms in a back-arc or at an oceanic spreading ridge. Since ophiolites are typically younger than 700 Ma and can have quite fresh mineralogy, most of the Sm-Nd geochronology to date has been carried out using internal mineral/whole-rock isochrons. They have been dated quite successfully with internal Sm-Nd isochrons because the original partitioning between primary phases is well preserved. The Rb-Sr system has been much less useful because nearly all ophiolite complexes have exchanged their igneous Sr with radiogenic seawater Sr during formation on the sea floor or during obduction. It is not clear that the Re-Os system will produce accurate ages on ophiolites. This should be the case based on the behavior of Re and Os in igneous systems. Seawater, however, has high Re and given the clear evidence for exchange from the Rb-Sr system, it may overprint the original Re content of ophiolites.

**Sr, Nd and Os initial ratio variations**

An important piece of information obtained from any isochron is the initial daughter isotopic ratio. Although a detailed discussion of initial 87Sr/86Sr, ɛ_{Nd} and 187Os/186Os of various groupings of igneous
rocks in different plate tectonic settings is beyond the scope of this short course, it is useful to summarize briefly how the initial isotopic ratios for the three systems derived from isochrons compare to one another and change throughout geologic time.

The extremely low $^{87}\text{Rb}/^{86}\text{Sr}$ of refractory inclusions in the Allende carbonaceous chondrite, the major phases in Angra dos Reis, plagioclases in lunar highlands rocks and basaltic achondrites have permitted the Rb-Sr system to be a sensitive indicator of the evolution of the early Solar System. Not enough age resolution is provided by the Rb-Sr system for these samples, so the $^{87}\text{Sr}/^{86}\text{Sr}$ evolution vs time history must be constructed using the most precise independent age information which is from Pb-Pb model ages. Details of early solar system Sr isotopic evolution have been discussed by Carlson and Lugmair (1988), Faure (1986), Tilton (1988) and Van Schmus (1981). Ca-Al-rich inclusions (CAI) in the Allende meteorite have the oldest Pb-Pb ages ($4559 \pm 4 \text{ Ma}$) and the most primitive $^{87}\text{Sr}/^{86}\text{Sr}$ of any early solar system materials. A regular increase in $^{87}\text{Sr}/^{86}\text{Sr}$ from that of the CAI's to that of the basaltic achondrites over the 20 Ma from 4559 to 4539 Ma suggests that the solar nebula evolved with a Rb/Sr (0.65) greater than chondritic (Faure, 1986; Tilton 1988; Van Schmus, 1981). The Sr isotopic composition of the oldest lunar highlands anorthosite 60025 (Carlson and Lugmair, 1988) suggests that either the moon formed within 20 Ma from material evolving along this evolution curve or that it formed 110 Ma later from material with a lower Rb/Sr more like that of the Earth. Carlson and Lugmair (1988) argued for the latter scenario and suggest that the composition of Angra dos Reis is a better starting composition from which to form both the Earth and the Moon.

The differentiation of the silicate portion of the Earth into a continental crust, an upper mantle and an oceanic crust represents a major, first-order fractionation of Rb from Sr (e.g. Fig. 1). On the scale of terrestrial Rb-Sr evolution, either the initial $^{87}\text{Sr}/^{86}\text{Sr}$ for basaltic achondrites or Angra dos Reis are reasonable starting points for the Sr isotopic evolution of the Earth's mantle. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the mantle, represented by Sr isotopic analyses of mantle-derived basaltic rocks, has grown at a relatively slow rate compared to the continental crust. Early initial Sr isotopic data for basaltic rocks compiled and summarized by Faure and Powell (1972) and Faure (1986) fall in a broad band that displays more rapid increase in $^{87}\text{Sr}/^{86}\text{Sr}$ from 4550 Ma to 2700 Ma (higher Rb/Sr) and less rapid growth of $^{87}\text{Sr}/^{86}\text{Sr}$ from 2400 Ma to the present (lower Rb/Sr). A family of growth curves can be drawn (e.g. Faure and Powell (1972), Fig. XII.2) suggesting that the mantle had a heterogeneous isotopic composition in the past and that there has been a marked lowering of the inferred time-averaged Rb/Sr from the early Archean to the Proterozoic.

A comparison of this envelope containing basaltic rocks with the data compiled for granitoids (Faure and Powell, 1972) shows granitoids evolve rapidly along growth curves with higher time-integrated Rb/Sr to more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$. Fully half of the granitoids in this compilation fall within the mantle Sr isotope envelope indicating that they can not contain significant amounts of old crust in their sources (Faure and Powell, 1972). Peterman (1977) has shown that Archean to Phanerozoic tonalites which are thought to have been derived from rapid remelting of basaltic crust have such low initial $^{87}\text{Sr}/^{86}\text{Sr}$ that an evolution curve drawn from them is indistinguishable from that of the depleted mantle. As discussed above, the Sr isotopic system is more affected by metamorphism and crustal mobility of Rb than is the Sm-Nd isotopic system or perhaps the Re-Os isotopic system. Although it is apparent that the Sr isotopic system has shown many of the systematic variations that have lead to more detailed models of mantle evolution in the Sm-Nd system, its open-system behavior during metamorphism has caused small but significant differences in initial $^{87}\text{Sr}/^{86}\text{Sr}$ to be suspect. Nonetheless, it is possible to use large differences in initial $^{87}\text{Sr}/^{86}\text{Sr}$ to characterize various present day mantle reservoirs (Table 1).

The Sm-Nd isotopic system is used much more widely now for looking at initial ratio variations in Precambrian rocks. For the Sm-Nd isotopic system, the initial $\varepsilon_{\text{Nd}}$ for chondritic meteorites (Jacobsen and Wasserburg, 1984) provides a well constrained starting point for solar system evolution. Since the range of $^{147}\text{Sm}/^{144}\text{Nd}$ in terrestrial and extraterrestrial whole-rocks is limited (e.g. Fig. 1) and both Sm and Nd are refractory, the first 20 to 100 Ma of the solar system does not have as profound an effect on Nd isotopic evolution as on Sr isotopic evolution. Evidence is gathering, however, that the earliest-formed rocks on both the Earth and the Moon had slightly higher initial $\varepsilon_{\text{Nd}}$ (+1.0) than the reference chondritic reservoir. The oldest lunar highlands rock, ferroan anorthosite 60025 has an initial $\varepsilon_{\text{Nd}}$ of +1.0, similar to 3 of 5 other high-Mg lunar highlands rocks (Carlson and Lugmair, 1988). The initial $\varepsilon_{\text{Nd}}$'s for all the terrestrial localities listed in Table 3 are plotted against age in Figs. 8a and 8b. These figures show that the first 800 Ma of preserved juvenile terrestrial crust also has a positive $\varepsilon_{\text{Nd}}$ regardless whether it is sialic or mafic. Such similarities seem to argue that the Earth and Moon were formed from a reservoir that behaved similarly, acquiring an early positive $\varepsilon_{\text{Nd}}$ signature. Carlson and Lugmair (1988) have discussed various explanations for this.
When initial \(\varepsilon_{Nd}\)'s for all the terrestrial studies discussed in the text are grouped according to rock type, some distinct differences in their \(\varepsilon_{Nd}\) evolution versus time emerge. With a few exceptions, supracrustal rocks show a distinctly positive \(\varepsilon_{Nd}\) throughout the Archean. As a group they are probably the least systematically contaminated and the most significant for tracking the evolution of the depleted mantle (Fig. 8a). Sialic high-grade gneisses are easily divisible into two groups: one that shows high and positive \(\varepsilon_{Nd}\)'s nearly identical to the supracrustal rocks and a second that shows \(\varepsilon_{Nd}\)'s ranging from positive to progressively more negative with time (Fig. 8b). A simple interpretation for this data is that the first group represent juvenile granitoids that were recycled too rapidly to diverge from depleted mantle compositions. The second group represents those gneisses that contain a large proportion of recycled continental crust. Mafic intrusive rocks (including gabbros, anorthosites and mafic layered intrusions) have more variable \(\varepsilon_{Nd}\) and, towards younger ages, show a greater proportion of lower initial \(\varepsilon_{Nd}\)'s. A likely explanation is that contamination is more prevalent in such crustal magma chambers. With only a few exceptions, flood basalts and ophiolites are restricted to late-Proterozoic to Phanerozoic occurrences. Flood basalts show the widest range in \(\varepsilon_{Nd}\) and some of the lowest initial \(\varepsilon_{Nd}\)'s. This is most likely due to contamination as they pass through continental crust, their derivation in lithospheric sources having some light REE enrichment or because their sources may involve upwelling mantle plumes whose sources show long-term light REE enrichment. Ophiolites have some of the highest initial \(\varepsilon_{Nd}\)'s yet analyzed, approaching that of modern MORB. Values for the Nd isotopic composition of modern terrestrial reservoirs are given in Table 1.

The Os isotopic evolution of solar system materials and the Earth is not as well known as for the Sm-Nd or Rb-Sr system because the number of analyses is small. Os isotopic composition of meteorites and metals from meteorites have not been measured with enough precision to examine fine-scale Os isotopic variations at the inception of the solar system. Also, the age of iron meteorites has not been determined precisely as is the case for stony meteorites using the Pb-Pb system. For the Earth, the few analyses that exist do constrain the evolution of various terrestrial reservoirs. The existing initial Os isotopic data is plotted against age in Fig. 9. Based on our level of present knowledge, the Earth's mantle could have evolved either along an evolution path from a chondritic initial \(^{187}\text{Os}/^{186}\text{Os}\) (Walker et al. 1989), along an evolution curve passing through osmiridiums (Allegre and Luck, 1980) or along an evolution curve passing through two of the most primitive ocean island basalts (Martin, 1991). The osmiridium growth curve is slightly lower than the chondritic growth curve and has a present day \(^{187}\text{Os}/^{186}\text{Os}\) close to 1.04 (Fig. 9) whereas the silicate earth evolution curve is higher than the chondritic curve and has a present-day \(^{187}\text{Os}/^{186}\text{Os}\) close to 1.10 (Fig. 9). Tentative evidence for the formation of depleted mantle reservoirs by the late Archean can be taken from the initial \(^{187}\text{Os}/^{186}\text{Os}\) of 2700 Ma old komatiites from Munro Township, Ontario which is distinctly lower than any of the mantle evolution curves. However, more work is needed to confirm this. Upwelling regions of the Earth's upper mantle identifiable as distinct plumes, appear to have radiogenic \(^{187}\text{Os}/^{186}\text{Os}\) (Fig. 9) as evidenced by the Gorgona komatiites and the composition of Hawaii and Iceland. Subcontinental mantle regions that are refractory due to depletion in melt components have the lowest initial \(^{187}\text{Os}/^{186}\text{Os}\) yet measured because of their long-term low Re/Os. Sialic crust, as yet only characterized indirectly, is likely to have a long-term history of high Re/Os and therefore a radiogenic initial \(^{187}\text{Os}/^{186}\text{Os}\). The values for present-day terrestrial reservoirs are compiled in Table 1.

References
Chase, C.G. and Patchett, P.J. (1988): Stored mafic/ultramafic crust and early Archean mantle depletion,
S.B. Shirey -- Rb-Sr, Sm-Nd and Re-Os Cosmo- and Geo-chronology

Earth Planet. Sci. Lett. 91, 66-72.


Nelson, B.K. and DePaolo, D.J. (1985): Rapid production of continental crust 1.7-1.9 b.y. ago: Nd and Sr isotopic evidence from the basement of the North American midcontinent. 96, 746-754.


Nyquist, L.E., Takeda, H., Bansal, B.M., Shih, C.-Y., Wiesmann, H. and Wooden, J. L. (1986): Rb-Sr and Sm-Nd Internal Isochron Ages of a Subophitic Basalt Clast and a Matrix Sample from the Y75011
S.B. Shirey -- Rb-Sr, Sm-Nd and Re-Os Cosmo- and Geo-chronology


Table 1: Comparison of Rb-Sr, Sm-Nd and Re-Os isotopic systems and reference reservoirs.

<table>
<thead>
<tr>
<th></th>
<th>Rb-Sr</th>
<th>Sm-Nd</th>
<th>Re-Os</th>
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<tr>
<td><strong>Element type</strong></td>
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<tr>
<td>Valence (VI-fold coordination)</td>
<td>+1</td>
<td>+3</td>
<td>+4,5,+6,+7</td>
</tr>
<tr>
<td>Ionic Radius (Å)</td>
<td>1.52</td>
<td>0.96</td>
<td>0.63,0.58,</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>0.63,0.58,0.55,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.53,0.39</td>
</tr>
<tr>
<td><strong>Decay Scheme</strong></td>
<td>$^{87}$Rb$\rightarrow ^{87}$Sr $\beta^-$</td>
<td>$^{147}$Sm$\rightarrow ^{144}$Nd $\alpha$</td>
<td>$^{187}$Re$\rightarrow ^{187}$Os $\beta^-$</td>
</tr>
<tr>
<td>Decay Constants</td>
<td>$1.42\pm0.01 \times 10^{-11}$</td>
<td>$6.54\pm0.05 \times 10^{-12}$</td>
<td>$1.52\pm0.04 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>$1.402\pm0.008 \times 10^{-11}$</td>
<td></td>
<td>$1.59\pm0.05 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.64\pm0.05 \times 10^{-11}$</td>
</tr>
<tr>
<td><strong>Reference Reservoirs</strong></td>
<td>$^{87}$Rb/$^{86}$Sr</td>
<td>$^{147}$Sm/$^{144}$Nd</td>
<td>$^{187}$Re/$^{186}$Os</td>
</tr>
<tr>
<td>Chondritic Reference Reservoir</td>
<td>0.08278</td>
<td>0.1966$^h$</td>
<td>3.3$^l$</td>
</tr>
<tr>
<td>Chondritic Reference Reservoir</td>
<td>$^{87}$Sr/$^{86}$Sr</td>
<td>$^{143}$Nd/$^{144}$Nd</td>
<td>$^{187}$Os/$^{186}$Os</td>
</tr>
<tr>
<td>Depleted Mantle (MORB)</td>
<td>0.704508</td>
<td>0.512638$^h$</td>
<td>1.06$^l$</td>
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<tr>
<td>Enriched Mantle (OIB)</td>
<td>0.7027$^+5/1$</td>
<td>0.5132$^+1/1$</td>
<td>1.04$^+2/1$</td>
</tr>
<tr>
<td>Convergent Margin (IAB)</td>
<td>0.7034$+7/1$, 0.7053$+7/1$</td>
<td>0.5130$+2$, 0.5126$+2/1$</td>
<td>1.10$+3/1$</td>
</tr>
<tr>
<td>Continental Crust (granite, sediment)</td>
<td>0.7039$+10/1$</td>
<td>0.5130$+2$, 0.5126$+2/1$</td>
<td>14$^n$</td>
</tr>
</tbody>
</table>

The term "chondritic reference reservoir" is only applicable to the Sm-Nd system (CHUR) and the Re-Os system. For the Rb-Sr system, this term is not directly applicable because the parameters are derived from the Sr-Nd mantle array for oceanic basalts and are distinctly different from the growth curve for chondrites. Data sources for this table are as follows: $^a$Steiger and Jäger (1977), $^b$Lugmair and Marti (1978), $^c$Luck and Allegre (1983), $^d$Lindner et al. (1986), $^e$Minster and Allegre (1982), Nyquist et al. (1986), $^f$Lindner et al. (1989), $^g$DePaolo (1988), $^h$Jacobsen and Waterburg (1984), Patchett (1989) (Values for fractionation correction to $^{146}$Nd/$^{144}$Nd = 0.72190), $^i$Morgan and Walker (1989), $^j$Morris and Hart (1983), $^k$Martin (1991), $^l$Faure (1986), $^m$Taylor et al. (1983) and $^n$Esser and Turekian (1990).
### Table 2: Comparative abundances of Rb, Sr, Sm, Nd, Re and Os and their ratios in rocks Earth reservoirs and rocks

<table>
<thead>
<tr>
<th></th>
<th>Rb</th>
<th>Sr</th>
<th>Rb/Sr</th>
<th>Sm</th>
<th>Nd</th>
<th>Sm/Nd</th>
<th>Re</th>
<th>Os</th>
<th>Re/Os</th>
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<tr>
<td>Primitive mantle</td>
<td>0.48&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.03</td>
<td>0.314&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.967&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.32</td>
<td>0.26&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.08</td>
</tr>
<tr>
<td>Oceanic crust</td>
<td>2.2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>130&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.02</td>
<td>3.3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.33</td>
<td>0.33 - 1.5&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.001 - 0.3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1 - 1500</td>
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<tr>
<td>Continental crust</td>
<td>32&lt;sup&gt;c&lt;/sup&gt;</td>
<td>260&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.12</td>
<td>3.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>16&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.22</td>
<td>0.40&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.041&lt;sup&gt;d&lt;/sup&gt;</td>
<td>10</td>
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<tr>
<td>C-1 chondrite</td>
<td>3.45&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.30</td>
<td>0.231&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.711&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.32</td>
<td>35.8&lt;sup&gt;b&lt;/sup&gt;</td>
<td>517&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.07</td>
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<td>Komatiite&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.8 - 3.6</td>
<td>7 - 36</td>
<td>0.10</td>
<td>0.4 - 0.86</td>
<td>0.86 - 1.9</td>
<td>0.47</td>
<td>0.5 - 1.3</td>
<td>1 - 2.2</td>
<td>0.5</td>
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<tr>
<td>MORB</td>
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<td>113&lt;sup&gt;f&lt;/sup&gt;</td>
<td>0.01</td>
<td>3.75&lt;sup&gt;f&lt;/sup&gt;</td>
<td>11.2&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>0.33 - 1.5&lt;sup&gt;d&lt;/sup&gt;</td>
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<tr>
<td>OIB</td>
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<td>3638</td>
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<td>0.4 - 0.8&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>Granite</td>
<td>159&lt;sup&gt;h&lt;/sup&gt;</td>
<td>163&lt;sup&gt;h&lt;/sup&gt;</td>
<td>0.98</td>
<td>5.67&lt;sup&gt;h&lt;/sup&gt;</td>
<td>28.7&lt;sup&gt;h&lt;/sup&gt;</td>
<td>0.20</td>
<td>0.04 - 0.34&lt;sup&gt;i&lt;/sup&gt;</td>
<td>0.01 - 0.02&lt;sup&gt;i&lt;/sup&gt;</td>
<td>4 - 17</td>
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Rb, Sr, Sm and Nd analyses are in ppm, Re and Os are in ppb. Data sources areas follows: <sup>a</sup>Taylor and McLennan (1981), <sup>b</sup>Morgan (1986), <sup>c</sup>Taylor and McLennan (1985), <sup>d</sup>Martin (1991), <sup>e</sup>Walker et al. (1988), <sup>f</sup>Hofmann (1988), <sup>g</sup>Newsom et al. (1986), <sup>h</sup>McCulloch and Chappell (1982) and <sup>i</sup>Walker et al. (1991).
<table>
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<tr>
<th>Sample Name</th>
<th>Sample Type</th>
<th>Sm-Nd Age</th>
<th>Type $^\text{E}_{\text{Nd}}(t)$</th>
<th>Ref</th>
<th>Rb-Sr Age</th>
<th>Type $^\text{Sr}^{87}/^\text{Sr}^{86}(t)$</th>
<th>Ref</th>
<th>Other age</th>
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<td>Angra dos Reis</td>
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### HIGH-GRADE GNEISSES AND GRANULITES

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**GABHAUS, ANORTHOSITES AND LAYERED INTRUSIONS**

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**OPHIOILITES**

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**Shawney et al.**, 1976; 2Papanassasiou and Wasserburg (1976); 3Carlson and Lugmair (1988), (note that this is one of many pristine lunar highlands rocks that have been studied in detail, see ref. 3 for summary); 4U-Pb and Pb-Pb ages from literature, (uncertainty due to assumptions in initial Pb isotopic composition, see discussion in Ref. 3); 5Lugmair et al. (1975); 6Papanassasiou et al. (1977); 7Nyquist et al. (1979); 8Shih et al. (1987); 9Carlson and Lugmair (1979); 10Nyquist et al. (1975); 11Lugmair and Marti (1977); 12Wasserburg et al. (1977), (Angra dos Reis, Allende and Babi initial 87Sr/86Sr corrected for interlaboratory bias as given in ref. 3); 13Jacobsen and Wasserburg (1984); 14Lugmair (1974); 15Lugmair et al. (1976); 16Unruh et al. (1977); 17Kamakura et al. (1977); 18Allegre et al. (1975); 19Tera et al. (1987); 20Lugmair et al. (1977); 21Pb-Pb isochron age (Tera et al., 1989); 22U-Pb ages on other monomict eucrites Berbea, Nuevo Laredo and Bouvante (Carlson et al., 1988 and ref 21); 23Average of Pb-Pb model ages from literature as given in Tilton (1988); 24U-Pb concordia (Manhes et al., 1984); 25Pb-Pb age (ref. 16); 26Gray et al. (1973) (corrected for interlab bias as given in ref. 3); 27Pb-Pb age (Chen and Wasserburg, 1981) (this age is for Ca-Al rich inclusions); 28Nyquist et al. (1974); 29Minster et al. (1982); 30Summary of best Pb-Pb model ages for chondrites as given in Tilton (1988); 31Kamakura et al. (1982); 32Papanassasiou and Wasserburg (1974), (corrected for interlaboratory bias as given in ref. 3); 33Shih et al. (1982), (note that the Sm-Nd internal isochrons for these meteorites were disturbed at 116-620 Ma and that no w-r Rb-Sr was obtained); 34Nyquist et al. (1986), (Sm-Nd isochron combines matrix, clasts and minerals from each, Rb-Sr isochron is that given for matrix); 35Hamilton et al. (1979); 36Jahn et al. (1982); 37Pb-Pb whole-rock isochron on least contaminated samples (Wilson and Carlson, 1988), (Note that the Nondweni greenstone belt displays three subparallel Sm-Nd isochrons with different initial ratios); 38Hegner et al. (1984), ("other age" listed is U-Pb zircon age on interbedded rhyolite); 39Carlson et al. (1983); 40Hamilton et al. (1981); 41Grau et al. (1987); 42Minimum age for Talga-Talga based on U-Pb zircon age of overlying Duffer Fm (Pigeon et al. (1978); 43Fletcher et al. (1984); 44McCulloch and Compston (1981); 45Pb-Pb isochron age (Rodwick, 1984); 46Cloue-Long et al. (1984); 47Chauvel et al. (1984), ("Other age" listed is Pb-Pb w-r age, including sulfides); 48Cloue-Long et al. (1988), (U-Pb zircon age on correlative chert horizon, accepted Gambalda age); 49Zindler (1982); 50Dupre et al. (1984); 51Basu et al. (1984);
52Hamilton et al. (1986); 53Cattell et al. (1984); 54Shirley and Hanson (1986); 55Xuan et al.; 56Drury et al. (1987); 57Balakrishnan et al. (in press); 58Hamilton et al. (1977); 59Hamilton et al. (1978); 60Skiold and Cliff (1984); 61Chauvel et al. (1986); 62Zindler (1982); 63Bokhari and Kramers (1981); 64Devlin et al. (1988); 65Walker et al. (1988). (Note that the "other age" is a Re-Os isochron age which agrees well with a 2720±20 Ma Pb-Pb age on nearby flows. See text.); 66Two Re-Os isochron ages obtained on eastern komatiites and tholeiites respectively (Walker et al. (in press)); 67Hamilton et al. (1979); 68Whitehouse (1988); 69Humphries and Cliff (1982); 70Cliff et al. (1983); 71Marcantonio et al. (1988). ("Other age" listed is U-Pb zircon age); 72Baadsgaard et al. (1986). ("Other ages" listed are the means of large number of conventional U-Pb zircon analyses); 73Collerson et al. (1989); 74Jahn et al. (1987b); 75Jahn et al. (1987a); 76Fletcher et al. (1988); 77Ion-microprobe U-Pb zircon age, (Kinny et al. 1988); 78McCulloch et al. (1983); 79Black and McCulloch (1987), ("Other age" listed is Pb-Pb whole-rock age); 80DePaolo (1981); 81Burwash et al. (1985); 82Windrim and McCulloch (1986); 83Mork et al. (1988); 84McCulloch et al. (1987); 85Korsch and Gulson (1986); 86Morrison et al. (1985). ("Other age" listed is U-Pb zircon age); 87DePaolo and Wasserburg (1979); 88Re-Os whole-rock, mineral isochron (Lambert et al. 1989); 89U-Pb zircon age (Lambert et al. 1990); 90Zindler et al. (1981); 91Hegner et al. (1989); 92DePaolo and Wasserburg (1984); 93DePaolo (1985); 94Ashwal et al. (1983); 95Hill (1988); 96Walker et al. (1991). ("Other ages" listed are three separate Re-Os isochrons with distinctly different initial Os isotopic compositions); 97Claesson et al. (1984); 98Jacobsen and Wasserburg (1979); 99Pin and Carme (1987); 100Edwards and Wasserburg; 101McCulloch et al. (1980); 102McKenna et al. (1987); 103Saleeby et al. (1989). ("Other age" listed is U-Pb zircon age); 104U-Pb zircon age (Krogh et al. 1984); 105Gruau et al. (1990); 106Ar 40/39 age (Lopez-Martinez et al. 1984); 107Evaporation single zircon Pb-Pb age (Krogh and Todt, 1988); 108Ion microprobe U-Pb zircon age (Armstrong et al. 1990).
Fig. 1: Abundances of parent vs daughter element (in ppm) for the Rb-Sr, Sm-Nd and Re-Os systems plotted on the same axes. Data and sources are given in Table 2. Dashed lines represent constant parent-daughter ratio. Cl=carbonaceous chondrites, PM=primitive mantle, K=komatiite, M=mid-ocean ridge tholeiite, O=Ocean island tholeiite, G=granite.
Fig. 2 Comparison of internal Rb-Sr and Sm-Nd isochrons on the achondrite Angra dos Reis. The Sm-Nd isochron is essentially a two-point isochron that gives an age equal to the formation of the solar system. The fractions analyzed for Rb-Sr work include whole-rock splits, pyroxene and the phosphate, whitlockite. They are extremely unradiogenic and do not regress to a precise age. They are consistent with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ that is clearly resolved as lower than the basaltic achondrite isochron but higher than the initial $^{87}\text{Sr}/^{86}\text{Sr}$ on Ca-Al rich chondrules from the Allende meteorite. Figure 2a is redrawn from Lugmair and Marti (1977). Figure 2b is redrawn from Wasserburg et al. (1977) and The Sm-Nd isotope systematics of Angra dos Reis have been reanalyzed by Jacobsen and Wasserburg (1984) with similar age results.
Fig. 3 Internal Rb-Sr and Sm-Nd isochrons for lunar troctolite 76535, a typical early cumulate from the lunar highlands. The Rb-Sr and Sm-Nd isochron ages are not in agreement. The current interpretation of the Sm-Nd age is as the age of crystallization, whereas the Rb-Sr age currently is interpreted as anomalously old (Carlson and Lugmair, 1988). All phases on the Rb-Sr isochron are unradiogenic and the slope appears to be controlled by olivine mixing with some old radiogenic component. In contrast, note the large range in $^{147}\text{Sm}/^{144}\text{Nd}$ of the magmatic phases on the Sm-Nd isochron. Fig. 3a is redrawn from Papanastassiou and Wasserburg (1976) and Fig. 3b is redrawn from Lugmair et al. (1976).
Fig. 4: Sm-Nd isochrons and ε Nd vs MgO relationships for volcanic rocks of the Nondweni greenstone belt, Kaapvaal Craton, South Africa. When grouped by composition (Fig. 4a), three isochrons with similar ages but different initial 143Nd/144Nd are apparent. Adding felsic volcanic rocks to this group isochron produces an artificially old age (Fig. 4b). The initial ε Nd of the samples varies directly with their MgO content (Fig. 4c), suggesting the lower ε Nd are produced by crustal contamination as shown by the assimilation-fractional crystallization curves. Tick marks indicate percentage of crustal input. Figs. 5a-c redrawn from Wilson and Carlson (1989).
Fig. 5: Sm-Nd, Rb-Sr and Re-Os whole-rock isochrons for komatiites from the Pyke Hill locality, Munro Township, Ontario. The komatiites show an extremely limited spread in $^{147}\text{Sm} / ^{144}\text{Nd}$ that does not regress to an isochron. The Rb-Sr systematics have clearly been reset at some time after crystallization. The Re-Os isochron shows substantial spread in $^{187}\text{Re} / ^{186}\text{Os}$ and gives the accepted crystallization age. Figures redrawn from Walker et al. (1988).
Fig. 6: Rb-Sr and Sm-Nd whole-rock isochrons for Amitsoq gneisses from the Isukasia area, southern West Greenland. The white and grey gneisses show such a limited spread in $^{147}$Sm/$^{144}$Nd that their Sm-Nd isochron ages are indistinguishable outside of errors. The mean age for the regressions, however, agree quite well with the individual Rb-Sr isochrons for each of the gneiss groups. Note the changes in scale for the Rb-Sr isochrons. Figures redrawn from Baadsgaard et al. (1986a).
Fig. 7: Initial $\varepsilon_{\text{Nd}}$ vs Nd/Sm and Re-Os whole-rock isochrons for whole-rocks from the Stillwater Igneous Complex, Montana. Differences are apparent in the initial $\varepsilon_{\text{Nd}}$ of the magmas (Fig. 7a). A large and apparently magmatic $^{187}\text{Re}/^{186}\text{Os}$ is displayed by ultramafic series sulfides, silicates and chromitites (Fig. 7b) allowing a precise age for the intrusion to be calculated. A significant difference exists, however, between anorthositic type magmas and ultramafic-type magmas (Fig. 7c) with substantial evidence for magma mixing. These figures are redrawn from Lambert et al. (1989).
Fig. 8: Initial $\varepsilon_{\text{Nd}}$ vs time for a majority of the mantle-derived rocks and crustally derived rocks from the literature that are discussed in the text. The data are plotted as individual samples from Sm-Nd isochron regressions with the age taken from the Sm-Nd isochron if it is the accepted age of crystallization. Supracrustal rocks in Fig 8a include both mafic and felsic major element compositions but are dominated by the former. Intrusive rocks include anorthosites, gabbros and mafic layered intrusions. High-grade gneisses are included with granitoids on Fig. 8b. Additional data on initial $\varepsilon_{\text{Nd}}$ in flood basalts has been added. Note the positive $\varepsilon_{\text{Nd}}$ growth curve for the mantle in the Archean. It is not clear from the data whether the mantle has evolved in continuous or a stepwise fashion. Note also the occurrence of various types of rocks during certain periods of Earth history. The granitoids are divided into two types. Juvenile granitoids clearly have a much higher initial $\varepsilon_{\text{Nd}}$. Note the time-scale change for Fig. 8b compared to 8a.
Fig. 9: Initial $^{187}$Os/$^{186}$Os vs time for Re-Os isotopic data from the literature. Three possible terrestrial growth curves are plotted: 1) a curve through osmiridiums (Allegre and Luck, 1980), 2) a curve calculated from the analyses for chondrites (Walker et al. 1989) and 3) a curve passing through primitive ocean island basalts (Martin, 1991). See text for details. Lithospheric peridotites have the lowest initial $^{187}$Os/$^{186}$Os, whereas upwelling plumes and enriched portions of layered intrusions have the highest $^{187}$Os/$^{186}$Os.
CHARACTERISTICS OF "GOOD" ISOCHRONs

THE THREE PRIMARY ASSUMPTIONS FOR VALID ISOCHRONs:

• All samples on an isochron formed at the same time.
• All samples had same initial isotopic composition at time of crystallization.
• System remained closed to parent-daughter diffusion.

ADDITIONAL CHARACTERISTICS TO HELP JUDGE ISOCHRON QUALITY:

• Clear geological relationship among samples on isochron.
• High degree of linearity on parent-daughter plot.
• Age agreement with precise data from another system.
• "Sensible" age that agrees with stratigraphy.
• Accurately and precisely date a real geological event (i.e. crystallization, high-T metamorphism, uplift).
• Isochron initial derivable from reasonable reservoirs.
## Practical Comparison of Isotope Systems (Cont.)

<table>
<thead>
<tr>
<th></th>
<th><strong>Rb-Sr</strong></th>
<th><strong>Sm-Nd</strong></th>
<th><strong>Re-Os</strong></th>
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<tbody>
<tr>
<td><strong>Amenable to Isochrons</strong></td>
<td>chondrites, sialic gneisses, granites, pegmatites, rhyolites, hydrothermal ores</td>
<td>meteorites, lunar samples, Pre-C volcanics, Pre-C gneisses, ophiolites, layered intrusions, anorthosites</td>
<td>iron meteorites, peridotites, komatiites, picrites, ophiolites, layered intrusions</td>
</tr>
<tr>
<td><strong>Not Amenable to Isochrons</strong></td>
<td>low vol. meteorites, lunar samples, Pre-C volc. rocks</td>
<td>granites, young rocks</td>
<td>diff. meteorites, lunar samples (basalts), (andesites), (granites)</td>
</tr>
<tr>
<td><strong>Amenable to Model Ages</strong></td>
<td>granites, gneisses</td>
<td>granites, alkalic rocks, eclogites</td>
<td>peridotites, molybdenites (basalts), (granites)</td>
</tr>
<tr>
<td><strong>Not Amenable to Model Ages</strong></td>
<td>Pre-C volc. rocks</td>
<td>komatiites, basalts</td>
<td>komatiites, chromitites</td>
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PRACTICAL COMPARISON OF ISOTOPE SYSTEMS

<table>
<thead>
<tr>
<th></th>
<th>Rb-Sr</th>
<th>Sm-Nd</th>
<th>Re-Os</th>
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<tr>
<td><strong>HOST MINERALS</strong></td>
<td>major</td>
<td>major and trace</td>
<td>ultratrace</td>
</tr>
<tr>
<td><strong>PAR./DAUGH. RANGE</strong></td>
<td>large</td>
<td>limited</td>
<td>profound</td>
</tr>
<tr>
<td><strong>METAMORPH. EFFECTS</strong></td>
<td>large</td>
<td>very limited</td>
<td>limited</td>
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<td><strong>MAIN USES</strong></td>
<td>hydrothermal uplift</td>
<td>crystallization mixing</td>
<td>crystallization hydrothermal PGE</td>
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<tr>
<td><strong>FACTOR/FAULT MOVEMENT</strong></td>
<td>high Rb systems</td>
<td>post-crystallization</td>
<td>post-crystallization</td>
</tr>
<tr>
<td><strong>LESSER USES</strong></td>
<td>crystallization</td>
<td>post-crystallization</td>
<td>post-crystallization</td>
</tr>
</tbody>
</table>
INTERNAL VS WHOLE-ROCK ISOCHRONS

THE INTERNAL ISOCHRON:
- Comprised of minerals separated from one sample.
  - Advantages:
    - All components of isochron formed at same time.
    - All components of isochron will have same initial.
  - Disadvantages:
    - Minerals are more susceptible to parent-daughter interdiffusion (more easily reset).

INTERNAL VS WHOLE-ROCK ISOCHRONS (CONT.)

THE WHOLE-ROCK ISOCHRON:
- Comprised of different whole-rock samples.
  - Advantages:
    - Components are too far apart for interdiffusion even on geologic time scales (more difficult to reset).
  - Disadvantages:
    - Components of may not have formed at same time.
    - Components may not have had the same initial ratio.
ISOCHRON AGES VS MODEL AGES

ISOCHRON AGES:
• Based on multi-sample least-squares regression line fit.
• Statistical treatment of systematics of fit possible.
• Validity of age uncertainty can be estimated.
• Disturbances to system can be discerned.
• Requires a large amount of data for each isochron.

ISOCHRON AGES VS MODEL AGES (CONT.)

MODEL AGES:
• Based on isotopic growth curve-reservoir intersection.
• No check of data with systematics possible.
• Age uncertainty is large and has no geological significance.
• Disturbances to system are not evident directly.
• Can be used on just one sample (this may be enough to decide between various petrogenetic processes.)
The hydrothermal stability of zircon: Preliminary experimental and isotopic studies

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(Received October 8, 1991; accepted in revised form June 16, 1992)

Abstract—Experimental investigations of the stability of the U-Pb isotopic system in nonmetamict zircons show that appreciable losses of Pb and U can be induced at amphibolite grade conditions (400°C to 600°C, 1 to 6 kb) in 2 M NaCl and 2% HNO₃ solutions. The severity of U loss and, to a lesser extent Pb loss, varies with solution composition: in this case the 2 M NaCl solution induced more Pb and U loss than the 2% HNO₃ solution at the same P-T conditions. Scanning electron microscopy of the run products also revealed a range of corrosion-related surface features, which suggest that some of the observed trends in Pb and U loss must be attributed to zircon dissolution. Backscattered electron (BSE) imaging of the run products further suggests that partial homogenization of chemical zoning patterns occurred during the experiments. Microprobe analyses of treated and untreated grains show that both populations have a similar range of Hf contents. Thus, the apparent loss of sharp, well-defined zoning features is most likely due to small-scale “smearing out” of formerly sharp chemical gradients and is perhaps related to the annealing of lattice defects caused by alpha-recoil damage. Thus, experimentally induced U-Pb isotopic discordance in zircon is a complex function of zircon stability and annealing effects.

INTRODUCTION

The chemical and isotopic response of zircons to changes in P and T may be complicated by primary intracrystalline chemical, structural, and isotopic inhomogeneities (e.g., Steiger and Wasserburg, 1966; Sommerauer, 1974, 1976; and others). Steiger and Wasserburg (1966) first suggested that the anisotropic response of zircon crystals to thermal events was due to the presence of discrete isotopic and physiochemical microdomains within each grain. Sommerauer (1974, 1976) demonstrated that zircons rich in trace elements (>1 mol% total) consist of two phases: a thermally stable structure with low trace element concentration and an amorphous, microheterogeneous mixture of SiO₂ and ZrO₂ which is enriched in trace components; an observation now more fully documented by the transmission electron microscopy studies of McLaren et al. (1991). Low temperature (ca. 350°C) annealing and loss or gain of radiogenic Pb, U, Th and other trace elements is likely due to small-scale “smearing out” of formerly sharp chemical gradients and is perhaps related to the annealing of lattice defects caused by alpha-recoil damage. Thus, experimentally induced U-Pb isotopic discordance in zircon is a complex function of zircon stability and annealing effects.

A number of geochronologic studies of metamorphic rocks (Gebauer and Grünfelder, 1976, 1979; Sinha and Glover, 1978; Williams et al., 1984) have shown that zircon-hosted U, Th, and Pb may undergo a considerable degree of redistribution at subsolidus conditions. In some instances, the zircon U-Th-Pb system remains undisturbed regardless of P-T conditions or kinematic regime (Peucat et al., 1985; Tilton et al., 1958). It is likely that variations in the degree of metamorphically induced U-Th-Pb discordance may be attributed to a number of factors: (1) growth of rims on preexisting zircon crystals implying either residual enrichment, or solution and transport of Zr during metamorphic or hydrothermal events (Gastil et al., 1967; Davis et al., 1968; Hart et al., 1968; Gulson and Krogh, 1973; Sinha and Glover, 1978; Peucat et al., 1985; Gebauer et al., 1981; van Bree man et al., 1987; Wayne et al., 1992); (2) radiation damage, hydroxylation, and subsequent structural annealing incurred prior to or during metamorphism (Gastil et al., 1967; Gebauer and Grünfelder, 1976; Corfu et al., 1985; Silver and Deutsch, 1963); (3) discontinuities in the bulk composition of the enclosing rocks or minerals (Gebauer and Grünfelder, 1979; Aleinikoff, 1983; Wayne et al., 1992); (4) high fluid pressure and activity during metamorphism (Gebauer and Grünfelder, 1976; Sinha and Glover, 1978; Schärer, 1980); (5) direct U adsorption without new crystal growth (Grauer et al., 1974); (6) decrease in structural integrity of zircon crystal structure through radiation damage (Holland and Gottfried, 1955; Ozkan, 1976; Yada et al., 1981) in association with volume changes may cause brittle failure (Chakoumakos et al., 1987) and enhanced leachability of U-Pb by fluids (Ewing et al., 1982; Krogh and Davis, 1973). From these studies, it is apparent that the significance of a particular discordance-generating circumstance or mechanism may vary, and that no single factor can be correlated to consistent trends of isotopic discordance. However, the importance of fluid/rock ratios during metamorphism and the ability of hydrothermal and metamorphic fluids to dissolve and transport Zr, Hf, U, Th, Pb, REEs, and other elements is undeniable (Gebauer and Grünfelder, 1976; Cuney, 1973;...

During a metamorphic episode involving fluids, the radiation-damaged portion of a zircon may be subject to a number of processes leading to isotopic discordancy. These processes include (1) preferential leaching of metamict zones due to the penetration of fluids along microfractures (cf. Wayne and Sinha, 1988), (2) annealing of metamict zones, or entire crystals during metamorphism (Gulson and Krogh, 1975), and (3) volume or grain boundary diffusion of Pb (or U) out of the zircon (Tilton, 1960; Wasserburg, 1963). The factors controlling the rate and extent of these processes must include (1) the physical and chemical nature of the zircons involved, (2) the intensity and duration of the P-T conditions of the metamorphic/hydrothermal episode, and (3) the composition and amount of fluid present.

Examples of discordancy generating mechanisms from mylonite zones, and regionally metamorphosed rocks will be described.


CRUSTAL EVOLUTION OF GRENVILLE TERRANES IN THE CENTRAL AND SOUTHERN APPALACHIANS: THE Pb ISOTOPE PERSPECTIVE FOR GRENVILLE TECTONICS

PARKS, Jane E., JENKS, Patrick J., SINHA, A.Krishna., Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

Grenville (1.0 b.y.) age rocks are recognized in eastern North America from Newfoundland to Texas have similarities and differences in terms of their time-integrated Th/U and U/Pb. Initial Pb isotopic compositions of the basement rocks of the Virginia Blue Ridge (of Group I) are used as a reference for comparing all other isotopic ratios. These reference isotopic values (the average of 25 whole rocks) are 206Pb/204Pb: 16.63-18.64 (average 17.27), 207Pb/204Pb: 15.38-15.58 (average=15.48), 208Pb/204Pb: 33.52-39.51 (average=36.50). The isotopic deviation in percent (Δ207/204, Δ208/204) show a remarkable separation of the basement massifs into separate U-Th-Pb provinces. For example, Δ207/204 and Δ208/204 values for other Group I rocks (such as the State Farm Gneiss of Virginia) range from -4.4 to 3.6 and -30.9 to 11.1 respectively. Rocks of Group II have a higher percent deviation from the reference. For example, the Carvers Gap Gneiss of North Carolina has a Δ207/204 range of 4.63-13.25 and a Δ208/204 range of 91.78-414.78 and defines a clearly distinct reservoir for Δ208/204 values.

Limited published lead isotopic data for other Grenville age basement massifs from Newfoundland to Texas have similarities and differences in terms of their time-integrated Th/U and U/Pb relative to the reference values presented here. For example, data from Texas have higher time-integrated Th/U and similar U/Pb while basement massifs from the Adirondacks have similar time-integrated Th/U but higher U/Pb.

The use of Pb isotopes to determine source region characteristics for crustal provinces has far reaching implications. Differences between juvenile crust and reworked older crust, leading to similarities or differences in reservoirs can be used as a method for determining the accretionary history of distinct terranes during the Grenville Orogeny.

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ARGON THERMOCHRONOLOGY OF MINERAL DEPOSITS
L.W. Snee

$^{40}\text{Ar}/^{39}\text{Ar}$ thermochronologic studies can be instrumental for understanding the genesis of mineral deposits. This method can easily establish the age of deposits that contain potassium-bearing alteration or gangue minerals. Equally or more important, however, is the capability to define the duration of and the number of thermal pulses during mineralization as well as gross estimates of the temperature during mineralization. Because analytical precisions are often on the order of 0.1% (absolute) and because the age-spectrum method enables evaluation of the argon systematics of each sample, fine-scale temporal resolutions are possible. I will discuss a few of our argon thermochronologic studies on selected mineral deposits and review the types of information derived for each and how the argon data were combined with other types of data, in some cases, to develop genetic models. Particular deposits to be discussed include the gold deposits within the Idaho batholith; the Juneau gold deposits, Alaska; tin-tungsten deposits of Panasqueira, Portugal, Geiju, China, and Cornwall, England; the Urad-Henderson molybdenum deposit, Colorado; and the Illinois-Kentucky fluorspar district.

Selected References:


Snee, L.W., and Hayes, T.S., 1992, \(^{40}\text{Ar}/^{39}\text{Ar}\) geochronology of intrusive rocks and Mississippi-Valley-type mineralization and alteration from the Illinois-Kentucky fluorspar district; U.S.G.S. Open-File Report 92-1, p.59-60.
AGE AND GENESIS OF PRECIOUS METALS DEPOSITS, BUFFALO HUMP DISTRICT, CENTRAL IDAHO: IMPLICATIONS FOR DEPTH OF EMPLACEMENT OF QUARTZ VEINS

KAREN LUND,* LAWRENCE W. SNEE,† AND KARL V. EVANS
U. S. Geological Survey, Box 25046, Mail Stop 922, Denver Federal Center, Denver, Colorado 80225

**Fig. 3.** Cooling curve for the Buffalo Hump district. 1 = amphibolite; 2 = muscovite-biotite granite; 3 = quartz vein: A = rapid cooling (about 95°C/m.y.) of amphibolite at about 9 km; B = emplacement of muscovite-biotite granite at 4 to 9 km; C = fracturing and gold mineralization at >4 km; D = slow cooling (about 3.5°C/m.y.) of region at about 4 km.

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40Ar/39Ar Thermochronology of Fracture-Controlled Mineral Deposits of the Idaho Batholith—Age, Thermal History, and Origin

By L.W. Snee, Karen Lund, K.V. Evans, C.H. Gammons, and M.J. Kunk

40Ar/39Ar age-spectrum dating is a highly precise (<0.25 percent absolute analytical uncertainty) and accurate isotopic technique that is a powerful tool for solving some long-standing problems in economic geology, including the age, duration, number of stages and (or) episodes, and temperature of mineralization. This method offers the temporal resolution necessary for dating different stages of mineralization and alteration in hydrothermal systems. An age-spectrum or isochron analysis of the data from a sample provides information about the distribution of argon in the analyzed mineral or whole rock and can indicate whether the dated material formed before, during, or after alteration. Duration of mineralization and number of episodes can be evaluated by comparing mineral data from veins that formed during multiple stages with data from associated wall rocks. 40Ar/39Ar age-spectrum dates are unique because the time when various minerals close to diffusion of argon can be related to temperature; thus, the dates provide a thermochronology. These time-temperature data are useful for understanding details of ore-forming processes and for planning mineral exploration. 40Ar/39Ar thermochronologic data have been used to provide valuable constraints on the age, thermal history, and origin of fracture-controlled mineral deposits of the Idaho batholith.
The age and origin of gold-bearing quartz veins hosted in Cretaceous rocks of the Idaho batholith or older rocks in central Idaho were the subject of debate prior to detailed isotopic dating. Eocene plutonic and dike rocks crop out in many of the mining districts, and, locally, disseminated gold deposits are present in Eocene volcanic rocks such as in the Thunder Mountain district. It has been long argued that the numerous gold-bearing quartz veins distributed throughout the Idaho batholith were genetically related to the Eocene plutonic and volcanic event.

Many quartz veins in the southern part of the Idaho batholith (within the Elk City, Challis, Hailey, and Twin Falls 1° x 2° quadrangles) are near the roof zones of Late Cretaceous (78–70 Ma), marginally peraluminous, granite-granodiorite (primarily biotite granodiorite and muscovite-biotite granite) plutons; other quartz veins are in older metaluminous granodiorite-tonalite plutons (93–87 Ma) and metamorphic rocks that were intruded by the younger plutons. The deposits are both in discrete quartz-filled fissure veins and in disseminated deposits along silicified shear zones. All the deposits are characterized by quartz flooding, episodic brecciation, and open-space filling. Wall-rock alteration is minor. The fissure-vein and shear-zone deposits contain sulfides and have produced gold, silver, copper, lead, zinc, molybdenum, tungsten, antimony, and mercury. Sulfide minerals of the veins vary from district to district, perhaps because of the depth of formation of the vein systems and possibly because of different sources of the metals. Although parallel Eocene dikes are common in several districts, the dikes cut mineralized rock and are neither silicified nor mineralized; thus, the Eocene dikes formed after the mineralization.

High-precision $^{40}\text{Ar}/^{39}\text{Ar}$ age-spectrum dates of muscovite and potassium feldspar from quartz veins and altered host rock from 15 districts range from 78 to 57 Ma. Ages of the deposits within any district tend to form clusters; locally, multiple mineralization events occurred in some districts (for example, Edwardsburg, Profile Gap, Yellow Pine, Atlanta). Ages of the deposits are slightly younger than cooling ages of the peraluminous granites in most districts. Therefore, the vein deposits are Cretaceous or, less commonly, Paleocene and were not formed by hydrothermal activity associated with Eocene plutons. Furthermore, the $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra for minerals from the deposits and the cooling history of the region after emplacement of Cretaceous granites quantify the thermal and spatial effects of younger events. In particular, age spectra of quartz-vein muscovites commonly show $^{40}\text{Ar}$ loss that occurred during younger Cretaceous and Paleocene mineralization; only those samples collected within a few meters of Eocene dikes, plutons, and volcanic centers display partial $^{40}\text{Ar}$ loss incurred during Eocene events. In addition, microcline from nearby Cretaceous plutons yields Late Cretaceous to Paleocene $^{40}\text{Ar}/^{39}\text{Ar}$ dates which indicate that the ambient temperature of host rocks and mineral deposits was already below about 150 °C (the argon closure temperature of microcline) before Eocene magmatic events. Thus, only Cretaceous or Paleocene mineral deposits that were cut by Eocene plutons or dike swarms show the effects of temperatures exceeding 150 °C. Mixed-layer illite/muscovite, which has an estimated argon closure temperature of less than 150 °C, was collected from two alteration zones adjacent to Eocene dikes and yielded $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 52 Ma. Therefore, metals were remobilized locally during Eocene magmatic activity, but the importance of such an event has not been evaluated.

In summary, most of the studied mineral deposits were episodically formed in fractures at or near the roof of marginally peraluminous, Cretaceous granite plutons, either in extensional fissures that opened during postemplacement cooling and uplift of the plutons or in preexisting and long-lived shear zones near the roof of the plutons. The Paleocene metallogenic activity may have been related to local slow cooling after the Cretaceous magmatic event or to undocumented Paleocene magmatism. Subsequently, most of these same fracture systems served as avenues for the emplacement of Eocene dikes and local remobilization of metals.
Thermochronology of Economic Mineral Deposits: Dating the Stages of Mineralization at Panasqueira, Portugal, by High-Precision $^{40}$Ar/$^{39}$Ar Age Spectrum Techniques on Muscovite

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Abstract

$^{40}$Ar/$^{39}$Ar age spectrum dates for 13 muscovites have been used to reconstruct the thermal history (thermochronology) of the Panasqueira, Portugal, tin-tungsten deposit, a deposit spatially associated with a belt of Hercynian plutons. Muscovite samples with an age difference as small as 2.2 m.y. (0.7% of the age) are statistically distinct. Statistics are even better for comparison of multiple samples from separate events; that is, a difference of 0.9 m.y. (0.3%) can be resolved in this ~300-m.y.-old deposit. The major tin and tungsten ore-forming stages, which are the oxide-silicate stage, the main sulfide stage, and greisenization, occurred between 296.3 ± 0.8 (1σ) and 291.6 ± 0.8 m.y. (1σ). The first substage of the oxide-silicate stage was a short-lived thermal pulse at 296.3 ± 0.6 m.y.; the fluids responsible may have emanated from the known granite cupola. The main sulfide stage was active at 294.5 ± 0.9 m.y. as a slightly longer lived pulse with oldest evidence for this stage (295.8 ± 0.6 m.y.) coming from areas farthest away from the known cupola and youngest evidence (293.5 ± 0.8 m.y.) closest to the cupola. A second substage of the oxide-silicate stage occurred as a short-lived thermal pulse at 292.9 ± 0.7 m.y., synchronous with greisenization of the cupola and alteration of the silica cap at 292.1 ± 0.4 m.y. The duration of activity of the oxide-silicate stage, the main sulfide stage, greisenization, and alteration of the silica cap based on the ages of all 13 muscovites was greater than 4.2 ± 0.5 m.y. (1σ). Minor argon loss from all dated muscovites occurred during later reheating, probably during the longer lived pyrrhotite alteration stage. A single center, the known cupola, had a prolonged role and was the source for main sulfide stage, oxide-silicate stage II, greisenization, and alteration of the silica cap and possibly oxide-silicate stage I and the pyrrhotite alteration stage; however, a separate source for these latter two stages cannot be ruled out.

This study is an example of a new and powerful application of $^{40}$Ar/$^{39}$Ar age spectrum dating of muscovite. Because of the high precision demonstrated in this study, it is now possible to establish time constraints necessary for solving some of the long-standing problems in economic geology. Beyond this, the unique geologic situation of Panasqueira has allowed us to quantify the thermal characteristics of muscovite. Published fluid inclusion data have been used to estimate a muscovite argon closure temperature of ~325°C during rapid cooling or short reheating and a temperature of ~270°C during slow cooling or extended reheating. Argon-loss patterns displayed by all dated muscovites resulted from reheating after original closure; the mechanism for this argon loss appears to have been argon transport by volume diffusion. Thus, $^{40}$Ar/$^{39}$Ar age spectrum dating of muscovite can be used to evaluate thermal conditions controlling argon diffusion as well as age, duration, and number of episodes of mineralization.
TABLE 3. Summary of ⁴⁰Ar/³⁹Ar Plateau Ages for Muscovites from Panasqueira, Portugal

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Stage of mineralization</th>
<th>Mean F</th>
<th>Percent of total ⁴⁰Ar on plateau</th>
<th>Apparent age (m.y.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL 503</td>
<td>OSS</td>
<td>21.67 ± 0.05</td>
<td>92.5</td>
<td>296.3 ± 0.8</td>
</tr>
<tr>
<td>PCL 207A</td>
<td>OSS</td>
<td>21.67 ± 0.05</td>
<td>76.3</td>
<td>296.3 ± 0.8</td>
</tr>
<tr>
<td>PCL 207B</td>
<td>OSS</td>
<td>21.43 ± 0.07</td>
<td>71.0</td>
<td>293.3 ± 1.0</td>
</tr>
<tr>
<td>PCL 2791</td>
<td>OSS</td>
<td>21.36 ± 0.05</td>
<td>58.7</td>
<td>292.4 ± 0.8</td>
</tr>
<tr>
<td>PGL 119</td>
<td>MSS</td>
<td>21.63 ± 0.03</td>
<td>71.4</td>
<td>293.8 ± 0.6</td>
</tr>
<tr>
<td>PGL 294</td>
<td>MSS</td>
<td>21.55 ± 0.05</td>
<td>78.1</td>
<td>294.8 ± 0.8</td>
</tr>
<tr>
<td>PGL 381</td>
<td>MSS</td>
<td>21.51 ± 0.03</td>
<td>97.4</td>
<td>294.3 ± 0.6</td>
</tr>
<tr>
<td>PCL 33</td>
<td>MSS</td>
<td>21.48 ± 0.05</td>
<td>89.6</td>
<td>293.9 ± 0.6</td>
</tr>
<tr>
<td>PGL 75</td>
<td>Greisen</td>
<td>21.45 ± 0.05</td>
<td>83.3</td>
<td>293.5 ± 0.8</td>
</tr>
<tr>
<td>PGL 354</td>
<td>Greisen</td>
<td>21.30 ± 0.06</td>
<td>85.6</td>
<td>291.6 ± 0.8</td>
</tr>
<tr>
<td>PGL 83</td>
<td>Greisen</td>
<td>21.35 ± 0.06</td>
<td>70.9</td>
<td>292.3 ± 0.9</td>
</tr>
<tr>
<td>PGL 86</td>
<td>Greisen</td>
<td>21.33 ± 0.06</td>
<td>63.9</td>
<td>292.0 ± 0.9</td>
</tr>
<tr>
<td>PGL 318</td>
<td>Silica cap</td>
<td>21.36 ± 0.05</td>
<td>100</td>
<td>292.4 ± 0.8</td>
</tr>
</tbody>
</table>

OSS = oxide-silicate stage, MSS = main sulfide stage; F = eq (3) in text.

Fig. 7. ⁴⁰Ar/³⁹Ar age spectrum diagrams for oxide-silicate stage I (PCL 503 and PCL 207A) and oxide-silicate stage II (PCL 207B and PCL 2791) muscovites.

Fig. 8. ⁴⁰Ar/³⁹Ar age spectrum diagrams for main sulfide stage muscovites.

Fig. 9. ⁴⁰Ar/³⁹Ar age spectrum diagrams for greisen and altered silica cap muscovites.

Fig. 10. Revised paragenesis of Panasqueira deposit showing results of detailed ⁴⁰Ar/³⁹Ar geochronology.
Rapid dewatering of the crust deduced from ages of mesothermal gold deposits

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The large-scale migration of fluids through the continental crust has been well documented, but there is no consensus regarding the timing of fluid migration relative to orogenic episodes, or rates of crustal dewatering. Here we present 40Ar/39Ar dates for muscovite from quartz veins along a major shear zone in southeast Alaska, which show that the veins were emplaced in the early Eocene, during the late stages of orogenic deformation. Hydrothermal activity took place for only about 1 Myr and along a distance of at least 200 km. The fluids were generated by metamorphic reactions in subducted crust along the North American plate margin, and were apparently trapped in the crust by the low permeabilities accompanying a convergent tectonic regime until 56 Myr ago. The rapid dewatering event coincided with a change in plate motion at ~56-55 Myr, which caused a shift from convergent to partly transcurrent tectonics. We suggest that this change in tectonic regime led to increased crustal permeabilities and hence the possibility of large-scale fluid migration.

Terrane accretion and subduction, thrusting, deformation, regional metamorphism and magmatic thickening of the Coast orogen characterized the northern North American cordillera between 110 and 50 Myr (ref. 2). Rapid uplift of the orogen core occurred during the last 15 million years of this period. The 700-km-long, northwest-trending Coast Range meganeament cuts medium- and high-grade metamorphic rocks 15-20 km west of the core of the orogen and of the Coast batholith in southeast Alaska and British Columbia. The meganeament has been defined in Alaska and British Columbia. The meganeament has been defined in Alaska as a prominent topographic zone, up to 10 km wide, formed by selective erosion along closely spaced joints, foliation, compositional layering and small faults. Farther south in British Columbia, this structure is recognized as a steep to vertical ductile shear zone. There the meganeament is interpreted to be the westernmost of several ductile shear zones that formed between 65-55 Myr and 50-48 Myr as a result of rapid differential uplift of the Coast orogen.

Gold-bearing quartz veins of the Juneau gold belt are widespread along the northern 200 km of the meganeament. These veins record a high fluid flux along this structure. Stable isotope data from silicate minerals in the veins can be used to calculate δ18O values for the ore fluid of 7.2-12.8% and δD values of -35 to -15% for δ18O = (18O/16O)sample/(18O/16O)standard - 1 and δD = (2D/1H)sample/(2D/1H)standard - 1. Fluid inclusion data indicate that the hydrothermal fluids were rich in H2O, CO2, CH4, N2 and H2S, and that the veins were formed at depths of at least 5 km and at temperatures of at least 250°C. These deposits are typical of mesothermal gold-bearing vein systems found throughout the Earth's orogenic belts.

Many different sources for the vein-forming fluids can be postulated, but existing data are only consistent with a metamorphic fluid. Interstitial pore fluids in the subducted, sedimentary rock-dominant terranes would have been expelled at shallow depths, long before the host rocks of the veins reached their maximum burial depths of perhaps 30-35 km (ref. 8). The lack of temporal and spatial association of the veins with specific igneous activity, and the consistently low salinity of the fluids, rule out the possibility of a magmatic fluid source. Calculated δD values for the fluid are incompatible with a meteoric water source and with any feasible water/rock regime. The stable-isotope and fluid-volatile chemistry, as well as the fact that the vein swarms are restricted to greenschist facies rocks, suggest that the fluid was generated during metamorphic reactions of greenschist and amphibolite facies.

The 40Ar/39Ar dates of hydrothermal muscovite from the five largest vein swarms in the gold belt show a remarkably narrow range, 55.0-56.1 Myr, for samples collected along 200 km (Fig. 1). Well-defined plateaus characterize all spectra of 39Ar release. The concordance of apparent ages might indicate that the dates of micas had been reset by a single thermotectonic episode or cooling of all veins through the 325°C isotherm at ~56-55 Myr. It could, however, indicate actual fluid ascension and vein deposition at geologically rapid rates; that is, extensive metamorphic dewatering and gold vein formation may be a relatively brief and late event during a much more prolonged period of orogenesis.

The resetting of all 40Ar/39Ar dates to 56-55 Myr from originally older dates is unlikely. Exposed igneous rocks in the immediate vicinity of the Juneau gold belt are clearly older than quartz veins. Veins cut through 105-Myr monzodiorite at Kensington and Juulian, Cretaceous monzodiorite at Treadwell and Mesozoic metagabbro at Alaska-Juneau. A belt of tonalitic plutons, generally 5 km east of the meganeament, is episodically emplaced from 68.2 ± 2.0 to 61 ± 1.5 Myr (refs 10-12). Granite and granodiorite of the Coast batholith were intruded between 54 ± 2 and 48 ± 2 Myr within a belt 20-50 km east of, and parallel with, the meganeament. This belt of plutons could in theory have reset the hydrothermal micas to 56-55 Myr, but the thermal effects of the magmatism apparently did not extend as far west as the meganeament (fig. 1). Hornblende and biotite K/Ar data for schist and amphibolite ~5 km east of the structure at the latitude of Juneau show no evidence of thermal overprinting. Farther south, near the Sumdum Chief mine, Ar-Ar studies indicate that the western margin of the belt of tonalite bodies has cooled below the 280 ± 40°C biotite blocking temperature by 59 ± 1 Myr.

It is unlikely that the micas were reset by circulation of meteoric water during uplift. Silicate δD values for country rocks near the meganeament attest to the lack of significant meteoric water circulation west of the Coast batholith. Furthermore, even if such circulation did occur, the undisturbed shape of the 39Ar spectra (Fig. 1) is evidence against resetting.

It is also doubtful that the 56-55 Myr concordance reflects uplift of previously formed veins across the 325 ± 25°C isotherm, which is the approximate blocking temperature for sericite.
Dates from \(^{40}\text{Ar}/^{39}\text{Ar}\) data for hydrothermal muscovite from gold-bearing veins at the five largest mines of the Juneau gold belt, ranging from 56.1 to 55.0 Myr. Ages obtained from the U/Pb ratio are 68-61 Myr (refs 8-10) for a tonalite sill to the east of the gold belt, indicating that it pre-dates the gold veining. U/Pb ages for the Coast batholith\(^1\) provide evidence that some magmatism may have been coeval with ore deposition. But K/Ar dates of metamorphic rocks to the east of Juneau\(^1\) and \(^{40}\text{Ar}/^{39}\text{Ar}\) dates from the southern part of the sill belt\(^1\) suggest that (1) the thermal effects of Eocene igneous activity were not felt as far west as the gold belt and (2) rocks near the gold belt had already cooled below the biotite blocking temperature of 280 °C before gold was formed. Dates labelled 'hbd' are from hornblende; bt, biotite.

Fluid inclusion studies\(^7\) suggest that vein formation temperatures were probably less than or close to 325 °C. Lower greenschist facies rocks\(^8\) that host the veins at the Treadwell mine on the west side of the megainseam never reached temperatures above ~325 °C. The uplift histories were probably notably different for rocks on opposite sides of the megainseam\(^9\),\(^10\), and there is no evidence that the sampled veins on both sides of the structure cooled through the 325 °C isotherm exactly the same time.

The most logical explanation for the exceptional concordance of calculated dates is that massive fluid circulation and vein formation occurred over a very brief time span in the early Eocene. This event took place over a length of at least 200 km along the Coast Range megainseam. Whether such an event affected other parts of the megainseam is uncertain. The lack of extensive gold-bearing quartz vein networks along the southern part of the structure might be explained by the fact that deeper crustal exposures of the megainseam and surrounding rocks occur to the south. If such veining did occur to the south, the evidence has long since been eroded away.

The widespread fluid event at 56-55 Myr might reflect an important change in crustal stress regime, as considerable changes in plate motion occurred at roughly that time (Fig. 2). Plate trajectory models\(^18\) show a counterclockwise swerve of the Kula plate concentrated in the 56-55 Myr interval, causing a shift from orthogonal subduction to a more oblique direction and the initiation of strike-slip motion. Structural and uplift studies\(^19\) along the southern part of the megainseam indicate that compressional tectonic events ceased between 60 Myr and 55 Myr. An abrupt change in the type and location of magmatism occurred near the megainseam between 54 and 48 Myr. The locus of magmatism shifted 20–50 km farther to the east-northeast, and plutons became more siliceous in composition and characterized by lower initial \(^{87}\text{Sr}/^{86}\text{Sr}\) ratios, pointing to changes in magma source\(^15\). It was suggested\(^13\) that these characteristics correlated with the change to a more extensional tectonic regime. The emplacement of the siliceous plutons in response to changing crustal stresses may be a more gradual process than fluid migration and quartz vein emplacement.

Our favoured scheme (Fig. 2) is one in which the vein-forming fluids may have formed over millions of years during devolatilization of subducted crust. A period of progressive Barrovian metamorphism from 70 Myr to ~60-55 Myr, superimposed on deeply buried, high-pressure, low-temperature prehnite-pumpellyite facies and lower greenschist facies rocks east of the megainseam\(^8\), is the event likely to have produced the large fluid volumes. The cause of this metamorphic event is uncertain. Re-equilibration of perturbed isotherms during uplift and/or during a declining rate of convergence\(^20\),\(^21\) is one possibility. Alternatively, thermal input from intrusion of the tonalites has been suggested\(^8\).

Rather than migrating upwards along the megainseam at various times, fluids might have ponded at depth below impermeable units. The mainly compressional environment kept permeabilities low along the western edge of the Coast orogen, even along any existing principal shear zones, including the

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**Fig. 2** Vein-forming fluids were released through devolatilization of subducted sedimentary and volcanic rocks during plate convergence before 56-55 Myr. Compressional tectonics maintained low crustal permeabilities, and therefore the released fluids probably collected below relatively impermeable units. A shift to a more oblique plate margin regime at 56-55 Myr (ref. 18) initiated considerable strike-slip motion and allowed hydrothermal fluids to ascend rapidly.
Coast Range megalineament (if it then existed). Seismic reflection data from present-day convergent margins provide evidence that large fluid volume may be trapped at mid-crustal levels during compressional events\(^1\). Hydrologic modelling\(^2\) of metamorphic fluids supports the seismic observations and indicates significant crustal porosities even long after peak metamorphism. The hydrology of deep crustal fluids is complex, however, and needs further study.

The trapped fluids were rapidly discharged along the megalineament over a period of \(\leq 10^6\) yr. Failure along the structure during some degree of relaxation of compression at 56-55 Myr reduced confining pressures and created pockets of fluid over-pressure, especially in zones of maximum dilation. Swarms of brittle-ductile shear veins\(^2\) formed in dilational sites within a few kilometres of the megalineament during large-scale crustal failure, probably according to the fault valve model of Sibson and others\(^3\).

Mesothermal gold-bearing quartz vein networks may delineate zones of metamorphic dewatering\(^4\) and are often spatially associated with principal crustal lineaments. Dating of gold-bearing, metamorphic quartz veins located along large-scale structures allow precise determination of the time of changes in crustal stresses and possibly in relative plate movement. Dewatering of the middle crust is a relatively instantaneous consequence of seismic failure, perhaps marking the start of a more transpressive type of plate margin regime. The discharge of non-meteoric fluids immediately following seismic events has been documented along many shear zones\(^2\). The isotope dates of 56-55 Myr from the Juneau gold belt are believed to define the onset of failure along the northern part of the Coast Range megalineament.

The formation of other Phanerozoic gold systems in western North America may also correlate with periods of considerable shift in plate motion. A marked change in the relative motion of the Farallon and North American plates at 133 Myr may be recorded by gold veining in the Klamath mountains\(^8\). Along the Melones fault zone of central California, K/Ar and Rb/Sr data from some of the mines in the Alleghany district, near the north end of the Melones fault zone, and from the Mother Lode district, ~200 km farther south on what may be the same structure, are statistically identical at 110-116 Myr (ref. 25). Plate reconstruction models\(^9\) for the southern Cordillera often include a shift from left-oblique to right-oblique convergence beginning at ~115 Myr. Although there is little evidence for Cretaceous strike-slip motion along the southern Melones fault zone\(^10\), the change in plate slip direction still may have been the driving force for localized opening of dilational jogs along the fault zone.

Our geochronological results from southeast Alaska clearly show that an episode of considerable fluid flow occurred relatively rapidly over great crustal lengths. We believe that the remarkable correlation between the time of this episode and that of significant shifts in plate motions is not coincidental. Rather, catastrophic crustal fluid flow and gold genesis along the outboard flank of an orogenic belt seem to be inherent tectonic processes, ultimately related to changing plate stresses in Cordilleran-type environments.

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The 320-km² Gejiu batholith, composed of more than 10 mafic and felsic intrusions, is well known for its large granite-hosted tin deposits but also is mined for Cu, Pb, Zn, W, Bi, Be, F, and S. The batholith is divided into eastern and western parts by the postmineralization, north-trending Gejiu normal fault. Intrusion compositions and mineral deposit types are distinctly different on opposite sides of the fault. Plutons in the west, grouped by age from oldest to youngest, include (1) gabbro, diorite, and monzonite; (2) granodiorite, granite porphyry, and granite; and (3) syenite and nepheline syenite. Lead and zinc are disseminated as galena and sphalerite in many western plutons; tin occurs as disseminated cassiterite in granite porphyry. East of the Gejiu fault, minor exposures of a large, subsurface granite body crop out within Triassic sedimentary rocks. Core drilling indicates that these outcrops represent parts of a continuous, 20-km-long granite pluton of relatively uniform composition but variable texture. Major tin deposits are associated with the numerous cupolas of this pluton and occur in skarn, greisen, and open-space veins.

Preliminary ⁴⁰Ar/³⁹Ar age spectra constrain the age and duration of tin mineralization and intrusive activity. Diorite in the west is 84.1±0.2 Ma. Granite emplacement and tin mineralization in the east took place between 82.6±0.2 and 80.6±0.1 Ma. Nepheline syenite was intruded in the west at 79.9±0.5 Ma. The age spectra show that tin mineralization and emplacement of associated granites occurred over at least 2 million years and that temporal-spatial relations among the tin-mineralized granites are resolvable. Relative age relations and isotopic data indicate that emplacement of nepheline syenite and formation of associated disseminated galena and sphalerite took place near the end of, or subsequent to, tin mineralization. Thus, because lead-bearing mineral deposits, associated with plutons that are older than the tin-mineralized granites, are also found west of the Gejiu fault, formation of lead deposits was either a multicycle phenomenon or occurred over a longer time period than formation of tin deposits.

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Compositional and isotopic data are available for approximately 200 samples of plutonic rocks, altered and unaltered country rocks, and minerals from the Gejiu area. The majority of the granitic rocks are weakly to moderately peraluminous; gabbro, diorite, and syenite are metaluminous. Mafic, intermediate, and syenitic plutons east of the Gejiu fault are not related by simple magmatic processes to granites east and west of the fault. Relative to other Gejiu plutons, granites are variably enriched in rubidium, cesium, tantalum, and uranium and depleted in barium, strontium, and hafnium. Concentrations of Rb, Cs, Ta, U, Hf, and Th are uniform in nongranitic plutons, but strontium and barium decrease with increasing SiO₂. Granites are depleted in light rare-earth elements (LREE) (<200 times chondrite abundance) and enriched in heavy rare-earth elements (HREE) (>20 times chondrite abundance) relative to nongranitic rocks (LREE=200-800 and HREE=5-20 times chondrite abundance). Large europium anomalies are characteristic of granites. Strontium initial ratios for all Gejiu plutons are elevated, but the ratios for western plutons are less than 0.712, whereas the ratios of eastern plutons are greater than 0.716. The strontium isotopic signature and the major and trace element compositions of all plutons were probably derived from a heterogeneous, chemically evolved, continental source.

Granitic plutons associated with Gejiu tin deposits are compositionally distinct from nonproductive granites. Productive granites are characterized by 69 to 75 weight percent SiO₂; Na₂O/K₂O of 0.59 to 0.74; enrichment in Rb (300-1,000 ppm), Cs (10-70 ppm), Ta (3-17 ppm), U (10-60 ppm), F (1,000-4,000 ppm), and Sn (10-30 ppm); and depletion in Ba (<300 ppm), Sr (<300 ppm), and Hf (<7 ppm). Rare-earth-element (REE) patterns of productive granites show relative depletion in LREE (35-110 times chondrite abundance), large europium anomalies, and enrichment in HREE (20-40 times chondrite abundance). REE patterns for biotite from these granites are similar to the REE patterns of the whole rock except that biotite, which forms about 10 modal percent of the rock, is enriched 10 times in total REE; thus, biotite is the principal REE carrier. In contrast, biotite from nonproductive plutons is not the primary REE carrier. The tin content of biotite from plutons that have less than 69 weight percent SiO₂ is less than 32 ppm. In contrast, the tin content of biotite from granites that have more than 69 weight percent SiO₂ is greater than 100 ppm to nearly 700 ppm. However, plutons that have significant tin deposits contain biotite having lower tin contents (that is, nearer 100 ppm).

A possible mechanism for tin mineralization that would account for these chemical characteristics might include (1) a plutonic source region relatively enriched in tin, (2) an evolved granitic magma that concentrated tin, (3) episodic thermal activity that occurred over at least 2 million years, and (4) either a late-stage fluid phase into which tin from the granitic magma was partitioned or a late-stage fluid phase that leached tin from biotite and concentrated tin in the altered host rock.
Deformation and age of the Red Mountain intrusive system (Urad-Henderson molybdenum deposits), Colorado: Evidence from paleomagnetic and $^{40}$Ar/$^{39}$Ar data

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ABSTRACT

Paleomagnetic and $^{40}$Ar/$^{39}$Ar age-spectrum data from most stocks of the Red Mountain intrusive system, in the northwest Colorado mineral belt, provide an improved understanding of the structural and cooling history of the suite of intrusions host to a world-class molybdenum deposit. Paleomagnetic data from five stocks at the surface and eight younger stocks exposed in the subsurface Hendeno Mine support field observations (for example, dike and vein orientations, stock geometries, and distribution of zones of mineralization) that imply moderate tilting (15°-25° down to the east-southeast) since latest Oligocene time after cooling and mineralization. Surface stocks contain magnetizations carried by both magnetite and hematite. The Red Mountain stock is the youngest surface intrusion and contains mostly normal polarity magnetizations (for example, $D = 321°$, $I = 59°$, $\alpha = 19°$, $N = 6$ samples, site RM9), whereas older East Knob and Rubble Rock breccia intrusions contain a nearly antipodal, well-characterized magnetization (East Knob stock: declination = $161°$, inclination = $-47°$, $\alpha = 13°$, $k = 23$, average of five site means). Polarity changed from reverse to normal during emplacement and cooling of the Red Mountain intrusions exposed at the surface. $^{40}$Ar/$^{39}$Ar age-spectrum data on biotite and orthoclase from the Red Mountain stock and stocks of the Henderson Mine indicate the reversal to be older than 30 Ma. All Henderson Mine stocks have normal polarity magnetizations (Primos stock: $D = 333°$, $I = 51°$, $\alpha = 5°$, $k = 44$, average of six site means) which, on the basis of $^{40}$Ar/$^{39}$Ar age spectra, were blocked between 28.7 and 27.6 Ma. Magnetite and magnesite are the major carriers of magnetization in these rocks.

On the basis of an $^{40}$Ar/$^{39}$Ar thermochronologic study of the Red Mountain intrusive system, thermal activity started at or just before 29.9 ± 0.3 Ma and ended at 26.95 ± 0.08 Ma. The age-spectrum data are interpreted to indicate that the porphyry of Red Mountain, one of the oldest stocks, was emplaced before 29.9 ± 0.3 Ma (possibly before 30.38 ± 0.09 Ma). Nearby lamprophyre dikes were emplaced at 29.8 ± 0.1 Ma; rhyolite dikes intruded at 29.4 ± 0.2 Ma. The Urut and Seriate stocks intruded after 29.8 Ma but before emplacement of the Vanquez stock at 28.71 ± 0.08 Ma. The system core cooled below 280 ± 40 °C (the argon closure temperature of biotite) at 27.59 ± 0.03 Ma. The last period of thermal activity involved pulses of magnetite-sericite alteration around the Seriate stock between 27.51 ± 0.03 and 26.95 ± 0.08 Ma; this activity did not thermally overprint unaltered parts of the intrusive system.

Tilting of the Red Mountain area is implied by a comparison between a grand mean (on the basis of 10 stock means, $D = 333°$, $I = 49°$, $\alpha = 5°$, $k = 78$) and a mid-Tertiary reference field. The Red Mountain intrusive system and host Precambrian rocks probably were deformed along a nearly north-south horizontal axis in response to northwest-side down, strike-slip faulting with displacement largely along the Woods Creek fault zone. Late Tertiary deformation of Precambrian-cored parts of the Front Range, host to numerous mineral deposits, was more complicated than simple, near-vertical uplift of the crust.
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**Porphyry of Red Mountain**

- Uradi, Seriate, Henderson, Ute, and Vasquez stocks
- System core, cooling below 280°C
- Magnetite-sericite alteration

**Rhyolite dike**

Figure 11. Composite $^{40}$Ar/$^{39}$Ar age-spectrum diagram for orthoclase, muscovite, and biotite from the Red Mountain intrusive system.

(One sigma analytical errors for data for most statistically significant temperature steps are between 0.05 and 0.10 Ma.) (A) Age-spectrum for orthoclase from porphyry of Red Mountain and potassium feldspar from a rhyolite dike emplaced into Precambrian host rocks. (B) Six (five orthoclase, one biotite) age spectra for minerals from the Uradi, Seriate, Henderson, Ute, and Vasquez stocks. (C) Six age spectra for biotites from Henderson, Ute, Vasquez, and Seriate stocks within the central part of the Red Mountain intrusive system. (D) Three age spectra for muscovite from the magnetite-sericite alteration zone around the Seriate stock.
Figure 12. Schematic block diagram of the Red Mountain intrusive system showing relative ages of stocks and cooling of emplacement (see Table 5); all ages in millions of years. Dashed lines represent approximate contacts between intrusions. Stippled region represents approximately the part of the system that cooled below ~200 °C at 27.59 ± 0.03 Ma on the basis of six biotite 40Ar/39Ar dates. Patterned region represents area of magnetite-sericite alteration formed between 27.51 ± 0.03 and 26.95 ± 0.08 Ma at the end of system cooling.

Figure 15. Geomagnetic polarity time scales for late Eocene and Oligocene time compared with zircon fission-track (F-T) dates, K/Ar isotopic and 40Ar/39Ar age-spectrum determinations for the Red Mountain intrusive system. Numbers adjacent to fission-track dates and isotopic age determinations correspond to sample numbers in Table 4. Vertical lines indicate error bars for the 40Ar/39Ar age-spectrum data. O, B, and M refer to orthoclase, biotite, and muscovite (sericite), respectively.
Determining the isotopic age of Mississippi-Valley-type (MVT) mineral deposits is difficult because datable phases with suitable isotopic integrity are generally absent from MVT ore. In the Illinois-Kentucky fluorspar district, numerous small igneous intrusions are exposed or have been intersected by drill core. Goldhaber and others (1991) presented new evidence supporting a thermal relationship between MVT deposits and igneous activity; their evidence includes the thermal zonation revealed by fluid inclusion homogenization temperatures in fluorites around Hick's Dome, Illinois. Biotite/phlogopite of lamprophyre and mica peridotite dikes and plugs of the district were visibly altered to sericite by the MVT mineralization. Many of the igneous rocks and two alteration phases in this area have been dated in the past but the isotopic dates range from 100 to nearly 400 Ma. Although many of these dates cluster in the mid-Permian, the analytical precisions generally span about 30 million years. We are using the $^{40}\text{Ar}/^{39}\text{Ar}$ age-spectrum technique to date primary and alteration phases from the Grants intrusive breccia (Illinois), the Hamp mine intrusive breccia (Illinois), a dike at the Hutson mine (Kentucky) and alteration phases from the West Morrison and Annabelle Lee mines (Illinois).

$^{40}\text{Ar}/^{39}\text{Ar}$ plateau dates for hornblende and biotite from unaltered Grants intrusive breccia, which is located about 2.5 miles south-southwest from the crest of Hick's Dome, are concordant at 271.7±0.7 and 272.7±0.7 Ma, respectively (fig. 1). Slightly altered biotite from the Hamp mine intrusive breccia yields a disturbed age spectrum but is approximately the same age or slightly older; less altered biotite from the Hamp mine breccia will soon be analyzed in an attempt to improve the age determination. Sericite that formed from alteration of biotite in the Hamp breccia during MVT mineralization yields equivocal $^{40}\text{Ar}/^{39}\text{Ar}$ results and is also being re-analyzed.

Figure 1. Composite $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum diagram for primary hornblende and biotite of the Grants intrusive breccia, Illinois-Kentucky fluorspar district.

Our preliminary $^{40}\text{Ar}/^{39}\text{Ar}$ data indicate that the best estimate for the emplacement age of the Grant intrusive breccia within the Illinois-Kentucky fluorspar district is 272±1 Ma. Because MVT mineralization altered primary phases within intrusive rocks of the district, the mineralization is younger. However, if the conclusions of Goldhaber and others (1991) that MVT mineralization is thermally related to these high-level intrusions is correct, the age of MVT mineral deposits is likely not much younger than 272 Ma.

REFERENCES USGS Open-File Report 92-1, p.59-60


Snee-14 210
The successful application of the Re-Os isotopic method (using negative ion thermal mass spectrometry) to evolved Climax-type magmatic systems shows that Re-Os has great potential for ore and magma petrogenesis studies related to economic geology.

A carefully collected sample suite from the 17 Ma Climax-type deposit at Mount Emmons includes specimens containing pyrite and magnetite from the higher temperature molybdenite ore shell and specimens containing pyrite, chalcopyrite, and sphalerite from the lower temperature, cross-cutting but presumably related, base metal halo peripheral to molybdenum ore. Concentrations of Re (~130 ppb) and Os (~50 ppt) for pyrite and chalcopyrite from the base metal halo are similar, and both yield 187Re/186Os around 100,000 and measured 187Os/186Os of 10-20. Pyrite associated with the molybdenite ore shell, on the other hand, has much lower Re (~10 ppb), indicating that Re is partitioned into molybdenite. In sharp contrast, sphalerite and magnetite provide a direct measure of initial 187Os/186Os because they have Os concentrations of 100-200 ppt (well above the 2-10 ppt Os blank) and Re concentrations <20 ppt; their 187Re/186Os is <10. Although Pb, Nd, and Sr isotopic data affirm a lower crustal origin for Climax-type melts in Colorado (Stein, 1985), the low initial 187Os/186Os for Mount Emmons magnetite and sphalerite (1.4 - 1.7) are consistent with accepted mantle compositions and preclude any upper crustal contribution. Alternatively, these low initial 187Os/186Os values may reflect granulitic lower crust in Colorado. Limited Re-Os abundance data for granulites have comparably low 187Re/186Os values (Morgan and Lovering, 1967).

No other radiometric dating method offers such a wide range of isotopic values as demonstrated by the Re-Os measurements in this study. These results show that the Re-Os method is no longer limited to mafic magmatic systems and ores enriched in Re and PGE, but that Re-Os can be used to unravel the origin of ore deposits formed from silicic-felsic systems containing Re and PGE in the ppb and ppt range.
Since its inception in the mid-1960’s, the \(^{40}\text{Ar}/^{39}\text{Ar}\) variant of the K-Ar method of geochronology has fostered an explosion of innovative applications to a wide variety of geologic problems. Applications run the gamut of most subdisciplines in geology. The purpose of this presentation is to briefly describe the \(^{40}\text{Ar}/^{39}\text{Ar}\) method and its variations, to show why its inception has fostered this explosion of possible applications, and finally to outline three applications that illustrate some of the major strengths and weaknesses of the method.

\(^{40}\text{Ar}/^{39}\text{Ar}\) dating technique

The \(^{40}\text{Ar}/^{39}\text{Ar}\) dating technique is a variant of the conventional K-Ar method. To obtain an age by this technique, the sample of unknown age and a standard of known age are irradiated together in a nuclear reactor to produce \(^{39}\text{Ar}\) from \(^{39}\text{K}\) by fast neutron bombardment. After irradiation, the \(^{40}\text{Ar}/^{39}\text{Ar}\) ratios of sample and standard are measured. The age of a sample can be calculated from its \(^{40}\text{Ar}/^{39}\text{Ar}\) ratio when compared to the \(^{40}\text{Ar}/^{39}\text{Ar}\) ratio of the standard. Most importantly, only the isotopic composition of argon need be measured and this is done by gas-source mass spectrometry, potentially a very precise analytical technique. In contrast, for a conventional K-Ar date, both \(^{40}\text{K}\) and \(^{40}\text{Ar}\) must be measured quantitatively. To do this, argon in one aliquant of the sample is measured by isotope-dilution, gas-source mass spectrometry. Potassium in a different aliquant of sample is determined by some other analytical method such as flame photometry, X-ray fluorescence, or isotope-dilution solid-source mass spectrometry. Thus, one inherent problem of the conventional K-Ar technique is the necessity of measuring isotopic abundances for separate aliquants of the same sample. This poses the danger that, because of sample inhomogeneity, different potassium and/or argon contents may exist in each aliquant. Two major advantages of the \(^{40}\text{Ar}/^{39}\text{Ar}\) dating method are: only isotopic ratios of argon need be determined, and all measurements are made on the same sample aliquant, thus avoiding the question of homogeneity. In addition, by the \(^{40}\text{Ar}/^{39}\text{Ar}\) method, it is possible to obtain a series of dates on a single sample when the argon is extracted by step heating. The combination of these advantages potentially increases the precision of the \(^{40}\text{Ar}/^{39}\text{Ar}\) method over the conventional K-Ar technique. However, the \(^{40}\text{Ar}/^{39}\text{Ar}\) technique will suffer if proper corrections are not made for interfering radiation-induced isotopes.
The \(^{40}\text{Ar}/^{39}\text{Ar}\) method was first used in total fusion experiments in which an irradiated sample was completely melted and all isotopes of argon measured in a single analysis to calculate an age for the sample. This total fusion age is roughly analogous to a conventional K-Ar age of the sample except that no isotopic concentration measurements are required. Very soon after the first uses of the \(^{40}\text{Ar}/^{39}\text{Ar}\) method, it was realized that a sample could be progressively degassed in temperature increments. An age could be calculated for each increment of gas released and the ages of all temperature increments of a sample were plotted against percent of released argon to form an age spectrum. The character of the spectrum can be evaluated within a theoretical framework to interpret the apparent distribution of potassium and argon within the sample. Early studies showed that some spectra of meteorites display characteristics that would be expected if volume diffusion were the dominant mechanism controlling the loss or argon from a sample in the geologic environment. Since that time, many studies have shown that meaningful ages of samples could be determined by the age spectrum technique even though some loss of \(^{40}\text{Ar}_R\) had occurred during the sample’s geologic history. It should be noted here that loss or gain of \(^{40}\text{Ar}_R\) by a sample is generally thermally controlled, samples from thermally complex regions should be analyzed by \(^{40}\text{Ar}/^{39}\text{Ar}\) age spectrum techniques.

\textbf{Ar/Ar Isotope Correlation (Isochron) Diagrams}

In recent years workers have demonstrated that samples from thermally complex geologic settings can incorporate extraneous \(^{40}\text{Ar}\) during heating, cooling, alteration, and/or recrystallization. If the \(^{40}\text{Ar}\) released from the sample in the laboratory by step-heating is a simple two-component mixture (inherited and radiogenic), it is possible that the argon isotopic data from the heating steps will define a straight line on a \(^{36}\text{Ar}/^{40}\text{Ar}\) vs \(^{39}\text{Ar}/^{40}\text{Ar}\) correlation diagram. This straight line can be interpreted as either a mixing line or an isochron. It is not yet clear why some minerals, especially hornblende, exhibit this type of behavior.

\textbf{Applications:}

- Stratigraphy - Mogollon - Datil Volcanic Field
- Tectonics - Southeastern New England
- Mineralization - Panasquiera, Portugal
Calibration of the latest Eocene–Oligocene geomagnetic polarity time scale using \(^{40} \text{Ar}/^{39} \text{Ar}\) dated ignimbrites

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ABSTRACT
A discontinuous record of late Eocene–Oligocene geomagnetic polarity has been determined using high-precision (±0.15 m.y.) \(^{40} \text{Ar}/^{39} \text{Ar}\) sanidine dating and paleomagnetic study of 37–27 Ma ignimbrites in New Mexico, Colorado, and Texas. This record provides age control for several geomagnetic polarity reversals that occurred during three periods of intense ignimbrite volcanism: 36.8–33.5 Ma, 32.7–31.4 Ma, 29.1–26.9 Ma. The relative timing of these polarity reversals permits four possible correlations with the geomagnetic polarity time scale (GPTS). The preferred correlation yields calibration ages for Chron C10R (28.0–29.0 Ma) and Chron C1OR (34.4–33.1 Ma) that indicate an Eocene–Oligocene boundary age near 33.4 Ma, some 0.3–0.6 m.y. younger than boundary ages indicated by other recently proposed GPTS calibrations based on terrestrial and marine sedimentary sequences.

INTRODUCTION
Radioisotopic calibration of the mid-Cenozoic geomagnetic polarity time scale (GPTS) has been the focus of much work during the past two decades. The number and relative lengths of Cenozoic geomagnetic polarity chrons have been well established using marine magnetic anomaly data (Manktnen and Dalrymple, 1979; Ness et al., 1980; Berggren et al., 1985; Harland et al., 1989), and these chrons have been reliably correlated with marine biostratigraphy (Lowe et al., 1982; Berggren et al., 1985). However, precise radiometric calibration points for the GPTS have proven elusive. Direct calibration of the GPTS by dating of sea-floor basalts is severely limited by problems of alteration and excess Ar retention (Berggren et al., 1985). Instead, terrestrial and marine stratigraphic sequences have been used to provide calibration points.

A particularly problematic period for radiometric calibration of the GPTS has been the late Eocene to Oligocene time. Published estimates of the age of the Eocene–Oligocene boundary have ranged from 32 to 38 Ma (Ness et al., 1980; Harland et al., 1989); this 20% variation considerably exceeds the precision and accuracy of available dating methods.

The widely cited 36.5 Ma Eocene–Oligocene boundary age of Berggren et al. (1985) was based largely on K-Ar data from volcanic ash within magnetostratigraphically studied terrestrial sedimentary sequences in North America (Berggren et al., 1985; Prothero, 1985; Prothero and Armentrout, 1985). A revised Eocene–Oligocene boundary age of 34 Ma has recently been proposed following redating of the same ash deposits using the \(^{40} \text{Ar}/^{39} \text{Ar}\) single-crystal laser-fusion method (Swisher and Prothero, 1990). This value is in general agreement with GPTS calibrations based on K-Ar, Rb-Sr, and \(^{40} \text{Ar}/^{39} \text{Ar}\) dating of biotites from bentonites within much-studied pelagic limestone sequences in Italy (boundary age = 33.7 Ma; Montanari, 1988; Montanari et al., 1988, 1991; Premoli Silva et al., 1988; Odin et al., 1991) and with \(^{40} \text{Ar}/^{39} \text{Ar}\) studies of microtektites in upper Eocene marine deposits in Barbados (boundary age = 34.4 Ma; Glass et al., 1986).

Herein we present a terrestrial volcanic calibration of the late Eocene–Oligocene GPTS using \(^{40} \text{Ar}/^{39} \text{Ar}\) dated ignimbrite sequences from the southwestern United States. This purely volcanic approach is analogous to the widely accepted calibration of the late Neogene GPTS using K-Ar ages and polarity determinations from terrestrial lava sequences (Cox and Dalrymple, 1967; McDougall et al., 1976; Harrison et al., 1979). It was previously impossible to extend this purely volcanic-based calibration method beyond 10–15 Ma, because errors in conventional K-Ar determinations become large relative to the lengths of individual polarity intervals (Berggren et al., 1985). Extension of this approach into mid-Cenozoic time is now made possible by the increased precision afforded by the \(^{40} \text{Ar}/^{39} \text{Ar}\) method, particularly for dating sanidine (e.g., Hess and Lippolt, 1986; Dalrymple and Duffield, 1988; McIntosh et al., 1990).

STUDY AREA
This study has focused on four late Eocene–Oligocene silicic volcanic fields: the Mogollon–Datil and Boot Heel fields in New Mexico, Thirtynine Mile field in Colorado, and Trans Pecos field in Texas (Fig. 1). The sequences at each of these volcanic fields include several (10–35) widespread (50–10,000 km²), voluminous (50–1300 km³), generally rhyolitic ignimbrites (ash-flow tuffs). The composite ignimbrite stratigraphy at each field has been established by detailed mapping, in some cases augmented by long-range correlations supported by \(^{40} \text{Ar}/^{39} \text{Ar}\) and paleomagnetic data (see references in Table 1). The Trans Pecos sequence includes several enigmatic widespread rhyolites that were probably emplaced as unusually fluid and voluminous...
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<td>7</td>
<td>$\pm 0.04$</td>
<td>$\pm 0.13$</td>
</tr>
<tr>
<td>Laser</td>
<td>Sanidine</td>
<td>Bloodgood Canyon</td>
<td>28.19</td>
<td>2*</td>
<td>$\pm 0.01$</td>
<td>$\pm 0.05$</td>
</tr>
<tr>
<td>Laser</td>
<td>Sanidine</td>
<td>Pahranagat Lakes</td>
<td>22.65</td>
<td>5</td>
<td>$\pm 0.02$</td>
<td>$\pm 0.08$</td>
</tr>
<tr>
<td>Laser</td>
<td>Sanidine</td>
<td>Nine Hill</td>
<td>25.11</td>
<td>5</td>
<td>$\pm 0.02$</td>
<td>$\pm 0.07$</td>
</tr>
<tr>
<td>Laser</td>
<td>Sanidine</td>
<td>New Pass</td>
<td>25.07</td>
<td>3</td>
<td>$\pm 0.04$</td>
<td>$\pm 0.15$</td>
</tr>
</tbody>
</table>

$n$, number of samples/unit; *$n$ too few for meaningful $\sigma$.

1, this study; 2, data compiled in Marvin et al. (1987); 3, Lanphere (1988); 4, Dalrymple and Duffield (1988); 5, Deino and Best (1988); 6, Deino (1989)
Fig. 5a–h. Representative age spectra from Mogollon-Datil sanidine samples. a Concordant plateau age spectrum and flat K/Ca spectrum typical of 80% of analyzed sanidines. b Concordant plateau age spectrum accompanied by a somewhat discordant K/Ca spectrum. c Age spectrum that climbs in age slightly with increasing temperature. d Steeply climbing age spectrum. e Steeply climbing age spectrum: both d and e indicate contamination by older K-feldspar. f Irregular discordant age spectrum of an altered sanidine. g Concordant plateau age spectrum of an apparently contaminated sample. h Somewhat discordant age spectrum, still meeting plateau criteria, of an apparently contaminated sample.

Fusion ages (Dalrymple and Duffield 1988; Deino and Best 1988; Deino 1989).

But how does \( \alpha X \) translate to actual resolution of ignimbrite correlation problems? Stratigraphic sequences offer the most rigorous tests of this question. In this study, the mean ages of better studied units \( (n \geq 3) \) all agree with independently established stratigraphic order, although the most closely erupted pair of well-constrained units (Kneeling Nun and Bell Top no. 1 Tuffs, Table 3) differ in mean age by 0.09 Ma. Good agreement with stratigraphic order is also shown by less well-constrained units in this study. The best examples are from a sequence of nine ignimbrites erupted over a 1.6-Ma period from calderas near the northern and western margins of the volcanic field (Fig. 7). The stratigraphic order of these units has been unequivocally demonstrated by detailed mapping (Osburn and Chapin 1983b; Ratté et al. 1984), augmented by paleomagnetic correlations (McIntosh 1989; McIntosh et al. 1986, in press). Except for one apparently contami-
CONTRASTING P-T-t PATHS: THERMOCHRONOLOGIC EVIDENCE FOR A LATE PALEOZOIC FINAL ASSEMBLY OF THE AVALON COMPOSITE TERRANE IN THE NEW ENGLAND APPALACHIANS

R. P. Wintsch,
J. F. Sutter,
M. J. Kunk,
J. N. Aleinikoff, and M. J. Doran

Abstract. Strongly contrasting pressure-temperature-time paths for the Avalon composite terrane and the structurally overlying Putnam-Nashoba zone in eastern New England obtained from thermochronologic and thermobarometric data are best explained by a late Paleozoic underthrusting of cover rocks by the Avalon composite terrane. We present new Ar and U-Pb thermochronologic data that show that in the southern Hope Valley zone, Permian (280 Ma) anatectic metamorphic conditions of 700°C and 6 kbar were quenched by relatively rapid cooling (12°C/m.y.) and exhumation (0.5 km/m.y.) for ~40 m.y. In contrast, peak metamorphic conditions in the Putnam-Nashoba zone predate Silurian intrusions, and slower cooling (3.5°C/m.y.) began at about 400 Ma. One-dimensional thermal modeling suggests that these two belts were not in thermal equilibrium during the Permian metamorphism of the Avalon composite terrane. Because of the absence of high-grade Alleghanian metamorphism in rocks overlying the Avalon terrane, we conclude that high-grade Alleghanian metamorphism in the Avalon terrane occurred east of rocks now overlying it and that significant motion between Avalon and this cover occurred after peak Alleghanian metamorphism. Similarly contrasting metamorphic histories between Avalon interiors (Willimanuc window, Massabesic complex gneiss, Pelham dome) and their cover rocks reveal the regional significance of this boundary. The core rocks all show Permian cooling, but the cover rocks show post-Acadian cooling ages decreasing from east to west to the Pelham area. where nonmetamorphic ages in Avalon and cover differ by only 35 m.y. Model calculations show that thermal equilibrium between instantaneously thrust blocks of rocks is generally obtained in tens of millions of years. Consequently, underthrusting of Avalon is constrained to be middle Mississippian or younger. Because the leading edge of the subduction zone would have been heated the longest and would have most closely approached thermal equilibrium with its cover, core rocks of the Pelham dome must have been relatively close to this leading edge. Thus Carboniferous to Permian underplating from a generally eastward direction best explains these thermochronologic relationships.

INTRODUCTION

One of the more persistent questions relating to the tectonic evolution of the New England Appalachians concerns the timing of the late Proterozoic Avalon terrane to the lithotectonic zones (of Zaranan [1988]) to the west that now overlie it: the Putnam-Nashoba, Merrimack Trough, Central Maine, and Bronson Hill (Figure 1). Some [e.g., Robinson and Hall, 1980; Skehan and Rast, 1990] have argued that the Middle Ordovician arrival of the Avalon terrane was responsible for the Taconic orogeny. Osberg [1978] and Williams and Hatcher [1983] argue that the accretion of Avalon occurred in the Early Devonian, when its arrival was responsible for the Acadian orogeny. Zen [1983], Wintsch and Sutter [1986], and Gromet [1989] have argued that at least the last stages of assembly were in the late Paleozoic. More recently, Stockmal et al. [1990] and van der Pluijm et al. [1990] proposed that initial collision occurred in the Silurian but continued in a protracted way to the late Paleozoic. Discrimination among these hypotheses has been stymied by the lack of temporal control of metamorphism of Avalon and adjacent rocks, and by the scarcity of fossils.

One approach to constraining the time of final juxtaposition of the Avalon terrane to the lithotectonic zones to the west is to establish the extent of Alleghanian metamorphism in eastern New England. If this metamorphism were later than important motion on terrane boundaries, then Permian isograds would cut across zone boundaries (as proposed by O'Hara [1986]), and the cooling histories of the rocks would be continuous across terrane boundaries. If, however, Alleghanian metamorphism in the Avalon terrane were earlier than final assembly, then major differences in cooling histories would exist, and the final juxtaposition of Avalon to the rocks now above it would postdate peak Alleghanian metamorphism.

In this paper we present thermochronologic data from the Avalon composite terrane and the adjacent Putnam-Nashoba zone showing that these two zones had distinct metamorphic and cooling histories from the Silurian to the Early Triassic. The slow cooling of the Putnam-Nashoba zone from high-grade Silurian metamorphism contrasts strongly with the peak Permian metamorphism and relatively fast Permian and Triassic cooling of the Avalon terrane. Similar discrepancies between the cooling histories of Avalonian inliers and their overlying rocks in east central New England constrain the time of final assembly of the Avalon terrane to the New England Appalachians to be late Paleozoic. We follow Zaranan's [1988] suggestion of using the neutral term 'zone' to refer to the various belts of rocks with common sedimentary, metamorphic, and/or plutonic histories. We break the Avalon composite terrane into the Edmond-Dedham, Hope Valley, Massabesic, and Pelham zones, with Avalonian rocks exposed in the Willimanuc window correlated with the Hope Valley zone. We refer to the parts of the Putnam-Nashoba zone as the Putnam belt (Connecticut) and the Nashoba belt (Massachusetts).

GEOLOGIC SETTING

The Avalon and Putnam-Nashoba zones lie on the eastern margin of New England (Figure 1). The Putnam-Nashoba zone contains late Proterozoic (?) pelitic metasedimentary and mafic
**88-313a**

Hornblende

Plateau Age = 339 ± 2 Ma
This study
2 Zartman & Naylor, 1984
3 Getty & Gromet, 1989
4 Hepburn et al., 1987b
Thermochronology of Economic Mineral Deposits: Dating the Stages of Mineralization at Panasqueira, Portugal, by High-Precision $^{40}\text{Ar}/^{39}\text{Ar}$ Age Spectrum Techniques on Muscovite

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Abstract

$^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum dates for 13 muscovites have been used to reconstruct the thermal history (thermochronology) of the Panasqueira, Portugal, tin-tungsten deposit, a deposit spatially associated with a belt of Hercynian plutons. Muscovite samples with an age difference as small as 2.2 m.y. (0.7% of the age) are statistically distinct. Statistics are even better for comparison of multiple samples from separate events; that is, a difference of 0.9 m.y. (0.3%) can be resolved in this ~300-m.y.-old deposit. The major tin and tungsten ore-forming stages, which are the oxide-silicate stage, the main sulfide stage, and greisenization, occurred between 296.3 ± 0.8 (1σ) and 291.6 ± 0.8 m.y. (1σ). The first substage of the oxide-silicate stage was a short-lived thermal pulse at 296.3 ± 0.6 m.y.; the fluids responsible may have emanated from the known granite cupola. The main sulfide stage was active at 294.5 ± 0.9 m.y. as a slightly longer lived pulse with oldest evidence for this stage (295.8 ± 0.6 m.y.) coming from areas farthest away from the known cupula and youngest evidence (293.5 ± 0.8 m.y.) closest to the cupula. A second substage of the oxide-silicate stage occurred as a short-lived thermal pulse at 292.9 ± 0.7 m.y., synchronous with greisenization of the cupula and alteration of the silica cap at 292.1 ± 0.4 m.y. The duration of activity of the oxide-silicate stage, the main sulfide stage, greisenization, and alteration of the silica cap based on the ages of all 13 muscovites was greater than 4.2 ± 0.5 m.y. (1σ). Minor argon loss from all dated muscovites occurred during later reheating, probably when the longer lived pyrrhotite alteration stage. A single center, the known cupula, had a prolonged role and was the source for main sulfide stage, oxide-silicate stage II, greisenization, and alteration of the silica cap and possibly oxide-silicate stage I and the pyrrhotite alteration stage; however, a separate source for these latter two stages cannot be ruled out.

This study is an example of a new and powerful application of $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum dating of muscovite. Because of the high precision demonstrated in this study, it is now possible to establish time constraints necessary for solving some of the long-standing problems in economic geology. Beyond this, the unique geologic situation of Panasqueira has allowed us to quantify the thermal characteristics of muscovite. Published fluid inclusion data have been used to estimate a muscovite argon closure temperature of ~325°C during rapid cooling or short reheating and a temperature of ~270°C during slow cooling or extended reheating. Argon-loss patterns displayed by all dated muscovites resulted from reheating after original closure; the mechanism for this argon loss appears to have been argon transport by volume diffusion. Thus, $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum dating of muscovite can be used to evaluate thermal conditions controlling argon diffusion as well as age, duration, and number of episodes of mineralization.

Introduction

ALTHOUGH there have been numerous geochronologic and geothermometric studies of economic mineral deposits, there have been few high-resolution thermochronologic studies of ore-forming processes. Until recently, isotopic techniques have been used only to date ore deposits, but they lacked the precision necessary for measurement of the total duration of mineralization or dating of the separate thermal pulses within an episode of mineralization. Moreover, the effects of chemical and/or thermal alteration on most isotopic systems were so poorly understood that criti-
Fig. 6. Diagrammatic cross section of a vein showing the paragenetic relation of samples PGL 207A and PGL 207B.
### Table 3: Summary of $^{40}$Ar/$^{39}$Ar Plateau Ages for Muscovites from Panasqueira, Portugal

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Stage of mineralization</th>
<th>Mean $F$</th>
<th>Percent of total $^{39}$Ar on plateau</th>
<th>Apparent age (m.y.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGL 503</td>
<td>OSS</td>
<td>$21.67 \pm 0.05$</td>
<td>92.5</td>
<td>$296.3 \pm 0.8$</td>
</tr>
<tr>
<td>PGL 207A</td>
<td>OSS</td>
<td>$21.67 \pm 0.05$</td>
<td>76.3</td>
<td>$296.3 \pm 0.8$</td>
</tr>
<tr>
<td>PGL 207B</td>
<td>OSS</td>
<td>$21.43 \pm 0.07$</td>
<td>71.0</td>
<td>$293.3 \pm 1.0$</td>
</tr>
<tr>
<td>PGL 279I</td>
<td>OSS</td>
<td>$21.36 \pm 0.05$</td>
<td>58.7</td>
<td>$292.4 \pm 0.8$</td>
</tr>
<tr>
<td>PGL 119</td>
<td>MSS</td>
<td>$21.63 \pm 0.03$</td>
<td>71.4</td>
<td>$295.8 \pm 0.6$</td>
</tr>
<tr>
<td>PGL 294</td>
<td>MSS</td>
<td>$21.55 \pm 0.05$</td>
<td>78.1</td>
<td>$294.8 \pm 0.8$</td>
</tr>
<tr>
<td>PGL 381</td>
<td>MSS</td>
<td>$21.51 \pm 0.03$</td>
<td>97.4</td>
<td>$294.3 \pm 0.6$</td>
</tr>
<tr>
<td>PGL 33</td>
<td>MSS</td>
<td>$21.48 \pm 0.05$</td>
<td>89.6</td>
<td>$293.9 \pm 0.8$</td>
</tr>
<tr>
<td>PGL 75</td>
<td>MSS</td>
<td>$21.45 \pm 0.05$</td>
<td>83.3</td>
<td>$293.5 \pm 0.8$</td>
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<tr>
<td>PGL 354</td>
<td>Greisen</td>
<td>$21.30 \pm 0.06$</td>
<td>85.6</td>
<td>$291.6 \pm 0.8$</td>
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<tr>
<td>PGL 83</td>
<td>Greisen</td>
<td>$21.35 \pm 0.06$</td>
<td>70.9</td>
<td>$292.3 \pm 0.9$</td>
</tr>
<tr>
<td>PGL 86</td>
<td>Greisen</td>
<td>$21.33 \pm 0.06$</td>
<td>63.9</td>
<td>$292.0 \pm 0.9$</td>
</tr>
<tr>
<td>PGL 318</td>
<td>Silica cap</td>
<td>$21.36 \pm 0.05$</td>
<td>100</td>
<td>$292.4 \pm 0.8$</td>
</tr>
</tbody>
</table>

OSS = oxide-silicate stage, MSS = main sulfide stage, $F = eq (3)$ in text
Isotopic standards have always played an important role in isotope ratio mass spectrometry. They allow results from different laboratories to be normalized so that data may be compared and combined. They provide a basis for correcting instrument measurement biases arising, for example, from non-linearities in the detection system. This can be especially important for elements which have isotopic abundances which span a large dynamic range. Isotopic standards provide a means of checking the validity of corrections for mass fractionation and mass discrimination during ion generation. They also play a role in chemistry, by allowing a researcher to evaluate isotope effects during separation chemistry. With the advent of the new generation of mass spectrometers capable of collecting multiple ion beams simultaneously, the need for calibrated or absolute isotopic standards for gain calibration, cup efficiency determinations, etc. is even more pronounced.

Standards can be divided into three types. The least stringently specified isotopic reference materials are the working standards. They are generally produced by a laboratory from material at hand for daily calibration and quality control. Values for a working standard are derived from a cross calibration with a primary standard which may be a reference material (RM) or a certified reference material (CRM).

Another kind of standard are the RMs. These are materials that have a wide distribution. They do not have certified isotopic values but instead have values set by a consensus survey of top laboratories. These samples are often measured concomitantly with unknowns, with the value of the unknowns expressed not in absolute units, but rather as relative deviations from a given standard. Excellent examples of this type of standard are the light stable isotopes of hydrogen, oxygen, nitrogen, carbon, sulfur and silicon distributed by the IAEA and NIST. These are listed in Table I. Isotope ratios of these elements, when measured on a gas isotope ratio mass spectrometer, are determined by switching back and forth between standard and unknown. The results of the unknown are then expressed as a relative deviation from a standard value. With this approach, highly precise data can be collected without the need for conversion to absolute values as long as everyone corrects to the same value for the standard. This kind of standard has also been important for solid source mass spectrometry. The former La Jolla and CIT neodymium standards and the Eimer and Amend strontium carbonate standard are examples of isotopic solutions prepared and distributed on a limited basis by early researchers in these fields. The current use of BCR-1 as a Nd isotopic interlab comparison standard is another example of an RM.

The last type of standard is the absolute isotopic reference material, designated Standard Reference Materials (SRM) by NIST and Certified Reference Materials (CRM) or Isotope Reference Materials (IRMs) by national standards labs in Europe such as CBNM. These standards differ from the previous two in that all known sources of measurement bias have been eliminated or corrected for. This means that the "true" value of the isotopic ratios lies...
within the error of the absolute determination. The production of an absolute isotopic reference material requires considerable effort and is, in fact, an atomic weight determination. After a pure, stoichiometrically definable form of the element being considered has been selected, pure separated isotopes of known assay of the same element must be found. Accurately known isotopic mixtures of the separated isotopes must be gravimetrically or volumetrically prepared. The principal factor limiting the overall accuracy of the absolute ratios is generally the quantitation during this step of the chemistry. At present, isotopic mixtures can be prepared on an absolute basis with an accuracy of a part in 10,000 or slightly better. Synthetic mixtures of the enriched isotopes are thus made that bracket the range of ratios in the candidate isotope reference material and are used to correct the measured ratios to an absolute basis. A rigidly defined mass spectrometric protocol specifying the sample form, amount, heating parameters, etc. is then followed from which simple correction factors for the measured isotope ratios are obtained. The absolute isotopic ratios and their uncertainties are derived from the corrected ratio data and a consideration of all the contributing sources of error or bias occurring during the certification process. Table II is a list of all the non-nuclear absolute isotopic standards currently available.
Table I. Light Stable Isotopic Reference Materials*

<table>
<thead>
<tr>
<th>Z El.</th>
<th>Reference Material</th>
<th>Type</th>
<th>( \delta^2H_{\text{VSMOW}} )</th>
<th>( \delta^{18}O_{\text{VSMOW}} )</th>
<th>( \delta^{13}C_{\text{VPDB}} )</th>
<th>( \delta^{15}N_{\text{AIR}} )</th>
<th>( \delta^{34}S_{\text{GSSM}} )</th>
<th>( \delta^{34}S_{\text{NBS28}} )</th>
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<td>0°</td>
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<td></td>
<td></td>
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</tr>
<tr>
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<td>Water</td>
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<td>Water</td>
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<tr>
<td>6 C</td>
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<td>Carbonate</td>
<td>+7.16</td>
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<tr>
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<td>16 S</td>
<td>Soufre de Lacq</td>
<td>Elemental S</td>
<td>+16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NZ1</td>
<td>Silver Sulfide</td>
<td>-0.3</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>NBS123</td>
<td>Sphalerite</td>
<td>+17</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>NBS127</td>
<td>Ba Sulfate</td>
<td>+9.4</td>
<td>+20.32</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Normalized Isotopic Compositions in parts per thousand (permil)*
Note: These materials are available through either:

I.A.E.A.
Section of Isotope Hydrology
P.O. Box 100
A-1400 Vienna
AUSTRIA

N.I.S.T.
Standard Reference Materials Program
Room 204, Building 202
Gaithersburg, MD 20899
USA

With the exception of the $^2$H/$^1$H ratio of VSMOW, none of these materials are certified on the basis of absolute isotopic ratios. However, they provide samples whose isotopic compositions are expressed as parts per thousand (permil) deviations from various light stable isotope standards. Thus, Vienna Standard Mean Ocean Water (VSMOW) is the reference standard for $^2$H/$^1$H and $^{18}$O/$^{16}$O ratios and is exactly defined as 0 for the two isotopic systems. Standard Light Antarctic Precipitation (SLAP) is also exactly defined as -428 for $\delta$D$_{VSMOW}$ and -55.5 for $\delta^{18}$O$_{VSMOW}$. The Vienna PeeDee Belemite (VPDB) is the reference standard for $^{13}$C/$^{12}$C ratios and is exactly defined as +1.95 for NBS19. Atmospheric N$_2$ (AIR) is the reference standard for $^{15}$N/$^{14}$N ratios, while the Canyon Diablo Troilite (CDT) is the reference standard for $^{34}$S/$^{32}$S ratios and NBS28 is the reference standard for $^{28}$Si/$^{29}$Si ratios.

Exactly defined ratios.
Table II. Absolute Isotopic Standards

<table>
<thead>
<tr>
<th>Z El.</th>
<th>SRM Name</th>
<th>Type</th>
<th>Source</th>
<th>Isotope Ratio</th>
<th>Certified Ratio</th>
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<tbody>
<tr>
<td>1 H</td>
<td>SMOW</td>
<td>Natural Water</td>
<td>IAEA</td>
<td>$^2\text{H}/^1\text{H}$</td>
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<td>3 Li</td>
<td>LSVEC</td>
<td>Li Carbonate</td>
<td>NIST</td>
<td>$^6\text{Li}/^7\text{Li}$</td>
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<td>IRM-015</td>
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<td>CBNM</td>
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<td></td>
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<td>CETAMA</td>
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<td></td>
<td>$^{25}\text{Mg}/^{24}\text{Mg}$</td>
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<td>$^{28}\text{Si}/^{29}\text{Si}$</td>
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<td>35 Br</td>
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<td>37 Rb</td>
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<td>Type</td>
<td>Source*</td>
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<td>---------</td>
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<tr>
<td>38 Sr</td>
<td>SRM 987</td>
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<td>NIST</td>
<td>⁸⁷Sr/⁸⁶Sr</td>
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<td>⁴⁴Sr/⁸⁶Sr</td>
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<td>47 Ag</td>
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<td>Ag Nitrate</td>
<td>NIST</td>
<td>¹⁰⁷Ag/¹⁰⁸Ag</td>
<td>1.07638</td>
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<td>75 Re</td>
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<td>NIST</td>
<td>¹⁸³Re/¹⁸⁷Re</td>
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<tr>
<td>81 Tl</td>
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<td>82 Pb</td>
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<td>²⁰⁶Pb/²⁰⁸Pb</td>
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<td>²⁰⁸Pb/²⁰⁸Pb</td>
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<td>SRM 991</td>
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<td>Atom % ²⁰⁸Pb</td>
<td>0.99979</td>
</tr>
</tbody>
</table>

* Note: These materials are available from:

**CBNM**
Central Bureau for Nuclear Measurements
Commission of the European Communities
Joint Research Centre
Geel, BELGIUM

**CETAMA**
Centre d'Etudes Nucléaires
60 - 68 Avenue du Général Leclerc
BP 6 - 92265 Fontenay aux Roses
FRANCE

**IAEA**
International Atomic Energy Agency
P.O. Box 100
A-1400 Vienna
AUSTRIA

**NIST**
National Institute of Standards and Technology
Standard Reference Materials Program
Room 204, Building 202
Gaithersburg, MD 20899
USA
ISOTOPIC REFERENCE MATERIALS - ABSOLUTE OR OTHERWISE

Workshop on the "Application of Isotope Systems to Geological Problems"

USGS Reston VA

Sept. 14-16, 1992

Robert D. Vocke, Jr., Inorganic Analytical Research Division, National Institute of Standards and Technology, A23/221, Gaithersburg, MD 20899
INTRODUCTION

Isotopic standards have always played an important role in isotope ratio mass spectrometry. They allow results from different laboratories to be normalized so that data may be compared and combined. They provide a basis for correcting instrument measurement biases arising, for example, from non-linearities in the detection system. This can be especially important for elements which have isotopic abundances spanning a large dynamic range. Isotopic standards provide a means of checking the validity of corrections for mass fractionation and mass discrimination during ion generation. They can also play a role in chemistry, by allowing a researcher to evaluate isotope effects during separation chemistry. Moreover, with the advent of the new generation of mass spectrometers capable of collecting multiple ion beams simultaneously, the need for additional and better calibrated or absolute isotopic standards is even more pronounced.

Isotopic standards can be divided into three types. The least stringently specified isotopic reference materials are the working standards. They are generally produced by a laboratory from material at hand for daily calibration and quality control. Values for a working standard are derived from a cross calibration with a primary standard which may be a reference material (RM) or a certified reference material (CRM).

Another kind of standard are the RMs. These are materials that have a wide distribution. Typical of RMs are the stable isotopes of the light elements distributed by IAEA and NIST. They do not have certified isotopic values but instead have values set by a consensus survey of selected laboratories. These samples are often measured concomitantly with unknowns, with the value of the unknowns expressed not in absolute units, but rather as relative deviations from a given reference standard.

The third type of standard is the absolute isotopic reference material, designated Standard Reference Materials (SRM) by NIST and Certified Reference Materials (CRM) or Isotope Reference Materials (IRMs) by national standards labs in Europe such as CBNM and CEA. These standards differ from the previous two in that all known sources of measurement bias have been eliminated or corrected for. This means that the "true" values of the isotopic ratios lie within the error of the absolute determinations.

The periodic table shown below characterizes the stable isotopic RMs and CRMs that are currently available worldwide.
### Periodic Table of Isotopic Reference Materials

<table>
<thead>
<tr>
<th>Element</th>
<th>Type</th>
<th>Isotopes</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>RM, CRM</td>
<td>2 nat</td>
<td>Certified Reference Material - absolute values</td>
</tr>
<tr>
<td>Li</td>
<td>CRM, RM</td>
<td>2 nat, spk</td>
<td>Reference Material - no absolute values</td>
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<tr>
<td>Na</td>
<td>CRM, RM</td>
<td>3 nat</td>
<td>Note: CRM is equivalent to SRM &amp; IRM</td>
</tr>
<tr>
<td>K</td>
<td>CRM, RM</td>
<td>3 nat</td>
<td>Shading highlights elements not suitable for stable IRMs</td>
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<td>CRM, RM</td>
<td>5 monoiso</td>
<td>Number of isotopes</td>
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<td>CRM, RM</td>
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<tr>
<td>V</td>
<td>CRM, RM</td>
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</tr>
<tr>
<td>Cr</td>
<td>CRM, RM</td>
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<td>CRM, RM</td>
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<td>Cs</td>
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<tr>
<td>Au</td>
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Note: Various symbols are used to indicate different isotopes and their properties, such as nat, spk, air, radio, and monoiso.
METHODOLOGY

Unlike CRMs, RMs can be homogeneous natural materials with complex matrices, as well as pure elemental separates. One important difference between RMs and CRMs is that RM values are generally consensus values and not absolute values and are thus subject to revision as more data becomes available. Despite this limitation, RMs are often able to fulfill the same objectives as CRMs by simply providing a universally available basis for normalization. The procedure for preparing a RM is schematically depicted below.

Excellent examples of RMs are the stable isotopes of hydrogen, oxygen, nitrogen, carbon, sulfur and silicon distributed by the IAEA and NIST. Isotope ratios of these elements, when measured on a gas isotope ratio mass spectrometer, are determined by switching back and forth between standard and unknown. The results of the unknown are then expressed as a relative deviation from a standard reference. With this approach, highly precise data can be collected without the need for conversion to absolute values.

RMs are also important in solid source mass spectrometry. The La Jolla and CIT neodymium standards and the former Eimer and Amend strontium carbonate standard are examples of isotopic RMs prepared and distributed by early researchers in these fields. Monitor standards for $^{40}$Ar/$^{39}$Ar and other noble gas measurements also fit this category.

The production of an absolute isotopic reference material requires considerable effort and is, in fact, an atomic weight determination. While many aspects of producing a CRM are similar to the protocol for producing a RM, a CRM must be based on measurements of fundamental units of matter, such as mass, and must be traceable to those units. A pure, stoichiometrically definable form of the element for the candidate isotope reference material must be selected, and pure separated isotopes of known assay of the same element must be found.

Accurately known isotopic mixtures of the separated isotopes must be gravimetrically or volumetrically prepared and become the accuracy basis for the mass spectrometry. The principal limit to the overall accuracy of the absolute ratios is generally the quantitation during this step of the certification. At present, isotopic mixtures can be prepared on an absolute basis with an accuracy of a part in 10,000 or slightly better. Synthetic mixtures of the enriched isotopes are made that bracket the range of ratios in the candidate isotope reference material and are used to correct the measured ratios to an absolute basis. A rigidly defined mass spectrometric protocol specifying the sample form, amount, heating parameters, etc. is then followed from which simple correction factors for the measured isotope ratios are obtained. The absolute isotopic ratios and their uncertainties are derived from the corrected ratio data and a consideration of all the contributing sources of error or bias occurring during the certification process. This procedure is schematically outlined in the diagram below.
Generalized Isotopic RM Production Scheme

**MASS SPECTROMETRY**
- Set up mass spectrometric procedure for isotope ratio measurements
- Identify sources of error and bias
- Develop a high precision mass spectrometric technique that minimizes error and controls bias
- Determine values of interest using mass spectrometric measurements from selected laboratories
- Compute "Consensus Value"

**STANDARD PREPARATION**
- Obtain material for standard
- Process standard material (eg. grind, purify, etc.)
- Distribute standard to participating laboratories

Generalized Isotopic SRM Certification Scheme

**MASS SPECTROMETRY**
- Set up mass spectrometric procedure for isotope ratio measurements
- Identify sources of error and bias
- Develop a high precision mass spectrometric technique that minimizes error and controls bias
- Determine accurate isotopic ratios for the SRM

**CLASSICAL CHEMISTRY**
- Develop accurate assay procedure
- Obtain enriched isotopes - Verify purity and assay
- Produce calibration mixes bracketing the isotope ratios of interest
In order to further their utility to the geochemical and environmental community, the currently available isotopic RMs and CRMs have been grouped into general categories below.
### Gas IRMS Reference Materials

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<tr>
<td>U</td>
<td>U-900</td>
<td>CRM</td>
<td>Synthetic Mixture</td>
<td>U Oxide</td>
</tr>
<tr>
<td>U</td>
<td>U-930</td>
<td>CRM</td>
<td>Synthetic Mixture</td>
<td>U Oxide</td>
</tr>
<tr>
<td>U</td>
<td>U-960</td>
<td>CRM</td>
<td>Synthetic Mixture</td>
<td>U Metal</td>
</tr>
<tr>
<td>U</td>
<td>U-970</td>
<td>CRM</td>
<td>Synthetic Mixture</td>
<td>U Oxide</td>
</tr>
</tbody>
</table>

### Sources

**CBNM**  
Central Bureau for Nuclear Measurements  
Joint Research Centre, Steenweg naar Reine  
B-2440 Geel  
BELGIUM  
Tel: (014) 571 211

**CIT**  
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BP 6 - 92265 Fontenay aux Roses  
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Tel: 33-146-54-71-17

**IAEA**  
International Atomic Energy Agency  
Section of Isotope Hydrology  
PO Box 110  
A-1400 Vienna  
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Tel: 43-2254-3361-226

**NBL**  
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USA  
ATTN: Reference Materials Sales  
Tel: (708) 972-2767

**NIST**  
National Institute of Standards and Technology  
Standard Reference Materials Program  
Room 204, Building 202  
Gaithersburg, MD 20899  
USA  
Tel: (301) 975-6776

**UCBerk**  
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La Jolla, CA 92093 USA

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This section has copies of the certificates for the currently available Certified Isotope Reference Materials.
National Institute of Standards & Technology

Report of Investigation

Reference Materials 8535-8537

8535: VSMOW (Vienna Standard Mean Ocean Water)
8536: GISP (Greenland Ice Sheet Precipitation)
8537: SLAP (Standard Light Antarctic Precipitation)

These Reference Materials (RMs) are intended to provide samples of known isotopic composition with deuterium and oxygen-18 isotope ratios stated in parts per thousand difference (‰) from the VSMOW isotope-ratio standard. These RMs are not certified, but their use allows comparability of stable hydrogen and oxygen isotope-ratio data obtained by investigators in different laboratories. RM 8535 (VSMOW) and RM 8537 (SLAP) are intended for stable hydrogen and oxygen isotope-ratio calibration of water samples and of mass spectrometers for isotope-ratio analysis of all other oxygen- or hydrogen-bearing substances. Each material is issued in units of 30 mL in a sealed glass ampoule.

These RMs are distributed on behalf of the International Atomic Energy Agency (IAEA), Vienna, Austria. The overall coordination of preparation for NIST distribution was carried out by T.B. Coplen, U.S. Geological Survey and R.D. Vocke, Jr., NIST Inorganic Analytical Research Division. The supporting aspects concerning the distribution by NIST of these RMs were coordinated through the Standard Reference Materials Program by J.S. Kane.

Material Preparation

RM 8535 (VSMOW) was prepared [1,2] by mixing distilled ocean water with small amounts of other water in order to adjust its isotopic composition as close as possible to that of Standard Mean Ocean Water (SMOW, [1]). RM 8536 (GISP) was prepared by W. Dansgaard, University of Copenhagen, from a sample of Greenland firn [3]. RM 8537 (SLAP) was obtained from a firn sample collected by E. Picciotto, Université Libre de Bruxelles, at Plateau Station, Antarctica in 1967 [2].

Storage

It is recommended that these RMs be used to calibrate internal laboratory standards immediately upon opening. After opening glass ampoules, RMs can be stored in small, dry, glass vials with conical plastic insert caps to prevent evaporation.

NOTE: Because very limited quantities of these materials exist, distribution is limited to one unit of each per three-year period of time. Users are strongly advised to prepare their own internal standards for daily use and calibrate these standards against these RMs.

Gaithersburg, MD 20899
June 22, 1992

William P. Reed, Chief
Standard Reference Materials Program

Isotope Abundances

RM 8535 (VSMOW) is the isotopic standard to which RM 8536 (GISP), RM 8537 (SLAP), and most other oxygen-bearing substances are compared [4]. The hydrogen isotope abundance of VSMOW is [5]:

\[ ^{1}H: 99.984426 \pm 0.001557 \text{ atom percent} \]
\[ ^{2}H: 0.015574 \pm 0.001557 \text{ atom percent} \]

The oxygen isotope abundance of VSMOW is [6,7]:

\[ ^{16}O: 99.76206 \text{ atom percent} \]
\[ ^{17}O: 0.03790 \text{ atom percent} \]
\[ ^{18}O: 0.2004 \text{ atom percent} \]

The oxygen and hydrogen isotope-ratio scales are defined in terms of VSMOW and SLAP such that the hydrogen and oxygen isotope composition of SLAP relative to VSMOW is -248‰ and -55.5‰, respectively. Participating scientists and laboratories included in the measurement of VSMOW and SLAP above are given in reference 2. The isotopic composition of GISP is given in reference 8. Therefore, the isotopic compositions of the three RMs in ‰ relative to VSMOW are:

<table>
<thead>
<tr>
<th>RM</th>
<th>( d_{\text{VSMOW}} )</th>
<th>( \delta^{18}O_{\text{VSMOW}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8535 (VSMOW)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8536 (GISP)</td>
<td>-189.8</td>
<td>-24.85</td>
</tr>
<tr>
<td>8537 (SLAP)</td>
<td>-428</td>
<td>-55.5</td>
</tr>
</tbody>
</table>

The uncertainties in the \( d_{\text{D}} \) and \( \delta^{18}O \) values of GISP are of the order of 0.5‰ and 0.05‰, respectively.

REFERENCES

Report of Investigation

Reference Materials 8538-8542

8538: NBS30 (biotite)
8539: NBS22 (tuff)
8540: PEF1 (polyethylene foil)
8541: USGS24 (graphite)
8542: Sucrose ANU (sucrose)

These Reference Materials (RMs) are intended to provide samples of known isotopic composition with D/H, H/D, 14C/12C, and 18O/16O isotope ratios stated in parts per thousand difference (‰) from the Vienna Standard Mean Ocean Water (VSMOW, RM 8535) or Vienna Pee Dee belemnite (VPDB, 1.2‰) isotope-ratio standards. These RMs are not certified, but their use allows comparability of stable hydrogen, carbon, and oxygen isotope-ratio data obtained by investigators in different laboratories. RM 8538 (NBS30) is intended for stable hydrogen and oxygen isotope-ratio calibration of silicates and is issued in units of 2 g. Hydrogen isotope ratios should be determined on the water fraction (3.5%). RM 8539 (NBS22), RM 8540 (PEFI), and RM 8542 (Sucrose ANU) are intended for stable hydrogen and carbon isotope-ratio calibration of organic materials and are issued in units of 1 mL, a few mg, and 1 g, respectively. RM 8541 (USGS24) is intended for standard carbon isotope-ratio analysis and is issued in units of 0.8 g.

These RMs are distributed on behalf of the International Atomic Energy Agency (IAEA), Vienna, Austria.

The overall coordination of preparation for NIST distribution was carried out by T. B. Coplen, U.S. Geological Survey and R. D. Vocke, Jr., NIST Inorganic Analytical Research Division.

The supporting aspects concerning the distribution by NIST of these RMs were coordinated through the Standard Reference Materials Program by J. S. Kane.

Material Preparation

NBS30 was prepared by L. Silver, California Institute of Technology, Pasadena. RM 8539 (NBS22) was prepared by J. Friedland, J. R. O’Neil, and G. Cebula of the U.S. Geological Survey from a sample of Lakeview tonalite (Southern California batholith) provided by L. Silver, California Institute of Technology, Pasadena. RM 8540 (PEFI) was prepared by H. Gerstenberger and M. Herrmann, Zentralinstitut für Isotopen- und Strahlenforschung, Leipzig, Germany [2]. RM 8541 (USGS24) was prepared by T. B. Coplen, U.S. Geological Survey from Baker technical grade graphite (96%, <44 μm). Prior to splitting with a sample splitter, six spatially separated 1-mg samples were analyzed to ensure isotopic homogeneity of the material. Peak-top-peak variation was 0.1‰. RM 8542 (Sucrose ANU) was supplied to the IAEA by H. Polach, Australian National University, Canberra, and was originally intended to replace NBS sucrose and used for 14C standardization [1].

Gaithersburg, MD 20899
June 22, 1992

William P. Reed, Chief
Standard Reference Materials Program

REFERENCES

5. Coplen, T.B., unpublished data.
These Reference Materials (RMs) are intended to provide samples of known isotopic composition for isotope-ratio analysis of lithium, carbon, oxygen, and silicon. RM 8543 (NBS18) is intended for δ^12C and δ^18O isotope-ratio analysis of carbonates with isotope ratios stated in parts per thousand difference (‰) from Vienna Pee Dee Belemnite (VPDB) or Vienna Standard Mean Ocean Water (VSMOW (RM 8535)), respectively. RM 8544 (NBS19) is intended for δ^13C and δ^18O isotope-ratio analysis of carbonates and is used to define the VPDB scale [1,2]. RM 8545 (LSVEC) is intended for lithium and carbon isotopic abundance calibrations. RM 8546 (NBS28) is the silicon isotope reference for reporting silicon isotope-ratio data, and it is also intended for oxygen isotope-ratio calibration of silicates. These RMs are issued in units of approximately 0.4 g each.

These RMs are distributed on behalf of the International Atomic Energy Agency (IAEA), Vienna, Austria.

The overall coordination of preparation for NIST distribution was performed by T. B. Coplen, U.S. Geological Survey and R.D. Vocke, Jr., NIST Inorganic Analytical Research Division.

The supporting aspects concerning the distribution by NIST of these RMs were coordinated through the Standard Reference Materials Program by J.S. Kane.

Material Preparation

RM 8543 (NBS18) and RM 8544 (NBS19) were prepared by J. Friedman, J.R. O’Neil and G. Cebula [3] of the U.S. Geological Survey. RM 8543 (NBS18), a carbonatite from Fen, Norway, was collected by B. Taylor, University of California, Davis, and crushed by H. Fricdriksen, University of Tubingen, Federal Republic of Germany. The fraction between 88 µm and 440 µm was stored and bottled as NBS18. RM 8544 (NBS19), also known in the literature as TS-Limestone, was obtained from a single slab of white marble of unknown origin. After crushing, the fraction between 177 µm and 325 µm was bottled. RM 8545 (LSVEC) was prepared by H. Svec, Iowa State University [4]. RM 8546 (NBS28) was obtained by I. Friedman, U.S. Geological Survey from Corning Glass Company. It was washed with acid to remove impurities and the fraction between 100 µm and 177 µm was separated and packaged.

Gainesburg, MD 20899
June 22, 1992

William P. Reed, Chief
Standard Reference Materials Program

Storage

It is recommended that these RMs be stored in the containers in which they are supplied to the user. To minimize the potential for oxygen isotope exchange of carbonate RMs with atmospheric water vapor, RM 8543 (NBS18) and RM 8544 (NBS19) can be stored in a desiccator.

NOTE: Because very limited quantities of these materials exist, distribution is limited to one unit of each per three-year period of time. Users are strongly advised to prepare their own internal standards for daily use and calibrate these standards against these RMs.

Isotope Abundances

The carbon isotopic abundance of NBS18 and NBS19 have been measured as [5]:

<table>
<thead>
<tr>
<th>RM</th>
<th>δ^12C (NBS18)</th>
<th>δ^13C (NBS19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8543</td>
<td>98.89 ± 0.0028</td>
<td>98.922 ± 0.0028</td>
</tr>
<tr>
<td>8544</td>
<td>1.1078 ± 0.0028</td>
<td>1.1078 ± 0.0028</td>
</tr>
</tbody>
</table>

The carbon isotopic composition of these carbonate RMs relative to VPDB, using the defined δ^12CVPDB value of +1.95‰ for NBS19, is [1,2]:

\[ \text{RM} \quad \delta^{12}C_{\text{VPDB}, \%} \]

<table>
<thead>
<tr>
<th>RM</th>
<th>\delta^{12}C_{\text{VPDB}, %}</th>
</tr>
</thead>
<tbody>
<tr>
<td>8543</td>
<td>−5.04 ± 0.06</td>
</tr>
<tr>
<td>8544</td>
<td>+1.95</td>
</tr>
<tr>
<td>8545</td>
<td>−46.7 ± 0.3</td>
</tr>
</tbody>
</table>

The oxygen isotopic composition of these RMs relative to VPDB using the defined δ^18O value of −2.20‰ for NBS19, is listed below [1,2]. Also listed is the δ^18O value relative to VSMOW using the relationship [6] that

\[ \delta^{18}O_{\text{VSMOW}} = 1.03092 \delta^{18}O_{\text{VPDB}} + 30.92 \]

<table>
<thead>
<tr>
<th>RM</th>
<th>\delta^{18}O_{\text{VPDB}, %}</th>
<th>\delta^{18}O_{\text{VSMOW}, %}</th>
</tr>
</thead>
<tbody>
<tr>
<td>8543</td>
<td>−23.05 ± 0.19</td>
<td>+7.16 ± 0.19</td>
</tr>
<tr>
<td>8544</td>
<td>−2.29</td>
<td>+28.65</td>
</tr>
<tr>
<td>8545</td>
<td>+9.58 ± 0.10</td>
<td>+9.58 ± 0.10</td>
</tr>
</tbody>
</table>

The lithium isotopic abundance ratio of LSVEC is [4]:

\[ \delta^{6}Li / \delta^{7}Li = 0.0832 ± 0.0002 \]

Although no absolute isotope abundance measurement of RM 8546 (NBS28) has been performed, this material has served as the reference for relative δ^28Si measurements for more than a decade; thus, δ^28SiNBS28 of RM 8546 = 0 ‰.
REFERENCES


Report of Investigation

Reference Materials 8547-8552

8547: IAEA-N1 (ammonium sulfate)
8548: IAEA-N2 (ammonium sulfate)
8549: IAEA-N3 (potassium nitrate)
8550: USGS25 (ammonium sulfate)
8551: USGS26 (ammonium sulfate)
8552: NSVEC (gaseous nitrogen)

These Reference Materials (RMs) are intended to provide samples of known isotopic composition with $^{15}N/^{14}N$ isotope ratios stated in parts per thousand difference ($\%_\text{e}$) from atmospheric nitrogen in air (AIR). These RMs are not certified, but their use allows comparability of stable nitrogen isotope-ratio data obtained by investigators in different laboratories. RM 8552 (NSVEC) is issued in units of 300 µmol and the other RMs are issued in units ranging from 0.4 to 2 g.

These RMs are distributed on behalf of the International Atomic Energy Agency (IAEA), Vienna, Austria. The overall coordination of preparation for NIST distribution was carried out by T.B. Coplen, U.S. Geological Survey and R.D. Vocke, Jr., NIST Inorganic Analytical Research Division.

The supporting aspects concerning the distribution by NIST of these RMs were coordinated through the Standard Reference Materials Program by J.S. Kane.

Material Preparation

RM 8547 (IAEA-N1) and RM 8548 (IAEA-N2) were prepared by E. Salati, Centro de Energia Nuclear na Agricultura, Brazil. RM 8549 (IAEA-N3) was prepared by A. Marinotti, Universidade P. and M. Curie, Paris, France. RM 8550 (USGS25) was prepared in 1991 by J.K. Böhlke, U.S. Geological Survey from Fisher® ammonium sulfate (A938-500, lot #915021) and Cambridge Isotopes® ammonium sulfate (99.95 percent; A938-500, lot BI-1328). RM 8551 (USGS26) was prepared in 1991 by J.K. Böhlke, U.S. Geological Survey from Fisher® ammonium sulfate (A938-500, lot #915021) and Cambridge Isotopes® ammonium sulfate (10 percent; A938-500, lot BI-11050). RM 8552 (NSVEC) was originally prepared by G. Junk and H.J. Svec, Iowa State University [1]; C. Keudell, U.S. Geological Survey then split the sample into several hundred aliquots.

Gaithersburg, MD 20899
June 22, 1992

William P. Reed, Chief
Standard Reference Materials Program

Storage

It is recommended that these RMs be stored in the containers in which they are supplied to the user. When RM 8552 (NSVEC, gaseous nitrogen) is opened, it should be used immediately for calibration. It can be stored in a glass container fabricated with an all-glass stopcock coated with Apiezon N® hydrocarbon-based stopcock grease. Because the salts are hygroscopic, they should be stored in a desiccator.

NOTE: Because very limited quantities of these materials exist, distribution is limited to one unit of each per three-year period of time. Users are strongly advised to prepare their own internal standards for daily use and to calibrate those standards against these RMs.

Isotope Abundances

The absolute isotope ratio of nitrogen in air, reported by Junk and Svec is [1]:

$^{15}N/^{14}N = 272.0 \pm 0.3$

Reference 2 lists the $\delta^{15}N$ values of several of these RMs relative to AIR are listed, but more precise values are available for many of the materials. By definition, $\delta^{15}N$ AIR of air is 0 $\%_\text{e}$.

<table>
<thead>
<tr>
<th>RM</th>
<th>$\delta^{15}N$, $%_\text{e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM 8547 (IAEA-N1)</td>
<td>+0.4 ± 0.2 [3]</td>
</tr>
<tr>
<td>RM 8548 (IAEA-N2)</td>
<td>+20.3 ± 0.2 [3]</td>
</tr>
<tr>
<td>RM 8549 (IAEA-N3)</td>
<td>+2 +0.4 [4]</td>
</tr>
<tr>
<td>RM 8550 (USGS25)</td>
<td>-30.4 ± 0.5 [5]</td>
</tr>
<tr>
<td>RM 8551 (USGS26)</td>
<td>+53.5 ± 0.5 [5]</td>
</tr>
<tr>
<td>RM 8552 (NSVEC)</td>
<td>-2.81 [6]</td>
</tr>
</tbody>
</table>

REFERENCES

The IRM is supplied with an atomic isotope ratio certified as

$$ \frac{^{6}\text{Li}}{^{7}\text{Li}} = 21.78 \pm 0.12 $$

This corresponds to an isotopic composition with following isotope abundances:

<table>
<thead>
<tr>
<th>Isotopic Atom</th>
<th>Isotopic Mass</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{6}\text{Li})</td>
<td>6.010</td>
<td>95.610</td>
</tr>
<tr>
<td>(^{7}\text{Li})</td>
<td>4.390</td>
<td>4.396</td>
</tr>
</tbody>
</table>

The atomic weight of the lithium is 6.015 121 4 \(\pm\) 0.000 001 4

The IRM is intended for use in calibrating Li isotope ratio measurements.

Notes:
1. All uncertainties indicated are accuracies, computed on a 2\(s\) basis.
2. The Reference Material consists of Li\(_2\text{CO}_3\) and is supplied in about 0.05 g units.
3. The atomic masses used in the calculation of mass % abundances and of the atomic weight, are:

\[
\begin{align*}
^{6}\text{Li} &: 6.015 121 4 \pm 0.000 001 4 \\
^{7}\text{Li} &: 7.016 003 0 \pm 0.000 001 8.
\end{align*}
\]
The IRM is supplied with an atomic isotope ratio certified as

\[
\frac{6_{\text{Li}}}{7_{\text{Li}}} = 0.08137 \pm 0.00034
\]

This corresponds to an isotopic composition with following isotope abundances:

<table>
<thead>
<tr>
<th>Isotopic Atom</th>
<th>Isotopic Mass</th>
<th>\pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6_{\text{Li}}$</td>
<td>6.521</td>
<td>0.079</td>
</tr>
<tr>
<td>$7_{\text{Li}}$</td>
<td>93.479</td>
<td>0.029</td>
</tr>
</tbody>
</table>

The atomic weight of the lithium is 6.940 69 \pm 0.000 29

The IRM is intended for use in calibrating Li isotope ratio measurements.

4. Certified values are based on thermionic mass spectrometric measurements on samples converted to LiF. The measurements were calibrated with the aid of synthetic mixtures of isotopically enriched Li isotopes. Full details of this procedure can be found in:

The preparation and characterisation of the synthetic isotope mixtures were performed by Jean Pauwels.

The development of a precise isotopic measurement procedure for Li, the isotopic measurements and their calibration with synthetic isotope mixtures, as well as the chemical preparation of samples for isotopic measurements were performed by Eddy Michiels.

B-2440 Geel
1 September 1984

PAUL DE BIEVRE
Head
CBNM Mass Spectrometry

NOTES
1. All uncertainties indicated are accuracies, computed on a 2s basis.

2. The Reference Material consists of Li$_2$CO$_3$ and is supplied in about 1 g units.

3. The atomic masses used in the calculation of mass % abundances and of the atomic weight, are:

<table>
<thead>
<tr>
<th>Isotopic Mass</th>
<th>\pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6_{\text{Li}}$</td>
<td>6.015 123 2 \pm 0.000 001 6</td>
</tr>
<tr>
<td>$7_{\text{Li}}$</td>
<td>7.016 004 5 \pm 0.000 001 8</td>
</tr>
</tbody>
</table>
The IRM is supplied with a molar concentration of $^6$Li certified to be

$$(3.825 \pm 0.027) \times 10^{-3} \text{ mol} \; ^6\text{Li} \cdot \text{kg}^{-1} \text{ of solution}$$

Other lithium isotopes present are related to the $^6$Li concentration through the following certified molar ratio:

$$^6\text{Li} / ^7\text{Li} : 21.78 \pm 0.12$$

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mole X</th>
<th>Mass X</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6$Li</td>
<td>95.610</td>
<td>94.916</td>
<td>$\pm 0.025$</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>4.390</td>
<td>5.084</td>
<td>$\pm 0.025$</td>
</tr>
</tbody>
</table>

The atomic weight of the lithium is $6.059 \pm 0.000 \text{ 22}$.

From the certified values, the following concentrations are derived:

$$(2.301 \pm 0.016) \times 10^{-5} \text{ kg} \; ^6\text{Li} \cdot \text{kg}^{-1} \text{ of solution}$$

$$(4.001 \pm 0.028) \times 10^{-3} \text{ mol} \; ^6\text{Li} \cdot \text{kg}^{-1} \text{ of solution}$$

$$(2.429 \pm 0.017) \times 10^{-5} \text{ kg} \; ^7\text{Li} \cdot \text{kg}^{-1} \text{ of solution}$$
Isotopic measurements by Thermal Ionisation Mass Spectrometry were carried out by André Lamerty.

Metrological aspects involved in the preparation and certification were performed by Frans Hendrickx.

The ampoulation of this IRM was accomplished by André Verbruggen and Adolfo Alonso-Muñoz.

The coordination of the preparation of this IRM was accomplished by André Verbruggen.

The overall coordination of the establishment leading to the certification and issuance of this IRM was performed by André Lamerty.
Certificate of Analysis

Standard Reference Material 951

Boric Acid

H₃BO₃, as determined by titration, weight percent 100.00 ± 0.01

Absolute Abundance Ratio, ¹⁰⁷B/¹¹⁷B 0.2173 ± 0.0002

Boron 10, atom percent 19.827 ± 0.013

Boron 11, atom percent 80.173 ± 0.013

The atomic weight of the boric acid, calculated from the absolute abundance ratios using the massic masses 10.0129 and 11.0093, is 10.812.

This lot of boric acid was prepared to ensure material of high purity and homogeneity. As received, it was slightly deficient (approximately 0.01 percent) in moisture, but adjusts to a stoichiometric composition in about 30 minutes exposure to a normal room humidity (approximately 35 percent relative humidity). Once adjusted to composition, the material is relatively insensitive (<0.01 percent) to moisture changes between 0 and 60 percent relative humidity, and absorbs only about 0.02 percent excess moisture in room temperature humidities as high as 90 percent. The material cannot be heated as it decomposes with the loss of considerable water.

Assay was by coulometric titration of samples varying in size from 0.2 to 1.0 g of boric acid dissolved in 100 ml of a perchloric solution 1.0 M in KCl and 0.75M in mannitol. The inflection point of the potentiometric curve obtained from measurements with a glass-calomel electrode system was taken as the end point. The pH of the maximum inflection point was taken as the end point. The pH of the maximum inflection point will vary from approximately 7.9 to 8.5 for the range of sample sizes given above, and the titration must, therefore, be conducted in the absence of carbon dioxide or carbonates. The indicated tolerance is at least as large as the 95 percent confidence level for a single determination of any sample in the lot of material, and the average essentially indicates a boron-hydrogen ion ratio of 1.0000, since separate examination shows the material contains less than 0.001 percent of free strong acid.

The abundance ratio was determined by single-filament solid-sodium mass spectrometry using the ion Na⁺/²¹⁰²²⁸B⁺. Mixtures of known ¹⁰⁷B/¹¹⁷B ratio (at a 1:4, 1:1, and 4:1 ratio) were prepared from high-purity separated isotope solutions and used as comparison standards. Correction was determined for the ¹⁰⁷B/¹¹⁷B ratio (¹⁰⁷B/¹¹⁷B ratio, -0.00079) by measuring mass 90 using the high-purity boron-11 separated isotope. The indicated tolerances are at least as large as the 95 percent confidence limits for a single determination which includes terms for inhomogeneity in the material as well as analytical error.

The material was prepared by the J. T. Baker Company of Phillipsburg, New Jersey, for the Argonne National Laboratory. Separated isotopes were purified and solutions prepared by K. M. Sappenfield and T. J. Murphy, coulometric titrations were made by C. Marinosko and C. E. Champion, mass-spectrometric measurements were made by E. J. Catanzaro and E. L. Garner, Analytical Chemistry Division. The various procedures developed have been published and available in Special Publication 240-A.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
February 21, 1969

W. Wayne Meinke, Chief
Office of Standard Reference Materials

(Revised October 12, 1971)
Certificate of Analysis

Standard Reference Material 952

Enriched Boric Acid

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute Abundance Ratio, (^{11}B/^{11}H)</td>
<td>18.80 ± 0.02</td>
</tr>
<tr>
<td>Boron 10, atom percent</td>
<td>94.94 ± 0.05</td>
</tr>
<tr>
<td>Boron 11, atom percent</td>
<td>5.05 ± 0.05</td>
</tr>
<tr>
<td>(\text{HBO}_3), acidimetric assay, weight percent</td>
<td>99.97 ± 0.02</td>
</tr>
</tbody>
</table>

The preparation furnished is an enriched boron-10 boric acid. It is slightly contaminated by unlabelled mother liquor but the assay value should make it useful for direct weighing for a "spiking" material for boron assays, as well as a useful material for the calibration of mass spectrometers. The atomic weight of the boron, calculated from the absolute abundance ratio and the nuclear masses 10.0129 and 11.0033, is 10.0033.

The abundance ratio was determined by single filament solid sample mass spectrometry, using the ion \(\text{Na}^{10} \text{BO}_3^+\). Mixtures of known \(^{11}B/^{11}B\) ratio were prepared from high-purity separated isotopes and used as comparison standards. Correction was determined for the \(^{11}B/^{11}H\) ratio (\(^{11}B/^{11}B\) ratio 0.00070) by measuring mass 90 using the high-purity boron 11 separated isotope. The indicated tolerance is at least as large as the 95 percent confidence limits for a single determination which includes terms for homogeneity in the material as well as analytical error.

Details of the preparations and measurements are available in Special Publication 200-17. The material was prepared by the Oak Ridge National Laboratory. The material and the separated isotopes were purified and solutions prepared by K. M. Sappenfield and T. J. Murphy, and mass-spectrometric measurements were made by G. Marzenko and C. E. Champion. Mass-spectrometric measurements were made by J. L. Calantaro and E. L. Garner, Analytical Chemistry Division.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. K. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D. C. 20234
February 28, 1969
Revised October 12, 1971

W. Wayne Meinke, Chief
Office of Standard Reference Materials
Certiﬁcate

ISOtOpIC REFERENCE MaTerial CRMM IKM-610

The IKM is supplied with an 10B atomic isotope concentration certiﬁed as

\[(2.718 \pm 0.00053) \times 10^2 \text{ n (atoms 10B)-kg}^{-1} \text{ (solution)}\]

from the certiﬁed isotope concentration, the following concentrations are derived:

\[3.683 \pm 0.00088 \text{ mole (10B)-kg}^{-1} \text{ (solution)}\]
\[3.687 \pm 0.00088 \text{ kg (10B)-kg}^{-1} \text{ (solution)}\]

Other Boron isotopes present are related to the 10B isotope concentration through the following molar ratio:

\[{}^{10}B/{}^{11}B = 18.80 \pm 0.02\]

This corresponds to an isotopic composition with following isotope abundances:

<table>
<thead>
<tr>
<th>mol %</th>
<th>mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>10B</td>
<td>94.949</td>
<td>± 0.0051</td>
</tr>
<tr>
<td>11B</td>
<td>5.050</td>
<td>± 0.0051</td>
</tr>
</tbody>
</table>

The atomic weight of the Boron is

\[10.063 \pm 0.000051\]

From the certiﬁed atomic isotope concentration, the following element concentrations are derived:

\[3.879 \pm 0.00091 \text{ mole (B)-kg}^{-1} \text{ of solution}\]
\[3.903 \pm 0.00094 \text{ kg (B)-kg}^{-1} \text{ of solution}\]

NOTES

1. All uncertainties indicated are accuracies, computed on a 2σ basis.

2. The IKM is a solution of HgBO3 in subboiled water and is supplied in quartz ampoules containing about 5 g of solution.

3. The Avogadro Constant used is \((6.022134 \pm 0.000012) \times 10^{23}\).

4. The atomic masses, used in the calculations, are

\[{}^{10}B = 10.0129369 \pm 0.000003\]
\[{}^{11}B = 11.0093054 \pm 0.000004\]

5. Using this Spike IKM, 10B concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the molar isotope dilution ratio \(Rg = 10B/11B\) in the blend. They should be computed with the aid of the following formula which allows an easy identiﬁcation of the sources of the uncertainties in the procedure:

\[C_{10} = \frac{R_X - R_Y}{R_X - R_Y} \times \frac{1}{R_F} \times \frac{M_X}{M_F} \times C_W\]

where

\[R_X = \text{molar isotope ratio } {}^{10}B/{}^{11}B \text{ in the unknown sample material}\]
\[R_Y = \text{molar isotope ratio } {}^{10}B/{}^{11}B \text{ in the spike material}\]
\[M_X = \text{mass of the unknown sample}\]
\[M_Y = \text{mass of the sample of spike solution used}\]
\[C_W = \text{number of atoms } {}^{10}B \cdot \text{kg}^{-1} \text{ spike material}\]
\[C_W = \text{number of atoms } {}^{11}B \cdot \text{kg}^{-1} \text{ sample solution.}\]
ISOTOPIC REFERENCE MATERIAL CBNM - IRM - U11

The IRM is supplied with an atomic isotope ratio certified as

\[ \frac{^{10}\text{B}}{^{11}\text{B}} = 0.24726 \pm 0.00037 \]

This corresponds to an isotopic composition with following isotope abundances:

<table>
<thead>
<tr>
<th>Isotopic Atom</th>
<th>Isotopic Mass %</th>
<th>Isotopic Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>10B</td>
<td>19.874</td>
<td>10.8359</td>
</tr>
<tr>
<td>11B</td>
<td>80.126</td>
<td>81.641</td>
</tr>
</tbody>
</table>

The atomic weight of the boron is 10.811 8 +/- 0.002 0

The IRM is intended for use in calibrating B isotope ratio measurements.

NOTES
1. All uncertainties indicated are accuracies, computed on a 2σ basis.
2. The Reference Material consists of \( \text{B}_2\text{O}_3 \) and is supplied in about 1 g units.
3. The atomic masses used in the calculation of mass % abundances and of the atomic weight, are:
   \[ ^{10}\text{B} : 10.012 938 0  \pm 0.000 001 0 \]
   \[ ^{11}\text{B} : 11.009 363 3  \pm 0.000 001 0 \]

4. Certified values are based on thermionic mass spectrometric measurements on samples converted to NaB\(_4\)O\(_7\). The measurements were calibrated with the aid of synthetic mixtures of isotopically enriched B isotopes. Full details of this procedure can be found in:


   The preparation and characterisation of the synthetic isotope mixtures were performed by Yves Le Noligou and Jan Bruulmans.

   The development of a precise isotopic measurement procedure for B, as well as the isotopic measurements and their calibration with synthetic isotope mixtures, were performed by Marc Gallet.

B-2440 Geel
1 June 1984

PAUL DE BIEVRE
Head
CBNM Mass Spectrometry
The IRM is supplied with a molar concentration of $^{11}$B certified to be:

$$(4.025 \pm 0.040) \times 10^{-3} \text{ mol} \text{ B-kg}^{-1} \text{ of solution}$$

Other Boron isotopes present are related to the $^{11}$B concentration through the following certified molar isotope ratio:

$$^{10}$B/$^{11}$B : 0.247 26 ± 0.000 32

This corresponds to an isotopic composition with the following abundances:

<table>
<thead>
<tr>
<th>Mole %</th>
<th>Mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{10}$B</td>
<td>19.024</td>
<td>± 0.020</td>
</tr>
<tr>
<td>$^{11}$B</td>
<td>80.176</td>
<td>+ 0.020</td>
</tr>
</tbody>
</table>

The atomic weight of the Boron is $10.81178 \pm 0.00030$.

From the certified values, the following concentrations are derived:

$$\begin{align*}
(4.431 \pm 0.044) \times 10^{-5} \text{ kg} \text{ B-kg}^{-1} \text{ of solution} \\
(5.020 \pm 0.050) \times 10^{-3} \text{ mol} \text{ B-kg}^{-1} \text{ of solution} \\
(5.478 \pm 0.054) \times 10^{-5} \text{ kg} \text{ B-kg}^{-1} \text{ of solution}
\end{align*}$$

NOTES

1. All uncertainties indicated are accuracies, computed on a 2s basis, taking into account both measurement reproducibilities and uncertainties of systematic nature estimated on a 2s basis.

2. The IRM is a solution of $^{10}$BD$_3$ in sub boiled water and is supplied in quartz ampoules each containing about 5g of solution.

3. The Avogadro Constant used is $(6.022 134 \pm 0.000 012) \times 10^{23} \text{ mol}^{-1}$.

4. The atomic masses, used in the calculations, are:

$$\begin{align*}
^{10}$B & : (10.012 936 9 \pm 0.000 012) \text{ u} \\
^{11}$B & : (11.009 305 4 \pm 0.000 000 4) \text{ u}
\end{align*}$$

5. Using this Spike IRM, $^{10}$B and $^{11}$B concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the molar isotope dilution ratio $R = ^{10}$B/$^{11}$B in the blend. They should be computed with the aid of the following equations for bi-isotopic elements which allow an easy identification of the sources of the uncertainties in the procedure:

$$c^{(10)}B = \frac{R - R_Y}{R - R_X} \times \frac{m_Y}{m_X}$$

$$c^{(11)}B = \frac{R - R_Y}{R - R_X} \times \frac{1}{1 + R} \times \frac{m_Y}{m_X}$$

where

- $R$ - molar isotope ratio $^{10}$B/$^{11}$B in the unknown sample material
- $R_X$ - molar isotope ratio $^{10}$B/$^{11}$B in the spike material
- $m_X$ - mass of the unknown sample
- $m_Y$ - mass of the sample of spike solution used
- $c^{(10)}B_X$ - number of moles $^{10}$B-kg$^{-1}$ of sample material
- $c^{(11)}B_X$ - number of moles $^{11}$B-kg$^{-1}$ of spike solution
- $c(B)_X$ - number of moles B-kg$^{-1}$ of sample material
- $c(B)_Y$ - number of moles B-kg$^{-1}$ of spike solution.
Isotopic measurements by thermal ionisation Mass Spectrometry were carried out by Veronica Holland.

Metrological aspects involved in the preparation and certification were performed by Frans Hendrickx.

The purity of H$_3$BO$_3$ was determined by Spark Source Mass Spectrometry by Willy Lycke.

The ampoulation of this IRM was accomplished by André Verbruggen and Adolfo Alonso Muñoz.

The coordination of the preparation of this IRM was accomplished by André Verbruggen.

The overall coordination of the establishment leading to the certification and issuance of this IRM was performed by Andree Lamberly.

B-2440 Geel
January 1990

Paul DE RIEVRE
Head
CBBM Mass Spectrometry
Certificate of Analysis

Standard Reference Material 980
Isotopic Standard for Magnesium

| Absolute Abundance Ratio, Mg-25 Mg-24 | 0.12663 ± 0.00013 |
| Absolute Abundance Ratio, Mg-26 Mg-24 | 0.13932 ± 0.00025 |
| Magnesium-24, Atom Percent           | 78.992 ± 0.025    |
| Magnesium-25, Atom Percent           | 10.003 ± 0.009    |
| Magnesium-26, Atom Percent           | 11.005 ± 0.019    |

The preparation furnished is a commercial sample of high-purity magnesium metal. Measurements are by triple filament (rhenium) mass spectrometry, using mixtures of known composition prepared from high-purity separated isotopes of magnesium as comparison standards. Overall limits of error are based on 95 percent confidence limits for the mean of the ratio measurements, and on allowances for the known sources of possible systematic errors. Details of the preparation and measurements are published by E. J. Catanzaro, T. J. Murphy, K. L. Garner and W. R. Shields, J. Research NBS 70A, No. 6, 453-458 (1966).
National Bureau of Standards
Certificate
Standard Reference Material 990
Assay-Isotopic Standard for Silicon

This Standard Reference Material is supplied in the form of a wafer 3 cm in diameter and 0.2 cm thick. It is intended to be used as a standard for assay and isotopic measurements of pure silicon material. The purity of this standard is established to be greater than 99.999 percent based on the determination of 22 impurities by isotope dilution-spark source mass-spectroscopy. The material was prepared from a single crystal of high purity silicon. This particular material has been used as the reference sample in the recent determination of Avogadro's number (1)

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom Percent</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon 28</td>
<td>92.2293 ± 0.00039</td>
<td></td>
</tr>
<tr>
<td>Silicon 29</td>
<td>1.6608 ± 0.00022</td>
<td></td>
</tr>
<tr>
<td>Silicon 30</td>
<td>6.1089 ± 0.00621</td>
<td></td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>28.086556 ± 0.000056</td>
<td></td>
</tr>
</tbody>
</table>

The indicated uncertainties are overall limits of error for a single analysis, based on 95% confidence limits of the mean and known sources of systematic bias.

Mass-spectrometric measurements were made by J. E. Barnes and L. J. Moore on samples prepared by L. A. Macdonald and T. J. Murphy.

The overall direction and coordination of the technical measurements leading to certification were under the chairmanship of J. E. Barnes.

The technical and support aspects concerning the preparation, certification, and release of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234  J. Paul Cal. Chief
August 1975  Office of Standard Reference Materials

The IRM is supplied with atomic isotope abundance ratios certified as:

\[
\begin{align*}
\frac{29S}{28S} & = 0.05069 \pm 0.00012 \\
\frac{30S}{28S} & = 0.03352 \pm 0.00010
\end{align*}
\]

This corresponds to an isotopic composition with the following isotope abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>28S</td>
<td>92.233</td>
<td>0.0014</td>
</tr>
<tr>
<td>29S</td>
<td>4.678</td>
<td>0.0011</td>
</tr>
<tr>
<td>30S</td>
<td>3.092</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

The atomic weight of silicon is 28.085 40 ± 0.000 19.

The IRM is intended for use in calibrating measurements of Si isotope abundance ratios.

NOTES

1. All uncertainties indicated are computed on a 2s basis, plus bounds to possible systematic errors due to the instrument and modelling.
2. The Reference Material consists of Si and is supplied in units of about 50 mg.
The IRM is supplied with atomic isotope ratios certified as

\[
\frac{\text{Si}^{28}}{\text{Si}^{29}} = 0.05083 \pm 0.00012 \\
\frac{\text{Si}^{30}}{\text{Si}^{28}} = 0.03336 \pm 0.00010
\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si^{28}</td>
<td>92.214</td>
<td>± 0.014</td>
</tr>
<tr>
<td>Si^{29}</td>
<td>4.688</td>
<td>± 0.011</td>
</tr>
<tr>
<td>Si^{30}</td>
<td>3.098</td>
<td>± 0.008</td>
</tr>
</tbody>
</table>

The atomic weight of the silicon is 28.08565 ± 0.00019

The IRM is intended for use in calibrating measurements of Si isotope abundance ratios.

NOTES

1. All uncertainties indicated are computed on a 2σ basis, plus bounds to possible systematic errors due to the instrument and modelling.

2. The Reference Material consists of SiO2 and is supplied in units of about 5 g.

3. The relative atomic masses used in the calculation of mass % abundances and of the atomic weight are

\[
\begin{align*}
\text{Si}^{28} & : 27.9769271 \pm 0.0000014 \\
\text{Si}^{29} & : 28.9764949 \pm 0.0000014 \\
\text{Si}^{30} & : 29.9737701 \pm 0.0000014
\end{align*}
\]

4. Certified values are based on gas isotope mass spectrometric measurements on SiO2 samples converted to SiF4 gas.

The chemical work on the IRM (i.e. conversions of SiO2 to SiF4) was carried out by S. Valkiers and G. Lenaers.

The development of a precise procedure for silicon isotopic measurements was carried out by S. Valkiers, G. Lenaers and W. De Bolle.

The measurements were calibrated with the aid of synthetic isotope mixtures prepared from three enriched Si isotopes.

The chemical development work and the preparation of the synthetic isotope mixtures were performed by G. Lenaers* and T.J. Murphy**.

The isotopic measurements (characterization of the synthetic mixtures and homogeneity verification of the IRM) and calibration of the IRM against the synthetic mixtures were performed by S. Valkiers.

Full details about the characterization of the IRM can be found in CBNM Internal Report GE/R/HS/11/89:

Characterization of two Silicon Isotope Reference Materials:
CBNM IRM-017 (Si) and CBNM IRM-018 (SiO2)
S. Valkiers, G. Lenaers and P. De Bievre

B-2440 Geel
1 May 1989
Paul DE BIEVRE
Head
CBNM Mass Spectrometry

* University of Antwerpen
** National Bureau of Standards, Gaithersburg MD, USA, - Visiting Scientist at CBNM 1986-1987
National Institute of Standards & Technology

Report of Investigation

Reference Materials 8553-8557

8553: Soufre de Lacq (elemental sulfur)
8554: NZ1 (silver sulfide)
8555: NZ2 (silver sulfide)
8556: NBS123 (sphalerite)
8557: NBS127 (barium sulfate)

These Reference Materials (RMs) are intended to provide samples of known isotopic composition with $^{32}$S/$^{34}$S and $^{18}$O/$^{16}$O isotope ratios stated in parts per thousand difference ($\permil$) from the Canyon Diablo Troilite (CDT) and the Vienna Standard Mean Ocean Water (VSMOW) (RM 8535) isotope-ratio standards, respectively. These RMs are not certified, but their use allows comparability of stable sulfur and oxygen isotope-ratio data obtained by investigators in different laboratories. RM 8553 (Soufre de Lacq) and RM 8556 (NBS123) are issued in units of 0.5 g and 1.5 g, respectively. RM 8557 (NBS127) is also intended for oxygen isotope-ratio calibration of sulfates and is issued in units of 0.5 g.

These RMs are distributed on behalf of the International Atomic Energy Agency (IAEA), Vienna, Austria.

The overall coordination of preparation for NIST distribution was carried out by T.B. Coplen, U.S. Geological Survey and R.D. Vocke, Jr., NIST Inorganic Analytical Research Division.

The supporting aspects concerning the distribution by NIST of these RMs were coordinated through the Standard Reference Materials Program by J.S. Kane.

Material Preparation

RM 8553 (Soufre de Lacq) was prepared by E. Roth, Centre d'Etudes Nuclceaires, Saclay, France. RM 8554 (NZ1) was prepared by B.W. Robinson, Department of Scientific and Industrial Research, Lower Hutt, New Zealand, from a sphalerite provided by S. Halas, University Maria Curie-Sklodowska University, Lublin, Poland, with $\delta^{34}$S$_{CDT}$ near 0 $\permil$. RM 8557 (NBS127) was prepared by J.R. O'Nell, U.S. Geological Survey, by ion exchange of sulfate in seawater from Monterey Bay, California.

Gatcbsburg, MD 20899
June 22, 1992

William P Reed, Chief
Standard Reference Materials Program

Storage

It is recommended that these RMs be stored in the containers in which they are supplied to the user.

NOTE: Because very limited quantities of these materials exist, distribution is limited to one unit of each per three year period of time. Users are strongly advised to prepare their own internal standards for daily use and calibrate these standards against these RMs.

Isotope Abundances

According to reference 2 the sulfur isotopic abundance of RM 8556 (NBS123) is:

\[
\begin{align*}
94.8871 \text{ atom percent } ^{32}\text{S} \\
0.7563 \text{ atom percent } ^{34}\text{S} \\
4.3463 \text{ atom percent } ^{33}\text{S} \\
0.0103 \text{ atom percent } ^{32}\text{S}
\end{align*}
\]

The sulfur isotopic composition of these RMs relative to CDT is:

\[
\begin{align*}
\delta^{34}\text{S}_{CDT}. \permil \\
\delta^{33}\text{S}_{CDT}. \permil \\
\delta^{32}\text{S}_{CDT}. \permil \\
\delta^{33}\text{S}_{CDT}. \permil
\end{align*}
\]

<table>
<thead>
<tr>
<th>RM 8553 (Soufre de Lacq)</th>
<th>+17.3 $\pm$ 0.2 $\permi M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM 8554 (NZ1)</td>
<td>-0.3 $\permi M$</td>
</tr>
<tr>
<td>RM 8555 (NZ2)</td>
<td>+21.0 $\permi M$</td>
</tr>
<tr>
<td>RM 8556 (NBS123)</td>
<td>+17.44 $\permi M$</td>
</tr>
<tr>
<td>RM 8557 (NBS127)</td>
<td>+20.32 $\pm$ 0.36 $\permi M$</td>
</tr>
</tbody>
</table>

The uncertainties on the first five items listed above are of the order of 0.3 $\permil$.

The oxygen isotopic composition of RM 8557 (NBS 127) relative to RM 8535 (VSMOW) is $+9.4 \pm 0.3 [1]$.

REFERENCES

Certificate of Analysis

Standard Reference Material 975
Isotopic Standard for Chlorine

Absolute Abundance Ratio, Cl-35/Cl-37
3.4272 ± 0.0079

Chlorine-35, atom percent
75.770 ± 0.011

Chlorine-37, atom percent
24.230 ± 0.016

The preparation furnished is a commercial sample of sodium chloride, formerly distributed as NBS Isotope Reference Sample No. 166. Measurements are by triple filament mass spectrometry, using mixtures of known composition prepared from high-purity separated isotopes as comparison standards. Overall limits of error are based on 95 percent confidence limits for the mean and on allowances for the effects of known sources of possible systematic error. Details of the applications and measurements are published by W. R. BĈellis, T. J. Murphy, E. L. Garner, and V. H. Hileman, J. ACS 84, 1519-1522 (1962).

W. Wayne Meinke, Chief

WASHINGTON, D. C. 20234
March 11, 1966.
Standard Reference Material 985
Assay-Isotopic Standard for Potassium

Fall, 1979

The NBS Office of Standard Reference Materials announces the availability of a new assay-isotopic standard for potassium, Standard Reference Material 985. This SRM is supplied as highly purified potassium chloride and is certified for assay (99.9%) and for isotopic composition.

SRM 985 is intended for use primarily by mass spectrometists for the calibration of isotope ratio mass spectrometers. The material may be dissolved by standard techniques to provide solutions of known purity and isotopic composition.

SRM 985 may be purchased from the Office of Standard Reference Materials, Room B311, Chemistry Building, National Bureau of Standards, Washington, D.C. 20234, for $50 per 10 gram sample.
National Bureau of Standards
Certificate of Analysis
Standard Reference Material 985
Assay-Isotopic Standard for Potassium

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atom Percent</th>
<th>Absolute Abundance Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium-39</td>
<td>91.258 ± 0.00029</td>
<td>13.8366 ± 0.0063</td>
</tr>
<tr>
<td>Potassium-40</td>
<td>0.01167 ± 0.00004</td>
<td>0.0617343 ± 0.0000061</td>
</tr>
<tr>
<td>Potassium-41</td>
<td>6.7302 ± 0.0029</td>
<td>0.20165 ± 0.000058</td>
</tr>
</tbody>
</table>

This Standard Reference Material is supplied as highly purified potassium chloride with a certified purity of 99.9 weight percent based on determination of the potassium content by a combination of gravimetric and isotope dilution analysis and the chloride content by a coulometric argentimetric procedure. The above value for the purity of the material is based on a sample dried over magnesium perchlorate for 24 hours. The absolute isotopic abundance ratios were determined by two analyses using two different mass spectrometers. Samples of known isotopic composition, prepared from nearly isotopically pure separated potassium-39 and potassium-41 isotopes, were used to calibrate the mass spectrometers. The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and allowances for the effects of known sources of possible systematic error. The details of the measurements are described in a published paper: J. Res. NBS(U.S.), 79A (Phys. and Chem.), No. 6, 713-725 (Nov.-Dec. 1975).

The overall direction and coordination of the analytical measurements leading to the certificate were performed in the Analytical Chemistry Division under the chairmanship of I. I. Barnes.

Mass spectrometric measurements were made by E. E. Garner and J. W. Gramlich on samples prepared by I. J. Murphy.

Assay measurements were made by I. J. Murphy and P. J. Pauken for potassium, and by G. Marumakno for chloride.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
August 31, 1979

George A. Utzmann, Chief
Office of Standard Reference Materials
# Certificate of Analysis

**Standard Reference Material 915**  
**Calcium Carbonate**

This Standard Reference Material is certified as a chemical of known purity. It is intended primarily for use in the calibration and standardization of procedures for calcium determinations employed in clinical analysis and for routine critical evaluation of the daily working standards used in these procedures.

The sample consists of highly purified calcium carbonate, and chemical assay as well as analysis for specific impurities indicate that the material may be considered to be essentially pure.

<table>
<thead>
<tr>
<th>Purity</th>
<th>99.9+ percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.01 ± 0.005 percent</td>
</tr>
</tbody>
</table>

Replicate samples taken from a randomly selected region of the undried material were assayed by a coulometric titrimetric procedure. The results from nine independent determinations, based on expression of the assay as calcium carbonate, indicate a purity of 99.99+ percent with a standard deviation of 0.003 percent. Samples equilibrated at a relative humidity of 75 percent and assayed by this coulometric procedure showed a maximum moisture adsorption of 0.02 percent as compared to samples that were dried for 6 hours at 210 °C. The moisture content, similarly measured, on samples equilibrated at 75 percent relative humidity, was found to be 0.01 percent. The water content was determined by the Karl Fischer method.


The overall direction and coordination of technical measurements leading to the certification were under the chairmanship of R. Schaffer.

The technical and support aspects concerning the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D.C. 20234  
March 4, 1969  
Revised November 21, 1973

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The material was examined for compliance with the specifications for reagent grade calcium carbonate as given in Reagent Chemicals, 4th edition, published by The American Chemical Society. The material was found to meet or exceed the minimum requirements in every respect. Examination by thermal gravimetric analysis indicated the loss of a minute proportion of weight below 175 °C (volatile matter) and the composition was stable above this temperature until a temperature of 625 °C, above which decomposition (evolution of CO₂) set in.

A semi-quantitative survey for trace contaminants by emission spectroscopy indicated the presence of less than 0.001 percent of copper, iron, magnesium, manganese and silicon in the material. By atomic absorption magnesium was evaluated at 1.0, sodium at 0.4, and strontium 2.1 parts per million (ppm); potassium was less than 0.4, lithium less than 0.05, and barium much less than 10 ppm. Neutron activation analysis indicated copper 0.9, manganese 0.6 and sodium 0.5 ppm. Copper was determined at 1 ppm by spectrophotometry.

This Standard Reference Material is intended for "in vitro" diagnostic use only.

This material is for use as a standard in clinical chemistry. It may be used to prepare calcium standard solutions for either atomic absorption or titrimetric methods of analysis.

**Standard stock solutions of calcium for atomic absorption (Reference Method) [1]:** Prepare a minimum of three concentrations at 2.00, 2.50, and 3.00 mmol of calcium per liter, with each to contain 140 mmol of sodium chloride and 5.0 mmol of potassium chloride per liter. To each of the three 1-liter volumetric flasks, add 8.18 g NaCl and 373 mg of KCl. To the first flask (2.00 mmol of Ca per liter) add 200.2 mg of SRM 915 (dried at 200 °C for 4 hours), to the second flask (2.50 mmol of Ca per liter) add 250.2 mg of SRM 915, and to the third flask (3.00 mmol of Ca per liter) add 300.3 mg of SRM 915. To each flask add a few milliliters of water and 1 ml of concentrated HCl. Make sure that all the calcium carbonate is in solution before diluting with water up to the neck. When at ambient temperature, dilute each flask to the calibrated volume and mix by inverting the flask 30 times. Pipettings and dilutions of this material should follow the instructions given in reference [1].

**Stock solution of calcium for titrimetric procedure:** Place 0.250 g of dried SRM 915 into a 1000-ml volumetric flask. Add approximately 9 ml of deionized water and 1 ml concentrated HCl. Shake until dissolved. Fill to the mark with deionized water and store in a pyrex bottle. This solution contains 10.0 mg per 100 ml or 5.00 meq per liter.

This Standard Reference Material should be stored in a well-stoppered bottle (preferably the original bottle) at room temperature. Calcium carbonate is a stable material. Under proper storage, experience at NBS indicates this material to be stable for at least 10 years. If the material purity degrades beyond the limits certified, purchasers will be notified by NBS. It is recommended that the material not be used after 5 years from the date of purchase.

Solutions prepared from SRM 915, Calcium Carbonate, are stable indefinitely when stored in an glass-stoppered bottle. All such solutions should be clear and display no turbidity.
References:


This Standard Reference Material has been measured and certified at the laboratories of the National Bureau of Standards, Gaithersburg, Maryland. All inquiries should be addressed to:

Office of Standard Reference Materials
B311, Chemistry Building
National Bureau of Standards
Washington, D. C. 20234

The date of issuance and certification of this Standard Reference Material was March 4, 1969.
Certificate of Analysis

Standard Reference Material 979
Isotopic Standard for Chromium

| Absolute Abundance Ratio, Cr $^{50}$ Cr $^{52}$ | 0.65186 ± 0.00004 |
| Absolute Abundance Ratio, Cr $^{53}$ Cr $^{52}$ | 1.1339 ± 0.0015 |
| Absolute Abundance Ratio, Cr $^{54}$ Cr $^{52}$ | 0.2822 ± 0.0004 |
| Chromium 50, atom percent | 1.315 ± 0.009 |
| Chromium 52, atom percent | 83.589 ± 0.12 |
| Chromium 53, atom percent | 9.501 ± 0.11 |
| Chromium 54, atom percent | 2.365 ± 0.05 |

The preparation furnished is a commercial sample of hydrated chromium nitrate [Cr(NO$_3$)$_3$·9H$_2$O]. Measurements are by single filament (platinum) mass spectrometry, using mixtures of known composition prepared from high-purity separated isotopes as comparison standards. Overall limits of error are based on 95 percent confidence limits for the mean of the ratio measurements, and on allowances for the known source of possible systematic errors. Details of the preparations and measurements are published by W. R. Shields, T. J. Murphy, E. J. Catanzaro, and E. L. Garner, J. Research NBS 70A (Phys. and Chem.) No. 2, 195–197 (1966).
The IRM is supplied with a molar isotope ratio certified as:

\[
\begin{align*}
\frac{n(54\text{Fe})}{n(56\text{Fe})} &= 0.06370 \pm 0.00027 \\
\frac{n(56\text{Fe})}{n(58\text{Fe})} &= 0.023096 \pm 0.000072 \\
\frac{n(58\text{Fe})}{n(56\text{Fe})} &= 0.003071 \pm 0.000029
\end{align*}
\]

This corresponds to an isotopic composition with the following abundances:

<table>
<thead>
<tr>
<th>Element</th>
<th>Mole %</th>
<th>Mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>54Fe</td>
<td>5.845</td>
<td>5.645</td>
<td>\pm 0.007</td>
</tr>
<tr>
<td>56Fe</td>
<td>91.754</td>
<td>91.902</td>
<td>\pm 0.003</td>
</tr>
<tr>
<td>57Fe</td>
<td>2.119</td>
<td>2.160</td>
<td>\pm 0.006</td>
</tr>
<tr>
<td>58Fe</td>
<td>0.281</td>
<td>0.292</td>
<td>\pm 0.002</td>
</tr>
</tbody>
</table>

The atomic weight of iron in this sample is 55.845 15 \pm 0.000 40.

This IRM is intended for use in calibrating measurements of iron isotope abundance ratios of iron (including those for isotope dilution).
The isotopic measurements on the enriched isotope carrier compounds, on the synthetic isotope mixtures and on the IRM was performed by Reinhold Haeck, at CBNM and the Los Alamos National Laboratories (for the enriched materials).

6. Full details of the characterisation of this IRM can be found in GE/MS/B/03/1992

U 2410 Geel
May 1992

Paul DE BIEUHE
Head
CBNM Mass Specrometry
This Standard Reference Material (SRM) is intended primarily for use as an isotopic standard. SRM 986 consists of 0.50 g of a commercial, high-purity nickel metal, 99.999 + % pure. The certified isotopic compositions are given below together with the atomic weight of nickel. The atomic weight is calculated from the isotopic composition given on this certificate.

Absolute Isotopic Abundance Ratios: $^{58}\text{Ni}/^{60}\text{Ni} = 2.596061 \pm 0.000072$

$^{61}\text{Ni}/^{60}\text{Ni} = 0.043469 \pm 0.000015$

$^{62}\text{Ni}/^{60}\text{Ni} = 0.138600 \pm 0.000045$

$^{64}\text{Ni}/^{60}\text{Ni} = 0.035295 \pm 0.000024$

Isotopic Composition:

$^{58}\text{Ni}$, Atom Percent 68.076886 ± 0.003919

$^{60}\text{Ni}$, Atom Percent 26.223146 ± 0.005144

$^{61}\text{Ni}$, Atom Percent 1.139194 ± 0.000333

$^{62}\text{Ni}$, Atom Percent 3.634692 ± 0.001442

$^{64}\text{Ni}$, Atom Percent 0.925546 ± 0.000359

Nickel Atomic Weight 58.6934 ± 0.0002

The indicated uncertainties are overall limits of error based on two standard deviations of the mean and allowances for the effects of known sources of possible systematic error.

The absolute abundance ratios of $^{58}\text{Ni}/^{60}\text{Ni}$, $^{60}\text{Ni}/^{60}\text{Ni}$, $^{62}\text{Ni}/^{60}\text{Ni}$ and $^{64}\text{Ni}/^{60}\text{Ni}$ were determined by thermal ionization mass spectrometry. Mixtures of synthetic isotopic standards were used to calibrate the mass spectrometers. These synthetic standards were gravimetrically prepared from chemically pure and nearly isotopically pure isotopes. The bias correction (calculated isotopic ratios/observed isotopic ratio), that these standards provide, allows absolute ratios to be calculated for the sample. Details of the preparation and measurements for this SRM are described by Gramlich, J.W., Machlan, L.A., Barnes, L.L., and Paulsen, P.J., "Absolute Isotopic Abundance Ratios and Atomic Weight of a Reference Sample of Nickel [1]."

The analytical measurements leading to the certification of this material were performed in the NIST Inorganic Analytical Research Division. Mass spectrometric measurements on the calibration mixes were made by J.W. Gramlich and L.L. Barnes. The calibration mixes were prepared by L.A. Macklan. The nickel metal used for SRM 986 was obtained from Atomergic Chemicals Corporation (Lot F-3625). Trace element impurities were determined by ICP-MS using isotope dilution and external standards.

Gaithersburg, MD 20899
May 1, 1990
William P. Reed, Acting Chief
Standard Reference Materials Program

Statistical analysis of the data was performed by K.R. Eberhardt and S.B. Schiller, NIST Statistical Engineering Division.

The overall direction and coordination of the technical measurements leading to certification were under the chairmanship of L.L. Barnes.

Issuance of this Standard Reference Material was coordinated through the Standard Reference Materials Program by J.C. Colbert.

REFERENCES
National Bureau of Standards
Certificate of Analysis
Standard Reference Material 976
Isotopic Standard for Copper

This Standard Reference Material (SRM) is intended for use as an isotopic standard. SRM 976 consists of 0.4 g of a commercial copper metal. The certified isotopic compositions are given below together with the atomic weight of copper. The atomic weight of this copper SRM was calculated from the isotopic composition and nuclidic masses, 62.929598 for $^{63}\text{Cu}$ and 63.927792 for $^{65}\text{Cu}$ reported by Wapstra and Audi [1].

Absolute Isotopic Abundance Ratio, $^{63}\text{Cu}/^{65}\text{Cu}$: 2.2440 ± 0.0021

Isotopic Composition:

$^{63}\text{Cu}$, Atom Percent: 69.174 ± 0.020
$^{65}\text{Cu}$, Atom Percent: 30.826 ± 0.020

Atomic Weight: 65.456 ± 0.0004

The indicated uncertainties are overall limits of error based on the sum of 95 percent confidence limits for the means and upper bounds for the effects of known sources of possible systematic error.

The absolute abundance ratio of $^{63}\text{Cu}/^{65}\text{Cu}$ was determined by thermal ionization mass spectrometry. Mixtures of known $^{63}\text{Cu}/^{65}\text{Cu}$ prepared from high-purity separated copper isotopes were used to calibrate the mass spectrometers. Details of the preparation and measurements of this SRM are described by Shields, W.R., Murphy, T.J., and Garner, E.L., "Absolute Isotopic Abundance Ratio and the Atomic Weight of a Reference Sample of Copper" [2].

The analytical measurements leading to certification of this material were performed in the NBS Inorganic Analytical Research Division (formerly the NBS Analytical Chemistry Division). Mass spectrometric measurements were made by W.R. Shields and E.L. Garner on calibration mixes prepared by T.J. Murphy.

Statistical analysis of the data was performed by H.H. Ku, NBS Statistical Engineering Division.

References


Gatersonburg, MD 20899
February 14, 1988
(Revision of Certificate
dated March 24, 1985)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials
Standard Reference Material 994, Gallium

Standard Reference Material 997, Thallium

The NBS Office of Standard Reference Materials announces the availability of two new Standard Reference Materials (SRM) for isotope composition: SRM 994, Gallium, and SRM 997, Thallium. These new SRMs, like previously issued isotopes, are intended for use in assessing small variations in isotope composition and for evaluating mass discrimination effects encountered in the operation of mass spectrometers. For SRM 994, the absolute abundance ratio of $^{67}$Ga/$^{69}$Ga was found to be 1.50076; while for SRM 997, the ratio of $^{203}$Hg/$^{205}$Hg was 2.3874. Both SRMs are high purity metals certified for isotopic composition, but neither are certified for chemical assay.

SRM 994, Gallium, is issued as a 0.25 g unit, and SRM 997, Thallium, is issued as a 0.5 g unit.

Both of these SRMs are available for $102 per unit from:

Office of Standard Reference Materials
Room B314, Chemistry Building
National Bureau of Standards
Gaithersburg, MD 20899

Telephone (301) 921-2015
This Standard Reference Material (SRM) is intended for use as an isotopic standard. SRM 994 consists of 0.25 g of a commercial, high-purity gallium metal. The certified isotopic compositions are given below together with the atomic weight of gallium. The atomic weight of this gallium SRM was calculated from the isotopic composition and nuclidic masses, 68.025880 and 70.9247005 reported by Wapstra and Audi [1].

### Absolute Isotopic Abundance Ratio, Ga/ Ga:

<table>
<thead>
<tr>
<th>Isotopic Composition</th>
<th>Atomic Percent</th>
<th>Atomic Percent</th>
<th>Atomic Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.1079 ± 0.00062</td>
<td>1.50676 ± 0.00039</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.8921 ± 0.00062</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The indicated uncertainties are overall limits of error based on the sum of 95% percent confidence limits for the means and upper bounds for the effects of known sources of possible systematic error. Details of the statistical analysis and deviation of the uncertainty limits are given by Eberhardt, K.R., “Statistical Evaluation of Uncertainties for the Absolute Isotopic Abundance and Atomic Weight of a Reference Sample of Gallium” [2].

The absolute abundance ratio of $^{68}\text{Ga} / ^{71}\text{Ga}$ was determined by thermal ionization mass spectrometry. Mixtures of known $^{68}\text{Ga} / ^{71}\text{Ga}$ prepared from nearly pure separated gallium isotopes were used to calibrate the mass spectrometers. Details of the preparation and measurements of this SRM are described by Machlan, L.A., Gramlich, J.W., Powell, L.J., and Lambert, G.M., “Absolute Isotopic Abundance and Atomic Weight of a Reference Sample of Gallium” [3].

The analytical measurements leading to the certification of this material were performed in the NBS Inorganic Analytical Research Division. Mass spectrometric measurements were made by J.W. Gramlich and L.J. Powell on calibration mixes prepared by L.A. Machlan. The purity of the separated isotopes was determined by G.M. Lambert using spark source mass spectrometry.

Statistical analysis of the data was performed by K.R. Eberhardt, NBS Statistical Engineering Division.

The overall direction and coordination of the technical measurements leading to the certification were under the chairmanship of J.R. DeVoe of the NBS Inorganic Analytical Research Division.

Issuance of this Standard Reference Material was coordinated through the Office of Standard Reference Materials by R.W. Seward.
Certificate of Analysis

Standard Reference Material 977

Isotopic Standard for Bromine

Absolute Abundance Ratio, Br-79/Br-81

1.02581 ± 0.00010

Bromine-79, atom percent
50.686 ± 0.025

Bromine-81, atom percent
49.314 ± 0.025

The preparation furnished is a commercial sample of sodium bromide, formerly distributed as NBS Isotopic Reference Sample No. 106. Measurements are by triple filament mass spectrometry, using mixtures of known concentrations prepared from high-purity separated isotopes as comparison standards. Overall limits of error are based on 95 percent confidence limits for the mean and on allowances for the effects of known sources of possible systematic error. Details of the preparations and measurements are published by E. J. Catanaro, T. J. Murphy, E. L. Garro, and W. R. Shaked, J. Research NBS 64A, (Phys. & Chem.) No. 6, 593-599 (1964).

W. Wayne Meinke,Chief,
Office of Standard Reference Materials

WASHINGTON, D.C. 20254
March 21, 1965.
Certificate of Analysis

Standard Reference Material 984
Rubidium Chloride

Rubidium, rubidium assay, weight percent ................. 99.98 ± 0.02
Absolute abundance ratio, 85Rb/87Rb .................. 2.593 ± 0.002

This lot of rubidium chloride was prepared to ensure material of intermediate purity and high homogeneity. The material is somewhat hygroscopic, absorbing approximately 0.6 percent moisture in a 75 percent relative humidity at room temperature, but can be dried to the original weight by desiccation over freshly exposed P2O5 or Mg(OH)2 for twenty-four hours. The material should therefore be stored with a desiccant such as P2O5.

The assay of this material is based on the determination of rubidium by a combination of gravimetry and isotope dilution analysis on eight samples of about 2 g each of the dried RbCl. More than 99% of the rubidium was precipitated, filtered and weighed as rubidium perchlorate. The weight of RbClO4 was corrected for potassium and cesium perchlorate. The soluble rubidium was determined by isotope dilution mass spectrometry. The total rubidium was the sum of the rubidium from the rubidium perchlorate and the rubidium from the filtrate. All weighings were corrected to vacuum and the atomic weights used in the calculations were from the 1969 Table of Atomic Weights. The indicated tolerances are at least as large as the 95 percent confidence level for a single determination.

Chloride was determined by silver coulometry to be 29.32 weight percent. Preferential oxidation of iodide and bromide showed that the material contains <0.0015% I and <0.0005% Br. Flame emission spectrometry indicated lithium, <0.02 ppm; sodium, 2.3 ppm; potassium, 420 ppm; and cesium 21 ppm. Emission spectrophotometric examination indicated, in addition, calcium, <10 ppm; magnesium, <10 ppm; sulfur, <10 ppm; and aluminum, detection questionable. The loss on ignition at 500 °C (20 hours) was 0.010% and the insoluble matter was 0.0001%. A material-balance shows that 99.99 ± 0.02 weight percent of the material is account for.

The absolute abundance ratio of 85Rb/87Rb was determined by triple-filament solid-sample mass spectrometry. Mixtures of known 85Rb/87Rb ratio, prepared from nearly isotopically pure separated rubidium isotopes, were used to calibrate the mass spectrometers. The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and allowances for the effects of known sources of possible systematic error. Details of the preparation and measurements are described in a published paper [J. Res. NBS, 73A, 511-516 (1969)].

The following members of the Analytical Chemistry Division contributed to the characterization of this material: T. J. Murphy and P. J. Paulsen, rubidium assay; G. Marinovko, chloride assay; T. L. Hanks and T. A. Rush, flame emission determinations; E. K. Hubbard, emission spectrophotographic analysis; and E. J. Fainstato and E. L. Garner, absolute ratio determination.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. H. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this standard reference material were coordinated through the Office of Standard Reference Materials by T. H. Hope.

Washington, D.C. 20234
July 27, 1970
J. Paul Calh, Acting Chief
Office of Standard Reference Materials
National Bureau of Standards
Certificate of Analysis
Standard Reference Material 987
Assay-Isotopic Standard for Strontium

SrCO₃, Alkalimetric assay, weight percent ......... 99.98 ± 0.02

Absolute Abundance Ratios

\[
\begin{align*}
^{88}\text{Sr}/^{86}\text{Sr} &= 8.37861 \pm 0.00113 \\
^{87}\text{Sr}/^{86}\text{Sr} &= 0.71034 \pm 0.00026 \\
^{86}\text{Sr}/^{84}\text{Sr} &= 0.5655 \pm 0.00014
\end{align*}
\]

which yields atom percents of:

\[
\begin{align*}
^{88}\text{Sr} &= 82.5845 \pm 0.00066 \\
^{87}\text{Sr} &= 7.0015 \pm 0.00026 \\
^{86}\text{Sr} &= 9.8566 \pm 0.00034 \\
^{84}\text{Sr} &= 0.5574 \pm 0.00015
\end{align*}
\]

The atomic weight calculated from these abundances is 87.6168 ± 0.00012.

This Standard Reference Material is certified for use as an assay and isotopic standard. The material consists of highly purified strontium carbonate and is of high homogeneity.

The assay was determined by using a coulometric procedure in which an excess of accurately standardized hydrochloric acid is reacted with a known weight of the dried sample and the excess hydrochloric acid is determined coulometrically. The results from eleven independent determinations showed a total alkalinity equivalent to 99.98 percent strontium carbonate.

This material was used as the reference sample in a determination of abundance ratios and atomic weight of strontium [1]. The indicated uncertainties are overall limits of error based on the 95 percent confidence limits for the means and allowances for the effects of possible systematic error.

The only detected impurities in the material are lithium, 4 ppm; sodium, 6 ppm; potassium, <1 ppm; magnesium, <2 ppm; calcium, 3 ppm; barium, <15 ppm; copper, <3 ppm; iron, <5 ppm; aluminum, <1 ppm; and silicon, <1 ppm.

The following members of the Center for Analytical Chemistry contributed to the characterization of this material: G. Marinello, E. E. Estrin, D. G. Friend, I. I. Barnes, I. J. Moore, I. C. Reims, I. A. Rush, I. A. Mathewson, I. J. Murphy, and P. J. Paulsen.

The overall direction and coordination of the technical measurements leading to the certification and current update of this SRM were performed under the chairmanship of I. I. Barnes and W. R. Shields.

*The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. W. Meers.


Washington, D.C. 20234
October 1, 1982

(A Revision of Certificates dated 11.871 & 3-6-72)
National Bureau of Standards
Certificate of Analysis
Standard Reference Material 988
Strontium-84 Spike Assay and Isotopic Solution Standard

This Standard Reference Material is certified for use as an assay and isotopic standard. SRM 988, Strontium-84 Spike, is a solution scaled in pure quartz ampoules. Each ampoule contains a nominal 10 grams of the solution, which is approximately 0.5N in UNO.

The isotopic composition and concentration of strontium in SRM 988 were determined using two mass spectrometers and two operators. The concentration was determined by comparison of ten Strontium-84 aliquots from five different ampoules with a series of solutions of SRM 987, Strontium Carbonate.

All isotopic measurements have been corrected for fractionation based on the pseudo absolute scale of a "natural" *Sr/*Sr ratio of 0.1194.

Isotopic Composition

<table>
<thead>
<tr>
<th>Measured Ratios</th>
<th>Atom Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr88/Sr86</td>
<td>Sr87/Sr86</td>
</tr>
<tr>
<td>0.8806 ± 0.0005</td>
<td>0.7104 ± 0.0004</td>
</tr>
<tr>
<td>0.8807 ± 0.0006</td>
<td>0.7101 ± 0.0004</td>
</tr>
<tr>
<td>0.8806 ± 0.0006</td>
<td>0.7106 ± 0.0004</td>
</tr>
</tbody>
</table>

Atomic Weight = 87.6165

*Estimated error limits because of the magnitude of the measured ratio.

Strontium Concentrationb

<table>
<thead>
<tr>
<th>Analyst 1</th>
<th>Analyst 2</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>gmoles/g of Solution</td>
<td>g/g of Solution</td>
<td>gmoles/g of Solution</td>
</tr>
<tr>
<td>1.1906 ± 0.0004</td>
<td>99.91 ± 0.03</td>
<td>1.1906 ± 0.0004</td>
</tr>
<tr>
<td>1.1908 ± 0.0005</td>
<td>99.92 ± 0.01</td>
<td>1.1907 ± 0.0005</td>
</tr>
</tbody>
</table>

b) Error limits are the 95% confidence limits for a single analysis.

For the analyst the following values were assumed from SRM 987:

<table>
<thead>
<tr>
<th>Ratios</th>
<th>Atom Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr87/Sr86 0.7552</td>
<td>Sr86/Sr87 0.005576</td>
</tr>
<tr>
<td>Sr86/Sr85 0.7104</td>
<td>Sr85/Sr86 0.090610</td>
</tr>
<tr>
<td>Sr85/Sr84 0.5655</td>
<td>Sr84/Sr85 0.670620</td>
</tr>
<tr>
<td>Sr84/Sr87 0.825003</td>
<td></td>
</tr>
</tbody>
</table>

Atomic Weight = 87.6167

The material for this SRM was supplied by the ORNL Isotope Development Center, Oak Ridge, Tennessee.

The following members of the NBS Analytical Chemistry Division participated in the characterization of SRM 988:

Isotope Measurements - L. L. Barnes and E. J. Moore Chemical Preparations - L. A. Macdon and J. R. Monny

The overall direction and coordination of the technical measurements leading to certification were under the chairmanship of W. R. Shields.

The technical and support aspects concerning the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. E. Reid.

Washington, D.C. 20234
May 21, 1973

J. Paul Cali, Chief
Office of Standard Reference Materials
The IKM is supplied with a $^{87}$Rb atomic isotope concentration certified as:

$$[6.753 \pm 0.010] \times 10^{19} \text{ atoms } ^{87}\text{Rb} \text{ kg}^{-1} \text{ of solution}$$

From the certified isotope concentration, the following concentrations are derived:

$$(1.121 \pm 0.001) \times 10^{-4} \text{ mol } ^{87}\text{Rb} \text{ kg}^{-1} \text{ of solution}$$

$$(9.743 \pm 0.015) \times 10^{-6} \text{ kg } ^{87}\text{Rb} \text{ kg}^{-1} \text{ of solution}$$

Other Rubidium isotopes present are related to the $^{87}$Rb atomic isotope concentration through the following atomic isotope ratio:

$$^{85}\text{Rb} / ^{87}\text{Rb} = 0.020498 \pm 0.000024$$

This corresponds to an isotopic composition with following isotope abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{87}$Rb</td>
<td>2.0087 \pm 0.00023</td>
</tr>
<tr>
<td>$^{85}$Rb</td>
<td>97.9913 \pm 0.00023</td>
</tr>
</tbody>
</table>

The atomic weight of the Rubidium is 86.869066 \pm 0.000045

from the certified isotope concentration, the following element concentrations are derived:

$$(1.144 \pm 0.001) \times 10^{-4} \text{ mol Rb kg}^{-1} \text{ of solution}$$

$$(9.940 \pm 0.015) \times 10^{-6} \text{ kg Rb kg}^{-1} \text{ of solution}$$

NOIFS

1. All uncertainties indicated are accuracies, computed on a 2s basis.
2. The IKM solution has a molality of 0.5 M HNO$_3$ (i.e. 0.5 mol HNO$_3$ kg$^{-1}$ of solvent) or a molarity of 0.5 M HNO$_3$ (i.e. 0.5 mol HNO$_3$ l$^{-1}$ of solution).
3. The Avogadro constant used is $(6.022 \pm 0.000) \times 10^{23}$.
4. The atomic masses, used in the calculations, are:
   $^{85}\text{Rb}$ 84.914 390 \pm 0.000 000
   $^{87}\text{Rb}$ 86.911 794 \pm 0.000 006
5. Using this Spike IKM, $^{85}$Rb concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the atomic isotope dilution ratio $R_y = ^{85}\text{Rb} / ^{87}\text{Rb}$ in the blend. They should be computed with the aid of the following formula which allows an easy identification of the sources of the uncertainties in the procedure:

$$C_8 = \frac{R_y - R_x}{R_x - R_y} \cdot \frac{M_x}{M_y}$$

where:
- $R_x$ = atomic isotope ratio $^{85}\text{Rb}/^{87}\text{Rb}$ in the unknown sample material
- $R_y$ = atomic isotope ratio $^{85}\text{Rb}/^{87}\text{Rb}$ in the spike material
- $M_x$ = mass of the unknown sample
- $M_y$ = mass of the spike solution used
- $N_8$ = number of atoms $^{85}\text{Rb}$ kg$^{-1}$ sample material
- $N_7$ = number of atoms $^{87}\text{Rb}$ kg$^{-1}$ spike solution.
Chemical preparation of this IRM was accomplished by André Verbruggen and Gaida Lapitajs.

Isotopic measurements by Thermal Ionisation Mass Spectrometry were carried out by Gaida Lapitajs.

Metrological aspects involved in the preparation and certification were performed by Frans Hendrickx.

The purity of $^{87}$RbCl was determined by Spark Source Mass Spectrometry by Willy Lycke.

The ampoulation of this IRM was accomplished by André Verbruggen, Adolfo Alonso-Muñoz and Gaida Lapitajs.

The overall coordination of the establishment leading to the certification and issuance of this IRM was performed by André Verbruggen.
The analytical measurements leading to the certification of this material were performed in the NHS Inorganic Analytical Research Division. Mass spectrometric measurements were made by J.W. Gramlich and I.J. Powell on calibration mixes prepared by T.J. Murphy. The purity of the separated isotopes and this SRM were determined by P.J. Pauelsen, using spark source mass spectrometry.

Statistical analysis of the data was performed by K.R. Eberhardt, NHS Statistical Engineering Division.

The overall direction and coordination of the technical measurements leading to the certification were under the chairmanship of E.L. Garner of the NHS Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by I.J. Powell.

Gaithersburg, MD 20899
September 21, 1984

(over)

Office of Standard Reference Materials
Stanley D. Rasberry, Chief

SRM 978a was prepared from SRM 748, Silver Vapor Pressure, which is high purity silver metal (greater than 99.99 percent) in rod form. SRM 748 was used by V.E.Bower and R.S. Davis to determine the electrochemical equivalent of silver [3]. Based on their work and the silver data presented here, the silver Faraday was recalculated with a high level of accuracy [4]. A portion of the metal was converted to silver nitrate and used as the isotopic reference sample for the determination of the atomic weight of silver [1]. Silver nitrate is non-hygroscopic up to about 80 percent relative humidity. As this relative humidity, or above, it will attract water and form a saturated solution. While this salt would not normally be exposed to such high humidities, as a precaution, it should be dried before use. Drying either in an oven for 1 hour at 105 °C or for approximately 15 hours in a desiccator over MgCl₂ is satisfactory.

National Bureau of Standards
Certificate of Analysis
Standard Reference Material 989
Assay-Isotopic Standard for Rhenium

Absolute abundance ratio, $^{185}\text{Re}/^{187}\text{Re}$: $0.56736 \pm 0.00009$

Rhenium-185, atom percent: $37.394 \pm 0.016$

Rhenium-187, atom percent: $62.602 \pm 0.016$

Atomic weight: $186.20679 \pm 0.00003$

The Standard Reference Material is supplied as a uniform metal in the form of a ribbon approximately 0.001 cm by 0.070 cm x 1.400 cm. The purity of this material is 99.9 percent based on impurities detected by isotope dilution spark source mass spectroscopy. The absolute abundance ratio of $^{185}\text{Re}/^{187}\text{Re}$ was determined by two analysts using two different mass spectrometers. Samples of known isotopic composition, prepared from nearly isotopically pure separated rhenium isotopes, were used to calibrate the mass spectrometers. The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and allowances for the effects of known sources of possible systematic error. The details of the measurements are described in a published paper: J. Res. NBS (U.S.), 73A (Phys. and Chem.), No. 6, 691-698 (Nov. Dec. 1983).

Mass-spectrometric measurements were made by W. Grazulis and J. Ancton on samples prepared by T. J. Murphy.

The overall direction and coordination of the technical measurements leading to certification were under the chairmanship of W. B. Sacks.

The technical and support aspects concerning the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. F. Hoad.

Washington, D.C., 20234
February 19, 1974
J. Paul LeBlanc, Chief
Office of Standard Reference Materials
Standard Reference Material 994, Gallium

Standard Reference Material 997, Thallium


These new SRMs, like previously issued isotopic SRMs, are intended for use in assessing small variations in isotopic composition and for evaluating mass discrimination effects in the operation of mass spectrometers. For SRM 994, the absolute abundance ratio of $^{69}$Ga to $^{67}$Ga was found to be 1.0036, while for SRM 997, the ratio of $^{203}$Tl to $^{205}$Tl was 2.0394. Both SRMs are high-purity metals certified for isotopic composition but neither are certified for chemical assay.

SRM 994, Gallium, is stocked as a 0.25 gram and SRM 997, Thallium, is stocked as a 0.5 gram.

Both SRMs are available for $150 per gram or more.

Office of Standard Reference Materials
National Bureau of Standards
Gaithersburg, MD 20899

Telephone: (301) 971 9101
National Bureau of Standards

Certificate of Analysis

Standard Reference Material 997

Isotopic Standard for Thallium

This Standard Reference Material (SRM) is certified for use as an isotopic standard. SRM 997 consists of 0.5 gram of a commercial, high-purity thallium metal. Note: While this SRM is a high-purity material for isotopic purposes, it oxidizes rapidly and cannot be used for assay purposes. The certified isotopic compositions are given below together with the atomic weight of thallium.

<table>
<thead>
<tr>
<th>Absolute Abundance Ratio</th>
<th>${}^{205}\text{Tl}/{}^{208}\text{Tl}$</th>
<th>$2.3874 \pm 0.00011$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotopic Composition</td>
<td>${}^{205}\text{Tl}$, Atom Percent</td>
<td>$29.5235 \pm 0.0088$</td>
</tr>
<tr>
<td></td>
<td>${}^{208}\text{Tl}$, Atom Percent</td>
<td>$70.4765 \pm 0.0088$</td>
</tr>
<tr>
<td>Thallium Atomic Weight</td>
<td>$204.38333 \pm 0.00018$</td>
<td></td>
</tr>
</tbody>
</table>

The above indicated uncertainties are the overall limits of error based on the sum of 95 percent confidence limits for the mean and allowances for the effects of known sources of possible systematic error.

This SRM was used in the determination of the absolute abundance ratio and atomic weight of thallium. The absolute abundance ratio of ${}^{205}\text{Tl}/{}^{208}\text{Tl}$ was determined by single filament thermal ionization mass spectrometry. Mixtures of known ${}^{205}\text{Tl}/{}^{208}\text{Tl}$, prepared from nearly pure separated thallium isotopes, were used to calibrate the mass spectrometers.

The analytical measurements leading to the certification of this material were performed in the NBS Inorganic Analytical Research Division. Mass spectrometric measurements were made by L.J. Powell and J.W. Gramlich on calibration mixes prepared by L.J. Powell. The purity of the separated isotopes was determined by P.J. Paulsen using spark source mass spectrometry.

Statistical analysis of the data was performed by H.H. Ku, NBS Statistical Engineering Division.

The overall direction and coordination of the technical measurements leading to certification of this SRM were performed under the chairmanship of I.L. Barnes, NBS Inorganic Analytical Chemistry Division, and W.C. Purdy, McGill University, Montreal, Quebec, Canada.

Issuance of this Standard Reference Material was coordinated through the Office of Standard Reference Materials by R.W. Seward.

Gainesburg, MD 20899
July 23, 1986

Stanley D. Raiberry, Chief
Office of Standard Reference Materials

Reference:

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 981
Common Lead Isotopic Standard

This Standard Reference Material (SRM) is intended primarily for use as an isotopic standard. SRM 981 consists of 1 gram of a commercially available, high purity lead metal, of 99.9+ percent purity, that was extruded into wire form. The atomic weight of the material is calculated to be 207.215 using the nuclidic masses 203.8194(4), 204.9730(2), 205.9744(3), and 207.976650. The certified isotopic compositions are given below.

Atomic Abundance Ratio, Lead-204/Lead-206 ... 0.0059042 ± 0.0000017
Atomic Abundance Ratio, Lead-207/Lead-206 ... 0.9146 ± 0.00013
Atomic Abundance Ratio, Lead-208/Lead-206 ... 2.1681 ± 0.0008
Lead-204, atom percent .................. 1.4255 ± 0.0012
Lead-206, atom percent .................. 24.1442 ± 0.0057
Lead-207, atom percent .................. 22.0833 ± 0.0027
Lead-208, atom percent .................. 52.3470 ± 0.0066

Overall limits of error are based on 95 percent confidence limits for the mean of the ratio measurements and on allowances for the known sources of possible systematic error.

Measurements for certification were by triple filament solid-sample mass spectrometry. Mixtures with known 204Pb/206Pb ratio, prepared from high-purity separated isotope solutions, were used as comparison standards. Details of the preparation and measurements were published by E.J. Catanzaro, T.J. Murphy, W.R. Shields, and E.L. Garner, J. Research NBS 72A, No. 3, 261 (1968).

The overall coordination of efforts leading to the update and revision of this document was performed by T. E. Gillis.

Germantown, MD 20899
March 25, 1991
(Revision of certificate dated 4-10-73)

William P. Reed, Chief
Standard Reference Materials Program

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 982
Equal-Atom Lead Isotopic Standard

This Standard Reference Material (SRM) is intended primarily for use as an isotopic standard. SRM 982 consists of 1 gram of a mixture of commercial and radiogenic lead to obtain essentially equal-atom amounts of Lead-204 and Lead-208. It is chemically pure to at least 99.9+ percent purity. The atomic weight of the material is calculated to be 206.9459 using the nuclidic masses 203.97044, 205.974468, 206.975903, and 207.976650. The certified isotopic compositions are given below.

Atomic Abundance Ratio, Lead-204/Lead-206 ... 0.027219 ± 0.000027
Atomic Abundance Ratio, Lead-207/Lead-206 ... 0.46707 ± 0.00020
Atomic Abundance Ratio, Lead-208/Lead-206 ... 1.00016 ± 0.00036
Lead-204, atom percent .................. 1.0912 ± 0.0012
Lead-206, atom percent .................. 40.0890 ± 0.0072
Lead-207, atom percent .................. 18.7244 ± 0.0023
Lead-208, atom percent .................. 40.0954 ± 0.0077

Overall limits of error are based on 95 percent confidence limits for the mean of the ratio measurements and on allowances for the known sources of possible systematic error.

Notice to User: SRM 982 is radioactive, containing Lead-210 4.2 × 10^3 Bq · g^-1 of natural origin (see attached Report of Test). All users and purchasers must comply with all state and federal regulations regarding the use and disposal of this material.

Measurements for certification were by triple filament solid-sample mass spectrometry. Mixtures with known 204Pb/206Pb ratio, prepared from high-purity separated isotope solutions, were used as comparison standards. Details of the preparation and measurements were published by E.J. Catanzaro, T.J. Murphy, W.R. Shields, and E.L. Garner, J. Research NBS 72A, No. 3, 261 (1968).

The overall coordination of efforts leading to the update and revision of this document was performed by T. E. Gillis.

Germantown, MD 20899
March 25, 1991
(Revision of certificate dated 6-1-68)

William P. Reed, Chief
Standard Reference Materials Program
Certificate of Analysis

Standard Reference Material 983
Radiogenic Lead Isotopic Standard

This Standard Reference Material (SRM) is intended primarily for use as an isotopic standard. SRM 983 consists of a wire that was prepared from radiogenic lead. It is chemically pure to at least 99.9% percent purity, and entailed samples of lead isotopic composition. The atomic weight of the material is calculated to be 206.0464 using the nuclidic masses 203.973044, 204.97441, 205.97593, and 207.976650. The certified isotopic compositions are given below.

<table>
<thead>
<tr>
<th>Atomic Abundance Ratio</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead-204/Lead-206</td>
<td>0.000371 ± 0.000020</td>
<td></td>
</tr>
<tr>
<td>Atomic Abundance Ratio, Lead-207/Lead-206</td>
<td>0.071201 ± 0.000040</td>
<td></td>
</tr>
<tr>
<td>Atomic Abundance Ratio, Lead-208/Lead-206</td>
<td>0.013619 ± 0.000024</td>
<td></td>
</tr>
<tr>
<td>Lead-204, atom percent</td>
<td>0.0342 ± 0.0020</td>
<td></td>
</tr>
<tr>
<td>Lead-206, atom percent</td>
<td>0.921497 ± 0.0041</td>
<td></td>
</tr>
<tr>
<td>Lead-207, atom percent</td>
<td>0.65611 ± 0.0025</td>
<td></td>
</tr>
<tr>
<td>Lead-208, atom percent</td>
<td>0.12550 ± 0.0022</td>
<td></td>
</tr>
</tbody>
</table>

Overall limits of error are based on 95 percent confidence limits for the mean of the ratio measurements and on allowances for the known sources of possible systematic error.

Notice to Users: SRM 983 is radioactive, containing 1 x 10^4 Bq g^-1 of natural origin (see attached Report of Test). All users and purchasers must comply with all state and federal regulations regarding the use and disposal of this material.

Measurements for certification were by triple filament solid-sample mass spectrometry. Mixtures with known Pb/Pb ratios, prepared from high-purity separated isotope solutions, were used as comparison standards. Details of the preparation and measurements were published by E.J. Catanzaro, T.J. Murphy, W.R. Shields, and E.L. Garner, J. Research NBS 72A, No. 3,261 (1968).

The analytical measurements leading to the certification of this material were performed in the NIST Inorganic Analytical Research Division.

The overall coordination of efforts leading to the update and revision of this certificate was coordinated through the Standard Reference Materials Program by T. J. Gill.
NOTES

A master solution containing a centimeter of lead wire was measured and dissolved in nitric acid. Gravimetric measurements were made for both the wire and the nitric acid. Liquid scintillation vials were prepared using a commercial scintillator and gravimetric aliquots of the active master solution.

The overall uncertainty was formed by taking three times the quadratic combination of the standard deviations of the mean, or approximations thereof, for the following:

- a) liquid scintillation measurements: 0.15 percent
- b) sample preparation: 0.10 percent
- c) gravimetric measurements: 0.15 percent
- d) detection efficiency: 3.0 percent
- e) background: 0.24 percent
- f) progeny contribution: 1.5 percent


Commercial counter with two phototubes which count in coincidence

For additional information please contact Jacqueline M. Calhoun at (301) 975-5518.
National Bureau of Standards
Certificate
Standard Reference Material 991
Lead 206 Spike Assay and Isotopic Solution Standard

This Standard Reference Material (SRM) is certified for use as an assay and isotopic standard. The primary intended use is as a spike for lead determinations by isotope dilution mass spectrometry. SRM 991, Lead 206 Spike, is a solution of lead nitrate sealed in opaque ampoules. Each ampoule contains a nominal 15 grams of solution, which is 0.5 N in HNO₃.

Concentration of Lead

\[ 0.3236 \pm 0.00012 \text{ micrograms/gram} \]

Isotopic composition (atom fraction)

- \(^{204}\text{Pb} = 0.00001 \text{ (3 ppm)}\)
- \(^{206}\text{Pb} = 0.00017\)
- \(^{207}\text{Pb} = 0.000001 \text{ (40 ppm)}\)
- \(^{208}\text{Pb} = 0.00013 \text{ (40 ppm)}\)

Atomic Weight 205.977

The concentration of lead in SRM 991 was determined by an isotope dilution mass spectrometry technique. A correction for isotopic fractionation was checked by analyzing SRM 901. The indicated uncertainty for the concentration is the 95 percent tolerance limit* for coverage of at least 99 percent of measured values of this lot of ampoules of SRM 991. In brief, if we had made concentration measurements on all the ampoules, almost all (at least 99 percent) of these measured values should fall within the indicated tolerance limits with a confidence coefficient of 95 percent (or probability = .95).

The mass spectrometry measurements at NBS were made by J. P. Moore and J. W. Grant in charge of a technique prepared by L. A. Macdonald.

The overall direction and coordination of the technical measurements leading to certification were under the chairmanship of L. L. Barnes.

The technical and support aspects concerning the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.


Washington, D.C. 20234
March 19, 1976

Office of Standard Reference Materials
PROVISIONAL CERTIFICATE

ISOTOPIC REFERENCE MATERIAL CBNM-IRM-060

The IRM is supplied with a $^{230}$Th atomic isotope concentration certified as:

$$(1.056 \pm 0.007) \times 10^{20} \text{ atoms } ^{230}\text{Th} \cdot \text{kg}^{-1} \text{ of solution}$$

From the certified isotope concentration, following concentrations are derived:

$$(1.755 \pm 0.013) \times 10^{-4} \text{ mol } ^{230}\text{Th} \cdot \text{kg}^{-1} \text{ of solution}$$

$$(4.038 \pm 0.030) \times 10^{-5} \text{ kg } ^{230}\text{Th} \cdot \text{kg}^{-1} \text{ of solution}$$

The $^{232}$Th isotope present is related to the $^{230}$Th atomic isotope concentration through the following atomic isotope ratio:

$$^{232}\text{Th}/^{230}\text{Th} = 0.0015 \pm 0.0005$$

This corresponds to an isotopic composition with the following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{230}\text{Th}$</td>
<td>99.85</td>
</tr>
<tr>
<td>$^{232}\text{Th}$</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The atomic weight of the thorium is:

$$230.0361 \pm 0.0010$$

From the certified atomic concentration, following element concentrations are derived:

$$(1.758 \pm 0.013) \times 10^{-4} \text{ mol Th} \cdot \text{kg}^{-1} \text{ of solution}$$

$$(4.044 \pm 0.030) \times 10^{-5} \text{ kg Th} \cdot \text{kg}^{-1} \text{ of solution}$$

5. $^{237}$Th concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, using this Spike IRM, through a measurement of the atomic isotope dilution ratio $R_B = ^{230}\text{Th} / ^{232}\text{Th}$ in the blend. They should be computed with the aid of the following formula which allows an easy identification of the sources of the uncertainties in the procedure:

$$\frac{C_{232}}{C_{230}} \cdot \frac{R_B - R_X}{R_Y - R_X} \cdot \frac{M_Y}{M_X}$$

where:

- $R_X$ = atomic isotope ratio $^{230}\text{Th}/^{232}\text{Th}$ in the unknown sample material
- $R_Y$ = atomic isotope ratio $^{230}\text{Th}/^{232}\text{Th}$ in the spike material
- $M_X$ = mass of the unknown sample
- $M_Y$ = mass of the sample of spike solution used
- $C_{232}$ = number of atoms $^{232}\text{Th} \cdot \text{kg}^{-1}$ spike material
- $C_{230}$ = number of atoms $^{230}\text{Th} \cdot \text{kg}^{-1}$ sample material

The isotopic measurements, as well as the overall technical coordination of the establishment of this IRM, were performed by Marc Gallet.

Chemical preparation of the samples for isotopic measurements was performed by André Verbruggen.

O-2440 GRIL
1 September 1984

Paul DE BIEVRE
Head
Mass Spectrometry
National Bureau of Standards
Certificate
Standard Reference Material 993
Uranium-235 Spike Assay and Isotopic Solution Standard

This Standard Reference Material (SRM) is certified for use as an assay and isotopic standard. The primary intended use is as a spike for uranium determinations by isotope dilution mass-spectrometry. SRM 993, Uranium-235 Spike, is a solution sealed in glass ampoules. Each ampoule contains a nominal 15 grams of solution, which is approximately 0.012% in UO3.

Concentration of Uranium
235U: 0.0112 ± 0.0001
238U: 0.0195 ± 0.0001
239Pu: 0.0571 ± 0.0001
240Pu: 0.0709 ± 0.0001

Isotopic composition (atom percent)

The concentration of uranium in SRM 993 was determined by an isotope dilution mass-spectrometry technique, which is described in NBS Technical Note 546. A correction for isotope fractionation was determined by analyzing SRM U-500. The indicated uncertainty for the concentration is the 95 percent confidence limit for coverage of at least 99 percent of measured values of this lot of ampoules of SRM 993.

The basic chemical and mass spectrometry procedures used for the uranium isotopic composition analysis are described in NBS Special Publication 280. The 235U and 238U values were determined by isotope dilution using 234U. The 238U value was determined by a direct measurement of 234U with respect to 235U. Corrections for isotope fractionation effects were obtained by analysis of SRM U-500 and a Belgian Congo natural uranium standard. As isotopic composition is independent of concentration, the indicated uncertainties are 95 percent confidence limits of the atom percent of the four isotopes.

The mass spectrometry measurements at NBS were made by F. L. Gatura using solutions prepared by L. A. Macdonald.

The overall direction and coordination of the technical measurements leading to certification were under the chairmanship of L. E. Barnes.

The technical and support aspects concerning the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.


In fact, if we had made concentration measurements on all the ampoules and all of these values should fall within the indicated tolerance limits with a confidence coefficient of 95 percent for probabilities of 95 percent.
National Bureau of Standards
Certificate of Analysis
Standard Reference Material 960
Uranium Metal

Uranium Assay 99.975 ± 0.017 Weight Percent

This metal standard of normal isotope composition is tested as a primary assay standard for uranium determinations. The value of the atomic weight of this material is 238.0289 as determined at NBS by thermal ionization mass spectrometry.

The uranium assay is based on the constant current coulometric reduction of uranium with electrogenerated tin(IV) in 7M sulfuric acid. The value of the assay has been corrected for 42 ppm of iron and 4 ppm of vanadium which are the titratable impurities present in the metal. The certified value, 99.975 weight percent, represents the mean of 21 determinations. The precision of the method, expressed in terms of the standard deviation of a single determination is 0.008 percent. The estimated value of the uncertainty of the mean assay is 0.006 percent. This figure includes the estimates of all known sources of error inherent to this determination: the random error component, 0.004 percent (the 95 percent confidence interval for the mean based on 20 degrees of freedom), and an additional 0.002 percent error term as an allowance for all known possible sources of systematic error. An overall mass balance of 99.9970 percent is obtained when the estimate of the total impurities present in the material (225 ppm) is taken into account.

The uncertainty attached to the certified assay value is the 95 percent confidence interval for a single determination.

The metal as received will contain a significant amount of surface oxide. In assaying the material, the oxide was removed from the uranium samples just prior to weighing. The metal surface was cleaned by the procedure outlined on the back of this certificate.

This material was prepared by the United States Atomic Energy Commission. Impurities were analyzed by the AECL Isotope Laboratory, Chalk River, Ontario. Analysis of the material was performed by G. Marinowski and E. S. Etz, the iron content was determined polarographically by E. J. Marzabal, and the atomic weight was determined by isotope ratio mass measurements performed by E. L. Garrard, all of the NBS Analytical Chemistry Division.

The overall direction and coordination of the technical measurement leading to the certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reev.

Washington, D.C. 20234
May 12, 1972

(P. Paul Celentano, Chief, Office of Standard Reference Materials)

Removal of Surface Impurities

The following cleaning procedure was used on all uranium assay samples after being cut to the approximate size for analysis. For accurate analytical work, this procedure or an equivalent one should be followed.

Dip the uranium sample in 1:1 HNO₃ for a period of up to 10 minutes to remove all visible surface oxide. Rinse in distilled water. Etch in 1:3 HCl for 5 minutes. Rinse thoroughly in distilled water. Remove excess surface water before placing the sample in a vacuum desiccator for attainment of constant weight. Removal of surface moisture is accelerated and re-oxidation of the metal surface is retarded by drying under vacuum for a suitable length of time (evacuation for 1/2 hour is sufficient).
National Bureau of Standards
Certificate of Analysis
Standard Reference Material U-970

Uranium Isotopic Standard
(Nominally 98% Enriched)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atom Percent</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{235}U$</td>
<td>92.797</td>
<td>92.176</td>
</tr>
<tr>
<td>$^{238}U$</td>
<td>0.714</td>
<td>0.747</td>
</tr>
<tr>
<td>$^{234}U$</td>
<td>0.0017</td>
<td>0.005</td>
</tr>
<tr>
<td>$^{234}U$</td>
<td>0.0017</td>
<td>0.005</td>
</tr>
</tbody>
</table>

This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

The material consists of highly purified uranium oxide, $U_3O_8$. The atomic weight of the material is calculated to be 235.197, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for $^{235}U$ and $^{238}U$ were calculated from measurements made at the National Bureau of Standards. The samples were spiked with high-purity $^{235}U$ to approximate the $^{234}U$ concentration, the ratios $^{235}U$ to $^{238}U$ and $^{235}U$ to $^{234}U$ were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits. Ratio determinations were corrected for mass discrimination by measurements made under similar conditions on SRM U-500.

The values for $^{234}U$ are calculated from measurements of the ratio $^{234}U$ to $^{238}U$, and calibrated by measurements of the same ratio on synthetic mixtures prepared from high-purity separated isotopes of $^{234}U$ and $^{238}U$ to approximate the composition of the sample. Because of the response time of the measuring circuit when switching from the $^{235}U$ peak to the $^{234}U$ peak, the $^{234}U$ peak was monitored for 1 minute and only data from the last 30 seconds, after the signal had stabilized, were used in the calculations. The value for $^{234}U$ is calculated by difference.

The indicated uncertainties for the isotopic compositions are at the 95-percent confidence level for a single determination, and include terms for the inhomogeneities of the material as well as analytical error. The $^{235}U$ to $^{238}U$ ratio for this standard, 1.6653, is known to at least 0.15 percent.

Measurements leading to the certification of this SRM were made by E. I. Garner and J. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

NOTE: In many industries traceability of their quality control process to the national measurement system is carried out through the mechanisms of SRM's. It may be therefore of interest to know the details of the measurements made at NBS in arriving at the certified values of this SRM. An NBS Special Publication, 260-27, is reserved for this purpose and is available from the NBS Office of Standard Reference Materials upon request.
National Bureau of Standards  
Certificate of Analysis  
Standard Reference Material U-900  
Uranium Isotopic Standard  
(Nominally 90% Enriched)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atom Percent</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{235}U$</td>
<td>0.7777</td>
<td>±0.0014</td>
</tr>
<tr>
<td>$^{236}U$</td>
<td>90.196</td>
<td>90.098</td>
</tr>
<tr>
<td>$^{238}U$</td>
<td>0.3327</td>
<td>±0.0010</td>
</tr>
<tr>
<td>$^{244}U$</td>
<td>8.693</td>
<td>8.795</td>
</tr>
</tbody>
</table>

This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

NOTE: In many industries traceability of their quality control process to the national measurement system is carried out through the mechanisms of SRM's. It may be therefore of interest to know the details of the measurements made at NBS in arriving at the certified values of this SRM. An NBS Special Publication, 260-27, is reserved for this purpose and is available from the NBS Office of Standard Reference Materials upon request.

Washington, D.C. 20234  
April 6, 1981  
(Official revision of Certificate dated 7-30-70)  
George A. Uriano, Chief  
Office of Standard Reference Materials
National Bureau of Standards
Certificate of Analysis
Standard Reference Material U-800
Uranium Isotopic Standard
(Nominally 80% Enriched)

<table>
<thead>
<tr>
<th></th>
<th>234U</th>
<th>235U</th>
<th>236U</th>
<th>238U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom Percent</td>
<td>0.6563</td>
<td>80.279</td>
<td>0.2445</td>
<td>18.820</td>
</tr>
<tr>
<td>Weight Percent</td>
<td>0.0013</td>
<td>80.021</td>
<td>0.0007</td>
<td>19.999</td>
</tr>
</tbody>
</table>

The Standard Reference Material (SRM) is certified for use as an isotope standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

The material consists of highly purified uranium oxide, UO₂. The atomic weight of the material is calculated to be 235.076, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for 234U and 238U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity 238U to approximate the 235U concentration, the ratios 235U to 234U and 238U to 234U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for 235U and 236U were calculated from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn.; at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the 235U to 234U ratio using triple-filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-900. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 50-50, and 90-percent 235U level prepared from high-purity 234U and 238U isotopes, that a constant bias for a given procedure can be maintained over the range of 5 to 95 percent 235U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the 235U concentration by oxide dilution and UF₆ analysis, and then the ratio calculated using the NBS values for 235U and 234U, and the 234U value obtained by difference.

The indicated uncertainties for the isotope concentrations are at 95-percent confidence level for a single determination. The 235U to 234U ratio for this standard, 4.266, is known to at least 0.1 percent, as the same time the pooled variance for the calibration system is significantly smaller.

Measurements leading to the certification of this SRM were made by E. L. Garner, L. A. Machlan, M. S. Richmond, and W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

NOTE: In many industries, traceability of their quality control process to the national measurement system is carried out through the mechanisms of SRM's. It may be therefore of interest to know the details of the measurements made at NBS in arriving at the certified values of this SRM. An NBS Special Publication, 260-27, is reserved for this purpose and is available from the NBS Office of Standard Reference Materials upon request.
**National Bureau of Standards**  
Certificate of Analysis  
Standard Reference Material U-500  
Uranium Isotopic Standard  
(Nominally 50% Enriched)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atom Percent</th>
<th>Weight Percent</th>
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<tbody>
<tr>
<td>$^{235}$U</td>
<td>51.81%</td>
<td>50.12%</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>49.06%</td>
<td>49.18%</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>0.0755%</td>
<td>0.17%</td>
</tr>
<tr>
<td>$^{236}$U</td>
<td>0.0658%</td>
<td>0.01%</td>
</tr>
<tr>
<td>$^{237}$U</td>
<td>0.0003%</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

The material consists of highly purified uranium oxide, $U_3O_8$. The atomic weight of the material is calculated to be 236.979, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for $^{235}$U and $^{238}$U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity $^{235}$U to approximate the $^{235}$U concentration, the ratios $^{235}$U to $^{234}$U and $^{238}$U to $^{234}$U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for $^{234}$U and $^{236}$U were calculated from measurements made at the National Bureau of Standards of the $^{235}$U to $^{238}$U ratio. The observed ratios were corrected for mass discrimination effects by intercomparison with five synthetic mixtures at the 50-percent $^{235}$U level prepared from high-purity $^{235}$U and $^{238}$U.

The indicated uncertainties, for the isotopic concentrations are at the 95-percent confidence level for a single determination. The $^{235}$U to $^{238}$U ratio for this standard, 0.9997, is known to at least 0.1 percent.

Measurements leading to the certification of this SRM were made by E. J. Garner, L. A. Machlan, M. S. Richmond, and W. R. Shields.

The indicated uncertainties, for the isotopic concentrations are at the 95-percent confidence level for a single determination. The $^{235}$U to $^{238}$U ratio for this standard, 0.9997, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Measurements leading to the certification of this SRM were made by E. J. Garner, L. A. Machlan, M. S. Richmond, and W. R. Shields.

Washington, D.C. 20234  
April 6, 1981  
(Revised reissue of  
Certificate dated 7-30-70)  
George A. Uranio, Chief  
Office of Standard Reference Materials

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**National Bureau of Standards**  
Certificate of Analysis  
Standard Reference Material U-350  
Uranium Isotopic Standard  
(Nominally 35% Enriched)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atom Percent</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}$U</td>
<td>0.2498%</td>
<td>24.76%</td>
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<tr>
<td>$^{235}$U</td>
<td>35.190%</td>
<td>35.190%</td>
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<tr>
<td>$^{238}$U</td>
<td>16.70%</td>
<td>16.70%</td>
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<tr>
<td>$^{239}$U</td>
<td>13.90%</td>
<td>13.90%</td>
</tr>
</tbody>
</table>

This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

This material consists of highly purified uranium oxide, $U_3O_8$. The atomic weight of the material is calculated to be 236.979, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for $^{234}$U and $^{239}$U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity $^{235}$U to approximate the $^{235}$U concentration, the ratios $^{235}$U to $^{234}$U and $^{239}$U to $^{234}$U were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for $^{238}$U and $^{235}$U were calculated from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the $^{235}$U to $^{238}$U ratio using triple-filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-100. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 30-, and 90-percent $^{235}$U level prepared from high-purity $^{235}$U and $^{238}$U isotopes, that a constant bias for a given procedure can be maintained over the range of 5- to 95-percent $^{235}$U. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the $^{235}$U concentration by oxide dilution and UF₆ analysis, and then the ratio calculated using the NBS values for $^{234}$U and $^{238}$U, and the $^{235}$U value obtained by difference.

The indicated uncertainties, for the isotopic concentrations are at the 95-percent confidence level for a single determination. The $^{235}$U to $^{238}$U ratio for this standard, 0.5465, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Measurements leading to the certification of this SRM were made by E. J. Garner, L. A. Machlan, M. S. Richmond, and W. R. Shields.

The indicated uncertainties, for the isotopic concentrations are at the 95-percent confidence level for a single determination. The $^{235}$U to $^{238}$U ratio for this standard, 0.5465, is known to at least 0.1 percent; at the same time the pooled variance for the calibration system is significantly smaller.

Measurements leading to the certification of this SRM were made by E. J. Garner, L. A. Machlan, M. S. Richmond, and W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D.C. 20234  
April 6, 1981  
(Revised reissue of  
Certificate dated 7-30-70)  
George A. Uranio, Chief  
Office of Standard Reference Materials
National Bureau of Standards
Certificate of Analysis
Standard Reference Material U-200
Uranium Isotopic Standard
(Nominally 20% Enriched)

<table>
<thead>
<tr>
<th>Atom Percent</th>
<th>234U</th>
<th>235U</th>
<th>238U</th>
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<tbody>
<tr>
<td></td>
<td>0.1246</td>
<td>20.013</td>
<td>79.651</td>
</tr>
<tr>
<td>±0.003</td>
<td>0.2116</td>
<td>79.651</td>
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</tbody>
</table>

Weight Percent

<table>
<thead>
<tr>
<th>Weight Percent</th>
<th>1229</th>
<th>19811</th>
<th>20021</th>
</tr>
</thead>
<tbody>
<tr>
<td>±0.20</td>
<td></td>
<td>79.856</td>
<td></td>
</tr>
</tbody>
</table>

This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

The material consists of highly purified uranium oxide, U\text{O}_3. The atomic weight of the material is calculated to be 237.440, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for 234\text{U} and 235\text{U} were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity 235\text{U} to approximate the 234\text{U} concentration, the ratios 234\text{U} to 238\text{U} and 235\text{U} to 238\text{U} were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for 232\text{U} and 233\text{U} were calculated from measurements made at the National Bureau of Standards, at Union Carbide Nuclear Co., Oak Ridge, Tenn., and at Goodyear Atomic Corp., Portsmouth, Ohio, each laboratory's value being given equal weight. Values obtained at NBS are the result of direct measurement of the 232\text{U} to 238\text{U} ratio using triple-filament thermal ionization. The observed ratios were corrected for mass discrimination effects by determining the system bias from measurements on standards U-500 and U-100. Experience at NBS has shown, through intercomparison of the standards, and synthetic mixtures at the 10-, 50-, and 90-percent 235\text{U} level prepared from high-purity 235\text{U} and 234\text{U} isotopes, that a constant bias for a given procedure can be maintained over the range of 0 to 95 percent 235\text{U}. Values from Union Carbide and Goodyear Atomic are based on direct determinations of the 235\text{U} concentration by oxide dilution and U\text{O}_3 analysis, and then the ratio calculated using the NBS values for 234\text{U} and 238\text{U}, and the 235\text{U} value obtained by difference.

The indicated uncertainties for the isotopic concentrations are at the 95-percent confidence level for a single determination. The 234\text{U} to 238\text{U} ratio for this standard, 0.25126, is known to at least 0.1 percent, at the same time the pooled variance for the calibration system is significantly smaller.

Measurements leading to the certification of this SRM were made by E. L. Garner, L. A. Machlan, M. S. Kulimond, and W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

Washington, D.C. 20234
April 6, 1981
(EDITORIAL REVISION OF CERTIFICATE DATED 1-30-70)

George A. Uriano, Chief
Office of Standard Reference Materials

National Bureau of Standards
Certificate of Analysis
Standard Reference Material U-100
Uranium Isotopic Standard
(Nominally 10% Enriched)

<table>
<thead>
<tr>
<th>Atom Percent</th>
<th>234U</th>
<th>235U</th>
<th>238U</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.0676</td>
<td>10.190</td>
<td>0.0079</td>
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<td>±0.0002</td>
<td>10.010</td>
<td>0.0001</td>
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</tbody>
</table>

Weight Percent

<table>
<thead>
<tr>
<th>Weight Percent</th>
<th>0.0666</th>
<th>10.075</th>
<th>0.376</th>
</tr>
</thead>
<tbody>
<tr>
<td>±0.0010</td>
<td>0.0379</td>
<td>89.704</td>
<td></td>
</tr>
</tbody>
</table>

This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

The material consists of highly purified uranium oxide, U\text{O}_3. The atomic weight of the material is calculated to be 237.741, using the nuclidic masses 234.0409; 235.0439; 236.0457; and 238.0508.

The values for 234\text{U} and 235\text{U} were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity 235\text{U} to approximate the 234\text{U} concentration, the ratios 234\text{U} to 238\text{U} and 235\text{U} to 238\text{U} were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The values for 232\text{U} and 233\text{U} were calculated from measurements made at the National Bureau of Standards. The samples were spiked with high-purity 235\text{U} to approach the 234\text{U} concentration, the ratios 232\text{U} to 238\text{U} and 233\text{U} to 238\text{U} were measured on a triple-filament equipped surface ionization mass spectrometer with d-c amplifier circuits.

The indicated uncertainties for the isotopic concentrations are at the 95-percent confidence level for a single determination. The 234\text{U} to 238\text{U} ratio for this standard, 0.11350, is known to at least 0.1 percent.

Measurements leading to the certification of this SRM were made by E. L. Garner, L. A. Machlan, M. S. Kulimond, and W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

NOTE: In many industries traceability of their quality control process to the national measurement system is carried out through the mechanisms of SRM's. It may be therefore of interest to know the details of the measurements made at NBS in arriving at the certified values of this SRM. An NBS Special Publication, 260-27, is reserved for this purpose and is available from the NBS Office of Standard Reference Materials upon request.

Washington, D.C. 20234
April 6, 1981
(EDITORIAL REVISION OF CERTIFICATE DATED 1-30-70)

George A. Uriano, Chief
Office of Standard Reference Materials
The material is a highly purified uranium oxide, \( U_3O_8 \). The atomic weight of the material is calculated to be 237.958 using the nuclidic masses: 234.0409, 235.0439, 236.0456, and 238.0508.

The values of 214U, 216U, 226U, and 238U were determined from measurements at the National Bureau of Standards using a thermal ionization mass spectrometer equipped with a triple-filament ion source and Faraday cage collector. The observed isotopic ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared from high-purity 214U and 216U separated isotopes, and blended to closely bracket the 214U/216U ratio of the SRM.

The abundances of the minor isotopes, 231, 232, and 236U, were determined by isotope dilution. The values for 214U and 216U were calculated from measurements made at the National Bureau of Standards using a surface ionization mass spectrometer equipped with a triple-filament ion source and Faraday cage collector. The values for 231, 232, and 236U were calculated from measurements made at the National Bureau of Standards using a surface ionization mass spectrometer equipped with a single-filament ion source and Faraday cage collector.

The values for 214U, 216U, 226U, and 238U were determined from measurements made at the National Bureau of Standards using a thermal ionization mass spectrometer equipped with a triple-filament ion source and Faraday cage collector. The observed isotopic ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared from high-purity 214U and 216U separated isotopes, and blended to closely bracket the 214U/216U ratio of the SRM.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields of the Inorganic Analysis Research Division. The statistical analyses were performed by E. F. Gomer and W. J. Mound of the Statistical Engineering Division. The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields of the Inorganic Analysis Research Division. The statistical analyses were performed by E. F. Gomer and W. J. Mound of the Statistical Engineering Division.
## National Bureau of Standards Certificate

### Standard Reference Material U-020a

**Uranium Isotopic Standard**

(Nominally 2.0% Enriched)

<table>
<thead>
<tr>
<th></th>
<th>$^{235}$U</th>
<th>$^{236}$U</th>
<th>$^{238}$U</th>
<th>$^{234}$U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom Percent</td>
<td>0.01732</td>
<td>2.0202</td>
<td>0.01179</td>
<td>97.9447</td>
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<tr>
<td>Weight Percent</td>
<td>±0.00003</td>
<td>±0.0011</td>
<td>±0.00007</td>
<td>±0.0011</td>
</tr>
<tr>
<td>Atom Percent</td>
<td>0.01703</td>
<td>2.0011</td>
<td>0.01169</td>
<td>97.9702</td>
</tr>
<tr>
<td>Weight Percent</td>
<td>±0.00003</td>
<td>±0.0011</td>
<td>±0.00007</td>
<td>±0.0011</td>
</tr>
</tbody>
</table>

This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

SRM U-020a is a highly purified uranium oxide, $U_3O_8$, which is certified for isotopic composition and $^{232}$U/$^{238}$U ratio. The atomic weight of the uranium is provided for informational purposes only and is calculated to be 237.989 using the nuclidic masses 234.0409, 235.0439, 236.0456, and 238.0508.

The indicated uncertainties for the isotopic concentrations are at the 95-percent confidence level for a single measurement and include allowances for inhomogeneities in the material as well as analytical error. The $^{235}$U/$^{238}$U ratio for this standard, 0.015565, is known to at least 0.1 percent.

Measurements leading to the certification of this SRM were made by J. W. Gramlich, J. A. Machlan, and J. R. Moody of the Inorganic Analytical Research Division.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T. E. Gillett.

Gaitersburg, MD 20899
March 1, 1985
(Revised Certificate dated July 12, 1984)

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## National Bureau of Standards Certificate

### Standard Reference Material U-015

**Uranium Isotopic Standard**

(Nominally 1.5% Enriched)

<table>
<thead>
<tr>
<th></th>
<th>$^{235}$U</th>
<th>$^{236}$U</th>
<th>$^{237}$U</th>
<th>$^{238}$U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom Percent</td>
<td>0.00850</td>
<td>1.5323</td>
<td>0.0164</td>
<td>98.443</td>
</tr>
<tr>
<td>Weight Percent</td>
<td>±0.00009</td>
<td>±0.0015</td>
<td>±0.0001</td>
<td>±0.0002</td>
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<td>Atom Percent</td>
<td>0.00836</td>
<td>1.5112</td>
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<td>98.462</td>
</tr>
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</table>

This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

The material is a highly purified uranium oxide, $U_3O_8$. The atomic weight of the material is calculated to be 238.004, using the nuclidic masses 234.0409, 235.0439, 236.0457, and 238.0508.

The values for $^{233}$U and $^{237}$U were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity $^{235}$U to approximate the $^{237}$U concentration, the ratio $^{233}$U to $^{237}$U and $^{233}$U to $^{238}$U were measured on a triple-filament equipped surface ionization mass spectrometer with ion-multiplier amplifier circuits. The values for $^{233}$U and $^{238}$U were calculated from measurements of the $^{233}$U to $^{238}$U ratio made at the National Bureau of Standards on a triple-filament, surface ionization mass spectrometer equipped with d-c amplifier circuits. The observed ratios were corrected for mass discrimination effects by intercomparison with synthetic mixtures prepared at the 1 percent $^{235}$U level from high-purity $^{235}$U and $^{238}$U.

The indicated uncertainties for the isotopic concentrations are at the 95-percent confidence level for a single determination, and include allowances for inhomogeneities in the material as well as analytical error. The $^{233}$U/$^{238}$U ratio for this standard, 0.015565, is known to at least 0.1 percent.

Measurements leading to the certification of this SRM were made by E. L. Garner, and J. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

NOTE: In many industries traceability of their quality control process to the national measurement system is carried out through the mechanisms of SRM's. It may be therefore of interest to know the details of the measurements made at NBS in arriving at the certified values of this SRM. An NBS Special Publication, 260-27, is reserved for this purpose and is available from the NBS Office of Standard Reference Materials upon request.

Washington, D.C. 20234
April 6, 1981
(Original revision of Certificate dated 7/30/80)

George A. Uriano, Chief
Office of Standard Reference Materials

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Stanley D. Rusberry, Chief
Office of Standard Reference Materials
National Bureau of Standards
Certificate
Standard Reference Material U-010
Uranium Isotopic Standard
(Nominal 1% Enriched)

<table>
<thead>
<tr>
<th>( ^{235}U )</th>
<th>( ^{234}U )</th>
<th>( ^{238}U )</th>
<th>( ^{239}U )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom Percent</td>
<td>0.00541</td>
<td>1.0037</td>
<td>0.00684</td>
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<tr>
<td>Weight Percent</td>
<td>0.00532</td>
<td>0.9911</td>
<td>0.00675</td>
</tr>
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This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

The material is a highly purified uranium oxide, \( U_3O_8 \). The atomic weight of the material is calculated to be 238.020, using the nuclidic masses 234.0409, 235.0439, 236.0457, and 238.0508.

The values for \( ^{234}U \) and \( ^{236}U \) were calculated from measurements at the National Bureau of Standards. The samples were spiked with high-purity \( ^{235}U \) to approximate the \( ^{235}U \) concentration. The ratios \( ^{235}U \) to \( ^{234}U \) and \( ^{236}U \) to \( ^{238}U \) were measured on a triple-filament equipped surface ionization mass spectrometer with ion-multiplier amplifier circuits.

The values for \( ^{235}U \) and \( ^{236}U \) were calculated from measurements of the \( ^{235}U \) to \( ^{234}U \) ratio made at the National Bureau of Standards on a triple-filament, surface ionization mass spectrometer equipped with d-c amplifier circuits. The observed ratios were corrected for mass discrimination effects by interpolation with synthetic mixtures prepared at the 1 percent \( ^{235}U \) level from high-purity \( ^{235}U \) and \( ^{236}U \).

The indicated uncertainties for the isotopic concentrations are at the 95-percent confidence limits for a single determination, and include allowances for inhomogeneities in the material as well as analytical error. The \( ^{235}U \) to \( ^{234}U \) ratio for this standard, 0.00104, is known to at least 0.1 percent.

Measurements leading to the certification of this SRM were made by E. L. Garner and J. A. Machlan.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of J. L. Hagler.

NOTE: In many industries traceability of their quality control process to the national measurement system is carried out through the mechanisms of SRM's. It may be therefore of interest to know the details of the measurements made at NBS in arriving at the certified values of this SRM. An NBS Special Publication, 200-27, is reserved for this purpose and is available from the NBS Office of Standard Reference Materials upon request.

Washington, D.C. 20234
April 6, 1981
(Revised Certificate dated July 12, 1984)
National Bureau of Standards
Certificate of Analysis

Standard Reference Material U-0002
Uranium Isotopic Standard
(Nominally depleted to 0.02%)

<table>
<thead>
<tr>
<th>Isotope</th>
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<tbody>
<tr>
<td>$^{234}\text{U}$</td>
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<td>0.0016</td>
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<td>$^{235}\text{U}$</td>
<td>0.01755</td>
<td>0.01733</td>
</tr>
<tr>
<td>$^{236}\text{U}$</td>
<td>&lt; 0.00001</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>99.9823</td>
<td>99.9825</td>
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</tbody>
</table>

This Standard Reference Material (SRM) is certified for use as an isotopic standard. The primary intended use is for the evaluation of mass discrimination effects encountered in the operation of a mass spectrometer.

The material is a highly purified uranium oxide, $\text{U}_2\text{O}_3$. The atomic weight of the material is calculated to be 238.0503 using the nuclidic masses 234.0409, 235.0489, and 238.0508.

The value for $^{235}\text{U}$ is calculated from measurements made on samples spiked with high purity $^{235}\text{U}$ to approximate the $^{235}\text{U}$ concentration, the ratio $^{235}\text{U}$ to $^{235}\text{U}$ was measured on a triple-filament equipped thermal ionization mass spectrometer with d-c amplifier circuits. Ratio determinations were corrected for mass discrimination by measurements made under similar conditions on SRM U-500.

The value for $^{238}\text{U}$ is calculated from measurements made on samples spiked with high purity $^{238}\text{U}$, the ratio $^{235}\text{U}$ to $^{238}\text{U}$ was measured on a two stage mass spectrometer using a pulse counting technique.

The indicated uncertainties are at the 95 percent confidence level for a single determination, and include allowances for the inhomogeneities of the material as well as analytical error.

Measurements leading to the certification of this SRM were made by E. I. Garner, L. A. Machlan, and L. J. Moore.

The overall direction and coordination of the technical measurements leading to certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects of the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by J. L. Hague.

NOTE: In many industries traceability of their quality control process to the national measurement system is carried out through the mechanisms of SRM's. It may be therefore of interest to know the details of the measurements made at NBS in arriving at the certified values of this SRM. An NBS Special Publication, 260-27, is reserved for this purpose and is available from the NBS Office of Standard Reference Materials upon request.

Washington, D.C. 20234
April 6, 1981
(Editorial revision of Certificate dated 7-30-70)

George A. Ursano, Chief
Office of Standard Reference Materials
Isotopic Reference Material CBNM IRM 072/1-15

Uranium Isotopic Reference Material for Testing Isotope Mass Spectrometers

The IRM set is supplied with atomic isotope ratios certified as:

<table>
<thead>
<tr>
<th>Code number</th>
<th>233U/235U</th>
<th>233U/238U</th>
<th>235U/238U</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1/- 0.03% of value)</td>
<td>(1/- 0.03% of value)</td>
<td>(1/- 0.000 20)</td>
</tr>
<tr>
<td>072/1</td>
<td>1.000 33</td>
<td>0.991 36</td>
<td>0.991 03</td>
</tr>
<tr>
<td>072/2</td>
<td>0.699 67</td>
<td>0.693 85</td>
<td>0.691 68</td>
</tr>
<tr>
<td>072/3</td>
<td>0.499 85</td>
<td>0.495 91</td>
<td>0.492 12</td>
</tr>
<tr>
<td>072/4</td>
<td>0.299 87</td>
<td>0.297 61</td>
<td>0.292 56</td>
</tr>
<tr>
<td>072/5</td>
<td>0.100 014</td>
<td>0.099 313</td>
<td>0.092 99</td>
</tr>
<tr>
<td>072/6</td>
<td>0.050 091</td>
<td>0.049 746</td>
<td>0.049 10</td>
</tr>
<tr>
<td>072/7</td>
<td>0.019 994</td>
<td>0.018 857</td>
<td>0.017 17</td>
</tr>
<tr>
<td>072/8</td>
<td>0.010 165</td>
<td>0.010 095</td>
<td>0.010 19</td>
</tr>
<tr>
<td>072/9</td>
<td>0.005 000</td>
<td>0.004 966</td>
<td>0.003 20</td>
</tr>
<tr>
<td>072/10</td>
<td>0.002 001</td>
<td>0.001 987</td>
<td>0.001 21</td>
</tr>
<tr>
<td>072/11</td>
<td>0.000 968</td>
<td>0.000 962</td>
<td>0.000 96</td>
</tr>
<tr>
<td>072/12</td>
<td>0.000 500</td>
<td>0.000 497</td>
<td>0.000 50</td>
</tr>
<tr>
<td>072/13</td>
<td>0.000 101</td>
<td>0.000 101</td>
<td>0.000 101</td>
</tr>
<tr>
<td>072/14</td>
<td>0.000 019</td>
<td>0.000 019</td>
<td>0.000 19</td>
</tr>
<tr>
<td>072/15</td>
<td>0.000 001</td>
<td>0.000 001</td>
<td>0.000 001</td>
</tr>
</tbody>
</table>

The IRM set is intended to verify and correct non-linearity of the entire mass spectrometer measurement system.

Notes:
1. All uncertainties indicated are accuracies, computed on a 2σ basis.
2. The atomic masses, used in the calculations, are:
   - 233U: 233.039 628 0 ± 0.000 006 0
   - 234U: 234.040 946 8 ± 0.000 004 8
   - 235U: 235.043 924 7 ± 0.000 004 7
   - 236U: 236.045 022 6 ± 0.000 004 6
   - 238U: 238.050 784 7 ± 0.000 004 6
3. The Reference Material consists of a uranyl nitrate solution. The amount of U per unit is 1.00 ± 0.02 mg contained in a 1.00 ± 0.02 ml solution.
4. The IRM solution has a molality of 6 m HNO₃ (i.e. 6 mol HNO₃ kg⁻¹ of solvent) or a molarity of 5 H₂HNO₃ (i.e. 5 mol HNO₃ l⁻¹ of solution).

Chemical purification of the 233U, 234U and 235U starting materials was performed by Frans Hendrickx and Willy Lycke. Characterization of the enriched isotopes from which the set was prepared, was performed by René Uamen and Kevin Rosman. Verification measurements on the mass spectrometer were done by René Uamen.

The overall technical coordination of the establishment of the IRM set was performed by Willy Lycke.

B-2440 Geel
September 1986

Paul De Bievre
Head
CBNM Mass Spectrometry
The IRM is supplied with an atomic isotope ratio certified as

\[
\frac{^{235}U}{^{238}U} = 0.0044036 \pm 0.0000022
\]

Other uranium isotopes present are related to the \(^{235}U\) isotope abundance through the following atomic isotope ratios:

\[
\frac{^{234}U}{^{235}U} = 0.00561 \pm 0.00045
\]

\[
\frac{^{236}U}{^{235}U} < 0.0005
\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic Atom</th>
<th>Isotopic Mass</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{234}U)</td>
<td>0.00246</td>
<td>± 0.00021</td>
</tr>
<tr>
<td>(^{235}U)</td>
<td>0.43842</td>
<td>± 0.00022</td>
</tr>
<tr>
<td>(^{236}U)</td>
<td>0.00010</td>
<td>± 0.00030</td>
</tr>
<tr>
<td>(^{238}U)</td>
<td>99.55912</td>
<td>± 0.00030</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is \(238.0317501 \pm 0.0000010\)

NOTES

1. All uncertainties indicated are accuracies, computed on a \(\%\) basis.

2. The material consists of purified UF\(_6\) and is supplied in vacui ampoules with about 20 g of material per ampoule.
The IRM is supplied with an atomic isotope ratio certified as

\[ \frac{^{235}U}{^{238}U} = 0.00072535 \pm 0.0000036 \]

Other uranium isotopes present are related to the \(^{235}U\) isotope abundance through the following atomic isotope ratios:

\[ \frac{^{234}U}{^{235}U} = 0.0023 \pm 0.0004 \]
\[ \frac{^{236}U}{^{235}U} < 0.0001 \]

This corresponds to an isotopic composition with the following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{234}U)</td>
<td>0.00527</td>
<td>0.00518</td>
</tr>
<tr>
<td>(^{235}U)</td>
<td>0.72009</td>
<td>0.71106</td>
</tr>
<tr>
<td>(^{236}U)</td>
<td>&lt; 0.00010</td>
<td>&lt; 0.00010</td>
</tr>
<tr>
<td>(^{238}U)</td>
<td>99.27464</td>
<td>99.29376</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is \(238.028921 \pm 0.000016\)

**NOTES**

1. All uncertainties indicated are accuracies, computed on a 2s basis.

2. The material consists of purified UF₆ and is supplied in molybdenum ampoules with about 20 g of material per ampoule.
The IRM is supplied with an atomic isotope ratio certified as

\[
\frac{^{235}U}{^{238}U} = 0.033863 \pm 0.000017
\]

Other uranium isotopes present are related to the \(^{235}U\) isotope abundance through the following atomic isotope ratios:

\[
\begin{align*}
^{234}U/^{235}U &= 0.01001 \pm 0.00021 \\
^{236}U/^{235}U &< 0.0003
\end{align*}
\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{234}U)</td>
<td>0.0328</td>
<td>± 0.00007</td>
</tr>
<tr>
<td>(^{235}U)</td>
<td>3.2343</td>
<td>± 0.00016</td>
</tr>
<tr>
<td>(^{236}U)</td>
<td>&lt; 0.0001</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>(^{238}U)</td>
<td>96.7335</td>
<td>± 0.0001</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is

\[237.951016 \pm 0.000055\]

Notes:

1. All uncertainties indicated are accuracies, computed on a 7s basis.

2. The material consists of purified IRM and is supplied in monel ampoules with about 20 g of material per ampoule.
CERTIFICATE

ISOTOPIC REFERENCE MATERIAL CBMM IRM 023A

The IRM is supplied with an atomic isotope ratio certified as

\[
\frac{235U}{238U} = 0.033882 \pm 0.000017
\]

Other uranium isotopes present are related to the \(^{235}U\) isotope abundance through the following atomic isotope ratios:

\[
\begin{align*}
\frac{234U}{235U} &= 0.010 \pm 0.000 21 \\
\frac{236U}{235U} &= < 0.000 03
\end{align*}
\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{234}U)</td>
<td>0.034 0</td>
<td>0.032 4</td>
</tr>
<tr>
<td>(^{235}U)</td>
<td>3.276 1</td>
<td>3.236 1</td>
</tr>
<tr>
<td>(^{236}U)</td>
<td>&lt; 0.000 1</td>
<td>&lt; 0.000 1</td>
</tr>
<tr>
<td>(^{238}U)</td>
<td>96.690 9</td>
<td>96.731 9</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is

\[237.950 955 \pm 0.000 055\]

NOTES

1. All uncertainties indicated are accuracies, computed on a 2s basis.

2. The material consists of purified UF₆ and is supplied in monel ampoules with about 20 g of material per ampoule.

3. The relative atomic masses, used in the calculations, are

\[
\begin{align*}
\frac{234U}{238U} &= 946.8 \pm 0.000 004 8 \\
\frac{235U}{238U} &= 924.2 \pm 0.000 004 8 \\
\frac{236U}{238U} &= 562.7 \pm 0.000 004 6 \\
\frac{238U}{238U} &= 784.7 \pm 0.000 004 6
\end{align*}
\]

4. This certificate announces better values and reduced uncertainties compared to the previous certificate (dated 1 September 1984) for the same material.

Mass spectrometry measurements were performed by H. De Boeck (\(^{235}U/238U\) by UF₆) and M. Gallet (IRMS) on solutions prepared by J. Bronthaerts.

B 2440 GEL
15 June 1988

Paul DE BLEY
Head,
CBMM Mass Spectrometry
CERTIFICATE

ISOTOPIC REFERENCE MATERIAL CNHM IRM 024

The IRM is supplied with an atomic isotope ratio certified as

\[ 235\text{U}/238\text{U} = 0.053 \pm 0.000027 \]

Other uranium isotopes present are related to the 235U isotope abundance through the following atomic isotope ratios:

\[ \frac{234\text{U}}{235\text{U}} = 0.00545 \pm 0.00016 \]
\[ \frac{236\text{U}}{235\text{U}} = 0.00970 \pm 0.00010 \]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic mass</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>234U</td>
<td>0.027 5</td>
<td>± 0.000 8</td>
</tr>
<tr>
<td>235U</td>
<td>5.050 6</td>
<td>± 0.002 4</td>
</tr>
<tr>
<td>236U</td>
<td>0.049 0</td>
<td>± 0.000 9</td>
</tr>
<tr>
<td>238U</td>
<td>94.872 9</td>
<td>± 0.002 7</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is\[ 237.896835 \pm 0.000 082 \]

NOTES

1. All uncertainties indicated are accuracies, computed on a 2\% basis.

2. The material consists of purified U3O8 and is supplied in monel ampoules with about 20 g of material per ampoule.

3. The relative atomic masses, used in the calculations, are

\[ ^{234}\text{U} \text{ 234.040} \text{946 8} \pm 0.000 004 8 \]
\[ ^{235}\text{U} \text{ 235.043} \text{924 2} \pm 0.000 004 8 \]
\[ ^{236}\text{U} \text{ 236.045} \text{562 7} \pm 0.000 004 6 \]
\[ ^{238}\text{U} \text{ 238.050} \text{784 7} \pm 0.000 004 6 \]

4. This certificate announces better values and reduced uncertainties compared to the previous certificate (dated 1 September 1984) for the same material.

Mass spectrometry measurements were performed by W. De Bolle (235U/238U by UP4) and M. Gallet (ThIMS) on solutions prepared by J. Broothaerts.

B-2440 GEEL
15 June 1988

Paul DE BIEVRF
Head,
CBNM Mass Spectrometry
The IRM is supplied with a molar concentration of $^{233}\text{U}$ certified to be

$$\left(4.0278 \pm 0.0072\right) \times 10^{-3} \text{ mol} \cdot \text{U} \cdot \text{kg}^{-1} \text{ of solution}$$

Other uranium isotopes present are related to the $^{233}\text{U}$ concentration through the following certified molar ratios:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Molar Ratio</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{234}\text{U}$/$^{233}\text{U}$</td>
<td>$0.009328 \pm 0.00000020$</td>
<td></td>
</tr>
<tr>
<td>$^{235}\text{U}$/$^{233}\text{U}$</td>
<td>$0.002108 \pm 0.0000056$</td>
<td></td>
</tr>
<tr>
<td>$^{236}\text{U}$/$^{233}\text{U}$</td>
<td>$0.000204 \pm 0.00000130$</td>
<td></td>
</tr>
<tr>
<td>$^{238}\text{U}$/$^{233}\text{U}$</td>
<td>$0.000040 \pm 0.00000130$</td>
<td></td>
</tr>
</tbody>
</table>

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mole %</th>
<th>Mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{233}\text{U}$</td>
<td>98.042</td>
<td>98.020</td>
<td>$\pm 0.005$</td>
</tr>
<tr>
<td>$^{234}\text{U}$</td>
<td>0.914</td>
<td>0.918</td>
<td>$\pm 0.002$</td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>0.214</td>
<td>0.216</td>
<td>$\pm 0.005$</td>
</tr>
<tr>
<td>$^{236}\text{U}$</td>
<td>0.024</td>
<td>0.024</td>
<td>$\pm 0.003$</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>0.001</td>
<td>0.002</td>
<td>$\pm 0.002$</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is

$$233.0410 \pm 0.00015$$

From the certified values, the following element concentrations are derived:

$$\left(9.3867 \pm 0.017\right) \times 10^{-4} \text{ kg} \cdot \text{U} \cdot \text{kg}^{-1} \text{ of solution}$$

$$\left(9.576 \pm 0.017\right) \times 10^{-4} \text{ kg} \cdot \text{U} \cdot \text{kg}^{-1} \text{ of solution}$$

$$\left(4.1092 \pm 0.0072\right) \times 10^{-3} \text{ mol} \cdot \text{U} \cdot \text{kg}^{-1} \text{ of solution}$$

NOTES

1. All uncertainties indicated are accuracies, computed on a 2s basis, taking into account both measurement reproducibilities and uncertainties of systematic nature estimated on a 2s basis.

2. The IRM solution has a molality of 6 m HNO$_3$ (i.e. 6 mol HNO$_3$ · kg$^{-1}$ solution) or a molarity of 5 M HNO$_3$ (i.e. 5 mol HNO$_3$ · L$^{-1}$ solution).

3. The Avogadro constant used is $(6.022136 \pm 0.000012) \times 10^{23}$ mol$^{-1}$.

4. The atomic masses, used in the calculations, are

$$\begin{align*}
^{233}\text{U} & = 233.0396293 \pm 0.0000071 \\
^{235}\text{U} & = 235.0439252 \pm 0.0000051 \\
^{236}\text{U} & = 236.0455629 \pm 0.0000018 \\
^{238}\text{U} & = 238.0507858 \pm 0.0000007
\end{align*}$$

5. Using this Spike IRM, $^{235}\text{U}$ concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the atomic isotope dilution ratio $R_{\text{dil}} = ^{233}\text{U} / ^{235}\text{U}$ in the blend. They should be computed with the aid of the following formula which allows an easy identification of the sources of the uncertainties in the procedure:

$$c(\text{U}) = c(233\text{U}) = \frac{R_{\text{dil}} - R_{\text{U}}}{R_{\text{U}} - R_{\text{M}}} \cdot \frac{m_{\text{M}}}{m_{\text{U}}} \cdot c(235\text{U}),$$

where

$$R_{\text{dil}} = \frac{R_{\text{dil}} - R_{\text{U}}}{R_{\text{M}} - R_{\text{U}}} \frac{m_{\text{M}}}{m_{\text{U}}} \cdot c(235\text{U}),$$

$$R_{\text{U}} = \text{Isotope abundance ratio}^{233}\text{U} / ^{235}\text{U} \text{ in the unknown sample material}$$

$$R_{\text{M}} = \text{molar isotope abundance ratio}^{233}\text{U} / ^{235}\text{U} \text{ in the spike material}.$$
The isotopic measurements by thermal ionisation Mass Spectrometry were performed by A. Alonso-Muñoz and K. Mayer.

Chemical preparation of the samples for isotopic measurements was performed by A. Verbruggen.

Metrological aspects involved in the preparation and certification were performed by F. Hendricks. The ampoulation of this IRM was accomplished by A. Verbruggen and A. Alonso-Muñoz.

The preparation of this IRM was coordinated by A. Verbruggen.

The overall coordination leading to the establishment, certification and issuance of this IRM, was performed by K. Mayer.

This IRM replaces IRM-040/1 (exhausted).
ISOTOPIC REFERENCE MATERIAL CBNM IRM 050

The IRM is supplied with a 235 U atomic isotope concentration certified as

\[(2.56203 \pm 0.00065) \times 10^{18} \text{ atoms} \times (235\text{U}) \times \text{kg}^{-1} \times (\text{solution})\]

From the certified isotope concentration, following concentrations are derived:

\[(4.2543 \pm 0.0011) \times 10^{-6} \text{ mole} (235\text{U}) \times \text{kg}^{-1} \times (\text{solution})\]

\[(9.9996 \pm 0.0005) \times 10^{-7} \text{ kg} (235\text{U}) \times \text{kg}^{-1} \times (\text{solution})\]

Other uranium isotopes present are related to the 235 U molar concentration through the following molar ratios:

\[234\text{U}/235\text{U} : 0.003360 9 \pm 0.0000052\]
\[236\text{U}/235\text{U} : 0.000096 \pm 0.0000010\]
\[238\text{U}/235\text{U} : 0.000129 6 \pm 0.0000003 0\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>mole %</th>
<th>mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>234\text{U}</td>
<td>0.036 1</td>
</tr>
<tr>
<td>235\text{U}</td>
<td>99.941 4</td>
</tr>
<tr>
<td>236\text{U}</td>
<td>0.009 6</td>
</tr>
<tr>
<td>238\text{U}</td>
<td>0.013 0</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is 235.044 047 ± 0.000 014.

From the certified molar concentration, following element concentrations are derived:

\[(4.2568 \pm 0.0011) \times 10^{-6} \text{ mole} (\text{U}) \times \text{kg}^{-1} \times (\text{solution})\]

\[(1.00055 \pm 0.00025) \times 10^{-6} \text{ kg} (\text{U}) \times \text{kg}^{-1} \times (\text{solution})\]

NOTES

1. All uncertainties indicated are accuracies, computed on a 2s basis.
2. The IRM solution has a molality of 5 M HNO3 (i.e. 5 mol HNO3 \times kg^-1 of solvent) or a molarity of 5 M HNO3 (i.e. 5 mol HNO3 \times L^-1 of solution).
3. The Avogadro Constant used is \( (6.022 134 \pm 0.000 012) \times 10^{23} \) mol\(^{-1}\).
4. The atomic masses, used in the calculations, are
   - 234\text{U} : 234.040 946 8 ± 0.000 004 8 u
   - 235\text{U} : 235.043 924 2 ± 0.000 004 8 u
   - 236\text{U} : 236.045 562 7 ± 0.000 004 6 u
   - 238\text{U} : 238.050 784 7 ± 0.000 004 6 u
5. Using this Spike IRM, 238 U concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the molar dilution ratio \( R_d = 235\text{U}/238\text{U} \) in the blend. They should be computed with the aid of the following formula which readily identifies the sources of uncertainty in the procedure:

\[ C = \frac{R_d \times R_m \times M_x}{R_x \times M_y} \]

where

- \( R_x \) = molar ratio 235\text{U}/238\text{U} in the unknown sample material
- \( R_y \) = molar ratio 235\text{U}/238\text{U} in the spike material
- \( M_x \) = mass of the unknown sample
- \( M_y \) = mass of the sample of spike solution used
- \( C_{238} \) = number of atoms 238\text{U} \times kg^-1 sample material
- \( C_{235} \) = number of atoms 235\text{U} \times kg^-1 spike solution.
6. Chemical preparation and manipulations of this IRM were accomplished by Willy
Lycke, Ado Alonso-Munoz, and Andre Verbruggen. The isolopic measurements were carried out by R. Gomes on samples chemically
prepared by Andre Verbruggen. Metrological weighings required in the preparation and certification were
performed by Frans Hendrickx. The general coordination of the procedures leading to the certification and
issuing of this IRM was performed by Andre Verbruggen.

B-2460 Geel
June 1990

Paul DE BIEVE
Head
CEBM Mass Spectrometry
The IRM is supplied with with atomic isotope ratios certified as:

\[
\frac{235u}{238u} < 0.000 000 1
\]
\[
\frac{234u}{238u} - 0.000 020 2 \pm 0.000 001 2
\]
\[
\frac{233u}{238u} - 0.003 215 7 \pm 0.000 001 6
\]
\[
\frac{233u}{238u} = 0.000 146 5 \pm 0.000 008 6
\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic Atom (%)</th>
<th>Isotopic Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>233u</td>
<td>0.000 01</td>
</tr>
<tr>
<td>234u</td>
<td>0.002 01</td>
</tr>
<tr>
<td>235u</td>
<td>0.320 49</td>
</tr>
<tr>
<td>236u</td>
<td>0.014 60</td>
</tr>
<tr>
<td>238u</td>
<td>99.662 90</td>
</tr>
</tbody>
</table>

This is equivalent to an atomic weight of uranium of

\[
238.040 00 \pm 0.000 018
\]

NUITS

1. All uncertainties indicated are accuracies, computed on a 2σ basis.

2. Values for isotope ratios, isotopic compositions and for concentrations are valid for 1985.10.10.

3. The IRM solution has a molality of 6 m HNO₃ (i.e. 6 mol HNO₃ - kg⁻¹ of solvent) or a molarity of 5 M HNO₃ (i.e. 5 mol HNO₃ - l of solution).

4. The Avogadro number used is \((6.022 136 9 \pm 0.000 000) \times 10^{23}\).

5. The relative atomic masses, used in the calculations, are:

\[
\begin{align*}
\frac{233u}{238u} & = 0.033 039 02 \pm 0.000 000 006 0 \\
\frac{234u}{238u} & = 0.040 046 8 \pm 0.000 004 8 \\
\frac{235u}{238u} & = 0.043 947 2 \pm 0.000 004 8 \\
\frac{236u}{238u} & = 0.045 562 7 \pm 0.000 004 6 \\
\frac{238u}{238u} & = 0.050 784 7 \pm 0.000 004 6 \\
\end{align*}
\]

6. The Reference Material consists of a uranyl nitrate solution. The amount of uranium per unit is 1 g.

Chemical preparation and ampoulation of this IRM were accomplished by Willy Lycke and Andre Verbruggen.

The isotopic measurements were carried out by Willy De Bolle \((\frac{233u}{238u} \text{ abundance ratio by IFF mass spectrometry})\) and René Dumen \((\text{all abundance ratios by thermionic mass spectrometry})\) on samples chemically prepared by Willy Lycke.

Metrological weighing required in the preparation was performed by Frans Hendricks.

The overall coordination of the technical work leading to the certification and issuance of this IRM was performed by Willy Lycke.

B-2440 Geel
1 December 1987

Paul DE RIVRE
Head
CBIM Mass Spectrometry
CERTIFICATE

ISOTOPIC REFERENCE MATERIAL CBMM-IRM 184

The IRM is supplied with with atomic isotope ratios certified as

\[
\begin{align*}
233\text{y}/238\text{y} &< 0.000 000 1 \\
234\text{y}/238\text{y} &< 0.000 000 000 03 1 \\
235\text{y}/238\text{y} &< 0.000 000 02 3 \\
236\text{y}/238\text{y} &< 0.000 000 000 2 \\
\end{align*}
\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>233y</td>
<td>&lt; 0.000 01</td>
</tr>
<tr>
<td>234y</td>
<td>0.005 24</td>
</tr>
<tr>
<td>235y</td>
<td>0.720 96</td>
</tr>
<tr>
<td>236y</td>
<td>0.000 02</td>
</tr>
<tr>
<td>238y</td>
<td>99.273 79</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is 238.078 896 ± 0.000 014

NOTES

1. All uncertainties indicated are accuracies, computed on a 2s basis.

2. Values for isotope ratios, isotopic compositions and for concentrations are valid for 1985.10.10.

3. The IRM solution has a molarity of 6 M HNO3 (i.e. 6 mol HNO3 kg⁻¹ of solvent) or a molarity of 5 M HNO3 (i.e. 5 mol HNO3 L⁻¹ of solution).
The IRM is supplied with atomic isotope ratios certified as:

\[
\begin{align*}
\frac{^{233}_{\text{U}}}{^{238}_{\text{U}}} &= 0.000 \pm 0.000 010 \\
\frac{^{234}_{\text{U}}}{^{238}_{\text{U}}} &= 0.001 173 \pm 0.000 006 0 \\
\frac{^{235}_{\text{U}}}{^{238}_{\text{U}}} &= 0.000 002 86 \pm 0.000 000 53 \\
\frac{^{236}_{\text{U}}}{^{238}_{\text{U}}} &= 0.000 000 01
\end{align*}
\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{233}_{\text{U}}$</td>
<td>0.000 01</td>
</tr>
<tr>
<td>$^{234}_{\text{U}}$</td>
<td>0.017 25</td>
</tr>
<tr>
<td>$^{235}_{\text{U}}$</td>
<td>1.966 75</td>
</tr>
<tr>
<td>$^{236}_{\text{U}}$</td>
<td>0.000 28</td>
</tr>
<tr>
<td>$^{238}_{\text{U}}$</td>
<td>98.016 72</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is 237.990 980 \(\pm 0.000 042\).

Notes:

1. All uncertainties indicated are accuracies, computed on a 2s basis.

2. Values for isotope ratios, isotopic compositions and for concentrations are valid for 1985.10.10.

3. The IRM solution has a molality of 6 M HNO₃ (i.e. 6 mol HNO₃ kg⁻¹ of solvent) or a molarity of 5 M HNO₃ (i.e. 5 mol HNO₃ l⁻¹ of solution).

4. The Avogadro number used is \((6.022 136 9 \pm 0.000 007 2) \times 10^{23}\).

5. The relative atomic masses, used in the calculations, are:

\[
\begin{align*}
^{233}_{\text{U}} &= 233.039 628 0 \pm 0.000 006 0 \\
^{234}_{\text{U}} &= 234.040 946 8 \pm 0.000 008 8 \\
^{235}_{\text{U}} &= 235.043 242 2 \pm 0.000 010 8 \\
^{236}_{\text{U}} &= 236.045 567 7 \pm 0.000 004 6 \\
^{238}_{\text{U}} &= 238.050 784 7 \pm 0.000 004 6
\end{align*}
\]

6. The Reference Material consists of a uranyl nitrate solution. The amount of uranium per unit is 1 g.

Chemical preparation and ampoulation of this IRM were accomplished by Willy Lycke and André Verbruggen.

The isotopic measurements were carried out by Willy De Bolle (\(^{235}\text{U}/^{238}\text{U}\) abundance ratio by UPG mass spectrometry) and René Damen (all abundance ratios by thermionic mass spectrometry) on samples chemically prepared by Willy Lycke.

Metrological weighing required in the preparation and certification was performed by Frans Hendrickx.

The overall coordination of the technical work leading to the certification and issuance of this IRM was performed by Willy Lycke.

8-2440 Geel
1 December 1987

Paul HC BILVRE
Head
CBNM Mass Spectrometry
The IRM is supplied with atomic isotope ratios certified as:

\[
\begin{align*}
\frac{^{233}U}{^{235}U} &< 0.000\,000\,01 \\
\frac{^{234}U}{^{235}U} &< 0.000\,000\,01 \\
\frac{^{235}U}{^{238}U} &< 0.000\,000\,09 \\
\frac{^{236}U}{^{238}U} &< 0.000\,000\,02
\end{align*}
\]

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^{233}U )</td>
<td>&lt; 0.000 01</td>
</tr>
<tr>
<td>( ^{234}U )</td>
<td>&lt; 0.000 01</td>
</tr>
<tr>
<td>( ^{235}U )</td>
<td>0.000 000</td>
</tr>
<tr>
<td>( ^{236}U )</td>
<td>0.000 000</td>
</tr>
<tr>
<td>( ^{237}U )</td>
<td>0.000 000</td>
</tr>
<tr>
<td>( ^{238}U )</td>
<td>0.000 000</td>
</tr>
</tbody>
</table>

4. The Avogadro number used is \((6.022\,136\,9 \pm 0.000\,000\,2) \times 10^{23}\).

5. The relative atomic masses, used in the calculations, are

\[
\begin{align*}
^{233}U & = 233.038\,626 \pm 0.000\,006 \\
^{234}U & = 234.010\,946 \pm 0.000\,004 \\
^{235}U & = 235.043\,924 \pm 0.000\,004 \\
^{236}U & = 236.045\,667 \pm 0.000\,004 \\
^{238}U & = 238.050\,784 \pm 0.000\,004
\end{align*}
\]

6. The Reference Material consists of a uranyl nitrate solution. The amount of uranium per unit is 1 g.

Chemical preparation and ampoulation of this IRM were accomplished by Willy Lycke and André Verbruggen.

The isotopic measurements were carried out by Willy Be 80He (\( ^{235}U/^{238}U \) abundance ratio by UHg mass spectrometry) and Rene Damen (all abundance ratios by thermionic mass spectrometry) on samples chemically prepared by Willy Lycke. Metrological weighing required in the preparation was performed by Frans Hendrickx.

The overall coordination of the technical work leading to the certification and issuance of this IRM was performed by Willy Lycke.

\[\text{O}-\text{2440 Geel} \]
1 December 1987

Paul DE RIEVRES
Head
CRNM Mass Spectrometry

\[\text{The atomic weight of the uranium is } 237.959\,861 \pm 0.000\,066\]

\[\text{NOTES}\]

1. All uncertainties indicated are accuracies, computed on a 2σ basis.

2. Values for isotope ratios, isotopic compositions and for concentrations are valid for 1985.10.10.

3. The IRM solution has a molarity of 6 M HNO₃ (i.e. 6 mol HNO₃·kg⁻¹ of solvent) or a molarity of 5 M HNO₃ (i.e. 5 mol HNO₃·l⁻¹ of solution).
The IRM is supplied with atomic isotope ratios certified as:

- $^{233}U / ^{238}U < 0.000 \pm 0.001$
- $^{234}U / ^{238}U = 0.000 \pm 0.002$
- $^{235}U / ^{238}U = 0.047 \pm 0.001$
- $^{236}U / ^{238}U = 0.000 \pm 0.004$

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{233}U$</td>
<td>&lt; 0.000 01</td>
</tr>
<tr>
<td>$^{234}U$</td>
<td>0.016 27</td>
</tr>
<tr>
<td>$^{235}U$</td>
<td>4.516 70</td>
</tr>
<tr>
<td>$^{236}U$</td>
<td>95.440 15</td>
</tr>
<tr>
<td>$^{238}U$</td>
<td>95.465 27</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is $237.913 \pm 0.004$.

NOTES

1. All uncertainties indicated are accuracies, computed on a 2s basis.

2. Values for isotope ratios, isotopic compositions and for concentrations are valid for 1985.10.10.

3. The IRM solution has a molality of 6 m HNO$_3$ (i.e. 6 mol HNO$_3$ / kg of solvent) or a molarity of 5 M HNO$_3$ (i.e. 5 mol HNO$_3$ / l of solution).
The IRM is supplied with atomic isotope ratios certified as:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>233U/238U</th>
<th>234U/238U</th>
<th>235U/238U</th>
<th>236U/238U</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.000 01</td>
<td>0.002 05</td>
<td>1.000 15</td>
<td>0.000 25</td>
</tr>
<tr>
<td></td>
<td>+/- 0.000 14</td>
<td>+/- 0.000 01</td>
<td>+/- 0.000 01</td>
<td>+/- 0.000 01</td>
</tr>
</tbody>
</table>

This corresponds to the isotopic composition:

<table>
<thead>
<tr>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>233U/235U</td>
<td>33.306 4</td>
</tr>
<tr>
<td>234U/235U</td>
<td>0.068 3</td>
</tr>
<tr>
<td>235U/238U</td>
<td>33.311 0</td>
</tr>
<tr>
<td>236U/238U</td>
<td>0.008 2</td>
</tr>
<tr>
<td>238U/238U</td>
<td>33.306 1</td>
</tr>
</tbody>
</table>

The atomic weight of the uranium is 235.377 23 +/- 0.000 49.

The concentration is specified as: 1.899 +/- 0.007 x 10^-3 kg U/kg solution.

The IRM is intended for:

1. Calibration of isotope dilution measurements
2. Verification of the dependence of mass discrimination upon mass.

Notes:

1. All uncertainties indicated are accuracies, computed on a 2s basis.
2. The relative atomic masses, used in the calculations, are:

<table>
<thead>
<tr>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>233U/235U</td>
<td>17.975 6</td>
</tr>
<tr>
<td>234U/235U</td>
<td>0.067 9</td>
</tr>
<tr>
<td>235U/238U</td>
<td>33.263 9</td>
</tr>
<tr>
<td>236U/238U</td>
<td>0.008 2</td>
</tr>
<tr>
<td>238U/238U</td>
<td>33.684 4</td>
</tr>
</tbody>
</table>

The overall technical coordination of the establishment of this IRM was performed by Willy Lycke.

The atomic weight of the uranium is 235.377 23 +/- 0.000 49.

3. The Reference Material consists of a uranyl nitrate solution, the amount of U per unit is 10 mg.
4. The IRM solution has a molarity of 6 M HNO3 (i.e. 6 mol HNO3 / kg of solvent) or a molarity of 5 M HNO3 (i.e. 5 mol HNO3 / kg of solution).

Chemical purification of the 233U, 235U and 236U starting materials was performed by Willy Lycke. Preparation of the mixture was performed by Frans Hendrickx and Willy Lycke. Isotopic measurements of the starting materials were performed by Kevin Rosman and René Damien. Verification measurements on the IRM were done by René Damien.

The overall technical coordination of the establishment of this IRM was performed by Willy Lycke.
The Standard Reference Material (SRM) is certified as an isotopic standard for use in isotopic measurements of plutonium. SRM 946 consists of approximately 250 mg of plutonium in the form of plutonium sulfate tetrahydrate packaged in a glass microbottle.

The plutonium isotopic distribution was determined by thermal ionization mass spectrometry at the National Bureau of Standards (NBS) on samples from which the americium and uranium were removed. Because high-purity plutonium isotopes have not been used to prepare known synthetic mixtures, the accuracy is dependent on uranium and plutonium exhibiting similar behavior. The observed mass spectrometer data were corrected for mass discrimination effects using data from the analysis of uranium isotopic SRMs that had been analyzed under similar conditions.

SRM 946 contains uranium and americium isotopes, including growing-daughters of plutonium that are isobaric with the plutonium isotopes. In addition, there may be radiation damage to the glass bottle and the tellurium cap liner resulting in small glass slivers. Therefore, in its use, a chemical separation that provides a purified plutonium fraction is essential to the attainment of high accuracy.

Measurements leading to the certification of this SRM were made in the Isotopic Analytical Research Division by T. A. Garner and I. S. Maclean.

The technical and support aspects involved in the revision of this Certificate were coordinated through the Office of Standard Reference Materials by T. E. Gillis.

<table>
<thead>
<tr>
<th>Date</th>
<th>239Pu</th>
<th>238Pu</th>
<th>237Pu</th>
<th>236Pu</th>
<th>235Pu</th>
<th>234Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>January 1, 1982</td>
<td>0.222</td>
<td>84.464</td>
<td>12.253</td>
<td>2.477</td>
<td>0.574</td>
<td></td>
</tr>
<tr>
<td>April 1, 1982</td>
<td>0.231</td>
<td>84.490</td>
<td>12.257</td>
<td>2.448</td>
<td>0.574</td>
<td></td>
</tr>
<tr>
<td>July 1, 1982</td>
<td>0.231</td>
<td>84.515</td>
<td>12.260</td>
<td>2.419</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>October 1, 1982</td>
<td>0.230</td>
<td>84.540</td>
<td>12.264</td>
<td>2.391</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>January 1, 1983</td>
<td>0.230</td>
<td>84.565</td>
<td>12.267</td>
<td>2.363</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>April 1, 1983</td>
<td>0.230</td>
<td>84.590</td>
<td>12.270</td>
<td>2.335</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>July 1, 1983</td>
<td>0.229</td>
<td>84.614</td>
<td>12.274</td>
<td>2.308</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>October 1, 1983</td>
<td>0.229</td>
<td>84.638</td>
<td>12.277</td>
<td>2.281</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>January 1, 1984</td>
<td>0.229</td>
<td>84.662</td>
<td>12.280</td>
<td>2.253</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>April 1, 1984</td>
<td>0.228</td>
<td>84.685</td>
<td>12.283</td>
<td>2.227</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>July 1, 1984</td>
<td>0.228</td>
<td>84.709</td>
<td>12.286</td>
<td>2.201</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>October 1, 1984</td>
<td>0.227</td>
<td>84.732</td>
<td>12.290</td>
<td>2.175</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>January 1, 1985</td>
<td>0.227</td>
<td>84.755</td>
<td>12.293</td>
<td>2.149</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>April 1, 1985</td>
<td>0.227</td>
<td>84.777</td>
<td>12.296</td>
<td>2.125</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>July 1, 1985</td>
<td>0.226</td>
<td>84.799</td>
<td>12.299</td>
<td>2.100</td>
<td>0.577</td>
<td></td>
</tr>
<tr>
<td>October 1, 1985</td>
<td>0.226</td>
<td>84.821</td>
<td>12.302</td>
<td>2.073</td>
<td>0.577</td>
<td></td>
</tr>
<tr>
<td>January 1, 1986</td>
<td>0.225</td>
<td>84.843</td>
<td>12.305</td>
<td>2.050</td>
<td>0.577</td>
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</tr>
<tr>
<td>April 1, 1986</td>
<td>0.225</td>
<td>84.864</td>
<td>12.307</td>
<td>2.036</td>
<td>0.577</td>
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</tr>
<tr>
<td>July 1, 1986</td>
<td>0.225</td>
<td>84.885</td>
<td>12.310</td>
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<td>0.577</td>
<td></td>
</tr>
<tr>
<td>October 1, 1986</td>
<td>0.224</td>
<td>84.906</td>
<td>12.313</td>
<td>1.979</td>
<td>0.577</td>
<td></td>
</tr>
</tbody>
</table>

95% Confidence Interval: ±0.001 ±0.001 ±0.001 ±0.001 ±0.001

The decay-adjusted values for the plutonium isotopic composition, in atom percent, are tabulated below. The half-life values, in years, used for the decay-adjustment are: 239Pu 87.74, 238Pu 24.119, 237Pu 6.560, 236Pu 14.34, and 235Pu 378.000.

[Table 1: Decay-Adjusted Plutonium Isotopic Composition]

<table>
<thead>
<tr>
<th>Date</th>
<th>239Pu</th>
<th>238Pu</th>
<th>237Pu</th>
<th>236Pu</th>
<th>235Pu</th>
<th>234Pu</th>
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</thead>
<tbody>
<tr>
<td>January 1, 1982</td>
<td>0.222</td>
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<td>0.574</td>
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<tr>
<td>April 1, 1982</td>
<td>0.231</td>
<td>84.490</td>
<td>12.257</td>
<td>2.448</td>
<td>0.574</td>
<td></td>
</tr>
<tr>
<td>July 1, 1982</td>
<td>0.231</td>
<td>84.515</td>
<td>12.260</td>
<td>2.419</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>October 1, 1982</td>
<td>0.230</td>
<td>84.540</td>
<td>12.264</td>
<td>2.391</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>January 1, 1983</td>
<td>0.230</td>
<td>84.565</td>
<td>12.267</td>
<td>2.363</td>
<td>0.575</td>
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</tr>
<tr>
<td>April 1, 1983</td>
<td>0.230</td>
<td>84.590</td>
<td>12.270</td>
<td>2.335</td>
<td>0.575</td>
<td></td>
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<tr>
<td>July 1, 1983</td>
<td>0.229</td>
<td>84.614</td>
<td>12.274</td>
<td>2.308</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>October 1, 1983</td>
<td>0.229</td>
<td>84.638</td>
<td>12.277</td>
<td>2.281</td>
<td>0.575</td>
<td></td>
</tr>
<tr>
<td>January 1, 1984</td>
<td>0.229</td>
<td>84.662</td>
<td>12.280</td>
<td>2.253</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>April 1, 1984</td>
<td>0.228</td>
<td>84.685</td>
<td>12.283</td>
<td>2.227</td>
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<td></td>
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<tr>
<td>July 1, 1984</td>
<td>0.228</td>
<td>84.709</td>
<td>12.286</td>
<td>2.201</td>
<td>0.576</td>
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</tr>
<tr>
<td>October 1, 1984</td>
<td>0.227</td>
<td>84.732</td>
<td>12.290</td>
<td>2.175</td>
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</tr>
<tr>
<td>January 1, 1985</td>
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<td>84.755</td>
<td>12.293</td>
<td>2.149</td>
<td>0.576</td>
<td></td>
</tr>
<tr>
<td>April 1, 1985</td>
<td>0.227</td>
<td>84.777</td>
<td>12.296</td>
<td>2.125</td>
<td>0.576</td>
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<tr>
<td>July 1, 1985</td>
<td>0.226</td>
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<td>12.299</td>
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95% Confidence Interval: ±0.001 ±0.001 ±0.001 ±0.001 ±0.001
National Bureau of Standards

Certificate of Analysis

Standard Reference Material 947

Plutonium Isotopic Standard

This Standard Reference Material (SRM) is certified as an isotopic standard for use in isotopic measurements of plutonium. SRM 947 consists of approximately 250 mg of plutonium in the form of plutonium sulfate tetrahydrate packaged in a glass microboule.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atom Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$Pu</td>
<td>0.278 ± 0.006</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>77.089 ± 0.022</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>18.610 ± 0.022</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>1.202 ± 0.006</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>20.004</td>
</tr>
</tbody>
</table>

As of January 1, 1982, refer to Table 1 for quarterly decay-adjusted values.

The plutonium isotopic distribution was determined by thermal ionization mass spectrometry at the National Bureau of Standards (NBS) on samples from which americium and uranium were removed. Because high-purity plutonium isotopes have not been used to prepare known synthetic mixtures, the accuracy is dependent on uranium and plutonium exhibiting similar behavior. The observed mass spectrometer data were corrected for mass discrimination effects using data from the analysis of uranium isotopic SRM's that had been analyzed under similar conditions.

SRM 947 contains uranium and americium isotopes, including growing-in daughters of plutonium that are isobaric with the plutonium isotopes. In addition, there may be radiation damage to the glass bottle and the Teflon cap liner resulting in small glass slivers. Therefore, in its use, a chemical separation that provides a purified plutonium fraction is essential to the attainment of high accuracy.

The technical and support aspects involved in the revision of this Certificate were coordinated through the Office of Standard Reference Materials by J.E. Gils.

August 19, 1982
Washington, D.C. 20234

George A. Urrano, Chief
Office of Standard Reference Materials

Table 1

<table>
<thead>
<tr>
<th>Date</th>
<th>$^{238}$Pu</th>
<th>$^{239}$Pu</th>
<th>$^{240}$Pu</th>
<th>$^{241}$Pu</th>
<th>$^{242}$Pu</th>
</tr>
</thead>
<tbody>
<tr>
<td>January 1, 1982</td>
<td>0.278</td>
<td>77.089</td>
<td>18.610</td>
<td>2.821</td>
<td>1.202</td>
</tr>
<tr>
<td>April 1, 1982</td>
<td>0.276</td>
<td>77.115</td>
<td>18.616</td>
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</tr>
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95% Confidence Limits: ±0.006 ±0.022 ±0.002 ±0.006 ±0.004
National Bureau of Standards
Certificate of Analysis
Standard Reference Material 948

Plutonium Isotopic Standard

The Standard Reference Material (SRM) is certified as an isotopic standard for use in isotopic measurements of plutonium. SRM 948 consists of approximately 250 mg of plutonium in the form of plutonium sulfate tetrahydrate packaged in a glass microbottle.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Atom Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>238Pu</td>
<td>0.010</td>
</tr>
<tr>
<td>239Pu</td>
<td>0.0010</td>
</tr>
<tr>
<td>240Pu</td>
<td>0.0010</td>
</tr>
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<td>241Pu</td>
<td>0.0001</td>
</tr>
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</table>

* As of January 1, 1982, refer to Table 1 for quarterly decay-adjusted values.

The plutonium isotopic distribution was determined by thermal ionization mass spectrometry at the National Bureau of Standards (NBS) on samples from which americium and uranium were removed. Because high-purity plutonium isotopes have not been used to prepare known synthetic mixtures, the accuracy is dependent on uranium and plutonium exhibiting similar behavior. The observed mass spectrometer data were corrected for mass discrimination effects using data from the analysis of uranium isotopic SRM's that had been analyzed under similar conditions. In addition, the value for 240Pu was checked by alpha-count of 239Pu, using the known value for 239Pu as a ratio check.

SRM 948 contains uranium and americium isotopes, including growing-in daughters of plutonium that are isobaric with the plutonium isotopes. In addition, there may be radiation damage to the glass bottle and teflon cap liner resulting in small glass slivers. Therefore, in its use, a chemical separation that provides a purified plutonium fraction is essential to the attainment of high accuracy.

Measurements leading to the certification of this SRM were made in the Isotopic Analytical Research Division by E. L. Garner, T. A. Macklan, and W. R. Shields.

The technical and support aspects involved in the revision of this Certificate were coordinated through the Office of Standard Reference Materials by E. E. Gibbs.

August 19, 1982
Washington, D.C. 20234
(Revision of Certificate dated 12-3-81)

George A. Urquhart
Chief, Office of Standard Reference Materials

---

Table 1

<table>
<thead>
<tr>
<th>Date</th>
<th>238Pu</th>
<th>239Pu</th>
<th>240Pu</th>
<th>241Pu</th>
<th>242Pu</th>
<th>243Pu</th>
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<td>7.923</td>
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<td>7.925</td>
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</table>

95% Confidence Limit

20.010
20.010
50.010
50.010
10.000
10.000
From the certified atomic isotope concentration, following element concentrations are derived:

\[(3.830 \pm 0.008) \times 10^6 \text{ mol Pu} \cdot \text{kg}^{-1} \text{ of solution}\]
\[(9.346 \pm 0.019) \times 10^7 \text{ kg Pu} \cdot \text{kg}^{-1} \text{ of solution}\]

**NOTES**

1. All uncertainties indicated are accuracies, computed on a 2s basis.
2. Values for isotope ratios, isotopic compositions and for concentrations are valid for 10 December 1986.
3. Due to radioactive decay, the Pu element concentration decreases by 0.003 3 % a⁻¹.
   The half lives, used in the calculations, are:
   238Pu (8.774 ± 0.009) 10⁶ a
   239Pu (2.411 ± 0.003) 10⁴ a
   240Pu (6.537 ± 0.010) 10³ a
   241Pu (1.433 ± 0.002) 10¹ a
   242Pu (3.763 ± 0.020) 10¹ a
   244Pu (8.2 ± 0.1) 10⁷ a
4. The IRM solution has a molarity of 6 mol HNO₃ (i.e. 6 mol HNO₃ · kg⁻¹ of solvent) or a molarity of 5 M HNO₃ (i.e. 5 mol HNO₃ · l⁻¹ of solution).
5. The Avogadro constant used is \((6.022 136 9 ± 0.000 007 2) \times 10^{23}\).
6. The atomic masses, used in the calculations, are:
   238Pu 238.049 554 6 ± 0.000 005 1
   239Pu 239.052 157 6 ± 0.000 005 1
   240Pu 240.053 808 2 ± 0.000 004 9
   241Pu 241.056 845 9 ± 0.000 004 8
   242Pu 242.058 737 3 ± 0.000 004 8
   244Pu 244.056 199 ± 0.000 005

The atomic weight of the plutonium is 244.006 306 ± 0.000 005
Using this Spike IRM, concentrations of unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the atomic isotope dilution ratio $R_y = \frac{\text{239Pu}}{\text{244Pu}}$ in the blend. They should be computed with the aid of the following formula which allows an easy identification of the sources of the uncertainties in the procedure:

$$C = \frac{R_x - R_y}{R_x - R_M} \cdot \frac{M_y}{M_x} \cdot \frac{C_y}{C_M}$$

where:

- $R_x$ = atomic isotope ratio $^{239}\text{Pu}/^{244}\text{Pu}$ in the unknown sample material
- $R_y$ = atomic isotope ratio $^{239}\text{Pu}/^{244}\text{Pu}$ in the spike material
- $M_x$ = mass of the unknown sample
- $M_y$ = mass of the sample of spike solution used
- $C_x = \text{number of atoms } ^{239}\text{Pu} \cdot \text{kg}^{-1}$ sample material
- $C_y = \text{number of atoms } ^{244}\text{Pu} \cdot \text{kg}^{-1}$ spike solution.

Chemical preparation and ampoulation of this IRM were accomplished by Willy Lycke and André Verbruggen.

The isotopic measurements were carried out by Marc Gallet on samples chemically prepared by André Verbruggen. Isotopic measurements were calibrated against synthetic plutonium isotopic mixtures prepared by Jan Broothaerts.

Metrological aspects involved in the preparation and certification were performed by Frans Hendrickx.

The overall coordination of the establishment leading to the certification and issuance of this IRM was performed by André Verbruggen.
The IRM is supplied with a $^{242}\text{Pu}$ atomic isotope concentration certified as:

$$ (1.100 \pm 0.003 3) \cdot 10^{17} \text{ atoms } 242\text{Pu} \cdot \text{kg}^{-1} \text{ of solution} $$

From the certified isotope concentration, following concentrations are derived:

- $$(1.820 \pm 0.006) \cdot 10^{-7} \text{ mol } 242\text{Pu} \cdot \text{kg}^{-1} \text{ of solution}$$
- $$(4.425 \pm 0.013) \cdot 10^{-8} \text{ kg } 242\text{Pu} \cdot \text{kg}^{-1} \text{ of solution}$$

Other plutonium isotopes present are related to the $^{242}\text{Pu}$ atomic isotope concentration through the following atomic isotope ratios:

- $^{238}\text{Pu} / 242\text{Pu} : 0.011 551 \pm 0.000 020$
- $^{239}\text{Pu} / 242\text{Pu} : 0.002 759 \pm 0.000 014$
- $^{240}\text{Pu} / 242\text{Pu} : 0.097 87 \pm 0.000 34$
- $^{241}\text{Pu} / 242\text{Pu} : 0.026 850 \pm 0.000 059$
- $^{243}\text{Pu} / 242\text{Pu} : 0.000 212 \pm 0.000 012$

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>1.013 9</td>
<td>0.998 1 \pm 0.001 6</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>0.242 1</td>
<td>0.219 4 \pm 0.001 2</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>8.590 7</td>
<td>8.528 1 \pm 0.027 0</td>
</tr>
<tr>
<td>$^{241}\text{Pu}$</td>
<td>2.356 8</td>
<td>2.349 4 \pm 0.004 4</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>0.777 9</td>
<td>0.866 3 \pm 0.031 0</td>
</tr>
<tr>
<td>$^{243}\text{Pu}$</td>
<td>0.010 8</td>
<td>0.018 7 \pm 0.001 0</td>
</tr>
</tbody>
</table>

The atomic weight of the plutonium is $241.015 33 \pm 0.000 60$.

From the certified atomic isotope concentration, following element concentrations are derived:

- $$(2.082 5 \pm 0.006 1) \cdot 10^{-7} \text{ mol } \text{Pu} \cdot \text{kg}^{-1} \text{ of solution}$$
- $$(5.035 6 \pm 0.001 4) \cdot 10^{-8} \text{ kg } \text{Pu} \cdot \text{kg}^{-1} \text{ of solution}$$

NOTES

1. All uncertainties indicated are accuracies, computed on a 2s basis.
2. Values for isotope ratios, isotopic compositions and for concentrations are valid for 8 August 1978.
3. Due to radioactive decay the Pu element concentration decreases by $0.12\times 10^{-4} \text{ a}^{-1}$.
   The half lives, used in the calculations, are:
   - $^{238}\text{Pu}$: (8.774 \pm 0.009) 10^{4} a
   - $^{239}\text{Pu}$: (2.411 \pm 0.003) 10^{5} a
   - $^{240}\text{Pu}$: (6.537 \pm 0.010) 10^{4} a
   - $^{241}\text{Pu}$: (1.433 \pm 0.002) 10^{4} a
   - $^{242}\text{Pu}$: (3.763 \pm 0.020) 10^{5} a
   - $^{243}\text{Pu}$: (8.2 \pm 0.1) 10^{4} a
4. The IRM solution has a molality of 6 m HNO_3 (i.e. 6 mol HNO_3 \cdot kg^{-1} of solvent) or a molality of 5 M HNO_3 (i.e. 5 mol HNO_3 \cdot 1^{-1} of solution).
5. The Avogadro constant used is $$(6.022 045 \pm 0.000 031) \cdot 10^{23}$$. 
6. The atomic masses, used in the calculations, are

\[
\begin{align*}
238_{\text{Pu}} & = 238.0495552 \pm 0.0000051 \\
239_{\text{Pu}} & = 239.0521578 \pm 0.0000051 \\
240_{\text{Pu}} & = 240.0538097 \pm 0.0000049 \\
241_{\text{Pu}} & = 241.0568469 \pm 0.0000048 \\
242_{\text{Pu}} & = 242.0587385 \pm 0.0000048 \\
244_{\text{Pu}} & = 244.0642000 \pm 0.0000010
\end{align*}
\]

7. Using this Spike IRM, \(^{239}\text{Pu}\) concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the atomic isotope dilution ratio \(R_B = \frac{^{239}\text{Pu}}{^{242}\text{Pu}}\) in the blend. They should be computed with the aid of following formula which allows an easy identification of the sources of the uncertainties in the procedure:

\[
C_{239} = \frac{R_B - R_X}{R_B - R_Y} \cdot \frac{N_Y - N_X}{M_Y - M_X} \cdot C_{242}
\]

where

- \(R_B\) = atomic isotope ratio \(\frac{^{239}\text{Pu}}{^{242}\text{Pu}}\) in the unknown sample material
- \(R_X\) = atomic isotope ratio \(\frac{^{239}\text{Pu}}{^{242}\text{Pu}}\) in the spike material
- \(N_Y\) = mass of the unknown sample
- \(N_X\) = mass of the sample of spike solution used
- \(C_{239}\) = number of atoms \(^{239}\text{Pu}\) kg\(^{-1}\) sample material
- \(C_{242}\) = number of atoms \(^{242}\text{Pu}\) kg\(^{-1}\) spike solution.

The isotopic measurements, as well as the overall technical coordination of the establishment of this IRM, were performed by Marc Gallet.

Chemical preparation of this IRM and of the samples for isotopic measurements was performed by Aadri Verbruggen.

Paul De BIEVRE  
Head  
CNRM Mass Spectrometry  

0-2440 GEEL  
16 September 1985
The IRM is supplied with a $^{242}$Pu atomic isotope concentration certified as:

$$(2.2920 \pm 0.0034) \times 10^{19} \text{ atoms} \cdot \frac{242\text{Pu}}{\text{kg}} \cdot \text{of solution}$$

From the certified isotope concentration, following concentrations are derived:

- $(3.8060 \pm 0.0057) \times 10^{-5} \text{ mol} \cdot \frac{242\text{Pu}}{\text{kg}} \cdot \text{of solution}$
- $(9.213 \pm 0.014) \times 10^{-6} \text{ kg} \cdot \frac{242\text{Pu}}{\text{kg}} \cdot \text{of solution}$

Other plutonium isotopes present are related to the $^{242}$Pu atomic isotope concentration through the following atomic isotope ratios:

- $^{238}\text{Pu}/^{242}\text{Pu} : 0.00009 \pm 0.000006$
- $^{239}\text{Pu}/^{242}\text{Pu} : 0.000827 \pm 0.000004$
- $^{240}\text{Pu}/^{242}\text{Pu} : 0.000108 \pm 0.000004$
- $^{241}\text{Pu}/^{242}\text{Pu} : 0.000009 \pm 0.000004$
- $^{244}\text{Pu}/^{242}\text{Pu} : 0.000015 \pm 0.000004$

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>0.000 9</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>0.082 6</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>0.010 8</td>
</tr>
<tr>
<td>$^{241}\text{Pu}$</td>
<td>0.000 9</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>99.303 3</td>
</tr>
<tr>
<td>$^{244}\text{Pu}$</td>
<td>0.001 5</td>
</tr>
</tbody>
</table>

The atomic weight of the plutonium is $242.056 \pm 0.000 028$.
Using this Spike IRM, \(^{239}\text{Pu}\) concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the atomic isotope dilution ratio \(R_y = \frac{^{239}\text{Pu}}{^{242}\text{Pu}}\) in the blend. They should be computed with the aid of the following formula which allows an easy identification of the sources of the uncertainties in the procedure:

\[
C_{\text{239}} = \frac{C_{\text{242}}}{C_{\text{242}}} R_y \frac{M_y}{M_x} \frac{C_{\text{242}}}{C_{\text{242}}} \frac{R_y}{R_x}
\]

where

- \(R_x\) = atomic isotope ratio \(^{239}\text{Pu}/^{242}\text{Pu}\) in the unknown sample material
- \(R_y\) = atomic isotope ratio \(^{239}\text{Pu}/^{242}\text{Pu}\) in the spike material
- \(M_x\) = mass of the unknown sample
- \(M_y\) = mass of the sample of spike solution used
- \(C_{\text{242}}\) = number of atoms \(^{242}\text{Pu}\) \(\cdot\) kg\(^{-1}\) sample material
- \(C_{\text{242}}\) = number of atoms \(^{242}\text{Pu}\) \(\cdot\) kg\(^{-1}\) spike solution.

Chemical preparation and ampoulation of this IRM were accomplished by Willy Lycke and André Verbruggen.

The isotopic measurements were carried out by Marc Gallet on samples chemically prepared by André Verbruggen. Isotopic measurements were calibrated against synthetic plutonium isotopic mixtures prepared by Jan Broothaerts.

Metrological aspects involved in the preparation and certification were performed by Frans Hendrickx.

The overall coordination of the establishment leading to the certification and issuance of this IRM was performed by André Verbruggen.

H 2440 Geel
September 1987

Paul DE BIEVRE
Head
CBNM Mass Spectrometry
The IRM is supplied with atomic isotope ratios certified as:

<table>
<thead>
<tr>
<th>Isotope Ratio</th>
<th>Value (certified)</th>
<th>Uncertainty (certified)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{235}\text{Pu}/^{244}\text{Pu}$</td>
<td>0.000 080</td>
<td>+/- 0.000 013</td>
</tr>
<tr>
<td>$^{239}\text{Pu}/^{244}\text{Pu}$</td>
<td>1.798 37</td>
<td>+/- 0.002 45</td>
</tr>
<tr>
<td>$^{240}\text{Pu}/^{244}\text{Pu}$</td>
<td>0.936 385</td>
<td>+/- 0.000 095</td>
</tr>
<tr>
<td>$^{241}\text{Pu}/^{244}\text{Pu}$</td>
<td>0.001 145</td>
<td>+/- 0.000 023</td>
</tr>
<tr>
<td>$^{242}\text{Pu}/^{244}\text{Pu}$</td>
<td>0.013 560</td>
<td>+/- 0.000 043</td>
</tr>
</tbody>
</table>

This corresponds to the isotopic composition:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>0.003 4</td>
<td>0.003 3</td>
<td>+/- 0.000 6</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>55.260 7</td>
<td>54.164 3</td>
<td>+/- 0.045 5</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>1.548 6</td>
<td>1.541 1</td>
<td>+/- 0.003 3</td>
</tr>
<tr>
<td>$^{241}\text{Pu}$</td>
<td>0.048 7</td>
<td>0.048 7</td>
<td>+/- 0.001 0</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>0.577 1</td>
<td>0.579 1</td>
<td>+/- 0.001 9</td>
</tr>
<tr>
<td>$^{244}\text{Pu}$</td>
<td>42.561 5</td>
<td>43.063 5</td>
<td>+/- 0.045 7</td>
</tr>
</tbody>
</table>

The atomic weight of the plutonium is 241.219 16 +/- 0.002 29.

The IRM is intended for:

a) determining Pu isotope fractionation using the certified $^{239}\text{Pu}/^{244}\text{Pu}$ ratio;

b) checking of isotopic contamination during chemical preparations and measurements using the $^{239}\text{Pu}/^{244}\text{Pu}$ and $^{242}\text{Pu}/^{244}\text{Pu}$ ratios.

NOTES

1. All uncertainties indicated are accuracies, computed on a 2s basis.

2. Values for isotope ratios and isotopic composition are valid for 10 September 1985.

3. The relative atomic masses used in the calculations are:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass (amu)</th>
<th>Uncertainty (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>238.049 554 6</td>
<td>+/- 0.000 002 4</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>239.052 157 6</td>
<td>+/- 0.000 002 4</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>240.053 808 2</td>
<td>+/- 0.000 002 3</td>
</tr>
<tr>
<td>$^{241}\text{Pu}$</td>
<td>241.056 845 9</td>
<td>+/- 0.000 002 3</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>242.058 737 3</td>
<td>+/- 0.000 002 3</td>
</tr>
<tr>
<td>$^{244}\text{Pu}$</td>
<td>244.064 199</td>
<td>+/- 0.000 005</td>
</tr>
</tbody>
</table>

4. The Reference Material consists of dried Pu nitrate. The amount of Pu per unit is (1.49 +/- 0.015) * 10^-7 kg.

5. No chemical redox cycle was performed on the material.

6. Due to radioactive decay, the Pu element concentration decreases by 0.004% /a.

   The half lives, used in the calculations, are:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half Life (years)</th>
<th>Uncertainty (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>8.774</td>
<td>+/- 0.009</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>2.411</td>
<td>+/- 0.003</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>6.537</td>
<td>+/- 0.010</td>
</tr>
<tr>
<td>$^{241}\text{Pu}$</td>
<td>1.433</td>
<td>+/- 0.002</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>3.763</td>
<td>+/- 0.020</td>
</tr>
<tr>
<td>$^{244}\text{Pu}$</td>
<td>8.2</td>
<td>+/- 0.1</td>
</tr>
</tbody>
</table>

Isotopic measurements, as well as the overall technical coordination of the establishment of this IRM, were performed by Marc Gallet.

Chemical preparation of this IRM and of the samples for isotopic measurements was performed by André Verbruggen.
The IRM is supplied with a $^{242}\text{Pu}$ atomic isotope concentration certified as:

$$\left(2.2698 \pm 0.0045\right) \times 10^{20} \text{atoms}^{242}\text{Pu} \cdot \text{kg}^{-1} \text{of solution}$$

From the certified isotope concentration, following concentrations are derived:

$$\left(3.7691 \pm 0.0075\right) \times 10^{-4} \text{mol}^{242}\text{Pu} \cdot \text{kg}^{-1} \text{of solution}$$

$$\left(9.123 \pm 0.018\right) \times 10^{-5} \text{kg}^{242}\text{Pu} \cdot \text{kg}^{-1} \text{of solution}$$

Other plutonium isotopes present are related to the $^{242}\text{Pu}$ atomic isotope concentration through the following atomic isotope ratios:

$$\frac{^{238}\text{Pu}}{^{242}\text{Pu}} : 0.00009 \pm 0.000006$$

$$\frac{^{239}\text{Pu}}{^{242}\text{Pu}} : 0.000827 \pm 0.000004$$

$$\frac{^{240}\text{Pu}}{^{242}\text{Pu}} : 0.00108 \pm 0.000004$$

$$\frac{^{241}\text{Pu}}{^{242}\text{Pu}} : 0.00009 \pm 0.000004$$

$$\frac{^{244}\text{Pu}}{^{242}\text{Pu}} : 0.000015 \pm 0.000004$$

This corresponds to an isotopic composition with following abundances:

<table>
<thead>
<tr>
<th>Isotopic atom %</th>
<th>Isotopic mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>0.000 9</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>0.082 6</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>0.010 8</td>
</tr>
<tr>
<td>$^{241}\text{Pu}$</td>
<td>0.000 9</td>
</tr>
<tr>
<td>$^{242}\text{Pu}$</td>
<td>0.993 3</td>
</tr>
<tr>
<td>$^{244}\text{Pu}$</td>
<td>0.001 5</td>
</tr>
</tbody>
</table>

The atomic weight of the plutonium is $242.056 \pm 0.000 020$.

From the certified atomic isotope concentration, following element concentrations are derived:

$$\left(3.1777 \pm 0.0007\right) \times 10^{-4} \text{mol} \text{Pu} \cdot \text{kg}^{-1} \text{of solution}$$

$$\left(9.132 \pm 0.018\right) \times 10^{-5} \text{kg} \text{Pu} \cdot \text{kg}^{-1} \text{of solution}$$

NOTES
1. All uncertainties indicated are accuracies, computed on a 2σ basis.
2. Values for isotope ratios, isotopic compositions and for concentrations are valid for 27 January 1987.
3. Due to radioactive decay, the Pu element concentration decreases by $0.00023 \%, \text{yr}^{-1}$.
4. The half lives, used in the calculations, are:
   - $^{238}\text{Pu}$: $(8.774 \pm 0.009) \times 10^4 \text{a}$
   - $^{239}\text{Pu}$: $(2.411 \pm 0.003) \times 10^4 \text{a}$
   - $^{240}\text{Pu}$: $(6.537 \pm 0.010) \times 10^3 \text{a}$
   - $^{241}\text{Pu}$: $(1.433 \pm 0.002) \times 10^3 \text{a}$
   - $^{242}\text{Pu}$: $(3.763 \pm 0.020) \times 10^2 \text{a}$
   - $^{244}\text{Pu}$: $(8.2 \pm 0.1) \times 10^1 \text{a}$
5. The IRM solution has a molarity of 6 M HN03 (i.e. 6 mol HN03 · kg⁻¹ of solvent) or a molarity of 5 M HN03 (i.e. 5 mol HN03 · l⁻¹ of solution).
6. The Avogadro constant used is $(6.022 136 9 \pm 0.000 007) \times 10^{23}$.
7. The atomic masses, used in the calculations, are:
   - $^{238}\text{Pu}$: $238.049 554 6 \pm 0.000 005 1$
   - $^{239}\text{Pu}$: $239.052 157 6 \pm 0.000 005 1$
   - $^{240}\text{Pu}$: $240.053 808 7 \pm 0.000 004 9$
   - $^{241}\text{Pu}$: $241.056 845 9 \pm 0.000 004 8$
   - $^{242}\text{Pu}$: $242.058 737 3 \pm 0.000 004 8$
   - $^{244}\text{Pu}$: $244.064 199 \pm 0.000 005$
Using this Spike IRM, $^{239}$Pu concentrations in unknown samples can be determined by Isotope Dilution Mass Spectrometry, through a measurement of the atomic isotope dilution ratio $R = \frac{^{239}\text{Pu}}{^{240}\text{Pu}}$ in the blend. They should be computed with the aid of the following formula which allows an easy identification of the sources of the uncertainties in the procedure:

$$C_{\text{am}} = \frac{C_{\text{am}}}{R_X} = \frac{M_Y}{M_X} \cdot C_{\text{am}}$$

where

- $R_X$ = atomic isotope ratio $^{239}\text{Pu}/^{240}\text{Pu}$ in the unknown sample material
- $R_Y$ = atomic isotope ratio $^{239}\text{Pu}/^{240}\text{Pu}$ in the spike material
- $M_X$ = mass of the unknown sample
- $M_Y$ = mass of the sample of spike solution used
- $C_{239}$ = number of atoms $^{239}\text{Pu}$·kg$^{-1}$ sample material
- $C_{240}$ = number of atoms $^{240}\text{Pu}$·kg$^{-1}$ spike solution.

Chemical preparation and ampoulation of this IRM were accomplished by Willy Lycke and André Verbruggen.

The isotopic measurements were carried out by Hare Gallet on samples chemically prepared by André Verbruggen. Isotopic measurements were calibrated against synthetic plutonium isotopic mixtures prepared by Jan Broothaerts.

Metrological aspects involved in the preparation and certification were performed by Frans Hendrickx.

The overall coordination of the establishment leading to the certification and issuance of this IRM was performed by André Verbruggen.
Applications of the Rhenium-Osmium Isotope System to Geologic Problems

Richard J. Walker, Isotope Geochemistry Laboratory, Department of Geology, University of Maryland, College Park, MD 20742

Recent advances in the mass spectrometry and chemical purification of the elements of Re and Os have now permitted this isotope system to take its place as a unique companion to the other long-lived radiogenic isotope systems. $^{187}\text{Re}$ decays to $^{187}\text{Os}$ by $\beta$ with a decay constant of approximately $1.639 \times 10^{11}\text{yr}^{-1}$. There is still approximately $\pm 3\%$ uncertainty in this decay constant, but it should be refined over the next several years as studies of terrestrial systems of known age are examined.

The Re-Os system serves as an isotopic tool with some singular uses, but primarily should be used in conjunction with other isotopic systems to be most effective. Many of its uses, for example geochronology, overlap with the uses of the Sm-Nd, Rb-Sr, Lu-Hf and U-Th-Pb systems. However, Re and Os are both siderophile and chalcophile elements, in geochemical contrast to the lithophile elements that comprise the other long-lived radiogenic isotope systems. Consequently, the "view" into geologic processes provided by this system is somewhat unique. A good example of this uniqueness is the behavior of the Re-Os isotope system in the mantle. Unlike the elements that comprise the other isotope systems, Os is usually retained in the mantle during melting events. Re, however, is moderately incompatible. This means that Os isotopes in the mantle are reasonably immune to the effects of short-term crustal recycling. In addition, most melting events in the mantle evidently leave Re-depleted residues with retarded $^{187}\text{Os}$ growth. We have shown that ancient subcontinental lithosphere is usually depleted in $^{187}\text{Os}$ relative to a model bulk Earth that approximates the isotopic evolution of carbonaceous chondrites.

A number of uses of the Re-Os system will be discussed. One important use of the system is in dating mafic and ultramafic rocks that are difficult to date using other techniques. Most basalts, for example, have relatively high Re/Os ratios, leading to extremely rapid growth of radiogenic Os relative to the common Os. This permits the dating of even young basalts via model age calculations and in some instances isochron dating. The system also has other unique geochronologic applications including the dating of molybdenites and iron meteorites. Os is one of the six platinum group elements, so the system serves as the best tracer of PGE that we will ever have. In one study, we have found the PGE in Sudbury (Ontario) sulfides to have been derived from ancient continental crust. In stark contrast, sulfides from the Noril'sk (Siberia) sulfides were dominantly derived from a mantle plume source.
Figure. Re-Os isochron plot and $\gamma_{Os}$ vs. Re/Os ratio plot for sulfide samples of the Kharaelakhsky orebody, Noril'sk region, Siberia. Data show closed-system behavior since the igneous event at approx. 250 Ma. $\gamma_{Os}$ values are all greater than zero (chondritic) and are consistent with derivation from a plume source.

The radioactive decay systems, U-Th-Pb, Rb-Sr, and Sm-Nd, when locked within individual minerals or hand specimen-sized whole-rocks, provide the basis for several well-established isotopic dating techniques. These same systems viewed at a larger scale serve to isotopically characterize terrestrial reservoirs, and function as natural tracers of geologic processes affecting those reservoirs. Applications can range from the study of local phase equilibrium (mm to m) through the identification of igneous rock/ore deposit source rock (m to 10 km) and the fingerprinting of tectonostratigraphic terranes (km to 10^2 km) to placing spatial and temporal constraints on planetary differentiation (10^3 km).

In this lecture we'll examine the basic theory underlying the Pb-Sr-Nd isotopic troika—so-called because its coupled relationships give rise to a number of correlation diagrams that emphasize parent-daughter fractionation trends (several other decay systems, such as Lu-Hf, Re-Os, and K-Ca, are also very useful in this respect). Although, historically, the three systems were developed more or less independently and spawned their own nomenclature and data-reporting conventions, some uniformity has been subsequently introduced with the ε_{Nd} and ε_{Sr} notation (parts per ten thousand deviation of isotopic ratios from reference values). No corresponding notation for lead has yet gained wide acceptance, but some advantages of the δ(6/4), δ(7/4), and δ(8/4) convention (parts per thousand deviation of isotopic ratios from reference values; first proposed by Stacey, 1986) will be discussed.

A vast body of isotopic data now exists, which invites a general synthesis into various petrogenetic models. At the largest scale and providing a framework for interpreting regional and local patterns are the terrestrial differentiation models. One such model—the plumbotectonic model of Doe and Zartman (1979) and Zartman and Doe (1981)—offers a planetary prospective that has proven helpful in describing first-
order Pb-Sr-Nd isotopic systematics among major Earth reservoirs (upper crust, lower crust, subcontinental lithosphere, mantle, orogene). Rather than by forcing a narrow tectonic scenario upon the observational data, the plumbotectonic model probably finds its greatest value in testing permissible ranges of reservoir compositions and of fluxes carrying material between reservoirs. Another model—the chemical geodynamics model of Allègre (1982) and Zindler and Hart (1986)—has been particularly effective in describing mantle heterogeneities by defining mantle end-member reservoirs (DMM, PREMA, BSE, HIMU, EM I, EM II).

Within the context of these broad terrestrial differentiation models one can then examine the various geologic phenomena that create and destroy isotopic differences. Observed isotopic patterns reflect a dynamic balance between these opposite tendencies and provide important constraints on the extent and timing of differentiation and mixing processes. Examples to be discussed are taken from studies of igneous rocks, ore deposits, seawater, and terrane identification.
Suggested Reading


Basic Equations

For a radioactive species $N$,

$$\frac{dN}{dt} = -\lambda N \rightarrow N = N_0 e^{-\lambda t}$$

resulting in the production of a radiogenic species $D$,

$$D = D_0 + N_0 - N = D_0 + N_0 (1 - e^{-\lambda t})$$
or, in terms of $N$ (today),

$$= D_0 + N(e^{\lambda t} - 1)$$

If $\lambda t \ll 1$, $D \approx D_0 + N \cdot \lambda t$

At $t = 0$ $[N_0, D_0, D']$

At $t = t$ $[N, D, D']$
The basic age equation is

\[ t = \frac{1}{\lambda} \cdot \ln[1 + (D-D_0)/N] \]

or, if \((D-D_0)/N \ll 1\), \[ t \approx \frac{1}{\lambda} \cdot \frac{(D-D_0)}{N} \]

Sometimes we want to calculate the amount of radiogenic daughter produced between two arbitrary times, \(t_1\) and \(t_2\).

\[ D(2) - D(1) = N(1') - N(2) = N(e^{\lambda t_1} - e^{\lambda t_2}) \]

Normalizing to a nonradiogenic isotope of the daughter element, \(D'\), we have

\[ \frac{D(2)}{D'} - \frac{D(1)}{D'} = \frac{N}{D'} \cdot (e^{\lambda t_1} - e^{\lambda t_2}) \]

For example,

\[ \frac{[^{206}\text{Pb}/^{204}\text{Pb}]} - \frac{[^{206}\text{Pb}/^{204}\text{Pb}]}{1} = \]

\[ \frac{[^{238}\text{U}/^{204}\text{Pb}]} \cdot (e^{\lambda t_1} - e^{\lambda t_2}) \]
## Decay Constants

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$\lambda \left(10^{-9} \text{ y}^{-1}\right)$</th>
<th>$t_{1/2} \left(10^{-9} \text{ y}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{U} \rightarrow ^{206}\text{Pb}$</td>
<td>0.1551</td>
<td>4.468</td>
</tr>
<tr>
<td>$^{235}\text{U} \rightarrow ^{207}\text{Pb}$</td>
<td>0.9849</td>
<td>0.7038</td>
</tr>
<tr>
<td>$^{232}\text{Th} \rightarrow ^{208}\text{Pb}$</td>
<td>0.04948</td>
<td>14.01</td>
</tr>
<tr>
<td>$^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$</td>
<td>0.0142</td>
<td>48.81</td>
</tr>
<tr>
<td>$^{147}\text{Sm} \rightarrow ^{143}\text{Nd}$</td>
<td>0.00654</td>
<td>106</td>
</tr>
</tbody>
</table>

335
ARABIAN REGION

LEAD TYPE

- OPHIOLITE
- ENSIMATIC ARC
- 630 Ma DIORITES
- MANTLE—L. CRUST MIX
- OLDER CONTINENT
Gold Hill, Utah

Southern stock (Jurassic)
- Feldspar
- Galena

$T_0 = 3700 \text{ Ma, } \mu_0 = 9.74$
$T_1 = 2700 \text{ Ma, } \mu_1 = 11.66$
$T_2 = 1640 \text{ Ma, } \mu_2 = 12.07$
$T_3 = 150 \text{ Ma}$

Northern stock (Oligocene)
- Feldspar
- Galena

$T_0 = 3700 \text{ Ma, } \mu_0 = 9.74$
$T_1 = 2700 \text{ Ma, } \mu_1 = 12.74$
$T_2 = 1640 \text{ Ma, } \mu_2 = 7.36$
$T_3 = 38 \text{ Ma}$
Gold Hill, Utah

Southern stock (Jurassic)

- Feldspar
- Galena

\[ T_0 = 3700 \text{ Ma, } \kappa_0 = 3.78 \]
\[ T_1 = 2700 \text{ Ma, } \kappa_1 = 4.31 \]
\[ T_2 = 1640 \text{ Ma, } \kappa_2 = 4.16 \]
\[ T_3 = 150 \text{ Ma} \]

Northern stock (Oligocene)

- Feldspar
- Galena

\[ T_0 = 3700 \text{ Ma, } \kappa_0 = 3.78 \]
\[ T_1 = 2700 \text{ Ma, } \kappa_1 = 4.00 \]
\[ T_2 = 1640 \text{ Ma, } \kappa_2 = 6.01 \]
\[ T_3 = 38 \text{ Ma} \]
JAPAN - A MODERN OROGEN

**TOTAL OROGENE**

**UPPER CRUST**

**PROXIMAL OROGENE**

**DISTAL OROGENE**

**MANTLE**

**SUBCRUST**

**MANTLE WEDGE**

**LOWER CRUST**

**MORB**

**EASTERN CHINA MANTLE LITHOSPHERE**

** подписи:**

$\varepsilon_{Nd} = +6$ to $-4$

$\varepsilon_{Sr} = -16$ to $+12$
Linju, Shandong Province

$^{207}$Pb / $^{204}$Pb vs. $^{206}$Pb / $^{204}$Pb

15.2 to 19.0
Consider the two uranogenic decay equations

\[
\left[\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right]_2 - \left[\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right]_1 = \left[\frac{^{238}\text{U}}{^{204}\text{Pb}}\right] \cdot (e^{\lambda t_1} - e^{\lambda t_2})
\]

\[
\left[\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right]_2 - \left[\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right]_1 = \left[\frac{^{235}\text{U}}{^{204}\text{Pb}}\right] \cdot (e^{\lambda t_1} - e^{\lambda t_2})
\]

Dividing, we have

\[
\frac{\left[\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right]_2 - \left[\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right]_1}{\left[\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right]_2 - \left[\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right]_1} = \frac{(e^{\lambda t_1} - e^{\lambda t_2})}{137.88 \cdot (e^{\lambda t_1} - e^{\lambda t_2})}
\]

For \( t_2 = 0 \) (today)

\[
\frac{\left[\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right]_2 - \left[\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right]_1}{\left[\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right]_2 - \left[\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right]_1} = \frac{(e^{\lambda t_1} - 1)}{137.88 \cdot (e^{\lambda t_1} - 1)}
\]
If we knew the parent and daughter element contents (actually parent-daughter ratio) and daughter element isotopic composition of the Earth at its time of formation, we would also know the average present-day isotopic composition of the daughter element. That is, despite the chemical fractionation and isotopic heterogeneity of its various reservoirs, the bulk Earth must have an isotopic composition commensurate with its overall parent-daughter ratio. Regarding the troika, it is commonly assumed that (1) the bulk Earth's rare-earth elements are unfractionated compared to chondritic abundances \( \frac{^{147}\text{Sm}}{^{144}\text{Nd}} = 0.1967 \), (2) the bulk Earth's Rb/Sr may be determined from the coupled \( \varepsilon_{\text{Nd}}(\theta) - \varepsilon_{\text{Sr}}(\theta) \) diagram for young basalts \( \frac{^{87}\text{Rb}}{^{86}\text{Sr}} = 0.0816 \), and (3) \( \frac{^{238}\text{U}}{^{204}\text{Pb}} \) must be about 9, although its exact value is not known; however, the coupled \( ^{238}\text{U} - ^{235}\text{U} \) decay schemes demand that bulk Earth lies on the Geochron.
Problems with Bulk Earth Constraints

1. Are important reservoirs hidden and/or isolated?

2. Did the Earth have an 'instantaneous' origin?

3. Are the bulk Earth's rare-earth elements unfractionated?

4. How valid is the assumption that the Sm-Nd and Rb-Sr systems are coupled?

5. How accurately can we determine the parent and daughter element contents and daughter element isotopic composition of individual reservoirs; i.e., can a meaningful summation of the parts be made so as to equal the whole?
## Decay Constants

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$\lambda \text{ (10}^{-9} \text{ y}^{-1})$</th>
<th>$t_{1/2} \text{ (10}^{9} \text{ y})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{U} \rightarrow ^{206}\text{Pb}$</td>
<td>0.1551</td>
<td>4.468</td>
</tr>
<tr>
<td>$^{235}\text{U} \rightarrow ^{207}\text{Pb}$</td>
<td>0.9849</td>
<td>0.7038</td>
</tr>
<tr>
<td>$^{232}\text{Th} \rightarrow ^{208}\text{Pb}$</td>
<td>0.04948</td>
<td>14.01</td>
</tr>
<tr>
<td>$^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$</td>
<td>0.0142</td>
<td>48.81</td>
</tr>
<tr>
<td>$^{147}\text{Sm} \rightarrow ^{143}\text{Nd}$</td>
<td>0.00654</td>
<td>106</td>
</tr>
</tbody>
</table>
STACEY (1986)

**DEFINE PARAMETERS**

\[ \delta (6/4) = \frac{X_f - X_t}{X_t - X_o} \times 1000 \quad \delta (7/4) = \frac{Y_f - Y_t}{Y_t - Y_o} \times 1000 \]

**FOR** \( t = 0 \text{ Ga} \)

\[ \delta (6/4) = \frac{X_f - X_t}{7.548} \times 1000 \quad \delta (7/4) = \frac{Y_f - Y_t}{2.630} \times 1000 \]
ZARTMAN & STACEY (1992)

\[ \delta (6/4) = \frac{X_f - X_t}{X_t} \times 1000 \]

\[ \delta (7/4) = \frac{Y_f - Y_t}{Y_t} \times 1000 \]

For \( t = 0 \text{ Ga} \):

\[ \delta (6/4) = \frac{X_f - X_t}{18.700} \times 1000 \]

\[ \delta (7/4) = \frac{Y_f - Y_t}{15.628} \times 1000 \]