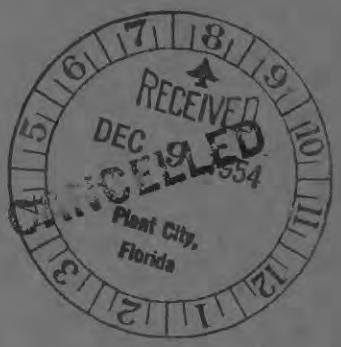

COMPARISON OF RADIOGENIC HELIUM AND LEAD IN ZIRCON

By Patrick M. Hurley, Esper S. Larsen, Jr., and David Gottfried

---

Trace Elements Investigations Report 475

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

IN REPLY REFER TO:

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

DEC - 7 1954

AEC-407/5

Dr. T. H. Johnson, Director
Division of Research
U. S. Atomic Energy Commission
16th Street and Constitution Avenue, N. W.
Washington 25, D. C.

Dear Dr. Johnson:

Transmitted herewith is one copy of TEI-475, "Comparison of radiogenic helium and lead in zircon," by Patrick M. Hurley, Esper S. Larsen, Jr., and David Gottfried, November 1954.

We plan to submit this report for publication in Geochimica et Cosmochimica Acta.

Sincerely yours,

Dwight M. Common

for W. H. Bradley
Chief Geologist

Geology and Mineralogy

This document consists of 12 pages.
Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

COMPARISON OF RADIOGENIC HELIUM AND LEAD IN ZIRCON*

By

Patrick M. Hurley, Esper S. Larsen, Jr., and David Gottfried

November 1954

Trace Elements Investigations Report 475

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

*This report concerns work done on behalf of the Division of Research of the U. S. Atomic Energy Commission.

USGS - TEI-475

GEOLOGY AND MINERALOGY

Distribution (Series A)	No. of copies
Argonne National Laboratory	1
Atomic Energy Commission, Washington	2
Battelle Memorial Institute, Columbus	1
Carbide and Carbon Chemicals Company, Y-12 Area	1
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Butte	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Douglas	1
Division of Raw Materials, Hot Springs	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, Phoenix	1
Division of Raw Materials, Richfield	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Washington	3
Division of Research, Washington	1
Dow Chemical Company, Pittsburg	1
Exploration Division, Grand Junction Operations Office	1
Grand Junction Operations Office	1
National Lead Company, Winchester	1
Technical Information Service, Oak Ridge	6
Tennessee Valley Authority, Wilson Dam	1
U. S. Geological Survey:	
Alaskan Geology Branch, Menlo Park	1
Fuels Branch, Washington	1
Geochemistry and Petrology Branch, Washington	15
Geophysics Branch, Washington	1
Mineral Deposits Branch, Washington	1
E. H. Bailey, Menlo Park	1
A. L. Brokaw, Grand Junction	1
J. R. Cooper, Denver	1
N. M. Denson, Denver	1
C. E. Dutton, Madison	1
W. L. Emerick, Plant City	1
L. S. Gardner, Albuquerque	1
M. R. Klepper, Spokane	1
A. H. Koschmann, Denver	1
R. A. Laurence, Knoxville	1
D. M. Lemmon, Washington	1
J. D. Love, Laramie	1
V. E. McKelvey, Menlo Park	1
P. C. Patton, Denver	1
J. F. Powers, Salt Lake City	1
Q. D. Singewald, Beltsville	1
J. F. Smith, Jr., Denver	1
A. E. Weissenborn, Spokane	1
TEPCO, Denver	2
TEPCO, RPS, Washington (Including master)	2
	70

COMPARISON OF RADIOGENIC HELIUM AND LEAD IN ZIRCON

By

Patrick M. Hurley, Esper S. Larsen, Jr., and David Gottfried

ABSTRACT

A direct comparison of helium and lead in nonmetamict zircon crystals has indicated a 25 percent discrepancy between these radiogenic constituents. It appears that the amount of helium is only three-quarters of the amount that should be present according to the content of lead. Approximately the same proportion was found in zircon having a wide range in age, activity, and total alpha irradiation and in large pegmatite zircon crystals as well as microscopic crystals from igneous rocks.

A study of helium age-ratios in zircon and sphene by Hurley (1952) seemed to indicate a uniform increase of helium loss from these minerals as the minerals had undergone increasing amounts of total alpha irradiation. Subsequent investigations revealed that in most samples of higher radioactivity the material is not homogeneous, some parts of the material being more radioactive and more damaged, or altered, than others. In the samples tested previously it was therefore not possible to obtain a precise relationship between alpha radiation damage and helium loss. In particular it was not clear whether helium ratios would agree exactly with lead ratios in material that had undergone negligibly small amounts of radiation damage, and if so, at what level of damage the helium would start to escape. It was believed that helium loss might prove to be a good indicator of the changes that occur in the process of metamictization.

A suite of gem zircon crystals from Ceylon seemed to be ideal for testing this question of helium retention. The radiogenic lead had been determined on these samples, which covered a wide range of radioactivity and therefore radiation damage. All of the samples showed the same lead age, approximately 600 million years, within limits of accuracy of the measurements. The samples were also reported to show a systematic variation in index of refraction, specific gravity, (Gottfried, 1953) and unit cell dimensions, in relation to an increasing amount of radiation damage (Holland and Gottfried, manuscript in process).

The results of the helium measurements on the Ceylon zircons are shown in table 1. The first seven samples, covering a range in irradiation from 94 to 593 x 10^{13} α/mg, all show the same helium ratio within the limits of experimental error. From a knowledge of the radiogenic lead in each of these samples, it is found that the helium is only 77 percent of the amount that should be present and that this proportion does not vary despite the range of damage in the samples. In the eighth sample (no. 3038), the irradiation was up to 1070 α/mg and the helium ratio showed the expected drop that had been observed in previous work.

A second suite of zircon samples of very different characteristics was tested in the same way. This suite is part of a group studied to determine the age of the Southern California, Sierra Nevada, and Idaho batholiths by the lead ratio method (Larsen et al., 1954). The samples were considered to be of interest for this helium investigation because they all showed agreement in lead age (average 105 million

Table 1.--Helium ratios of Ceylon zircon of different activities.

Sample no.	USGS no.	Alpha activity α/mg/hr	Total irradiation 10^{13} α/mg	Helium 10^{-5} cc/g	Helium age-ratio (million years)
3031	4-33	182	94	2560	435
3001	1/	344	177	5400	485
3002	1/	401	207	6490	495
3036	3-11	525	270	7850	460
3035	2-37	678	349	10400	475
3037	2-18	890	458	13130	455
3027	2-17	1150	593	17000	455
3038	1-2	1870	1000	7870	130

Average helium age-ratio of first seven samples: 466 million years

Average lead age-ratio of first seven samples: 600 million years

Helium ratio/lead ratio 0.77

1/ Samples supplied by H. Holland, Princeton University.

years) and are nonmetamict, microscopic, accessory zircon, as opposed to the large gem crystals from Ceylon. The samples were not all homogeneous and a few of them had to be treated with hot 1:1 aqua regia to remove highly radioactive grains that may have been thorite. However, after acid treatment the crystals remaining were low enough in both activity and age so that the radiation damage was within the range of interest.

The results of the helium measurements on these samples are given in table 2.

Crystals of accessory zircon in igneous rocks are small enough so that a significant fraction of the alpha particles emerge from the crystals before coming to rest. This fraction is measured by a count of alpha particles per unit time emitted by a single layer of whole crystals of known weight. Thus if I is the total activity of a sample of accessory zircon, and E is the whole-space whole-crystal emission, then I minus E gives the rate at which the number of helium atoms is increased within the boundaries of the zircon crystals.

From the results in table 2 it again appears that the radiogenic helium is a constant proportion of the amount that should be present according to the radiogenic lead. In this case the proportion averages 70 percent, despite a range in irradiation from 11 to 66 x 10^{13} α/mg, which again indicates that an extrapolation to zero radiation damage would still give the same fraction.

Table 3 gives the helium ratios on a group of pegmatite zircon samples from Ontario. These samples are very low in activity (Hurley, 1952) and therefore they probably do not contain highly radioactive zones or inclusions. They have been remeasured after acid treatment to remove any possible traces of highly active contaminant. They have

Table 2.--Helium ratios of accessory zircon from the Southern California, Sierra Nevada, and Idaho batholiths.

Sample no 1/	Alpha activity (α/mg/hr) I	Whole crystal emission (α/mg/hr) E	Rate of helium increase (α/mg/hr) I - E	Total irradiation 2/ 10^{13} α/mg	Helium 10^{-5} cc/g	Helium age-ratio (million years)
			Southern California batholith			
3026	160	55	105	14.7	233	68
1986A	182	49	133	16.7	272	63
3033	184	48	135	16.9	342	78
1989A	237	73	164	21.8	382	72
3025	452	150	303	41.6	803	82
3030	545	183	362	50.0	805	68
1890	725	210	515	66.5	1265	76
			Sierra Nevada batholith			
1988A	260	46	214	23.9	566	81
1990A	523	172	351	48.0	805	71
			Idaho batholith			
1908	122	20	102	11.2	244	74
1893A	134	20	114	12.3	256	72

Average helium age-ratio: 73
Average lead age-ratio: 105
Helium ratio/lead ratio: 0.70

1/ For sample descriptions, see next page.
2/ Alpha activity times age.

Table 2.--Helium ratios of accessory zircon from the Southern California, Sierra Nevada, and Idaho batholiths--Continued.

Sample no.	USGS no.	Sample Notes
3026	G-11	Green Valley quartz diorite. Southern California batholith.
1986A	G-15	Granite of Cottonwood Springs, Southern California batholith. Treated with aqua regia.
3033	S-1	Lakeview quartz diorite, Southern California batholith.
1989A	G-13 (Acid)	La Posta quartz diorite, Southern California batholith. Treated with aqua regia.
3025	S-2	Woodson granodiorite, Southern California batholith.
3030	G-48T	Stonewall quartz diorite, Southern California batholith. Treated with acid.
1890	Z-14B	Rubidoux granite, Southern California batholith.
1988A	PB-7	Palisade granodiorite, Sierra Nevada, Treated with aqua regia.
1990A	PB-1	Albite granite near Bishop, Calif. Sierra Nevada. Treated with aqua regia.
1908	Z-39A	Zircon concentrate from stream placer sands from the Idaho batholith. Treated with hot 1:1 aqua regia.
1893A	Z-39	Another sample from same locality as above. Treated with aqua regia.

Table 3.--Helium ratios of low activity zircon from Ontario pegmatites. Similar samples from the same district have been dated by lead ratios.

Sample no.	Locality	Alpha activity (α/mg/hr)	Helium 10^{-5} cc/g	Helium age-ratio (million years)
1659	Renfrew County, Ontario	31	780	770
1777	Do.	32	797	770
1660	Brudenell Township, Ontario	32	742	715
1681	S. Burgess, Leeds County, Ontario	32	715	700
1670	Lanark County, Ontario	68	1618	730
1901	Fresh part of zoned zircon from Oklahoma (treated with acid)	150	2190	450
	Average lead age of same crystal: 635 million years Helium ratio/lead ratio 0.71			

Average helium age-ratio of first five samples: 737 million years

Average lead age of pegmatites from same region: 1000 million years

Helium ratio/lead ratio 0.73

been included in this investigation, together with the fresh part of a sample of zoned zircon from Oklahoma (Larsen, Waring, and Berman, 1953), because of a good knowledge of their age by lead ratio determination. Again it appears that the average helium ratio is approximately three-quarters of the value that would be expected according to the age and activity of the sample.

The accuracy of the measurements listed in the tables must be stated in qualitative terms. The measurements of activity have a basic precision set by counting statistics: generally counts are made so that this error is not greater than 2 percent standard deviation. In addition, a variation in source area and in inhomogeneity in the sample may raise the total error in precision to about 5 percent per analysis. Exceptionally inhomogeneous material may show greater variations. The determination of the activity in thick sources of the samples requires the use of a source absorption factor. In zircon, a factor of 0.493 was calculated for the conversion from $\alpha/cm^2/hr$ to $\alpha/mg/hr$ for an assumed Th/U ratio of 1. This factor is known to be approximately correct from independent measurements of uranium and thorium. However, in this investigation an error in this factor, or in the activity measurements themselves, is not significant as the same values are used for both the helium and lead ratios.

The helium measurements normally have a precision of about 6 percent as determined by replicate measurements of materials containing amounts of helium in this range. The absolute accuracy of the helium analysis is believed to be within 5 percent. The McLeod gauge was calibrated well within this limit by weight of mercury; and the calibration of the entire analysis procedure, using measured samples of helium introduced

in blank fusions, has established the calibration constant for the system over a period of years. An independent measurement using a new pipette for the introduction of a known amount of helium gave a result agreeing within 3 percent of the standard calibration value. As the helium analyses listed show the same ratio despite a variation in helium content of the sample from 240 to 17,000 x 10^{-5} cc/g, there seems to be little possibility that the analyses are low because of incomplete release of helium in the fusion.

A process of helium loss that would leave the same proportion of helium remaining in the crystalline material despite differences in helium content and age, is not yet visualized by the authors. The question will have to remain open until other evidences can be brought to bear on it.

ACKNOWLEDGMENTS

The writers wish to thank Professor Heinrich Holland of Princeton University for the samples supplied by him. This research was conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission. The instruments used in the investigation were made available by the Office of Naval Research, U. S. Department of Defense.

Gottfried, David, 1953, The age and relationships of radioactivity, lead content, and physical properties of zircon crystals from Ceylon (abs.): Am. Geophys. Union Trans., v. 34.

Hurley, P. M., 1952, Alpha ionization damage as a cause of low helium ratios: Am. Geophys. Union Trans., v. 33, p. 174-183.

Larsen, E. S., Jr., Gottfried, David, Jaffe, H., and Waring, C. L., 1954, The age of the Southern California, Sierra Nevada, and Idaho batholiths (abs.): Geol. Soc. America Bull., v. 65 (in press).

Larsen, E. S., Jr., Waring, C. L., and Berman, J., 1953, Zoned zircon from Oklahoma: Am. Mineralogist, v. 38, p. 1118-1125.