United States Department of the Interior

Geological Survey

Abundances of Li, Rb, and Sr in W-2, BCR-1, and AC-E Determined By Isotope Dilution Mass Spectroscopy

by

N. Rait, F. G. Walthall, and J. A. Philpotts

Open-File Report 93-267

1993

Abundances of Li, Rb, and Sr in W-2, BCR-1, and AC-E Determined By Isotope Dilution Mass Spectroscopy

N. Rait, F. G. Walthall, and J. A. Philpotts

Abstract

We have determined abundances of Li, Rb, and Sr in AC-E using isotope-dilution Mass-spectrometery. The well characterized rock standards W-2 and BCR-1 were also analyzed in order to monitor the procedure. AC-E, a microgranite from Ailsa Craig Island (Harrison et al 1987, Potts and Holbrook 1987) in southwest Scotland, is being characterized for use as an international reference standard.

Introduction

The Ailsa Craig (AC-E) microgranite was proposed as a reference material for trace elements by P.J. Potts (1983). This proposal initiated investigations and analyses by various methods and at numerous international laboratories. Resulting data was compiled by Govindaraju (1987). As a contribution to this data base, we have used stable isotope dilution mass spectroscopy to analyze for Li, Rb, and Sr in AC-E. BCR-1 and W-2 were used as standards and analyzed along with AC-E.

Apparatus and Reagents

Mass Spectrometer - 60^{o} National Bureau of Standards (NBS now NIST) solid source circa 1968, equipted with a 15 cm Hall probe
detector - Faraday cup
recorder - Leeds and Northrup Co.* strip chart
Filaments - Rhenium, width = 0.762 mm, thickness = 0.0305 mm, United Mineral and Chemical Corp.*
Ion Exchange Column - polypropylene, 7 mm dia., resin height 9.5 cm
Resin - Bio Rad* Analytical Cation Exchange AG 50W-X8, 100-200 mesh, hydrogen form
Distilled deionized water
6M hydrochloric acid, redistilled
2M hydrochloric acid, from 6M redistilled hydrochloric acid and distilled deionized water
70% Perchloric Acid
48% Hydrofluoric Acid
Spike - Composite of isotopically enriched tracers (Ba, Sr, Rb, Li, rare earths) prepared from Oak Ridge National Laboratory* standards

* Company and trade names are included for information purposes only and do not constitute an endorsement by the U.S. Geological Survey.

Procedure

A three mL solution of the composite spike, was added to the weighed sample in a Teflon* evaporating dish. Then 20 mL of hydrofluoric (HF) acid and 1 mL of perchloric acid ($HClO_4$) were added. The mixture was heated slowly, fumed, evaporated to dryness, and cooled. Fifteen mL of 2M hydrochloric acid (HCl) were added and heated in order to dissolve the residue. The solution was then transferred to a small uncovered bomb and evaporated to dryness. Two mL of 2M HCl were added to the residue, the bomb was covered, heated for one hour, then cooled. The cooled solution was passed through an ion exchange column and eluted, initially with 2N HCl then with 6N HCl. Separate fractions were collected for Li; Rb; Sr; Lu; and the rare earths;however, only Li, Rb, and Sr are discussed in this manuscript. The eluted fractions were collected in polypropylene beakers, and evaporated to dryness on a steam bath. The beakers were then covered with Parafilm* for storage. Two hundred microliters of 2M HCl were added to each fraction in order to dissolve the sample. About 25 uL of this solution were loaded onto each of the two side filaments of a triple rhenium filament source and evaporated to dryness.

The sample was then run on the mass spectrometer. A minimum of three runs, each consisting of about 10 scanning sets of mass spectra, were made for each element. Data was collected for masses 6 and 7 for Li; 85 and 87 for Rb; and 84, 86, 87, and 88 for Sr. A single scanning set for an element consists of a spectra being scanned (by varying the magnetic field current) from low mass to high mass then from high mass back down to the low mass. The temperature of the filaments was increased for each run by varying filament current. The concentrations of Li, Rb, and Sr in each sample were calculated (Philpotts 1991) using appropriate isotopic compositions and concentrations. The mean values and standard deviations were calculated for each run, and the averages and standard deviations (Tables 1,2,3) were calculated from all the run means. All results not within two standard deviations of the mean were dropped and a new mean (preferred mean) was calculated. The working results for Li, Rb, and Sr for AC-E were calculated from reported data compiled by K. Govindaraju (1987).

Calculations

The following definitions are used in the equations.
E denotes element
X = Isotope X
Y = Isotope Y
R = ratio of isotope X to isotope Y
n denotes sample
s denotes spike
N = micrograms of normal element E in sample (to be determined)
S = micrograms of spike element E added to the sample (known)
$(\%^{X}E)_n$ = % weight abundance of isotope X in normal element E
$(\%^{Y}E)_n$ = % weight abundance of isotope Y in normal element E
$(\%^{X}E)_s$ = % weight abundance of isotope X in spike
$(\%^{Y}E)_s$ = % weight abundance of isotope Y in spike

The measured ratio of isotope X to isotope Y is given by eq. 1

$$1)\ R = \frac{\text{peak height isotope X} - \text{background at isotope X}}{\text{peak height isotope Y} - \text{background at isotope Y}} * \frac{\text{scale factor X}}{\text{scale factor Y}}$$

The scale factors include any correction factors.
If the isotopes represent a single element and there are no additional correction factors (eg. mass fractionation) then

$$2)\ R = \frac{N * (\%^{X}E)_n + S * (\%^{X}E)_s}{N * (\%^{Y}E)_n + S * (\%^{Y}E)_s}$$

Since the quantities of each isotope of an element varies, their ion current will vary. By varing the resistance to the input current for each isotope the recorder scale will change (White 1968).

3) N/S can be solved for from eq. 2.

$$\frac{N}{S} = \frac{(\%^{X}E)_{s} - R * (\%^{Y}E)_{s}}{R * (\%^{Y}E)_{n} - (\%^{X}E)_{n}}$$

The micrograms N of element E in the sample is the only unknown in eq. 3.

Solving eq. 3 for N,

$$4)\ N = \frac{(\%^{X}E)_{s} - R * (\%^{Y}E)_{s}}{R * (\%^{Y}E)_{n} - (\%^{X}E)_{n}} * S = \text{total ug of E}$$

$$5)\ \text{ppm of E in sample} = \frac{\text{N in ug - blank in ug}}{\text{Wt. sample in grams}}$$

Results

The results of the analyses for Li, Rb, and Sr in W-2, BCR-1, and AC-E are listed in Tables 1, 2, and 3, respectively. The values for Li, Rb, and Sr in a single blank analysis are listed in Table 3. The standard deviation are counting errors only. The values found for Li in W-2, BCR-1, and AC-E were 9.12 ppm, 13.2 ppm, and 94.9 ppm, respectively. They are within the range of the recomended values (Flanagan 1984, Gladney et al 1990, Flanagan 1976, Govindaraju 1987.), of 9.56 ± 0.54 ppm, 12.9 ± 0.4 ppm, and 95.8 ± 4.4 ppm, respectively. The values found for Rb in W-2, BCR-1, and AC-E were 19.6 ppm, 46.9 ppm, and 146 ppm, respectively; the recomended values are 20.9 ± 1.1 ppm, 47.2 ± 0.6 ppm, and 152 ± 6 ppm, respectively. The Rb value for AC-E is within 2 standard deviations of the recomended value. The Sr values for W-2, BCR-1, and AC-E were 207 ppm, 319 ppm, and 1.81 ppm, respectively. The Sr recomended values are 192 ± 3 ppm, 330 ± 5 ppm, and 3 ± 1 ppm, respectively. The Sr value for BCR-1 is at the lower boundary of twice the standard deviation.The recomended value for Sr in AC-E which had been calculated from 61 analyses varied from 1 ppm to 13 ppm (Govindaraju, 1987), and as a result, the recomended value may not be valid due to sample inhomogenity. The value for Sr in AC-E is within 2 standard deviations of the recomended value.

References

Sidney Abby,1983, Studies in "Standard Samples" of Silicate Rocks and Minerals 1969-1982: Geological Survey of Canada Commission Geologique du Canada, paper 83-15, pp 114.

F.J. Flanagan, 1976, Descriptions and analysis of eight new U S G S Rock Standards: Geological Survey Professional Paper 840, pp 192.

F.J. Flanagan, 1984, Three U S G S Mafic Rock Reference Samples, W-2, DNC-1, and BIR-1: U. S. Geological Survey Bulletin 1623, pp 54.

E. S. Gladney, E. A. Jones, E. J. Nichell, and I. Roelandts, July 1990, 1988 Compilation of Elemental Concentration Data for U. S. G. S. Basalt BCR-1: Geostandards Newsletter, Vol 14 no. 2, p 209 to 359.

K. Govindaraju, October 1987, 1987 Compilation Report on Ailsa Craig Granite AC-E with Participation of 128 GIT-IWG Laboratories: Geostandards Newsletter Vol 11 no.p 203 to 255.

R.K. Harrison, P. Stone, I.B. Cameron, R.W. Elliot and R.R. Harding, 1987, Geology, petrology and geochemistry of Ailsa Craig, Aylshire: British Geological Survey Report Vol. 16 #9, pp 29.

J. A. Philpotts, 1991, Isotope Dilution Mass Spectrometry,
P. A. Baedecker Ed., Methods for Geochemical Analysis,
U. S. Geological Survey Bulletin 1770, p k1-k5.

P.J. Potts, 1983, Proposal for the Adoption of a Microgranite from Ailsa Craig, S.W. Scotland as a Trace Element Rock Reference Sample: Geostandards Newsletter, Vol.7 no 2, p 345 to 346.

P. J. Potts and J. R. Holbrook, October 1987, Ailsa Craig - The History of a Reference Material, Geostandards Newsletter, Vol. 11, No. 2, p 257 to 260.

F.A. White, 1968, Mass Spectrometry in Science and Technology, John Wiley and Sons, Inc., New York, pp 352.

Table 1. Li, Rb, and Sr determined in W-2 compared to their recomended values.

W-2 values in ppm			weight W-2 = 0.13985 g
element(E)	determined	recomended (1)	(E in blank /E in sample)%
Li	9.12 ± 0.08	9.56 ± 0.54	0.059
Rb	19.6 ± 0.1	20.9 ± 1.1	0.110
Sr	207 ± 5	192 ± 3	0.023

1) F.J. Flanagan 1984

Table 2. Li, Rb, and Sr determined in BCR-1 compared to their recomended values.

BCR-1 values in ppm			weight BCR-1=0.12573 g
element	determined	recomended (1,2)	(E in blank/E in sample)%
Li	13.2 ± 0.6	12.9 ± 0.4, 12.8	0.045
Rb	46.9 ± 1.6	47.2 ± 0.6, 46.6	0.005
Sr	319 ± 4	330 ± 5, 330	0.016

1) E. S. Gladney et al 1990
2) F.J. Flanagan 1976

Table 3. Li, Rb, and Sr determined in AC-E compared to their recomended values, and the blank values for Li, Rb, and Sr.

AC-E values in ppm			weight AC-E = 0.14056 g	
element	determined	recomended (1)	ug Blank	E in blank / E in sample %
Li	94.9 ± 2.5	95.8 ± 4.4	0.020	0.006
Rb	146 ± 4	152 ± 6	0.003	0.002
Sr	1.81 ± 0.02	3 ± 1	0.120	2.59

1)Data from K. Govindaraju, 1987. Instead of using the median value given, statistical calculations were made on the data given. All values greater then two standard deviations were dropped.