Lead isotopic composition in the geochemical reference rock JG-1

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The isotopic composition of lead in the geochemical reference rock JG-1 (granodiorite), which was prepared and distributed by the Geological Survey of Japan, was determined in this study by surface ionization mass spectrometry using ultra-clean analytical techniques. A large numbers of data on the concentrations of trace metals in the JG-1 reference sample was compiled and in many metals the consensus means and/or average values were given by Ando et al. (1974). The JG-1 is available as a reference material for concentration measurements of many elements in silicate rocks and it would be advantageous to use this reference sample for isotopic analyses as well. Isotopic compositions of metals in this standard rock have been reported for strontium, whose $87/86$ ratios determined by several investigators agree with each other within analytical errors (Ando et al., 1974). In order to obtain reliable isotopic composition data of lead in rocks and minerals which contain Pb concentration levels of $\mu\text{g/g}$ or less, it is necessary not only to accurately measure its ratios but also to practice strict contamination control during sample preparation by using the clean analytical techniques in a clean laboratory. It should be realized that there may be a significant error in isotopic Pb data because of artificial lead contamination to a sample

by the blanks from reagents and laboratory equipment used, by Pb aerosol in a room and by the analyst himself through handling and analytical processes if he treats it with conventional chemicals and articles in an ordinary laboratory. The isotopic composition of lead in JG-1 presented here was determined using a high resolution surface thermal ionization mass spectrometer and microanalytical methods of strict contamination control at ultra-clean laboratory.

Sample preparation and chemical analysis

An aliquot of rock powder of the JG-1 (split 7 position supplied by the G.S.J.) was taken and finely ground in an agate mortar, which was washed before with dilute hydrofluoric acid, nitric acid and doubly quartz-distilled water (QDW) at a clean laboratory at the Muroran Institute of Technology. The fine powder was stored until further aliquotting in an acid-cleaned (Patterson and Settle, 1976a) polyethylene bottle which was triple wrapped with acid-cleaned polyethylene bags to keep it free from lead contamination.

Chemical separation and purification of lead in the sample was carried out at the ultra-clean laboratory of Dr. C.C. Patterson at the California Institute of Technology. A

20 to 50 mg aliquot of the material in the bottle was placed into an FEP teflon beaker using a stainless steel spatula cleaned with hot nitric acid. A mixture of HNO_3 , HClO_4 and HF was added to the sample. The beaker was covered with a teflon watchglass and stood at room temperature for several hours. Then the beaker from which the cover was removed was placed in a TFE-teflon oven flushed with filtered nitrogen gas, and was heated until strong fumes of perchloric acid formed. One milliliter of HF was added to the sample which was then evaporated to dryness. The residue was twice redissolved with conc. nitric acid and evaporated again to convert any perchlorates to nitrates, then redissolved in dilute nitric acid, and transferred into a teflon separately funnel. The lead from this aqueous solution was extracted into a dithionite-chloroform solution at pH 9 in the presence of both $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and KCN. The separated chloroform layer was washed with slightly ammoniated QDW and back-extracted with dilute nitric acid. The sample solution was further purified by repeating the extraction procedure and dithionite traces were removed from the aqueous phase by washing it with CHCl_3 . The final solution was drained into an FEP beaker, evaporated to dryness inside a teflon oven in an atmosphere of pure N_2 . The remaining spec of sample residue was dissolved with several μl of QDW and loaded onto an outgassed rhenium filament with silica gel and phosphoric acid for analysis in a mass spectrometer.

Prior to the extraction procedure, the separately funnel used was preconditioned by extracting the QDW, adjusted to pH 9, with Dz-CHCl_3 . This particular step reduces effectively the level of the Pb blank contributed by the funnel (D. Settle,

personal communication, 1980). The level of artifact Pb contamination from teflon containers and transfer quartz pipettes used is largely lowered by soaking them for several days in three acid baths which contain concentrated analytical grade, 1% triply distilled, and 0.1% purest nitric acids, respectively (Patterson and Settle, 1976a). Throughout the sample preparation and analytical processes the laboratory articles were touched and handled only with untalced polyethylene gloves. As a result of these and other measurements of contamination control (Patterson and Settle, 1976a, b), the total procedural contamination of lead was evaluated to be insignificant with respect to samples containing tens of ng of Pb or more: the overall contamination effects are estimated to be less than 1 ng Pb.

Mass spectrometry and results

A high resolution surface thermal ionization mass spectrometer equipped with an automatic digital reading and computation system was used to determine the Pb isotopic composition at the Caltech laboratory. Isotope ratio determinations of 206/208, 206/207 and 206/204 were made at three different filament temperatures. At a given filament temperature sets of ten peak height measurements (10 seconds integration time during scanning) were done, first for the ratios of 206/208 and 206/207, subsequently for 206/204. Baseline readings were taken immediately before and after each data set. The mean ratios were corrected for shunt errors and for velocity discrimination effect (root mass) since an electron multiplier was used. The isotopic ratios of lead in the reference material were calculated for each analysis by averaging the corrected means of these data sets.

Table 1-a Lead isotope ratios of the JG-1 rock standard, obtained by five individual analyses

Sample size(mg)	Sample run	206/208	206/207	206/204
48	1	0.48130 $\pm$ 0.000145*	1.1914 $\pm$ 0.00046*	18.479 $\pm$ 0.0382*
29	2	0.48084 $\pm$ 0.000121	1.1907 $\pm$ 0.00097	18.450 $\pm$ 0.0337
36	3	0.48095 $\pm$ 0.000101	1.1915 $\pm$ 0.00009	18.490 $\pm$ 0.0152
22	4	0.48102 $\pm$ 0.000117	1.1918 $\pm$ 0.00035	18.515 $\pm$ 0.0128
31	5	0.48077 $\pm$ 0.000206	1.1908 $\pm$ 0.00070	18.496 $\pm$ 0.0240
	mean	0.48098 $\pm$ 0.000205	1.1912 $\pm$ 0.00047	18.486 $\pm$ 0.0240

* Standard deviation (2σ).

Table 1-b Calculated ratios

Sample run	207/204	208/204
1	15.510	38.393
2	15.495	38.371
3	15.518	38.444
4	15.536	38.492
5	15.533	38.471
mean	15.518 $\pm$ 0.0168*	38.434 $\pm$ 0.0512*

* Standard deviation (2σ).

Five aliquots of the powder (20 to 50 mg each) were individually processed and analyzed within a couple of weeks. The results obtained are listed in table 1-a. In most sample run the ratios 206/208 and 206/207, and 206/204 were determined with a precision better than $\pm 0.06\%$ and $\pm 0.1\%$ in relative standard deviation (2σ), respectively. The table 1-b represents the 207/204 and 208/204 ratios calculated from the data given in the table 1-a. In spite of relatively small sample sizes, the isotope ratios obtained in five individual experiments were in good agreement. The average isotopic composition of the reference sample and the overall limit of uncertainty (2σ) are given in the bottom line of table 1-b. The result presented here suggests that even if an aliquot of tens of mg is taken from a sample powder to be analyzed, it would be able to precisely determine its

Pb isotope ratio if the sample material is reduced very finely, mixed thoroughly and treated chemically in lead contamination free environment, and that the JG-1 sample can be used as a suitable reference material for evaluating an analytical method, from sample preparation through mass spectrometer run, employed to measure isotopic composition of lead in a given silicate rock sample.

I am indebted and sincerely grateful to Dr. Clair C. Patterson at the California Institute of Technology for allowing me to use his ultra-clean laboratory and mass spectrometer, and for his helpful advice and criticism. Thanks are also due to Dr. Bernhard Schaule for reading the manuscript and to Dorothy M. Settle at Caltech for profitable suggestions. The reference standard used in this study was provided by

Dr. Ando of the Geological Survey of Japan.
This work is partly supported by the Toyota Science Fund (Grant 79-1-092).

Reference

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地球化学的標準岩石 JG-1 の鉛同位体比

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厳密に重金属汚染が制御されたクリーン実験室で地球化学的標準岩石 JG-1 (Split 7 position) 中の鉛を抽出・精製し、レニウムシングルフィラメントにシリカゲル及びリン酸とともに塗布後、高分解能表面電離型質量分析計で同位体比を測定した。全分析操作を通じ試料への鉛汚染量は 1 ng 以下に保たれた。20~50 mg ずつ分取した 5 粉末試料の鉛同位体比は変動係数約 0.1% 以内で一致した。得られた同位体比は次の通りである：

206/204; $1.8486 \pm 0.0240^*$, 207/204; 15.518 ± 0.0168 , 208/204; 38.434 ± 0.0512 ,

206/208; 0.48098 ± 0.000205 , 206/207 1.1912 ± 0.00047

*standard deviation (2σ)。