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Differential Lead Retention in Zircons: Implications for Nuclear Waste Containment

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Abstract. *An innovative ultrasensitive technique was used for lead isotopic analysis of individual zircons extracted from granite core samples at depths of 960, 2170, 2900, 3930, and 4310 meters. The results show that lead, a relatively mobile element compared to the nuclear waste–related actinides uranium and thorium, has been highly retained at elevated temperatures (105° to 313°C) under conditions relevant to the burial of synthetic rock waste containers in deep granite holes.*

We report here the measurement of Pb isotope ratios of whole, undissolved zircons, which were loaded directly onto the rhenium filament of a thermal ionization mass spectrometer. This innovation eliminates the Pb contamination introduced in standard chemical dissolution procedures. By using this technique, we were able to measure contamination-free Pb isotope ratios on single, microscopic (~ 50 to 75 μm) zircon crystals, which we estimate contained only ~ 0.2 to 0.5 ng of Pb. We applied this ultralow-level detection method to study the differential retention of Pb in zircons ($ZrSiO_4$) extracted from Precambrian granite core samples (*1*) taken from depths of 960, 2170, 2900, 3930, and 4310 m. These depths correspond to presently recorded temperatures of 105°, 151°, 197°, 277°, and 313°C, respectively (*2*). We measured about the same $^{206}Pb/^{207}Pb$ ratio for zircons from all five depths, and we found that the total number of Pb counts measured per individual zircon was, to the limit of our experimental procedures, independent of depth. Taken together, these results strongly suggest that there has been little or no differential Pb loss which can be attributed to the higher temperatures existing at greater depths. As discussed below, this evidence for high Pb retention under adverse environmental conditions appears to have immediate and practical application to the question of long-term containment of hazardous nuclear wastes.

Samples of granite (*2*) from Los Alamos National Laboratory drill holes GT-2 and EE-2 from all five depths were individually crushed and then passed through different heavy liquid (methylene iodide) separatory funnels to obtain the high-density fraction containing the zircons. This procedure was repeated several times with different samples from each depth. The high-density fraction was then washed thoroughly with acetone to eliminate the methylene iodide residue before being placed on a standard 1 by 3 inch glass microscope slide. Under a polarizing microscope, the zircons were picked out of the high-density fraction with a fine-tipped needle and then loaded either onto pyrolytic graphite disks for ion microprobe analysis or onto V-shaped rhenium filaments, which were mechanically compressed before mass spectrometric measurements. (Surficial residues on the zircons burned off at temperatures well below that used to measure Pb from within the zircons.) Some zircons were analyzed by x-ray fluorescence before mass analysis.

Our efforts to measure lead isotope ratios in zircons with an Applied Research Laboratory ion microprobe failed because of molecular ion interferences. We then concentrated on determining relative abundances of U, Th, and Zr, using mostly an $^{16}O^-$ primary ion beam. Ion count rates were obtained on the $^{90}Zr^+$, $^{232}ThO^+$, and $^{238}UO^+$ peaks. The data were then quantified with sensitivity factors obtained from six different National Bureau of Standards glass standards containing Zr, Th, and U. Two or three zircons from three depths were analyzed, and usually four determinations were made from each zircon. Frequently, there were significant differences in the U and Th concentrations from two different locations on the same zircon. The results are given in Table 1 as a range of values obtained from each zircon.

The most important results came from the thermal ionization experiments. The thermal ionization mass spectrometer used in this work is similar to others described previously (*3*). It has a single magnet with 90° deflection and a 30-cm central radius of curvature. It is equipped with a pulse-counting detection system to allow complete isotopic analyses to be made on small quantities (<1 ng) of suitable elements ionized from a single filament. The filaments, made of V-shaped rhenium foil 0.64 cm long and 0.08 cm deep (*4*), were baked out at 2000°C before loading the zircons. Ions are formed by resistive heating of the filament; typical temperatures for this work were 1400° to 1470°C (uncorrected pyrometer readings).

Table 1. Ion microprobe determinations of U and Th concentration ranges in atomic parts per million on separate zircons from 960, 3930, and 4310 m. Calculations were based on a comparison of $^{238}UO^+$, $^{232}ThO^+$, and Zr^+ peak sizes and on the assumption that the zircons were pure $ZrSiO_4$.

Zircon depth (m)	Th (ppm, atomic)	U (ppm, atomic)
4310	40–85	125–210
4310	63–175	110–550
3930	63–120	83–220
3930	60–90	90–110
960	220–750	465–1130
960	100–275	1250–3300
960	800–2000	240–5300

Previous work done to develop a technique for analyzing small lead samples led to the use of silica gel to enhance ionization efficiency (*5*). Because individual zircons are chemically somewhat similar to silica, we decided to try to analyze lead from individual zircons loaded directly on the rhenium filament. Such a technique would have several advantages over traditional methods: contamination would be essentially eliminated because no chemical separation would be required and, since the zircons are small (~ 50 μm in diameter), they would provide an approximate point source of ions, which is known to optimize ion-optical conditions in the mass spectrometer (*6*).

Test experiments with zircons from other localities (*7*) were uniformly successful; ion signals were observed at masses (*m*) 206, 207, and 208 which could definitely be ascribed to Pb isotopes. To help ensure that we were at the correct ion lens conditions, we focused on the $^{138}BaO^+$ peak (the zircons contained some Ba), which was reasonably intense at 1200°C. Surficial residues left on the zircons after the acetone wash burned off before the operating temperature of 1450°C, where the lead signal was measured. Great care had to be exercised to avoid making the temperature too high; very rapid evaporation of the lead occurred only a little above the operating temperature. Typical count rates were 100 to 3000 counts per second for $^{206}Pb^+$. Traces of thallium ($m = 203$ and 205) were sometimes observed, but burned out more rapidly than the lead. Other than thallium, lead gave the only substantive peaks in the range $m = 202$ to 210. There was, however, a general background generated by the sample; chemically unseparated samples such as these zircons almost always yield such backgrounds. This background has little effect on the 206, 207, and 208 peaks, but made precise measurement of the ^{204}Pb signal, which was very small, impossible. For example, in an analysis typical of these experiments, 1.6×10^5 counts from ^{206}Pb were collected; the back-

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ground correction was about 40 counts and, after correction, 18 counts remained at mass 204. Although these counts are listed as ^{204}Pb counts in Table 2, more work is needed to determine how much may be uncompensated background.

Table 2. Results of thermal ionization mass measurements for zircons with a ^{204}Pb/total Pb ratio of less than 2×10^{-3}. The background correction was taken from the 208.5 mass position; it was applied to the raw data to obtain the isotopic abundances, which were used to compute the isotopic ratios. Standard deviations are listed with the Pb isotopic ratios.

Zircon depth (m)	Filaments analyzed	Average zircons per filament	Total Pb counts	Counts of ^{204}Pb	$\frac{^{204}\text{Pb}}{\text{total Pb}}$	Average ^{206}Pb/^{207}Pb	Range ^{206}Pb/^{208}Pb
960	4	~ 10	1.2×10^{6}	235	2×10^{-4}	9.6 ± 0.3	6.5–9.2
960	4	1	1.3×10^{5}	35	2.7×10^{-4}	9.9 ± 0.4	5.8–14
2170	3	~ 5	8.9×10^{5}	269	3×10^{-4}	10.0 ± 0.4	6.4–12.4
2900	3	~ 4	4.1×10^{5}	114	2.8×10^{-4}	11.2 ± 0.3	4–11.4
3930	2	~ 10	6.5×10^{5}	132	2×10^{-4}	11.0 ± 0.4	5.9–8.7
3930	2	1	8×10^{4}	46	5.8×10^{-4}	10.4 ± 0.1	3.1–6.9
4310	7	~ 10	5.6×10^{6}	1400	2.5×10^{-4}	9.7 ± 0.6	3.4–9.8
4310	2	1	1.6×10^{5}	100	6×10^{-4}	9.8 ± 0.4	4.5–10.7

Table 2 shows the results of our mass analyses of filaments loaded with single and multiple zircons from five granite cores. The range of ^{206}Pb/^{208}Pb values reflects the fact that this ratio varied from one group of zircons to another, and sometimes varied during measurements on a single zircon. These variations are not surprising in view of the ion microprobe analyses, which showed significant U/Th variations at different points on a single zircon (^{232}Th decays to ^{208}Pb and ^{238}U decays to ^{206}Pb). These variable ^{206}Pb/^{208}Pb ratios do not furnish any direct information on differential Pb retention in these zircons. For that purpose, it is generally accepted that the radiogenic ^{206}Pb/^{207}Pb ratios derived from ^{238}U/^{235}U decay are more specific. We note that Zartman's (*8*) isotopic measurements of Pb, which was chemically extracted from zircons taken from the GT-2 core at 2900 m, yield an adjusted ^{206}Pb/^{207}Pb ratio (*9*) that approximates our ratios.

In a conventional chemical extraction of lead from zircons, the lead measured in the mass analysis is considered to be a combination of radiogenic lead (from U and Th decay) and nonradiogenic lead (from common lead contamination and from some initial lead in the zircon). The radiogenic component is obtained by subtracting out a nonradiogenic component proportional to the amount of ^{204}Pb. In our experiments, however, the direct loading procedure virtually eliminated the common lead contamination, and we circumvented the need to make adjustments for initial lead in the zircons by accepting only analyses (*10*) showing a ratio of ^{204}Pb to total Pb of less than 2×10^{-3}. Thus the ^{206}Pb/^{207}Pb ratios shown in Table 2 represent highly radiogenic lead and hence are potential indicators of Pb retention.

We consider that the most important observations on the data in Table 2 are: (i) the fact that the ^{206}Pb/^{207}Pb ratios on single zircons closely approximate the ratio obtained when a group of similar zircons was loaded simultaneously on a single filament, (ii) the relative uniformity of the ^{206}Pb/^{207}Pb ratios for zircons from all depths, and (iii) the fact that the total number of Pb counts per zircon (the counts in column 4 of Table 2 divided by the product of columns 2 and 3) shows no systematic decrease with depth, as would be expected if differential Pb loss had occurred at higher temperatures. Taken together, items (ii) and (iii) provide strong evidence for high Pb retention in zircons even for a prolonged period in an environment at an elevated temperature. These results have possible implications for long-term nuclear waste disposal.

For example, Ringwood (*11, 12*) has suggested that highly radiation-damaged minerals that have successfully retained U, Th, and Pb (*13*) over a significant fraction of earth history might also serve to immobilize high-level nuclear waste in synthetic rock (SYNROC) containers, which could be buried in deep granite holes. Even though zircons are not envisioned as part of Ringwood's special type of synthetic rock waste container, our results are relevant since they show that Pb, which is much more mobile in zircons than U and Th (*12, 14*), has been highly retained at depths (960 to 4310 m) which more than span the proposed burial depths (1000 to 3000 m) for synthetic rock containers in granite (*11*). The inclusion of this elevated temperature effect in our samples means that our results provide data which have heretofore been unavailable in support of nuclear waste containment in deep granite. In addition, the contamination-free method we used to analyze the zircons for radiogenic Pb may prove valuable in searching for other minerals suitable for synthetic rock waste containment.

Because it has been suggested that temperatures in the granite formation are rising (*15*), we do not know precisely how long the zircons have been exposed to the present temperatures. However, by using diffusion theory and the measured diffusion coefficient of Pb in zircon (*16*), we can estimate future loss of Pb by diffusion in synthetic rock–encapsulated zircons buried at the proposed depths of 1000 to 3000 m (*11*) if we assume a temperature profile similar to that in the drill holes. At a burial depth of 3000 m (~ 200°C), we calculate that it would take 5×10^{10} years for 1 percent of the Pb to diffuse out of a 50-μm crystal. At 2200 m (~ 150°C) it would take 7.4×10^{13} years, and at 1000 m (~ 100°C) it would take 7.7×10^{17} years for 1 percent loss to occur (*16*). Since all these values greatly exceed the 10^{5} to 10^{6} years estimated for waste activity to be reduced to a safe level (*11*), and since, as noted earlier, U and Th are bound even more tightly than Pb in zircons (*12, 14*), our results appear to lend considerable support to the synthetic rock concept of nuclear waste containment in deep granite holes.

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9. If the ^{204}Pb in Zartman's (*8*) Pb isotopic abundances in his zircons is attributed to common lead, the corrected ^{206}Pb/^{207}Pb ratio for the zircons from 2900 m is 11.03.
10. This criterion resulted in the rejection of four single zircon analyses whose average ^{206}Pb/^{207}Pb ratio was 8.8 ± 1.3. These lower ratios imply that some zircons contain more initial Pb than others, as noted in some other runs.

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16. In general, if R is the gas constant, T is the absolute temperature, and D and Q are, respectively, the diffusion coefficient and activation energy of a certain nuclide in a given diffusing medium, then $D = D_0\, e^{-Q/RT}$, where D_0 is a temperature-independent parameter. In particular, if C_0 is the initial concentration of that nuclide within a sphere of radius a, then the average nuclide concentration $\overline{C}$ within that sphere at some later time t is given by

$$\overline{C}/C_0 = \frac{6}{\pi^2}\sum_{1}^{\infty}\frac{e^{-(n^2\pi^2 Dt/a^2)}}{n^2}$$

[see L. O. Nicolaysen, *Geochim. Cosmochim. Acta* **11**, 41 (1957)]. We used measured values of $D_0 = 2.2 \times 10^{-2}$ and $Q = 58$ kcal/mole for diffusion of Pb in zircon [see Sh. A. Magomedov, *Geokhimiya* **2**, 263 (1970)] and a computer program to calculate the times when $\overline{C}/C_0 = 0.99$ for $T = 100°$, 150°, and 200°C.

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