

Differential Lead Retention in Zircons: Implications for Nuclear Waste Containment

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 (ZrSiO₄) 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 ²⁰⁶Pb/²⁰⁷Pb 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 graph-

ite disks for ion microprobe analysis or onto V-shaped rhenium filaments, which were mechanically compressed before mass spectrometric measurements. (Surface 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 ¹⁶O⁻ primary ion beam. Ion count rates were obtained on the ⁹⁰Zr⁺, ²³²ThO⁺, and ²³⁸UO⁺ 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

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 ²³⁸UO⁺, ²³²ThO⁺, and Zr⁺ peak sizes and on the assumption that the zircons were pure ZrSiO₄.

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

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).

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 ¹³⁸BaO⁺ peak (the zircons contained some Ba), which was reasonably intense at 1200°C. Surface 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 ²⁰⁶Pb⁺. 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 ²⁰⁴Pb signal, which was very small, impossible. For example, in an analysis typical of these experiments, 1.6 × 10⁵ counts from ²⁰⁶Pb were collected; the back-

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 shows the results of our mass analyses of filaments loaded with single and multiple zircons from five granite cores. The range of $^{206}\text{Pb}/^{208}\text{Pb}$ 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 $^{206}\text{Pb}/^{208}\text{Pb}$ ratios do not furnish any direct information on differential Pb retention in these zircons. For that purpose, it is generally accepted that the radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ratios derived from $^{238}\text{U}/^{235}\text{U}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$ 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

Table 2. Results of thermal ionization mass measurements for zircons with a $^{204}\text{Pb}/\text{total Pb}$ 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	$^{204}\text{Pb}/\text{total Pb}$	Average $^{206}\text{Pb}/^{207}\text{Pb}$	Range $^{206}\text{Pb}/^{208}\text{Pb}$
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

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 ($\sim 200^\circ\text{C}$), 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 ($\sim 150^\circ\text{C}$) it would take 7.4×10^{13} years, and at 1000 m ($\sim 100^\circ\text{C}$) 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 $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for the zircons from 2900 m is 11.3.
10. This criterion resulted in the rejection of four single zircon analyses whose average $^{206}\text{Pb}/^{207}\text{Pb}$ 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 particu-

lar, if C_0 is the initial concentration of that nuclide within a sphere of radius a , then the average nuclide concentration \bar{C} within that sphere at some later time t is given by,

$$\bar{C}/C_0 = \frac{6}{\pi^2} \sum_1^{\infty} \frac{e^{-(n^2\pi^2 D t/a^2)}}{n^2}$$

[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 $\bar{C}/C_0 = 0.99$ for $T = 100^\circ, 150^\circ,$ and 200°C .

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Ramón and Maya Ruins: An Ecological, Not an Economic, Relation

Abstract. *Economically important trees such as ramón have been shown to have a high density in the civic-ceremonial core zone of ancient Maya ruins. The distribution of such trees is probably the result of their requirements for growth and reproduction, which are optimal on the ruins, and not because they are the descendants of trees planted by the Maya aristocracy.*

The role that the *ramón* tree (*Brosimum alicastrum*) played in Maya culture has been the subject of intriguing speculation. Early reports (1) noted that *ramón* is a common tree on all Maya ruins, leading Puleston (2) to propose that *ramón* was a subsistence alternative for the Classic Maya of the central southern lowlands. Puleston also suggested that its occurrence in the ceremonial precincts and on housemounds at Tikal, Guatemala, was evidence of its cultivation in residential areas. Some Mayanists appear to have accepted this proposal (3); others (4) doubt that the Maya would

have depended entirely on such a resource. Folan *et al.* (5) have suggested that the Maya aristocracy maintained and controlled the distribution of economically important fruit, fiber, bark, and resin trees in the city centers. They also contend the present trees are descendants of those planted by the ancient Maya and that their distribution today corresponds to that in Classic times.

Ramón and other economically important species were used by the indigenous people in the past as well as today. But the trees grow on Maya ruins because their requirements for growth and repro-

duction are probably optimal on the ruins, not because the Maya may have cultivated them 1000 years ago. The data from Tikal and from Cobá in the Yucatán, Mexico, we suggest, are probably biased to the *ramón* and associated species (5). If all tree species had been considered, as at Lamanai, Belize, then the frequency and density or dominance of useful trees would probably be no greater than those of nonuseful trees.

We have already described six forest associations commonly occurring at Lamanai (6). *Ramón* occurred in nine transects in only two of the associations—on ruins and in highbush forest. In the latter it was present in only two of eight sampled transects. Three more transects are now included in the data: two ruin sites and a naturally occurring limestone outcrop 12 km south of Lamanai. Even though *ramón* was present in all 12 transects, it was dominant only in two stands.

A correlation matrix (7) with important values (8) was used to determine whether there were naturally occurring groupings in the 12 transects. A dendrogram (Fig. 1) identifies high and low structures among the ruins and highbush forest. On the basis of the measure of similarity the forest-covered limestone outcrop, where there was no evidence of structures, is closer to the high structures than to the low ones.

Six species can be described as being associated with high structures. They are *Brosimum alicastrum* (*ramón*), *Protium copal* (*copal*), *Bursera simaruba* (*chacha*), *Pimenta dioica* (*naba kook*), *Talisia ovaliformis* (*kinep*), and *Allophylus camptostachys* (*bikhach*). Four species, *Spondias mombin* (*hu hu*), *Cryosophila argentea* (*akuum*), *Guazuma ulmifolia* (*pixoy*), and *Stemmadenia donnelsmithii* (*chalkin*), were more common on the low structures and throughout the highbush forest (9).

The density of *ramón* trees is greatest on the steep sides of the highest structures, where the soil rarely exceeds 15 cm in depth and covers identifiable structures or collapsed structural limestone material. Because of the softness of the local limestone, roots have caused extensive damage to structures. Soil moisture content is low even during the rainy season, and drainage is rapid from the steep sides of the structures. Because the limestone base is close to the soil surface, there are high concentrations of exchangeable Ca (24,500 ppm) and Mg (500 ppm) as well as high cation exchange capacity and pH (7.5).

Soil depth increases to approximately 25 cm on low structures and plazas. Soil

Table 1. Comparison of the distribution and dominance of *ramón* at three Maya ceremonial centers. Abbreviation: N.A., not available.

Designation of vegetation units	Area sampled (ha)	Number of <i>ramón</i> per hectare	Total trees per hectare	Important trees (percent of total)
<i>Tikal</i>				
0 to 0.5 km	5	63		
0.5 to 1.0 km	5	49		
2.5 to 3.0 km	5	4	N.A.	N.A.
4.5 to 5.0 km	5	71		
<i>Cobá</i>				
A	19.3	56		
B	25.7	13		
E	49.3	1.3		
H	45	6	N.A.	N.A.
I	50	8		
K	50.5	4		
<i>Lamanai</i>				
High structures	15	106	780	53
Outcrop	20	33	780	32
Low structures	25	17	655	17
Highbush	30	12	685	6