

Reports

Uranium and Lead Isotopic Stability in a Metamict Zircon under Experimental Hydrothermal Conditions

Abstract. *Disturbance of the uranium-lead isotopic system in a metamict Ceylon zircon has been produced in a 2 molal NaCl solution at 500°C and 1000 bars fluid pressure. Loss of radiogenic lead to the extent of 61 percent in 13 days was the most significant effect. The experimental results support the episodic rather than continuous lead-loss interpretation of natural zircon systems utilized in geochronology.*

The stability of uranium-lead isotope systems in zircons under a variety of geological conditions has fundamental significance in the interpretation of observed U-Pb isotope ratios in geochronological applications. For many years investigators have known that natural zircon displayed a great range of physical and chemical properties reflecting radiation damage to its crystalline structure and accumulating in the process known as metamictization. Silver and Deutsch (1) and Silver (2) have demonstrated the existence of a systematic relation between radioactivity and U-Pb isotope ratios in cogenetic zircon suites. The degree of isotopic disturbance has been observed to vary directly with the amount of radioactivity in zircon fractions from a single rock sample for which all the variables of geologic

history are essentially the same. This fundamental relation prevails in more than 200 natural zircon suites of diverse ages and geographic origins analyzed by one of us (L.T.S.).

We now report results of an investigation of the effects of laboratory hydrothermal conditions on uranium and lead concentrations in samples of a highly radioactive and completely metamict zircon "pebble" from the Ceylon placer gravels. This zircon (provided by H. D. Holland) is an end member in the series studied by Holland and Gottfried (3) in their work on the correlation of physical properties with radiation damage in Ceylon zircons. It shows no x-ray diffraction pattern, has an index of refraction of about 1.83, and is apparently isotropic. This physical state was presumed to provide a relatively susceptible system for iso-

topic disturbance under hydrothermal conditions. Other factors leading to the selection of the sample were its nearly concordant U-Pb isotopic ratios reflecting only slight prior isotopic disturbance, its high degree of homogeneity, and its provision of a relatively abundant supply for experimentation.

Hydrothermal experiments in sealed gold capsules were performed. Both coldseal and Morey bombs were used, and all experiments were run at 1000 bars fluid pressure. Quench times were from 5 to 15 minutes. The environmental solution was 2 molal sodium chloride and the experiments were performed at 500°C for durations of 1, 11, 79, and 312 hours.

The procedure for the analyses of lead and uranium in the zircons and the environmental solutions follows closely that developed by Tilton *et al.* (4). The specific procedure is described in the papers by Silver *et al.* (5) and Silver and Deutsch (1). Isotopic analyses were made on a 30-cm radius, 60° sector, single-focusing mass spectrometer with electron multiplier. Silver and Deutsch (1) discuss the reproducibility of uranium-lead analyses on zircon with this instrument and also the choice of a common correction for lead.

It is difficult to assign an overall experimental error to our uranium and lead concentration analyses. For instance, weighing errors attributable to the use of 20-mg samples for analyses have added considerably to the normal procedural uncertainty. We estimate ± 3 percent as the maximum overall experimental error.

The Ceylon zircon "pebble" was

Table 1. Lead-uranium isotopic analyses of zircon from hydrothermal experiments at 500°C and 1000 bars fluid pressure in 2 molal NaCl.

Expt. No.	Duration (hr)	Analyzed phase	U ($\mu\text{g/g}$)*	Radiogenic Pb ($\mu\text{g/g}$)*	Radiogenic Pb (atomic percentage)			Ratio		
					Pb ²⁰⁶	Pb ²⁰⁷	Pb ²⁰⁸	Pb ²⁰⁶ /U ²³⁸	Pb ²⁰⁷ /U ²³⁵	Pb ²⁰⁷ /Pb ²⁰⁶
(13-2)	1	Natural zircon	6000	460	92.41	5.32	2.27	0.0824	0.654	0.0576
		Zircon	5700	421				0.0789	0.630	
(13-1)	11	Solution	3.1	12.6						
		Zircon	5650	225				0.0424	0.339	
(12-1)	79	Solution	4.3	221						
		Zircon	5700	210				0.0388	0.310	
(10-1)	312	Solution	0.6	151						
		Zircon	5740	171	91.89	5.34	2.77	0.0319	0.256	0.0581
	312	Solution	0.2	173						

* Data reported in units per gram of zircon treated.

prepared for experimentation by heating it in distilled concentrated nitric acid and then rinsing it repeatedly in distilled water. The pebble was crushed and mechanically separated into fractions of various sizes. Our experiments were performed on the -100 to +200 mesh fraction.

The results of uranium and lead isotope dilution analyses on all zircon samples, and on the recovered sodium chloride solutions which formed the hydrothermal environments, are included in Table 1. Results of analyses of the solutions are reported as micrograms of uranium or lead per gram of zircon used in the experiment. This table also includes the radiogenic isotope ratios Pb^{206}/U^{238} , Pb^{207}/U^{235} , and Pb^{207}/Pb^{206} .

Lead isotopic compositions are reported for the natural zircon and for the zircon subjected to the hydrothermal conditions for 312 hours. The determination of composition on the experimental material was of relatively poor quality, and because of lack of sample the analysis could not be repeated. The uncertainty is largest for the Pb^{206}/Pb^{204} ratio, and the corrections for common Pb must be assigned errors which preclude recognition of a significant difference between the two Pb compositions. Concentration calculations are based on the natural zircon composition, but use of the other composition would have no effect on the concentration values outside the assigned errors.

Lead concentration measurements show that significant amounts have been removed from the zircon during the experiments. Under the experimental conditions for 1 hour, the zircon lost 4 percent of its radiogenic Pb, whereas after 11 hours 48 percent of the Pb was lost. After 79 and 312 hours, the zircon Pb concentrations were reduced by 53 and 61 percent, respectively. A representation of cumulative Pb loss as a function of time is presented in Fig. 1. These losses are reflected also in the changing ratios of U to Pb (Fig. 2). The recovered solutions have significant Pb contents (Table 1). The lack of material balance in some experiments (such as experiment 10-1) between Pb in the zircon and that in the environmental solution could be due to weighing errors, loss of Pb from solution before spiking, or to physical loss of solution during the opening of the capsule. As great care was taken to assure com-

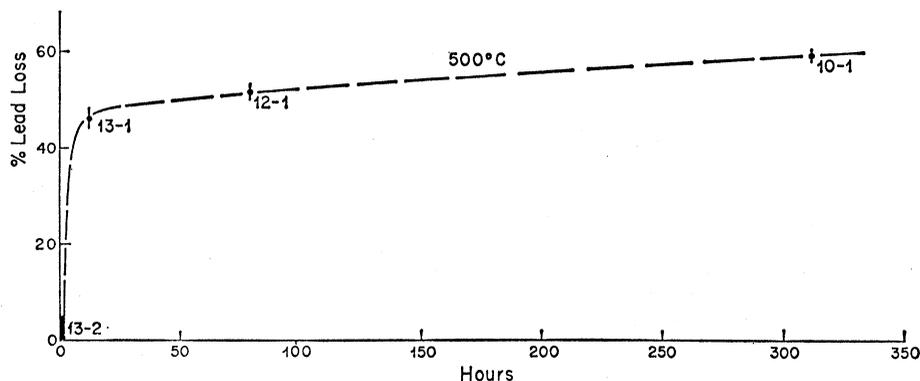


Fig. 1. Lead loss from Ceylon zircon (6500) (-100 to +200 mesh). Sealed in gold capsules in 2 molal NaCl, at a fluid pressure of 1000 bars. Error bars, ± 3 percent of lead concentration.

plete recovery of the solution, physical loss seems unlikely.

Uranium concentration measurements on all zircon samples, regardless of the duration of hydrothermal treatment, fall within ± 3 percent of the mean value. All of the experimental samples have lower average U concentrations than the natural zircon, suggesting slight U loss during the experiments. However, there is no correlation of the apparent U loss with duration of the hydrothermal conditions. This suggests that the apparent loss may be a reflection of experimental error, to a significant degree.

Measurements of the U concentrations of the environmental solutions in no case exceed $4.3 \mu\text{g}$ per gram of zircon in the experiment. These amounts are significantly greater than the blank ($< 0.1 \mu\text{g}$) but insufficient to explain the apparent U loss from the zircon. As with the U in the zircons, the concentrations found in the

solutions do not correlate with the duration of the experimental conditions. Possible explanations include intermittent contamination, dissolution of the zircon itself, or loss of U from solution at some time before spiking. Independent cross checks on the U procedure and an unsuccessful search for zirconium in the solutions argue against the first two suggestions. Uranium loss from the solution upon quench by precipitation or plating appears more probable.

The observed isotopic disturbance of a metamict zircon under experimental hydrothermal conditions has significant implications in the understanding of disturbed U-Pb isotopic systems in natural zircons.

At present two models are advocated to explain the discordant U-Pb isotopic systems found in natural zircons. The first, proposed by Wetherill (6) for U-Pb systems in general, is known as "the episodic-loss

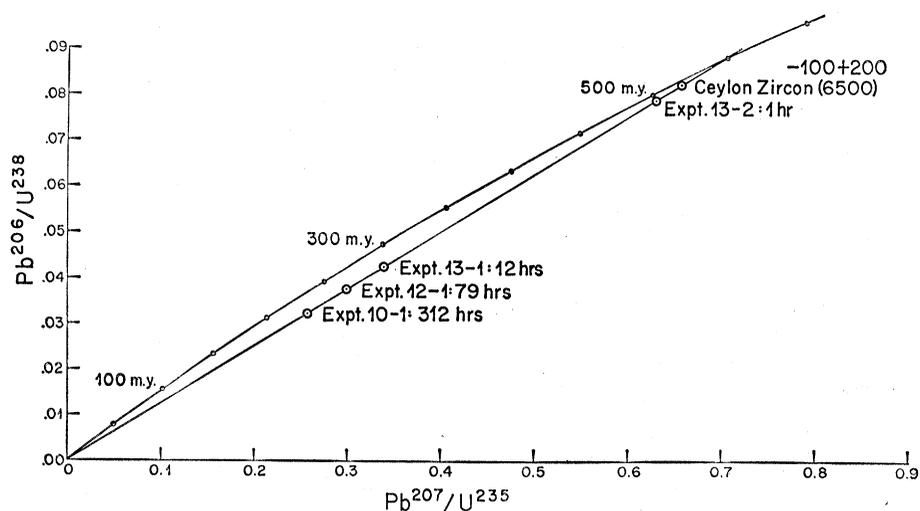


Fig. 2. Concordia plot of Ceylon zircon (6500) (-100 to +200 mesh) after hydrothermal experiments at 500°C in 2 molal NaCl at 1000 bars fluid pressure.

model." From this model the observed spread of Pb-U ratios from U-Pb systems of the same original age is attributed to Pb loss or U gain during an episodic event. The second, known as "the continuous diffusion model," has been developed in various forms by Nicolaysen (7), Tilton (8), Wasserburg (9), and Wetherill (10). From this model the linear spread of Pb-U ratios on a concordia plot is interpreted as a function of continuous Pb loss by diffusion; the diffusion loss pattern on a concordia plot being nearly linear over much of its range.

The first application of the episodic loss interpretation to U-Pb isotope relations in cogenetic zircons was that of Silver and Deutsch (1). This mechanism has been advocated by Silver (2) as the most appropriate explanation for discordant Pb-U ages in numerous cogenetic Precambrian zircon suites from the southwestern United States.

Under the experimental hydrothermal conditions the metamict Ceylon zircon has undergone a significant and systematic Pb loss and also a possible minor loss of U. The Pb-U ratios show a systematic correlation with the duration of the experimental conditions, and, on a concordia plot, they form a linear array passing through the original zircon point and the origin (Fig. 2). These isotopic disturbances have been induced by a modern hydrothermal episode. A geological event reproducing the magnitude of the various experimental conditions would produce major episodic Pb losses from the natural metamict zircon and a pattern similar to that shown in Fig. 2. It can be argued that, since such effects are not observed in this zircon, the material has not been exposed to conditions of comparable severity in that it has become significantly metamict (for example, in the last 200 to 300 million years). This suggests that detailed examinations of the state of isotopic disturbance compared with the degree of metamictization in zircons may provide useful limiting data on the thermal history of the mineral.

The decrease in rate of Pb loss as the duration of the experimental conditions increases suggests that a second significant reaction or process may be interfering with or inhibiting the Pb-loss mechanism. From investigations of natural zircons we believe this may be related to the re-

crystallization process. An experimental study of the relation of Pb loss to recrystallization is proceeding as part of this current laboratory program.

In conclusion, a metamict zircon has undergone systematic episodic Pb loss with possible minor loss of U during a series of hydrothermal experiments in 2 molal NaCl at 500°C and 1000 bars fluid pressure for various durations. From this one sample of zircon and this one set of experiments it is impossible to generalize for all zircon U-Pb isotope systems. However, from the experimental evidence alone, episodic Pb loss is confirmed as a significant process and is supported as a possible explanation for many discordant U-Pb isotope relations observed in natural zircon suites.

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Deep-Sea pH

Abstract. *In the northeastern Pacific Ocean, north of 22°N and east of 180°W, a deep-sea pH maximum of 7.9 exists near 4000 meters. The effect of hydrostatic pressure on the dissociation constants of carbonic acid in sea water appears to be important in its formation.*

What controls the pH of the ocean has been a topic of discussion in recent years. Sillen (1), Garrels (2), and Mackenzie and Garrels (3) stress that the reactions between silicate minerals and sea water are of great importance in maintaining the pH of sea water near 8. The pH is also altered by reactions occurring in the oceanic carbon dioxide system (4), and it can be influenced biologically by production and consumption of carbon dioxide or of organic acids and bases (5).

Until now, however, there have been few reliable *in situ* pH data for the oceanic environment, especially for the deep-sea water. Scarcity of reliable data has been attributed to the contamination of water samples by brass water-sampling bottles (Nansen bottles) used in the past (6). Recently, the brass contamination has been minimized by coating the inside of the bottles with Teflon. A better method is to measure pH directly *in situ*, as attempted by Manheim (7), down to a depth of 16 m. However, no application of his method

References and Notes

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has been reported for deep-sea pH measurements. All *in situ* pH data for the ocean, including data for this report, are from shipboard analysis.

During a recent cruise of R. V. *Yaquina* of Oregon State University, April-July 1966, I measured approximately 3000 pH values for sea water in the northeastern Pacific Ocean by the method described in the manual of Strickland and Parsons (8). The area covered was between 22° and 57°N and 135° and 180°W (9). In this area depth profiles of the *in situ* pH possess two maxima and one minimum (Fig. 1). A deep-sea pH maximum over such a broad area in the Pacific has not been reported previously.

In general, the first pH maximum (8.2 to 8.3) exists intermittently near the surface within the first 100 m. The second maximum, of about 7.9, frequently exists near 4000 m. The pH minimum, with a value of 7.5 to 7.7, has a wide depth range of 200 to 1200 m; it generally exists at the depth of oxygen minimum (Fig. 1). The near-