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SEPARATION OF Pb FROM YOUNG ZIRCONS BY SINGLE-BEAD ION EXCHANGE

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Abstract

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If Pb is separated from zircons containing < 5 ppm Pb by a single pass through an ion-exchange column, other substances following Pb may suppress and render unstable the emission of Pb ions. This problem can be overcome by adsorbing Pb as the $PbBr^2{}_4{}^-$ ion onto a single bead of macroporous resin weighing ~ 300 μg. Although the kinetics are slow, taking 8–12 hr. to reach equilibrium, and although the low solubility of Zr salts and K_D-values between 600 and 800 in 0.6 *M* HBr lead to recoveries between 50% and 60%, the procedure justifies itself by producing Pb of sufficient purity to give strong stable ion beams after a single separation. Insofar as minimal quantities of reagents are required, the procedure has the potential of yielding very small blanks.

1. Introduction

The Pb content of late Cretaceous–early Tertiary zircons is typically 1–5 ppm. Although sufficient mineral can be purified to yield 100–200 ng Pb without undue difficulty (a large proportion of zircons of this age are diamagnetic) it has been my experience that separation of Pb with HBr using a single 0.2-ml ion-exchange column yields a large residue of inorganic material that suppresses the ionization of Pb by a factor between 100 and 1000. Whether other laboratories have experienced this problem is not clear from the analytical techniques they report, but it is generally accepted that, whenever Pb is present in low concentration with respect to a matrix, two passes through an ion-exchange column are needed to obtain Pb of sufficient purity for precise isotopic analysis. Thus Tera and Wasserburg (1975) used anion and cation columns of 0.15-ml capacity to separate Pb from various lunar materials. Chen et al. (1986) used a 1-ml column followed by an 0.1-ml column to separate Pb from seawater containing 20–66 ppb Pb. Göpel et al. (1985) found it necessary to pass 5–10 g of FeNi meteorite containing 20–100 ppb Pb through a 1-ml column followed by three passes through an 0.01-ml column. As an alternative to multicolumn techniques, which can only add to the blank, I present here a method whereby Pb is adsorbed onto a single ion-exchange bead. Although developed primarily for zircon chemistry, it may be used wherever small amounts of

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Pb are to be separated from large amounts of matrix.

A single-bead ion-exchange technique differs from an elution technique in that a bead is stirred in the solution containing the ion to be extracted until equilibrium is attained. The final amount of the ion on the bead is then governed by the mass of the bead, M_B, the mass of the liquid, M_L, and the distribution coefficient, K_D. The efficiency of the extraction may be expressed as the ratio of the ions bound to the bead, I_B, to those initially present in the liquid, I. The exact relationship is:

$$I_B/I = (1 + M_L/K_D M_B)^{-1}$$

Some ions like that formed by Pu in HNO_3 have K_D-values of the order of 10^4 and are almost totally adsorbed by ion-exchange beads, permitting a cheap and convenient means of storing and shipping radioactive products (Walker et al., 1974; Smith et al., 1982). In another application, Koide et al. (1984) reported quantitative extractions onto a single bead of several trace metals from 1 ml of seawater. In their work, however, K_D was increased by using cyanide or thiocyanide as complexing agents.

The extraction of Pb from zircon by a single bead has several attractive aspects.

(1) A resin such as Dowex® *1X8* can bind one-third its weight of Pb. Thus all the 10–100 ng of Pb necessary for an isotopic analysis can, at least in principle, be held by a bead weighing $< 1\ \mu g$.

(2) By using the smallest practical volume of resin, retention of weakly bound or occluded interfering ionic species is minimised.

(3) The volumes of reagents are those necessary to dissolve the Zr salts, the bead itself, and the volume of water into which the Pb is back-extracted. Thus the reagent blank can be kept to the smallest possible size.

(4) A miniature stirring apparatus is no more difficult to handle and clean than is a miniature ion-exchange column.

The method, however, has the limitation that the mass of the liquid depends on the rather low solubility of the salts formed by the decomposition of zircon in HF. To compensate for this, K_D must be large, which excludes use of HCl media in which the maximum K_D-value for the complex Pb ion is $\sim$ 30 (Kraus and Nelson, 1956). In 0.5 *M* HBr, K_D is $\sim$ 821 (Strelow, 1978), suggesting the feasibility of using a single resin bead to extract Pb from zircon. Experiments were, therefore, conducted to measure K_D, the recovery of Pb, and the blank, and also to investigate the factors affecting attainment of equilibrium. The approach closely follows that of Koide et al. (1984).

2. Experimental

A standard solution was prepared from SRM *981* (National Bureau of Standards, Washington, D.C.).

Deionized H_2O and doubly distilled HBr were the only reagents used. Both had Pb contents of < 10 pg ml^{-1}. All Pb concentration measurements were made by stable-isotope dilution using a ^{206}Pb spike and 30-cm-radius mass spectrometers. The loading blank associated with the silica gel–phosphoric acid emitter was 10 pg Pb.

For the reasons of strength, density and opacity given by Koide et al. (1984), single beads of a macroporous resin, Amberlite®IRA-*900* (Sigma Chemical Corporation), were used. The resin, 16–50 mesh, was passed through a 20-mesh polypropylene screen, and the coarse fraction was retained. The resin was cleaned by repeated overnight washings in doubly distilled 6 *M* HCl, followed by a wash in deionized water, before being dried at 80°C. In some experiments, Dowex® *1X8*, 200–400 mesh was used because of its more rapid attainment of equilibrium. Beads and liquids were stirred magnetically in either 3- or 7-ml screw-cap Teflon® PFA jars (Savillex Corporation) on a specially constructed apparatus using a 6-V variable-speed DC motor. Teflon®-coated stirring bars, 2 × 7 mm or 3 × 10 mm were used (Cole-Parmer Inc.). Care must be taken with the smaller bars

because the Teflon® coating on them has a tendency to split. Dry beads were handled with a pair of stainless-steel tweezers, but a hooked piece of 0.5-mm Pt wire mounted in a holder was used to retrieve the beads from the liquid.

A macroporous resin like Amberlite® IRA *900* has much slower kinetics than a gel-type resin like Dowex® *1X8*, and Koide et al. (1984) have shown that 16–20-mesh beads require 12 hr. to attain equilibrium. This presented a problem in Texas, U.S.A., where this work was begun, because the cooling system of the building was shut off overnight and a significant amount of the small quantities of liquid used in single-bead extractions were evaporated by the heat of the stirring motor and condensed on the walls of the Teflon® jars, resulting in a change in strength and volume of the acid. To avoid this problem, most extractions were carried out over an 8-hr. period, at which point the data of Koide et al. (1984, fig. 3) indicate that 96% of the final equilibrium distribution will be attained. The distribution coefficient measured in this way will be referred to as the "8-hr. K_D" value.

3. Results

3.1. K_D vs. HBr concentration

Although it has been known for many years that K_D for Pb in HBr peaks somewhere between 0.5 and 1.0 *M* (Andersen and Knutsen, 1962), the only detailed measurement of K_D and its variation with acid strength appears to be that of Strelow (1978) who stated that K_D peaks at 0.5 *M* HBr, but this fact is not obvious from his data owing to the rather wide interval between acid strengths he chose. In order to find the acid strength at which it peaks, K_D was measured at increments of 0.1 in molarity in the range 0.3 to 1.0 *M* by stirring for 2 hr. 10 mg of Dowex® *1X8*, 200–400 mesh in 3 ml of acid containing initially 10 μg Pb. A 200-μl aliquot of the solution was withdrawn, its Pb content measured, and K_D calculated. The results are shown in Fig. 1 and show a surprising amount

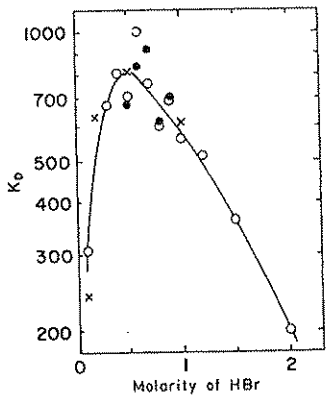

Fig. 1. Distribution coefficient, K_D, of Pb between anion-exchange resin and HBr as a function of HBr molarity [*open circles* = Dowex® *1X8*, 200–400 mesh; *closed circles* = Amberlite® IRA *900*, 16–20 mesh; *crosses* = data of Strelow (1978)].

of scatter considering that Pb concentrations were measured by isotope dilution and that Dowex® *1X8*, 200–400 mesh, was used in this experiment because of its rapid kinetics and the averaging effect of many resin beads. The reason for this scatter is not understood, unless in this batch of resin large differences in cross-linking existed, but the results are similar to those of Strelow (1978), who used approximately the same Pb concentration (4 $\mu g\ ml^{-1}$). The experiment was then repeated using Amberlite® IRA-*900*, 16–20 mesh, stirred for 12 hr., and essentially the same result was obtained (Fig. 1). In all the following experiments, 0.6 *M* HBr was used because at this strength the highest values of K_D were measured.

3.2. Effect of hydration and bead size

In this experiment beads of different weights were taken and the apparent K_D-value was measured after 6 hr. of stirring when, according to Koide et al. (1984), ~ 90% of equilibrium should be attained. Differences in the "6-hr. K_D" value should then give an indication as to the effect of bead size on kinetics. The experiment was then repeated to check the reproducibility of the measurements.

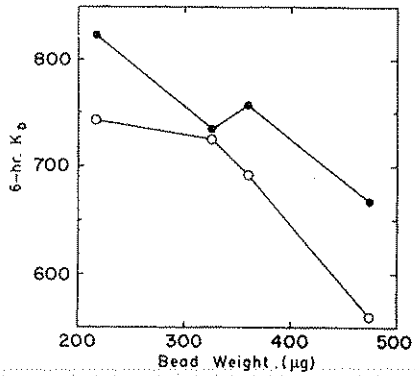

Fig. 2. Distribution coefficient of Pb in 0.6 *M* HBr as measured after 6 hr., "6-hr. K_D", as a function of bead weight (*open circles* = measurements performed on dry beads; *closed circles* = repeat measurements performed on the same, but now hydrated, beads).

The dry resin beads were weighed on a microbalance and transferred to a 3-ml screw-cap jar containing 200 μl of 0.6 *M* HBr with an initial Pb content of 500 ng. After stirring, the bead was removed and the Pb content of the acid was measured. Pb was back-extracted from the bead by stirring for 8 hr. in 200 μl of water. The experiment was repeated using the hydrated bead. The results are shown in Fig. 2.

It is seen that: (1) the "6-hr. K_D" value of the dry bead is always less than that of the hydrated bead; (2) halving the weight of the bead increases the "6-hr. K_D" value by an average of 30% in both the dry and hydrated beads; and (3) the projected K_D-value of beads weighing ~ 300 μg, i.e. "6-hr. K_D"/0.9, is 829, implying that the smallest bead weighing 217 μg with a "6-hr. K_D" value of 824 attained equilibrium in 6 hr.

Once beads are hydrated, the K_D-values can be duplicated to within ± 5%.

3.3. K_D *vs. Pb concentration*

The "8-hr. K_D" values of hydrated beads with dry weights between 300 and 350 μg were measured in solutions of 0.6 *M* HBr with initial Pb concentrations between 0.05 and 100 μg ml^{-1} and were found to increase from 560 to 1000

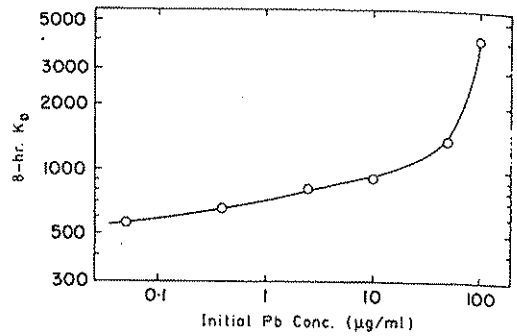

Fig. 3. Distribution coefficient as measured after 8 hr., "8-hr. K_D", as a function of the initial concentration of Pb in 0.6 *M* HBr.

from 0.05 to ~ 16 μg ml^{-1} and then increase very rapidly to 4000 at 100 μg ml^{-1} Pb (Fig. 3). For most zircon work concentrations between 0.2 and 2 μg ml^{-1} may be expected, leading to K_D-values between 600 and 800.

3.4. *Rate of uptake of Pb*

The "8-hr. K_D" values of hydrated beads whose dry weights varied between 300 and 350 μg were measured in duplicate, then the beads were stirred for various lengths of time up to 8 hr. and the apparent K_D-values were measured. The uptake expressed as the ratio of the apparent K_D to "8-hr. K_D" is shown in Fig. 4. After 6 hr. the uptake is more than 90% of that at 8 hr.

3.5. *Recovery from zircon*

To test the technique on a real sample, an Archean metamict zircon from a pegmatite was

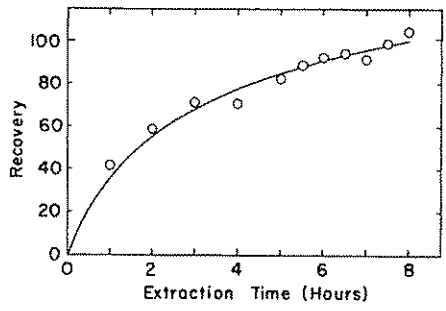

Fig. 4. Percent recovery of Pb from 0.6 *M* HBr as a function of extraction time.

TABLE I

Recovery of Pb from solutions of zircon (20 mg in 100 μl) with different Pb contents

Weight of bead (μg)	K_D	Pb_i (ng)	Pb_L (ng)	K'_D	Pb_R (ng)	Recovery (%)	Unrecovered Pb (ng)
299	759	27.7	7.9	838	14.8	53	5.0
289	626	42.9	14.7	664	22.2	52	6.0
308	640	63.1	20.2	690	35.7	57	7.2
314	670	84.0	26.9	676	47.3	56	9.8
465	554	103.5	27.2	603	69.7	67	6.6

K_D = duplicate values measured for extraction from 0.6 *M* HBr; Pb_i = Pb initially present in solution; Pb_L = Pb remaining in liquid phase after extraction; K'_D = "8-hr. K_D" for extraction from zircon solution; Pb_R = Pb back-extracted from bead; Unrecovered Pb = $Pb_i - Pb_L - Pb_R$.

dissolved in HF and passed through an ion-exchange column which reduced its Pb content from 1013 ppm to 1.3 ppm. The solution was divided into 5 equal portions each corresponding to 20 mg of zircon and ^{206}Pb was added to four to make concentrations corresponding to 1.3, 2.2, 3.2, 4.2 and 5.2 ppm Pb in the undecomposed zircon. The aliquots were dried and dissolved in 100 μl of 0.6 *M* HBr. Pb was then extracted for 8 hr. onto hydrated beads whose "8-hr. K_D" values had already been measured. The amount of Pb remaining in the solution was measured with a ^{208}Pb spike, and the "8-hr. K_D" value calculated. Recovery was checked by back-extracting the Pb adsorbed on the bead in 200 μl of water. The results are summarized in Table I. It is seen that: (1) the presence of Zr does not reduce the "8-hr. K_D" value; (2) the values of "8-hr. K_D" are with one exception in the range of 600–700; (3) recovery is between 53% and 67%; and (4) between 5 and 10 ng Pb are lost, presumably by being irretrievably bound to the bead.

3.6. *Blanks*

Blanks of 4–5 pg Pb per bead were estimated by extracting 40 ng of 99.98% enriched ^{206}Pb onto 10 beads and then back-extracting into water. No attempt was made to improve on this figure as the blank associated with dissolving 20 mg of zircon is 10 times larger. However, by using cleaner reagents a blank of < 1 pg should be attainable without much difficulty.

4. Suggested procedure

Zircons are spiked with ^{235}U before dissolution using HF in a Teflon® bomb at 200 °C. The solution is transferred to a 3-ml screw-cap Teflon® jar. A 10% aliquot is withdrawn, weighed into another 3-ml jar, spiked with 20 ng ^{208}Pb, and dried. The dried salts are dissolved in a minimal quantity ($\sim$ 20 μl) of 0.6 *M* HBr. A bead that had been soaked overnight in 0.6 *M* HBr is then added and stirred for 6–8 hr. The bead is removed, dried on a piece of filter paper and transferred to a flat-bottomed 1-ml Teflon® TFE beaker (Chemplast)®. A small quantity (3–4 μl) of 0.6 *M* HBr is placed on the bead, and the drop is then slowly rotated for 2 hr. The purpose of this step is to wash out any salt that had diffused into the bead. The bead is removed and dried as before, and the beaker and stirrer are rinsed before back-extracting the Pb into 100 μl of water.

To extract Pb from the unspiked aliquot the same procedure is followed, with the dried salts being again dissolved in a minimal quantity of 0.6 *M* HBr. The remaining liquid from either or both extractions is used for the U analysis. Some beads may release an organic residue which, if it is loaded, drastically suppresses ionization. In such cases, a 1-ml TFE beaker is washed and

placed without touching by hand inside a clean 7-ml screw-cap jar. The organic residue is dissolved in a minimal quantity of dilute HNO_3, transferred to the 1-ml beaker, and is dried. Two drops of conc. $HClO_4$ are placed in the bottom of the 7-ml jar which is then tightly closed and placed in an oven at 200°C for 4 hr. The organic material is completely destroyed in the $HClO_4$ vapour and the sample is ready to be loaded.

Although recoveries are only slightly more than 50%, this disadvantage is more than offset by the purity of the Pb obtained and the absence of inorganic substances that might suppress ionization. Zircons containing 2 ppm Pb that gave unusable runs after separation on an 0.2-ml column even though 100 mg of zircon had been dissolved, yielded high-precision analyses after a single-bead extraction from 20 mg of zircon. If recovery is deemed a problem, it could possibly be enhanced by: (1) only partially dissolving the Zr salts because PbF_2, being highly soluble, should be totally contained in the liquid phase, (2) extracting with several beads, or (3) obtaining Pb from the bead by ashing rather than by back-extracting.

The method can, of course, be used on zircons with greater contents of Pb. Because smaller volumes of acid are required to dissolve the Zr salts, recovery is greater, and smaller beads can be used, leading to faster equilibration.

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