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ISOTOPIC COMPOSITION OF URANIUM IN ZIRCON

BRUCE R. DOE AND MARCIA F. NEWELL[1]
U. S. Geological Survey, Denver, Colo.; Washington, D. C.

ABSTRACT

Twenty analyses were made of the isotopic abundances of U^{238}, U^{235}, and U^{234} in 13 selected zircon samples by mass spectrometry. Five samples were checked for U^{238}/U^{234} by alpha spectrometry. Variations in U^{238}/U^{235}, do not exceed 0.5 per cent of the ratio. The range in U^{235}/U^{234} is about 9 per cent. Variations in U^{235}/U^{234} cannot be correlated with age, grain size, per cent discordance in the isotopic ages, type of discordance (positive or negative), uranium content, or radiation damage.

The ratio, U^{236}/U^{234}, for two of four samples could not be reproduced within analytical uncertainties, suggesting lack of sample homogeneity or problems arising from chemical procedures. The range in U^{235}/U^{234} is not large enough to account for discordant U-Pb ages in zircons by radioactive disequilibrium between U^{238} and U^{234}. Most zircon concentrates are obtained from surface rocks that are at least incipiently weathered. Use of U^{235}/U^{234} as a weathering indicator leads to the conclusion that incipient weathering has little or no effect on zircons.

INTRODUCTION

The mineral zircon which first came into prominence in geochronology through the lead-alpha (Larsen) method of age determination is becoming increasingly important in U-Pb isotopic work because of the resistance of zircon to metamorphism. The U^{235}, U^{238} and Th^{232} decay systems permit theoretical analysis of the isotopic data, and this analysis affords a most promising technique for the study of rocks that have been affected by metamorphism.

All theoretical treatments assume the ratio U^{238}/U^{235} is constant, an assumption based in part on theory and in part on the observed lack of variations greater than 0.1 per cent of the ratio in uranium ores where uranium is a major element (Senftle *et al.*, 1957; Shields, 1960; Smith, 1961; Smith *et al.*, 1961). The only previous studies, to our knowledge, of U^{238}/U^{235} of uranium as a trace element are the investigations of weathered granite and sandstone (Rosholt *et al.*, 1964a, b). No variation of U^{238}/U^{235} was found in those studies exceeding the analytical precision of 0.5 per cent at the 99.5 per cent confidence level.

The recent discoveries of variations in U^{238}/U^{234} from bone, waters, uranium ores, and some minerals (Chalov, 1959; Cherdyntsev *et al.*, 1961; Isabaev *et al.*, 1960; Thurber, 1962; Rosholt *et al.*, 1963) have reopened the possibility mentioned by Russell and Ahrens (1957) that some or all discordant uranium-lead ages in zircons may be explained by loss of intermediate daughter products. Russell and Ahrens specifically referred

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to pitchblende, uraninite and monazite but zircon must also be considered. The decay chain proceeds $U^{238} \rightarrow Th^{234} \rightarrow Pa^{234} \rightarrow U^{234} \rightarrow \cdots \rightarrow Pb^{206}$. Although observed discordant ages cannot be accounted for solely by the loss of U^{234}, investigations of variations in U^{234} abundance may help one decide if problems with intermediate daughters must be considered in the interpretation of isotopic ages determined by the U-Th-Pb method.

ANALYTICAL TECHNIQUES

Measuring technique. U^{238}/U^{235} and U^{235}/U^{234} were measured on a solid source, 12-inch, Nier-type mass spectrometer utilizing an electron multiplier. U^{238}/U^{234} was also measured on five samples by alpha-spectrometry. Mass spectrometry may yield ratios too small compared to the true value, expecially in trace isotopes, owing to interference from impurities with the same value of mass/charge. On a clean sample, however, U^{235}/U^{234} may be measured to 0.75 per cent or better on a 20–30 μg uranium sample using a triple filament mode of ionization. Alpha-spectrometry may also yield ratios too small owing to interference with other radioactive isotopes such as thorium that yield alpha particles having the same energy. Measurement may not be made as precisely as by mass spectrometry, at best has an error of about 1 per cent, and in general, a larger sample of uranium is required to reduce the counting time to a reasonable limit. The two methods support one another in that interferences are of a radically different nature so that agreement of the results forms a strong inductive proof that the measured values are correct.

Sample processing and chemical technique. The rock was crushed and a heavy mineral concentrate was gathered on a Wilfley table. The zircon was purified from other heavy minerals by bromoform, methyl iodide, and magnetic separations. Pyrite and uranothorite were removed by heating in hot concentrated HNO_3. Approximately 0.5 g of zircon was poured from a bottle for analysis. Anderson (personal communication, 1965) reports that the purity of the M series samples is close to 100 per cent with perhaps a small amount of apatite (<1 per cent) the only impurity. B70 contains a small amount of sphene (<1 per cent) as impurity, and perhaps a small amount of barite. Stern (pers. comm.) reports the other separates to be 99+ per cent pure with sphene the main impurity.

The zircon was fused in sodium tetraborate. For samples labeled "a" in Table 1 uranium was purified and isolated by methyl isobutyl ketone (hexone) solvent extractions by using conventional $Al(NO_3)_3$ and NH_4NO_3 salting agents. Such a separation does not quantitatively re-

Table 1. Δ238/235 and Δ235/234 for Selected Zircons.

Sample No.	Pb^{206}/Pb^{207} age (m. y.)	α-activity (dis./mg. hr.)	% Discordance[1]	Δ238/235	Δ235/234	
					mass spec.	α-spec.
MA115a	3220	276	−17	+0.15[3]	+1.0	—
b[2]				−0.44[3]	−0.3	—
B70a	650	265	+16	−0.73[3]	+0.1	—
b[2]				—	+0.8	—
KA345 +100 mesh[2]	2650	190	−10	+0.73[3]	−0.8	—
−200 mesh[2]	2650	165	−6	−0.15[3]	−1.5	—
MA114a 1st fusion	2600	340	−20	+0.66[3]	+1.8	—
b[2]				+0.15[3]	+1.1	—
MA114 2nd fusion	—		—	+0.37	−0.3	0.0
421-4	1420	350	−137	+0.73[3]	+0.5	—
423—1st fusion	900	3700	−1850	−0.44[3]	−2.0	—
423—2nd fusion	—		—	0.00	+1.5	—
M5220	—	105	—	−0.22	+3.2	+3.7
M7029	2460	—	−33	+0.14	+5.7	—
M5219 −100 mesh +200 mesh	2630	85	−5	+0.14	+2.4	—
M5222	2480	135	−23	+0.22	+2.3	—
RP-1—1st fusion	1510	1185, 1070	−172	+0.22	+6.8	+7.5
2nd fusion	—	—	—	0.00	+7.5	+7.3
383	590	7380	−190	−0.07	+3.8	+4.1
541	1800	—	−17	0.00	0.0	—
Instrumental uncertainty (in per cent):				0.25	0.75	1.0

[1] Per cent discordance = [U^{238}/Pb^{206} age-Pb^{206}/Pb^{207} age]×100/(U^{235}/Pb^{207} age)

[2] No resin column step for the quantitative removal of thorium.

[3] Low intensity measurements with an uncertainty of about 0.75 per cent.

move all the thorium. To determine if thorium might have any effect on the mass spectrometer, several aliquots of samples were run through an anion exchange column in the chloride form to eliminate the thorium

(Sample labeled "b" in Table 1). All other samples were processed through anion exchange resin columns, and the remaining iron was removed by a hexone solvent extraction from 6.2N HCl. A portion of the fused sample was used to determine U-Th-Pb relations, and another portion was analyzed for uranium isotopic abundance measurements. Portions of zircon samples with extreme isotopic results were refused, reprocessed, and reanalyzed, or analyzed by alpha spectrometry.

DATA

The data on U^{238}/U^{235} and U^{235}/U^{234} are presented in Table 1. As an electron multiplier was used and there exists about a 5 per cent tail under U^{234} from U^{238} (U^{235}/U^{234} is roughly 134), the analytical results are subject to bias which is eliminated by expressing the data relative to a standard (NBS 950 U_3O_8 standard):

$$\Delta 238/235 = \left[\left(\frac{U^{238}}{U^{235}}\text{ sample}\Big/\frac{U^{238}}{U^{235}}\text{ reference}\right) - 1\right] \times 100$$

and

$$\Delta 235/234 = \left[\left(\frac{U^{235}}{U^{234}}\text{ sample}\Big/\frac{U^{235}}{U^{234}}\text{ reference}\right) - 1\right] \times 100.$$

$\Delta 238/235$ data are of two qualities. In the first set of samples, the multiplication of the electron multiplier was held constant so that the intensity of the uranium signal for measurements of U^{238}/U^{235} was about 1/30 that for measurements of U^{235}/U^{234}. This results in such a small signal for U^{235} that precise measurements could not be made, and the range in $\Delta 238/235$ observed for these analyses of about 1.5 per cent must be considered to be within analytical uncertainties even though 1.5 per cent is about three times the range observed in the reference sample. Nonuniform purity of the samples relative to the reference could account for the significant differences at such small signals.

To check on the validity of this conclusion, the second set of samples were analyzed to that the intensity of the uranium signal for U^{238}/U^{235} was about half that for U^{235}/U^{234} measurements. This large signal for U^{238} in addition necessitated a corresponding reduction in the multiplication factor for the electron multiplier which gave better analytical data for U^{238}/U^{235} in the second set of data but equivalent analytical data for U^{235}/U^{234}.

From the second set of data, there is no evidence for any variation in U^{238}/U^{235} much more than 0.5 per cent for trace quantities of uranium in the mineral zircon. Three spectrometric analyses were made from two fusions of MA114 and two analyses from two fusions of KA345, 423, and RP-1. The multiple analyses of MA114 and 423 suggest that isotopic variations in U^{238}/U^{235} at the 0.5 per cent level cannot be ruled out by the present data.

Variations in U^{235}/U^{234} are noted that cover a range of about 9 per cent, and values agree well between mass spectrometry and alpha spectrometry. Results on the second fusions of MA114 and RP-1 are in excellent agreement with the first fusions but second fusions of MA114 and 423 disagree markedly with the results on the first fusions. The disagreement is well beyond the instrumental uncertainties of about 0.75 per cent and is apparently related to natural sample inhomogeneity, to the HNO_3 washing, or to prior steps in the sample treatment. Because of nuclear recoil U^{234} is probably not in the same lattice sites as U^{235} and U^{238} so that it is possible to separate to some degree U^{234} from U^{235} and U^{238} by laboratory procedures. Overall laboratory uncertainties might require differences in U^{235}/U^{234} greater than two per cent for significant variations.

Discussion of Variations in U^{235}/U^{234}

No correlation is recognized between $\Delta 235/234$ and age, grain size, per cent discordance in the isotopic ages, type of discordance (positive or negative), or uranium content. Nor is there any simple correlation between radiation damage inferred from the alpha activity and $\Delta 235/234$. Samples MA114, M7029, KA345 (-200 mesh), KA345 ($+100$ mesh), and M5222 are all nearly the same age but range in alpha activity by about a factor of 20. About 80 per cent of the total range in $\Delta 235/234$ is represented by these five samples. The extremes in $\Delta 235/234$ have uranium contents that differ by only 15 per cent, and the extremes in uranium content have $\Delta 235/234$ within analytical uncertainties. Sample 423 probably has undergone the greatest radiation damage because of an extreme alpha activity; yet, the $\Delta 235/234$ is not particularly unusual.

In order for uranium series disequilibrium to have any marked effect on isotopic ages, the disequilibrium must be maintained for long periods of time. Episodic losses will have an insignificant effect. It has been demonstrated that U^{234} in zircon may be depleted by a few per cent in some zircons at the present time, and depleted perhaps by as much as 9 per cent in unusual cases. These data point to the possibility of long term uranium series disequilibrium. The important point is that the magnitude of the disequilibrium presently observed down through U^{234} is inadequate to explain the discordant U-Pb ages, and that it may only be important in interpreting U-Pb ages when the discordance is less than 10 per cent.

Most zircon concentrates are obtained from surface rocks that are at least incipiently weathered. Rosholt *et al.* (1964a) found a 23 per cent depletion in $\Delta 235/234$ for a slightly weathered granite. Use of $\Delta 235/234$ as a weathering indicator leads to the conclusions that incipient weathering has little or no effect on zircons.

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