Short Communication

Application of two-tracer isotope dilution mass spectrometry in the determination of uranium in geological samples

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ABSTRACT

The determination of the uranium concentration in mineral samples using two tracer (^{233}U and ^{235}U) mass spectrometric isotope dilution techniques is described. The precision and accuracy are discussed and results are compared with those obtained by x-ray fluorescence and instrumental neutron activation methods. Based on the two independent values obtained for the same dilution, parameters such as the chemical procedures adopted, effect of mass fractionation and uranium distribution in minerals are evaluated. The ability of the method to distinguish between the analytical errors and heterogeneous distribution of uranium is discussed.

The accurate and precise determination of the concentration of uranium in geological samples is necessary in many contexts in the earth sciences. Of the many methods that are used, stable isotope dilution by thermal ionization mass spectrometry offers high sensitivity, freedom from matrix effects and does not require calibration standards [1]. Generally for geological samples the tracer used is the isotope enriched in ^{235}U, whereas for highly radioactive solutions the ^{233}U-enriched tracer is used, eliminating the need for the separate determination of the isotope composition of the sample [2]. A ^{233}U tracer has been successfully employed [3] in the determination of uranium in geological materials. However, the non-homogeneous distribution of uranium in the materials [4,5] poses a major problem, making it difficult to distinguish between the analytical errors and sample heterogeneity when analyses are repeated. If two independent values can be obtained within a single analysis, then a comparison of the values

should yield information on the analytical and sampling errors. Such an attempt was made in this work, in which two independent tracers enriched in ^{235}U and ^{233}U were employed in isotope dilution analysis. The experimental procedures involved in the determination of uranium in minerals using two tracers are described. Based on the precision and accuracy of the values obtained, parameters such as the chemical procedures adopted, distribution of uranium in minerals and the effect of mass fractionation in thermoionic isotope dilution mass spectrometry are evaluated.

Experimental

Preparation and calibration of tracer solutions.
The tracer solutions were prepared from the isotopic standard enriched in ^{233}U supplied by the CEA (Fontanay, France) and the isotopic standard enriched in ^{235}U supplied by the National Bureau of Standards (Washington, DC, U.S.A.). These solutions were calibrated by mass spectro-

metric isotope dilution using the uranium isotopic standard (NBS SRM 950[a]) with the isotopic abundance of natural uranium. The calculated concentration of ^{233}U and ^{235}U in the tracer solutions were found to be $(0.92 \pm 0.3) \times 10^{-5}$ and $(9.76 \pm 0.03) \times 10^{-6}$ g g^{-1}, respectively.

Chemical procedures. Depending on the concentration of uranium in the sample, a known amount of each tracer solution was weighed and added to the previously weighed sample. The sample and the tracer solutions were dissolved according to the scheme of Patchett and Tatsumoto [6] using PTFE pressure bombs. This procedure ensures complete dissolution of even the most resistant minerals studied in this work. The separation and the purification of the uranium were done using the two-stage ion-exchange method. In the first stage, uranium was separated from thorium [7] using Dowex 1 − X8 (200–400 mesh) resin in the chloride form and in the second stage iron, alkali metals and other elements were separated using the same resin after Fe(III) had been reduced to Fe(III) using iodic acid [8].

Mass spectrometric procedure. The mass spectrometer employed in the isotopic measurements was a Varian TH-5 solid-source single-focusing instrument coupled to a microcomputer for data acquisition and processing [9]. Samples were loaded in the nitrate form on one of the side filaments of a double-filament assembly using an automatic sample deposition unit [10], while the other filament was used to ionize the atoms emitted from the sample filament. Amounts of 5–10 μg of sample were loaded onto the filament and the ion current was measured with a Faraday detector. The data were processed by a microcomputer, which listed the isotope ratios and relative standard deviations.

Results and discussion

Table 1 gives the uranium values $C_{A^{233}}$ and $C_{A^{235}}$ calculated for the sample at the same dilution using the isotope tracers ^{233}U and ^{235}U, respectively. The isotope dilution equations used to calculate the concentration of uranium take into consideration the presence of ^{238}U in the tracer solutions. The blank values are also corrected for. It can be seen that the internal standard devia-

TABLE 1

Uranium concentrations in minerals determined by two-tracer isotope dilution mass spectrometry

Sample	Dilution	Concentration (mg kg^{-1})	
		$C_{A^{233}} \pm SD_{in}$ [a]	$C_{A^{235}} \pm SD_{in}$ [a]
Feldspar	1	3.23 ± 0.02	3.17 ± 0.01
	2	2.46 ± 0.01	2.498 ± 0.020
	3	2.32 ± 0.01	2.36 ± 0.008
Phosphorite	1	102.4 ± 0.3	103.7 ± 0.4
	2	103.2 ± 0.3	103.5 ± 0.5
	3	102.6 ± 0.3	103.1 ± 0.8
Zircon	1	244.8 ± 0.7	246 ± 1
	2	231 ± 1	230 ± 1
	3	254.2 ± 0.8	251 ± 1
Monazite	1	1929 ± 6	1952 ± 10
	2	1885 ± 6	1891 ± 7
	3	1862 ± 10	1865 ± 10
Caldasite	1	3848 ± 30	3836 ± 25
	2	3857 ± 10	3878 ± 20
	3	3860 ± 20	3850 ± 20

[a] SD_{in} = internal standard deviation for three runs on eight isotope ratios for one filament loading (calculated by law of error propagation).

tions of the calculated uranium concentration are of the order of 0.5% for both tracers. The precision is independent of the concentration levels of uranium (2–4000 mg kg^{-1}) and depends mainly on the precision with which isotope ratios are measured. The two independent values of uranium ($C_{A^{233}}$ and $C_{A^{235}}$) for the same dilution agree to within 1% for all the concentration levels. Such an agreement reflects the accuracy of the chemical procedures adopted. In the calculation of $C_{A^{233}}$ and $C_{A^{235}}$, the isotope ratios employed (^{233}U/^{238}U and ^{235}U/^{238}U) have mass differences of 5 ($\Delta M = 238-233$) and 3 ($\Delta M = 238-235$), respectively, yet the uranium values obtained are concordant, indicating the negligible effect of mass fractionation. This is in conformity with the observation of Webster [11], who suggested that if tracer calibration is also done by isotope dilution, then mass fractionation effects can be neglected.

From Table 2, the total relative standard deviation for triplicate analyses of the samples shows that for phosphorite and caldasite it is about 0.5%, whereas for feldspar, zircon and monazite it is

TABLE 2

Comparison of average uranium concentrations obtained by two-tracer isotope dilution mass spectrometry (IDMS) with other methods

Sample	Concentration (mg kg^{-1})			
	IDMS		XRF [b]	INAA [c]
	$C_{A^{233}} \pm SD_t$ [a]	$C_{A^{235}} \pm SD_t$ [a]		
Feldspar	2.67± 0.49	2.68± 0.43	< 5	2.21
Phosphorite	102.7 ± 0.4	103.4 ± 0.2	107	101
Zircon	243 ±12	242 ±11	210	257
Monazite	1892 ±35	1903 ±46	1740	1780
Caldasite	3855 ±16	3854 ±21	4000	3850

[a] SD_t = total standard deviation of three independent determinations.

[b] XRF = x-ray fluorescence spectrometry.

[c] INAA = instrumental neutron activation analysis.

17%, 5% and 2%, respectively. An estimate of the total precision was obtained with the application of the F-test [12,13] adopting a 95% confidence level. This large variation in the three samples is due to the heterogeneous distribution of uranium in the samples, as the close agreement of the $C_{A^{233}}$ and $C_{A^{235}}$ values rules out the possibility of analytical errors. The heterogeneous distribution of uranium in geological samples has been documented by many investigators [3–5] and a study of the sampling errors in the determination of uranium caused by mineral distributions in rocks [4] has shown that the errors can be of the order of 100% or more. All these studies have shown a heterogeneous distribution of uranium in rock samples, as uranium is generally concentrated in accessory minerals such as zircon or apatite. This study indicates that even in accessory minerals uranium is likely to be distributed heterogeneously.

Table 2 also gives the uranium concentrations obtained by x-ray fluorescence and instrumental neutron activation analysis. It can be seen that the values are in good agreement for phosphorite and caldasite, whereas for other samples there is a larger scatter, indicating that here the uranium distribution is the major factor contributing to the errors. The $C_{A^{233}}$ and $C_{A^{235}}$ value shown in Table 2 clearly distinguish the mineral samples (feldspar,

zircon and monazite), where the sampling errors are higher owing to the heterogeneous distribution of uranium. The two-tracer technique therefore appears to be an important method for distinguishing between analytical and sampling errors. A major implication of this result is in the field of U–Pb geochronology, where uranium and lead isotope analysis should be carried out in the same aliquot of sample to avoid sampling errors.

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