G

Geochemical Journal, Vol. 22, pp. 133 to 137, 1988

LETTER

Error in neutron activation analysis from recoil-implanted fission products from uranium in aluminum foil

RANDY L. KOROTEV

Department of Earth and Planetary Sciences
and McDonnell Center for the Space Sciences
Washington University, St. Louis, MO 63130, U.S.A.

(Received July 12, 1988; Accepted October 19, 1988)

Commercial aluminum foil may contain a high concentration of uranium, up to 1.4 $\mu g/g$. Samples or sample tubes in contact with aluminum foil during neutron irradiation can be contaminated with recoil-implanted fission products of ^{235}U from uranium in the foil. This can lead to errors in the determination of Zr, Mo, La, Ce, Nd in neutron activation analysis.

INTRODUCTION

We recently analyzed a 243 mg diamond by instrumental neutron activation (INAA) in order to determine its uranium concentration, as part of a study of noble gas isotopes in diamonds (Honda *et al.*, 1987). We would normally encapsulate samples in tubes of ultrapure fused silica for irradiation (Korotev, 1987). However, the diamond was too large to fit in available tubing, so we simply wrapped it in aluminum foil.

Gamma-ray spectrometry at 9 days following irradiation produced some confusing results. As we did not expect diamond to be a good host for most trace elements, we expected very low levels of most radionuclides. Thus, we were not surprised that we were unable to detect any gamma-ray lines for ^{239}Np, the usual analytical isotope for U analysis, which is produced by the (n, γ) reaction on ^{238}U followed by beta decay. We were surprised, however, that significant signals were observed for several other radionuclides, most of which were fission products of ^{235}U. Taken at face value, these results implied that the diamond had a much greater $^{235}U/^{238}U$ ratio than normally encountered in nature. As that seemed unlikely, we sought another explanation. Having previously observed concentrations of U in Al metal that were high compared to those of other trace elements, we suspected that the fission products observed in the diamond sample were implanted by recoil from fission of ^{235}U in the Al foil in contact with the diamond. To test this hypothesis, two experiments were done.

EXPERIMENTAL

For the first experiment, we analyzed samples from four rolls of Al foil and a roll of Al utility wire that were available in our laboratory for packaging samples for irradiation. All four foils were consumer brands sold for household use. For comparison, we also analyzed a piece of sheet aluminum from a soft drink can and a sample of bauxite, an aluminum ore. Analytical procedures were similar to those described by Korotev (1987).

The second experiment was to reproduce the observations of the diamond experiment under controlled conditions. Two tubes were prepared from the stock of silica tubing that we use for encapsulation and radioassay of samples (T21

Suprasil©, Heraeus-Amersil, Sayreville, New Jersey, U.S.A.). The tubes, which had an outside diameter of 5 mm, were cut to about 4.5 cm length, soaked in aqua regia for several hours, and sealed shut on both ends with a natural gas-oxygen flame. The two tubes were each wrapped entirely with two layers of aluminum foil having a thickness of approximately 10 μm (foil 4 in Table 1). Thus, the foil contacted a surface area of silica of approximately 7 cm^2. A tube that was not wrapped in foil was also included. All three tubes (along with a large number of sample tubes for a different experiment) were irradiated with a thermal neutron flux of 4.9×10^{13} cm^{-2} s^{-1} for 48 hours in the University of Missouri Research Reactor in a canister filled with water. After irradiation, the Al foil was removed and the tubes were washed in 6 M $HNOg_3$ for 5 minutes and rinsed with water and acetone. The tubes were radioassayed approximately 10 days following irradiation.

RESULTS

Results of the analysis of U in the Al metal samples and bauxite are listed in Table 1 along with results for Ce. Cerium, like uranium, behaves as an incompatible trace element and is not strongly fractionated from U in many geochemical systems. For example, the U/Ce ratio in the bauxite (0.05) is similar to the average ratio for the terrestrial crust (0.03-0.04), indicating little fractionation of the two elements has occurred during formation of the ore. However, the U/Ce ratios are 4 to 46 times greater in the Al samples than in the bauxite, indicating that U is not as efficiently separated from Al as is Ce during the production and purification of Al metal.

Photopeaks for a number of radionuclides were detected in the empty silica tubes. In Tables 2 and 3, the count-rate data obtained for the most intense radionuclides have been converted to equivalent nanograms of element, assuming that each radionuclide was produced by neutron capture. Detection limits are listed for some elements for which no photopeak was observed.

Table 1. Uranium and cerium concentrations in samples of alminum metal and (U.S.) National Bureau of Standards (NBS) Standard Reference Metarial 69b (bauxite, Arkansas)

	U (μg/g)	Ce (μg/g)	U/Ce
Al foil 1	0.52 ±0.02	0.47 ±0.02	1.1
Al foil 2	0.096±0.003	0.50 ±0.02	0.2
Al foil 3	1.40 ±0.04	0.71 ±0.03	2.0
Al foil 4	0.39 ±0.02	0.41 ±0.04	1.0
Al wire	0.016±0.002	0.007±0.002	2.3
Al sheet	0.63 ±0.02	0.72 ±0.03	0.9
NBS 69b	12.2 ±0.3	247. ±3.	0.05

Table 2. Results of the silica-tube experiment for elements without (n, fission) interferences

	not foil wrapped (ng)	wrapped in Al foil (ng)
Sc	0.0045 ± 0.0003	0.0038 ± 0.0004
Cr	1.56 ± 0.06	1.82 ± 0.10
Fe	46. ± 3.	52. ± 5.
Co	0.068 ± 0.005	0.129 ± 0.010
Sb	0.174 ± 0.006	0.010 ± 0.004
Yb	<0.01	<0.01
Lu	<0.0014	<0.0015
Hf	0.006 ± 0.003	0.011 ± 0.005
Ta	<0.03	<0.02
Th	<0.008	<0.008
U	<0.03	<0.03

Uncertainties (1σ) and upper limit estimates (2σ) are based on counting statistics. The values in the table are the apparent mass of each element (in nanograms) associated with the 1.2 g silica tubes.

Table 3. Results of the silica-tube experiment for elements with (n, fission) interferences and equivalent mass of uranium required to produce the signal if the signal derives entirely from fission of ^{235}U

	not foil wrapped (ng)	wrapped in Al foil (ng)	equivalent mass U (ng)
Zr	<4.	14. ±3.	1.4 ±0.3
Mo	<0.3	1.34 ±0.14	1.05±0.11
La	<0.05	0.149±0.011	1.52±0.11
Ce	0.052±0.023	0.33 ±0.06	1.2 ±0.2
Nd	<0.13	0.19 ±0.09	0.9 ±0.4
Sm	<0.007	0.009±0.003	2.2 ±1.0
weighted mean			1.28±0.07

Because results treated in this manner were essentially the same for both tubes wrapped in Al foil, only the mean values are reported. For conceptual convenience, the values in Tables 2 and 3 can be regarded as the contribution from the silica tube (tube blank error) to the total observed concentration in units of nanograms of element per milligram of sample (i.e., ppm) for a sample weighing 1 mg encapsulated in such a tube. For example, if a tube had contained a sample weighing 1 mg, then the error in Fe concentration calculated for the sample resulting from ^{59}Fe associated with the tube would have been about 50 μg/g (Table 2). If the tube had contained a sample weighing 100 mg, then the error would have been only 0.5 μg/g.

Several of the radionuclides observed, namely, ^{46}Sc, ^{51}Cr, ^{59}Fe, ^{60}Co, ^{122}Sb, and ^{181}Hf, are not (n, fission) products, but result from (n, γ) reactions upon impurities in the silica tubing or contaminants introduced during preparation of the tubes. Results for these elements in all three tubes were similar, except Sb, for which concentrations were considerably higher in the tube that was not in contact with Al foil (Table 2). (Among blank tubes we have included in many previous experiments, results for Sb have been more variable than those for other elements.) Because the actual masses of the silica tubes were 1.2 g each, the values in Table 2 are the approximate concentrations in ng/g of contaminants associated with the silica glass. (Accurate estimates of the concentrations of impurities in the silica glass are difficult to obtain for several reasons. One problem is contamination prior to irradiation because of the very low concentrations involved. This may be the cause of the erratic Sb blanks. Another problem is matching the geometry of the tube and standard during radioassay. The volume of the empty tubes is usually much larger than the volume of the elemental standard contained in another such tube.)

In addition to the radionuclides discussed above, photopeaks for ^{95}Zr, ^{95}Nb, ^{99}Mo, ^{140}La, ^{141}Ce, ^{147}Nd, and ^{153}Sm were observed in the two foil-wrapped tubes, but not in the tube that was not in contact with Al. Three possibilities exist for the presence of these radionuclides in the foil-wrapped tubes.

(1) Each of the radionuclides is a fission product of ^{235}U. Thus, the two foil wrapped tubes may have contained an impurity or contaminant of U not present in the tube that was not wrapped in foil. This possibility can be eliminated because the quantity of U in the silica is too small to have produced the observed activity of fission products. Correction for interferences from fission products of ^{235}U from uranium contained in a sample is usually made from the U concentration obtained from (n, γ) activation of ^{238}U, using correction factors such as those listed by Korotev and Lindstrom (1985), Glascock *et al.* (1986) and Landesberger (1986). Using these factors, the activities of ^{95}Zr, ^{99}Mo, ^{140}La, ^{141}Ce, ^{147}Nd and ^{153}Sm observed in the foil-wraped tubes were each those expected from about 1.3 ng U (Table 3). As was observed in the diamond discussed in the introduction, however, no peaks of ^{239}Np were observed in the silica. (A peak at 228 keV was that of ^{132}Te, a fission product, not ^{239}Np.) Based on background noise in the vicinity of 106 keV, the location of the most sensitive photopeak of ^{239}Np, an upper limit of 0.03 ng was calculated for the ^{238}U content of the silica (Table 2). Thus, the quantity of U necessary to produce the observed count rates of fission-product isotopes in the silica (1.3 ng of U) far exceeded the actual U content of the silica, so if the radionuclides derived from fission of ^{235}U, then the uranium must not have been that contained in the silica glass.

(2) Each of the radionuclides in question is also a product of neutron capture. Thus, they may result instead (totally or in part) from impurities in the silica or contamination of the silica glass by material containing Mo, Zr, and rare earth elements prior to irradiation. For several reasons, however, neutron capture cannot be the principal source of these radionuclides. First, as in the case above, it would require the coincidence that the impurity or contamination affected both foil-wrapped tubes to the same extent and affected the unwrapped tube

to a much lesser extent. Second, if these radionuclides were produced in large part by neutron capture by tube impurities, it would be a remarkable coincidence that the observed quantity of each radionuclide corresponds to a quantity of uranium (1.3 ng/g) that is the same for all elements, within experimental uncertainty (Table 3). Third, signals for ^{131}I, ^{132}I, ^{132}Te, and ^{103}Ru were also observed in the tubes which had been wrapped in Al foil. These radionuclides are fission products, but not neutron-capture products. Finally, the Zr/Hf ratio in rocks and minerals, such as the quartz from which the high-purity silica was presumably made, is remarkably constant at about 35–40. The signal for ^{181}Hf, an (n, γ) product, corresponded to 0.011 ± 0.005 ng of Hf (Table 2); thus the actual mass of Zr in the tube would probably not exceed about 0.7 ng. The observed signal for ^{95}Zr, however, was equivalent to that expected from 14 ng of Zr (Table 3) if all of it had resulted from neutron capture. Thus, most of the ^{95}Zr cannot have resulted from neutron capture by ^{94}Zr.

(3) The only remaining possibility is that the radionuclides are fission products implanted in the silica by recoil from fission of ^{235}U outside the tube, most likely from the Al foil in contact with the silica tubes. If the fission-products were merely surficial contamination, they would probably have been removed by the acid wash following irradiation. The mass of foil wrapped around each tube was about 65 mg. Thus, the fission products observed in the silica derived from about $1.3/65 = 0.02$ nanograms of U per mg of foil, or about 5% of the ^{235}U contained in the foil (foil 4, Table 1).

Discussion

In our laboratory (and many others) it is common practice to encapsulate samples in ultrapure silica tubes for neutron irradiation, and then radioassay the samples in the same tubes. This procedure is used because it minimizes the need to transfer and weigh radioactive material (often powders) into unirradiated counting vials and because for all elements determined, blank concentrations in high-purity silica are negligibly small for most types of samples. To hold the tubes together during irradiation, they are wrapped with aluminum foil, so foil is in contact with all tubes on the outside of the bundle.

For samples that fill a significant fraction of a tube, the data in Table 3 indicate that the error from implanted fission products would be negligibly small for most types of samples. For example, the error in the Zr concentration would be only 0.14μg/g for a 100 mg sample in a tube totally wrapped in Al foil containing 0.4μg/g U, as in the experiment described here. This would be a negligible error for most geologic samples. In the following circumstances, however, the error might be significant: (1) the sample mass is small, (2) the sample has low concentrations of Mo, Zr, or light rare-earth elements, (3) a large surface area of a sample or tube is in contact with the foil, or (4) the foil is particularly rich in uranium. The case of the diamond discussed in the introduction is a worst case; the analytical error resulting from the implanted fission products could have led to an overestimation of the concentrations of several elements by at least a factor of ten, had the error not been noted.

Aluminum is a preferred material for many reactor experiments. Thus, fission products from U in Al metal may also be a potential source of error in other experiments, such as those in which U concentrations or crystallization ages of rocks and minerals are determined from fission tracks following neutron irradiation. It is clear from Table 1 that U concentrations in Al metal are highly variable. The potential for error can be minimized by selecting Al foil with a low U concentration.

References

Glascock, M. D., Nabelek, P. I., Weinrich, D. D. and Coveney, R. M., Jr. (1986) Correcting for uranium fission in instrumental neutron activation analysis of high-uranium rocks. *J. Radioanal. Nucl. Chem. Art.* **99**, 121–131.

Honda, M., Reynolds, J. H., Roedder, E. and Epstein, S. (1987) Noble gases in diamonds: Occurrences of solarlike helium and neon. *J. Geophys. Res.*, **92** (B12), 12507–12521.

Korotev, R. L. (1987) National Bureau of Standards coal flyash (SRM 1633a) as a multielement standard for instrumental neutron activation analysis. *J. Radioanal. Nucl. Chem., Art.* **110**, 159–177.

Korotev, R. L. and Lindstrom, D. J. (1985) Interferences from fission of ^{235}U in INAA of rocks. *Trans. Am. Nucl. Soc.* **49**, 177–178.

Landesberger, S. (1986) Spectral interferences from uranium fission in neutron activation analysis. *Chem. Geol.* **57**, 415–421.