

CORRECTING FOR URANIUM FISSION IN INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF HIGH-URANIUM ROCKS

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Failure to correct for fission products of ^{235}U is shown to result in significant errors in the measured concentrations of La, Sm, Nd, Ba, Zr, and Mo by Instrumental Neutron Activation Analysis of high uranium rocks. Measured and calculated correction factors are presented as the ratio of the fission product to parts per million by weight of uranium in the rock. Potential errors in petrogenetic interpretations of uncorrected data are outlined.

Introduction

Instrumental neutron activation analysis (INAA) is commonly used by geologists and geochemists for the analysis of trace elements in rocks to study the physical and chemical processes operating during formation. Accurate trace element abundances for the rare earth elements (REE), Ba and Zr are particularly critical for petrogenetic modeling calculations. However, some REE data published as chondrite-normalized patterns are not smooth, especially for granitic rocks. This is partly because results which are uncorrected for nuclides formed by the fission of ^{235}U are sometimes published. Here we correct such deficiencies and outline situations where the presence of appreciable uranium may lead to erroneous petrogenetic interpretations. Furthermore, our experimental method gives correction factors which are in excellent agreement with parametric values which can be easily calculated.

Experimental

Five replicates of the individual element standards and ten replicates of uranium were prepared from known stock solutions which were calibrated to within $\pm 1\%$. For each sample, 50 λ (0.050 ml) of liquid was put into high purity quartz vials.

Each vial was weighed carefully after inserting the 50 λ of stock solution to insure that the proper amount had been transferred. To wash the liquid down from the interior walls of the vials, another 50 λ of distilled water was added. The vials were spun on a centrifuge and the quartz was then sealed by torch. The amount of element in each vial was: Zr:100 μg , Mo:0.050 μg , Ru:2.115 μg , Ba:700 μg , La:1.18 μg , Ce:17.72 μg , Cd:19.66 μg , U:1.801 μg (prepared from a uranium stock with ^{235}U at the natural abundance level of 0.72%).

In addition to the individual element standards, five replicates each of well characterized reference materials were prepared in quartz vials. About 75 mg of each reference material was precisely weighed into the vials. The materials used were: SRM-1633a (NBS Fly Ash; U=10.3 ppm), RGM-1 (U.S. Geological Survey, Rhyolite glass; U=5.84 ppm), MQSB-1 (Mecca Quarry shale; U=125 ppm).

Reference materials SRM-1633a and RGM-1 are well-known interlaboratory standard obtained, respectively, from the U.S. National Bureau of Standards and the U.S. Geologic Survey. Sample MQSB-1 is our own intralaboratory standard, originating from a 10 kg block of metal-rich bed B of the Mecca Quarry shale member of the Linton Formation of Indiana.¹ Standard MQSB-1 has been pulverized by grinding in a steel ball mill to a maximum grain size of approximately 200 μm .

Flux monitors of Co and Zr in triplicate, placed in quartz vials, were used to obtain data for the proposed calculations and assurance of proper irradiation conditions. Sample were continuously irradiated for a total of 12 hours in position B2(10-20) at the Univer of Missouri Research Reactor (MURR). The bundle of samples was rotated continuously by an automatic rotary system at a rate of nine revolutions per hour to insure uniform irradiation of all samples. The flux monitors were analyzed three days after irradiation to determine the thermal and epithermal neutron fluxes. These were determined to be: $\Phi_{\text{th}} = 5.28 (\pm 0.11) \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and $\Phi_{\text{epi}} = 1.06 (\pm 0.09) \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ respectively.

Samples were counted at two separate times using a 20% efficiency Princeton Gamma Tech detector with 1.80 keV resolution. The first counting for 3600 seconds each occurred from 3-5 days after irradiation ended to measure the isotopes ^{140}La , ^{99}Mo , ^{97}Zr , and ^{143}Ce . The second count for ^{103}Ru , ^{95}Zr , ^{131}Ba , ^{141}Ce , and ^{147}Nd was made 33-35 days after irradiation. All data were acquired and processed by a Nuclear Data ND6620 analyzer system with its associated software.

Results

The experimentally measured amounts of fission products produced during irradiation in the uranium samples are given relative to the amount of total uranium as correction factors M_x/M_U in Table 1. Inspection of the Table indicates that the corrections differ depending on which isotope is being counted.

Table 1
Experimentally determined correction factors
for contribution of uranium to various isotopes

Isotope	Gamma-ray energy, keV	Correction factor M_x/M_U	
^{95}Zr	756.7	11.3	(± 0.2)
^{97}Zr	743.4	26.6	(± 0.9)
^{99}Mo	140.5	1.41	(± 0.05)
	739.5	1.39	(± 0.05)
^{103}Ru	497.1	0.126	(± 0.003)
^{131}Ba	496.2	3.37	(± 0.07) $\cdot e^{0.0402 \cdot T_d}$
^{140}La	1596.5	0.0028	(± 0.0002) $\cdot [e^{0.35593 \cdot T_d} - 1]$
^{141}Ce	145.4	0.287	(± 0.008)
^{143}Ce	293.3	1.35	(± 0.04)
^{147}Nd	91.1	0.21	(± 0.01)

For example, both ^{95}Zr and ^{97}Zr are produced during the fission of ^{235}U . Corrections for both are extremely large, with M_x/M_U ratios of 11.3 for ^{95}Zr and 26.6 for ^{97}Zr . Corrections for ^{99}Mo and the REE isotopes, ^{141}Ce , ^{143}Ce and ^{147}Nd , are much smaller, but may be significant if the true amount of the element present in the rock is comparable to uranium. These isotopes are direct products of ^{235}U fission and the interference correction factors are applicable for any decay time following the irradiation. To obtain the correct element concentrations in the presence of these interferences, the amount of uranium in the rock must be determined first and then multiplied by the M_x/M_U factor. This interference contribution is then subtracted from the measured concentrations for the element.

Two nuclides, ^{140}La and ^{131}Ba , are special cases because their correction factors are dependent on the length of decay between irradiation and counting. ^{131}Ba itself is not a fission product of ^{235}U . However, the most commonly analyzed ^{131}Ba peak occurs at 496 keV and it cannot be resolved from the 497 keV peak of ^{103}Ru , a fission product of ^{235}U . The contribution to the 497 peak by ^{103}Ru cannot be readily calculated by using another peak from ^{103}Ru because it is the only peak with sufficient intensity to be measured. ^{103}Ru has a half-life different from ^{131}Ba and the apparent M_x/M_U for ^{131}Ba of 3.37 at the end of irradiation needs to be adjusted for ^{103}Ru decay by the factor $e^{0.0402 \cdot T_d}$ where 0.0402 is $\lambda^{131}\text{Ba} - \lambda^{103}\text{Ru}$ and T_d is time after irradiation, both in units of days. The correction becomes greater with time because the half-life of ^{103}Ru is larger than that of ^{131}Ba . Other ^{131}Ba peaks at 216 and 373 keV can be used as a check on the results from applying the interference correction to the 497 keV peak. However, the analytical precision of

these peaks are smaller than on the 496 keV peak even if the latter needs to be corrected for ^{103}Ru interference.

Because ^{140}La is a daughter of fission-produced ^{140}Ba (12.8 d), the concentration of ^{140}La needs to be corrected for the time of decay following irradiation. When $T_d=0$, M_x/M_U is 0.0028. This value increases with time by a factor of $e^{0.35893 \cdot T_d} - 1$. Large corrections can be avoided by counting for ^{140}La as soon as possible after irradiation when the adjustment is usually less than 1%, given the typical abundances of La in rocks. The correction for ^{140}La produced during irradiation is independent of the duration of irradiation at least to the point where ^{140}Ba nears saturation. In that case, corrections for ^{140}La produced during irradiation need to be applied.^{2,3}

It is noted that we did not attempt to determine the correction factor for samarium as a more severe interference results from the ^{239}Np 103.8 KeV peak on the ^{153}Sm 103.2 keV peak. KOROTEV and LINDSTROM⁴ suggest that the interference factor due to fission is only 0.004.

Parametric correction

The experimentally determined correction factors were compared to parametrically determined values. These values can be calculated if thermal and epithermal neutron fluxes for a particular irradiation are known. The parameters used for the calculation are given in Table 2 and the results are given in Table 3. The saturation activity (SA_s) in $\mu\text{Ci}/\text{mg}$ of the element standard can be calculated using:

$$SA_s = \frac{1.628 \times 10^{16}}{M} \theta [\phi_{th} \cdot \sigma_{th} + \phi_{epi} \cdot I_o] \quad (1)$$

where M — atomic weight of the element standard,
 θ — isotopic abundance of the target isotope,
 ϕ_{th} — thermal neutron flux (see experimental procedures),
 ϕ_{epi} — the epithermal neutron flux,
 σ_{th} — thermal neutron cross section,
 I_o — the resonance integral.

To calculate the activity at saturation of the fission isotope per milligram of uranium (SA_f), Eq. (1) is used, but the result needs to be multiplied by the fission

Table 2
Nuclear parameters for (n, γ) reaction products which have interferences from ^{235}U (n, f) reaction products

Reaction	Atomic weight	Isotopic abundance	Thermal neutron cross section, barns	Resonance integral, barns	Isotopic half-life, d	Gamma-ray energy, keV	Branching ratio, %	Fission yield, %
$^{94}\text{Zr}(n, \gamma)^{95}\text{Zr}$	91.22	0.1739	0.052	0.306	64.0	756.7	54.6	6.50
$^{96}\text{Zr}(n, \gamma)^{97}\text{Zr}$	91.22	0.028	0.020	5.6	0.70	743.4	92.8	5.93
$^{98}\text{Mo}(n, \gamma)^{99}\text{Mo}$	95.94	0.241	0.13	6.9	2.75	739.4	12.6	5.78
$^{102}\text{Ru}(n, \gamma)^{103}\text{Ru}$	101.07	0.316	1.20	4.4	39.35	497.1	86.4	3.04
$^{130}\text{Ba}(n, \gamma)^{131}\text{Ba}$	137.33	0.00106	11.00	263	12.0	496.2	42.0	*
$^{139}\text{La}(n, \gamma)^{140}\text{La}$	138.9	0.999	9.20	11.4	1.68	1596.2	95.5	6.35**
$^{140}\text{Ce}(n, \gamma)^{141}\text{Ce}$	140.12	0.885	0.57	0.47	32.5	145.5	48.4	5.80
$^{142}\text{Ce}(n, \gamma)^{143}\text{Ce}$	140.12	0.111	0.97	1.15	1.375	293.3	42.0	5.95
$^{146}\text{Nd}(n, \gamma)^{147}\text{Nd}$	144.24	0.172	1.30	2.85	11.0	91.1	27.2	2.23
$^{235}\text{U}(n, f)$	238.03	0.0072	584	280	—	—	—	—

*There is no fission yield for ^{131}Ba . The 497 keV gamma-ray from ^{131}Ba cannot be resolved from the 496 keV gamma-ray from fission produced ^{103}Ru .

**Formed by decay of ^{140}Ba (12.8 d).

Table 3
Calculated correction factors for interference from the
 $^{235}\text{U}(n, f)$ reaction

Isotope	Gamma-ray	Correction factor, M_x/M_U
^{95}Zr	756.7	10.5
^{97}Zr	743.4	26.1
^{99}Mo	739.4	1.53
^{103}Ru	497.1	0.135
^{131}Ba	496.2	2.74 $\cdot e^{0.0402 \cdot T_d}$
^{140}La	1596.5	0.00274 $\cdot e^{0.35893 \cdot T_d - 1}$
^{141}Ce	145.5	0.283
^{143}Ce	293.3	1.35
^{147}Nd	91.1	0.26

yield factor, η . The saturation activities are converted to end of irradiation activities (A_s and A_f) by:

$$A = SA \cdot (1 - e^{-\lambda T_i}) \tag{2}$$

where T_i is the time of irradiation, in our case 0.5 days. To obtain the interference factor for each element, M_x/M_U , A_f for the fission isotope needs to be divided by A_s for the standard. However, the time-dependent correction factor for the 496.2 peak of ^{131}Ba needs to be calculated using:

$$\frac{M_x}{M_U} = \left[\frac{SA^{103}\text{Ba}}{SA^{131}\text{Ba}} \right] \cdot \left[\frac{1 - e^{-\lambda^{103}\text{Ru} \cdot T_i}}{1 - e^{-\lambda^{131}\text{Ba} \cdot T_i}} \right] \cdot \left[\frac{b^{103}\text{Ru}}{b^{131}\text{Ba}} \right] \tag{3}$$

where b is the branching ratio.

The parametric correction factor for ^{140}La formed by the decay of fission produced ^{140}Ba can be derived from the general radioactivity equations (DE SOETE⁵) which account for the ^{140}La produced during irradiation and after the end of irradiation. For practically all counting experiments in which ^{140}La from fission produced ^{140}Ba is measured the ^{140}La produced after the end of irradiation is the only important term. The correction factor for ^{140}La is then best approximated by the expression in Table 3. The experimentally determined value in Table 1 is deemed superior as it agrees well with that of KOROTEV and LINDSTROM⁴ who obtained 0.00248 ± 0.00003 .

Comparison of measured and calculated correction factors indicates an excellent agreement. The only appreciable discrepancy is in the correction value for ^{131}Ba .

We recommend using the experimentally determined values for all the elements because they are independent of the neutron flux measurements and other nuclear parameters which are not necessarily known to a high degree of accuracy. Furthermore, our measured correction factor for barium is in excellent agreement with the value of 3.33 ± 0.06 reported by KOROTEV and LINDSTROM.⁴

Analysis of rocks and errors in interpretation of data

Concentrations of REE and the other analyzed elements were obtained for several rock samples to illustrate potential errors in petrogenetic interpretations due to uncorrected data (see Table 4). The chondrite-normalized REE patterns are shown in Figs 1–3. For REE heavier than Nd, SRM–1633a fly ash was used as the standard.

It is readily observed that only small corrections are required for the light REE

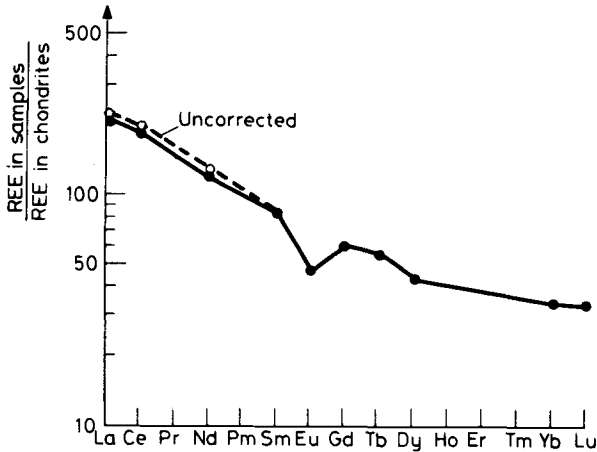


Fig. 1. Chondritic normalized abundances for NBS Fly Ash SRM–1633a

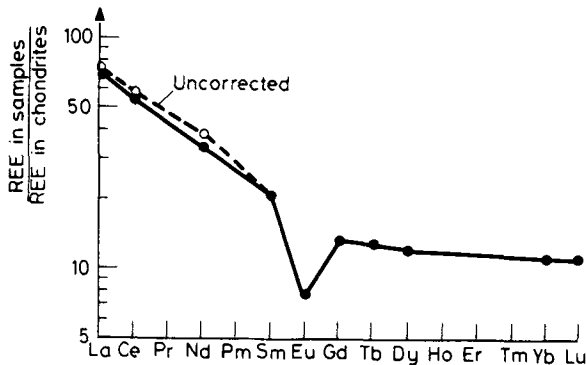


Fig. 2. Chondritic normalized abundances for RGM–1 geological reference material

Table 4
Analytical results for standard samples

Sample	Element	Uncorrected concentration, ppm	Corrected concentration, ppm
SRM-1633a	La	75.1 (\pm 0.8)	74.7 (\pm 0.7)
	Ce	177 (\pm 4)	174 (\pm 4)
	Nd	80 (\pm 4)	78 (\pm 4)
	Sm		16.6 (\pm 0.1)
	Eu		3.50 (\pm 0.04)
	Gd		16.0 (\pm 0.2)
	Tb		2.69 (\pm 0.07)
	Dy		14.6 (\pm 0.3)
	Yb		7.68 (\pm 0.09)
	Lu		1.15 (\pm 0.02)
	Zr	497 (\pm 52)	380 (\pm 47)
	Ba	1403 (\pm 84)	1259 (\pm 75)
	Mo	39 (\pm 3)	25 (\pm 2)
	U		10.3 (\pm 0.3)
RGM-1	La	24.4 (\pm 0.6)	24.2 (\pm 0.5)
	Ce	52 (\pm 1)	50 (\pm 1)
	Nd	24 (\pm 1)	22 (\pm 1)
	Sm		4.14 (\pm 0.04)
	Eu		0.58 (\pm 0.03)
	Gd		3.50 (\pm 0.05)
	Tb		0.63 (\pm 0.03)
	Dy		4.1 (\pm 0.3)
	Yb		2.51 (\pm 0.11)
	Lu		0.402 (\pm 0.007)
	Zr	352 (\pm 19)	290 (\pm 17)
	Ba	894 (\pm 34)	810 (\pm 31)
	Mo	9 (\pm 1)	1 (\pm 1)
	U		5.8 (\pm 0.2)
MQSB-1	La	32.2 (\pm 0.7)	28.5 (\pm 0.6)
	Ce	91 (\pm 4)	55 (\pm 3)
	Nd	62 (\pm 4)	35 (\pm 3)
	Sm		6.17 (\pm 0.11)
	Eu		1.25 (\pm 0.02)
	Gd		5.9 (\pm 0.2)
	Tb		0.93 (\pm 0.03)
	Dy		5.0 (\pm 0.3)
	Yb		2.99 (\pm 0.07)
	Lu		0.45 (\pm 0.03)
	Zr	1466 (\pm 50)	43 (\pm 45)
	Ba	2446 (\pm 113)	733 (\pm 96)
	Mo	1831 (\pm 20)	1655 (\pm 18)
	U		125 (\pm 2)

in SRM-1633a and RGM-1, since they contain only moderate amounts of uranium, 10.3 and 5.8 ppm, respectively. In fact, the corrections required are within the error of the analysis. The uncorrected REE pattern is slightly concave downward and would appear to be more so if the sample contained more uranium. Typically, concave-down patterns are associated with minerals such as clinopyroxene, hornblende, or sphene,

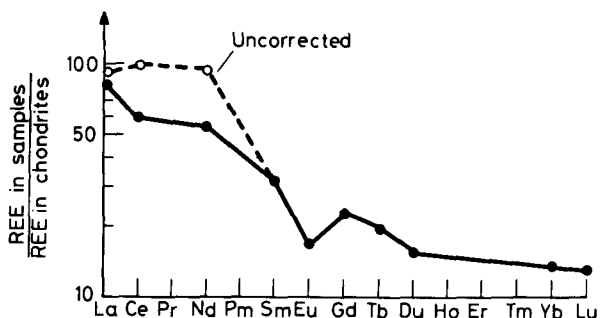


Fig. 3. Chondritic normalized abundances for Mecca Quarry Shale MQSB-1

which have generally stronger affinity for the middle REE.⁶ Thus an uncorrected rhyolite pattern, such as RGM-1, could be erroneously interpreted as to have resulted from accumulation of any of these phases.

The false concave-down pattern is especially well illustrated by the Mecca Quarry Shale (MQSB-1) data. This sample contains 125 ppm uranium, and therefore, the corrections for light REE become extremely large. The uncorrected pattern is significantly enriched in light REE and the light REE side appears to be decisively concave-downward. Such a pattern may be interpreted to be the result of accumulations of a mineral, such as allanite, which is commonly called upon to explain light REE enriched patterns. The corrected pattern is clearly different and even exhibits a slight negative cerium anomaly. This is consistent with the depositional environment of this brackish-water shale⁷ as it is known that rocks which form in sea water commonly have negative cerium anomalies.^{8,9}

The largest corrections are for zirconium: 11.3 for ⁹⁵Zr and 26.6 for ⁹⁷Zr. It is thus clearly advantageous to analyze for ⁹⁵Zr. The correction is particularly critical for modeling the petrogenesis of granitic melts as these often form in equilibrium with zircon in the residue¹⁰ and zircon is an important host for uranium in such rocks. The magnitudes of the correction factors suggest that some reported sympathetic Zr and U relationships may be erroneous if the Zr values were not corrected for fission-produced Zr. For example, in RGM-1, the apparent Zr concentration is 352, but the true value is 290, a 21% error. The error for SRM-1633a

is 30% and for MQSB-1 it is 3309%. So correction factors for U contributions to Zr peaks can be appreciable. Corrections as large as that of MQSB-1 are, in fact, unacceptable and we suggest that INAA cannot be used to analyze for Zr in such uranium-rich samples.

The correction for barium is also relatively large and the concentrations may be significantly overestimated in uraniferous samples. For example, failure to correct for fission produced ^{103}Ru introduces 235% error in MQSB-1 if it is counted 36 days after irradiation. Such uncorrected data may affect the interpretation of petrogenetic processes, because barium is an element commonly used for numerical modeling of sources for granitoids and other uranium-rich rocks.

Molybdenum is seldom used to model petrogenesis of granitoids because its abundance is generally small and there is little information regarding mineral/melt partition coefficients. However, conventional Mo ore deposits are for the most part associated with granitoids, some of which may contain high uranium concentrations. Mining cut-off grades for granitoid-hosted deposits are near 500 ppm Mo, and, as most granites contain less than 10 ppm U, the error introduced by INAA analysis for Mo in an ore deposit will be relatively small. However, for solving the petrogenesis of an ore deposit, workers may sometimes analyze possible source rocks which contain little Mo. For example, most granitoids contain only 1–2 ppm Mo as reported by TUREKIAN and WEDEPOHL,¹¹ a value that is of the same order or less as typical U contents. Hence, in many cases, INAA data for typical granitoids would show substantial contributions to the Mo Peak from U fission. In some cases, nearly all of this Mo may be a fission product of uranium. For example, the uncorrected concentration of Mo in RGM-1 is about 9 ppm, whereas the true value for natural Mo is 1 ppm.

In addition to the Mecca Quarry shale discussed here, there are numerous cases of simultaneous enrichment of Mo and U in black shales. For example, there are the eastern Devonian age shales of SHAFFER et al.¹² and LEVENTHAL¹³ and various Western shales described by DESBOROUGH and POOLE.¹⁴ In all such cases, care must be taken to assess the contribution of the Mo peak by uranium fission in order to arrive at a valid Mo assay.

Another geological setting where uranium may be a particularly significant contribution to the Mo peak would be in Colorado Plateau-type (roll-front) uranium deposits where high Mo values are spatially associated with U–Se–V enrichments. In such cases, the highest (ore-grade) uranium values are not typically coincident with the largest concentrations of molybdenum. However, the peak values for both elements are commonly juxtaposed—a circumstance that suggests the need for caution in interpreting INAA results.

Conclusions

Both experimentally determined and separately calculated correction factors presented in this paper demonstrate the necessity of adjusting INAA measured concentrations of La, Ce, Nd, Zr, Ba, and Mo to compensate for isotopes produced by fission of uranium in the sample during irradiation. The experimentally determined correction factors are independent of the reactor and detector specifications and therefore of general use. Moreover, an independent assessment of the correction factors can be easily calculated if the flux of thermal and epithermal neutrons is known. It is shown that uncorrected results can potentially lead to incorrect petrogenetic modeling conclusions, particularly if zirconium and barium concentrations are used and that molybdenum assays may be deleteriously affected by the presence of large amounts of uranium. Perhaps most importantly, REE plots, which ordinarily are based on NAA data, may show misleading trends unless proper corrections are made.

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