

Determination of Rare Earth Element Distribution Patterns in Rocks and Minerals by Neutron-Activation Analysis*

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Neutronenaktivierungsanalytische Bestimmung der Verteilung der Seltenen Erden in Gesteinen und Mineralien. Ein Routineverfahren für die Bestimmung von 11 Elementen der Seltenen Erden in natürlich vorkommenden Mineralien und Gesteinen wird beschrieben. Die Proben werden mit thermischen Neutronen bestrahlt und anschließend die Substanzen nach Zusatz von Trägerelementen (Seltene Erden) mit Na_2O_2 aufgeschlossen. Die Seltenen Erden werden dann als Gruppe mittels eines Hydroxid-Fluorid-Trennverfahrens isoliert. Silicium wird als Gel abgetrennt. Die Messung der Aktivitäten in den Lanthanidenkonzentraten erfolgt mit einer Ge(Li) Gamma-Spektrometer-Meßanordnung hoher Auflösung. Die bei der chemischen Abtrennung der Seltenen Erden erzielte Ausbeute wird anschließend durch Bestrahlung der Anreicherungsprodukte und Messung der Aktivitäten der Trägerelemente bestimmt.

Die Reproduzierbarkeit und Genauigkeit der Methode wurde durch die mehrfache Analysierung bestimmter Proben und von Standardgesteinen (z. B. W-1) geprüft. Mit leichten Änderungen wurde das Verfahren an über 100 Gesteins- und Mineralproben erprobt. Es hat sich gezeigt, daß mit den 11 durch Neutronenaktivierung quantitativ bestimmten Seltenen Erden die Verteilung dieser Elementgruppe in natürlich vorkommenden Mineralien und Gesteinen hinreichend gut beschrieben werden kann.

Summary. A routine procedure for determining eleven of the fourteen naturally occurring rare earth elements (REE) in rocks and minerals is described. Following thermal neutron activation the samples are decomposed, in the presence of REE carriers, by fusion with Na_2O_2 . The REE are separated as a group using a gel removal technique for silica and a conventional hydroxide-fluoride cycle. The REE concentrates are then counted with a high resolution Ge(Li) spectrometer system. Chemical yields are determined by reirradiation and counting of the carrier.

The high precision and accuracy of the technique have been proven through replicate analyses and through analyses of the U.S. Geological Survey standard rock, W-1. The technique, with slight modifications, has been tested to date on more than a hundred rock and mineral samples. Experience has shown that the eleven REE determined by this technique more than adequately describe the total distribution patterns for the REE in naturally occurring samples.

Best. von Seltenen Erden in Gesteinen und Mineralien; Aktivierungsanalyse, Neutronen.

The REE are highly dispersed in the common rocks and rock-forming minerals, with concentrations for individual elements ranging from about 100 ppm to the sub-ppb level. Sample size also is often limited by availability. Because of the extremely low levels of

the REE in many natural materials and of possible limitations on sample availability, the need for developing new analytical methods has grown. Mass spectrometry (e.g. [6]) and neutron-activation analysis (NAA) (e.g. [4]) are perhaps the only two techniques that are presently capable of meeting these two restrictions.

The present technique, using destructive NAA, is not completely unique. It comprises some of the best and most appropriate techniques of others (see esp. [8] and [1]) and is designed to give maximum sensitivity and relative speed. The method will be

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described as presently performed on silicate samples. For other sample types, depending upon their physical and chemical state, some modifications may be necessary.

Experimental

Stock solutions of the individual REE, with the exception of Ce, are prepared from their respective Spec-pure oxides by dissolution in HCl or HNO₃. The dissolution of CeO₂, which proceeds only very slowly by this method, warrants further description:

10 ml of 96% H₂SO₄ are added to a beaker containing approximately 1.5 g CeO₂. The powder is stirred until all small clumps are broken up. Then 10 ml of 47% HBr are poured very slowly into the beaker. The beaker is covered, and the solution heated carefully to approximately 80°C. When the escape of the brown Br₂ vapor has ceased, the solution is cooled, an additional 10 ml HBr added, and the heating procedure repeated. When the Br₂ vapor is again no longer visible and the solution allowed to cool, Ce₂(SO₄)₃ precipitates from the saturated solution. This precipitate dissolves when the solution is diluted with 150–180 ml H₂O and warmed slightly, thus ensuring that the reduction of Ce⁴⁺ to Ce³⁺ is complete. The resulting solution is then transferred to a platinum dish and heated slowly to drive off the excess H₂SO₄. The dry Ce₂(SO₄)₃ is dissolved in 20–30 ml H₂O and diluted to the desired final volume for the stock solution.

The concentrations of the stock solutions are determined by back titration of EDTA following the method of Haskin *et al.* [4]. A standard monitor solution and a carrier solution are prepared from the stock solutions to concentrations similar to those recommended by Denechaud *et al.* [1].

Sample materials, consisting of 200–500 mg of finely ground powders, are weighed into 1 ml polyethylene vials and heat-sealed. The REE standard solution is either similarly encapsulated or sealed in quartz tubing. The standard and five or six sample vials are arranged symmetrically in an aluminium irradiation capsule. The capsules are irradiated for 3–7 days (depending upon the expected REE content of the samples) in the thermal column of the reactor FR-2 of the Kernforschungszentrum Karlsruhe at a flux of 2.2×10^{11} n/cm²-sec. The flux dose is either homogenized by means of a rotating sample holder or monitored by a 10–20 mg piece of iron wire wrapped around each sample and standard vial.

After irradiation the samples are allowed to cool for 18–24 h before chemical handling (see Fig. 1). The sample vials are then opened and the contents placed in nickel crucibles in which 2 ml of the REE carrier solution and 5 to 10 mg each of Sc, Cr, and Co chloride have been evaporated. The Sc, Cr, and Co act as hold-back carriers to facilitate removal of the activated species of these elements from the sample during chemical processing. The samples are fused to red heat with approximately five times their volume Na₂O₂. While still warm, each crucible is placed in a beaker containing 80–100 ml H₂O. The fusion cake is dissolved with concentrated HCl, and hydroxides are precipitated using concentrated NH₄OH and solid NH₄Cl as a buffer. This precipitation procedure effects an early removal of the intense Na and K activities in the supernatant solution. Following the method of Denechaud *et al.* [1], the hydroxides are then dissolved

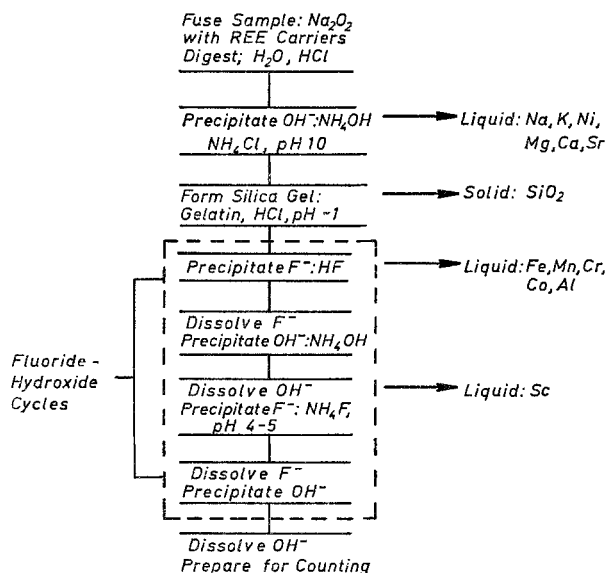


Fig. 1. REE separation scheme

with HCl, the solution evaporated until silica gel forms, and approximately 25 mg gelatin added to aid the coagulation of silica gel. The supernatant solution and washings of the gel mixture are then carried through a three times repeated cycle of fluoride and hydroxide precipitations. The first fluoride precipitate is effected with 48% HF and the two subsequent precipitations with a 6 N solution of NH₄F, following the recommended procedure of Stevenson and Nervik [7] for elimination of Sc impurities. During the hydroxide-fluoride cycle, the REE fluorides are dissolved with a few ml of saturated H₃BO₃ solution and about 1 ml of 2 N HNO₃. The final hydroxide precipitate is dissolved with 2 N HCl; and the solution is placed in a clean, 2 ml polyethylene vial for counting. The resulting solution contains only the REE with occasionally detectable impurities of Sc and Ba. An aliquant of the standard solution is weighed into a similar polyethylene vial and prepared for counting. Two experienced workers can fully process five to six samples in approximately 6 h. For readers desiring further description of the chemical separation procedure a detailed flow chart is available from the authors.

Gamma-ray counting of the samples is performed with a 40 cm³ Ge(Li) detector coupled to a 1024 channel analyzer. Peak resolution of the system for the 1.33 MeV Co⁶⁰ gamma-ray is 2.5 keV. The samples are mounted in a specially designed plexiglass holder which permits precise positioning of the samples at variable distances from the detector face. The sample holder and detector are housed within a graded lead shielding (i.e. 5 cm thick walls of Pb lined successively with 0.5 mm thick sheets of Sn and Cu). Samples are counted at three separate decay times (see Table 1) to optimize the peak to background ratios for the nuclides of various half lives. At all times the analyzer dead time is kept at or below 10%. All peaks used lie in the energy range 80–350 keV, thus utilizing the energy region of maximum detector efficiency and resolution.

The yield of the chemical separation is determined by reirradiation of an aliquant of the REE concentrate from each sample. After the final counting each sample vial is

Table 1. Summary of counting conditions

Count set	Days after end of irradiation	Nuclide	Half-life	Energies of γ -rays used (keV)	Interference requiring removal
I	3	^{166}Ho	26.9 h	80.6	
		^{153}Sm	47.0 h	103.2	
		^{140}La	40.2 h	328.8	
II	10	^{147}Nd	11.1 d	91.1	
		^{177}Lu	6.7 d	208.4	
		^{175}Yb	4.21 d	282.6	
III	30—40	^{170}Tm	130 d	84.3	Tb 86.8 keV
		^{153}Gd	242 d	97.4	+ Eu-back-scatter
		^{141}Ce	33 d	145.4	
		^{160}Tb	72.1 d	298.5	Eu 296.0 keV
		^{152}Eu	12.7 yr.	344.4 or 121.8	
Yield	8	^{153}Sm	47.0 h	103.2	
		^{152}Eu	12.7 yr.	121.8	
		^{177}Lu	6.7 d	208.4	
		^{175}Yb	4.21 d	282.6	
		^{160}Tb	72.1 d	298.5	Eu 296.0 keV
		^{140}La	40.2 h	328.8	

opened, and its contents transferred to a 100 ml volumetric flask. The solution is brought to volume by the addition of 10 ml concentrated HCl and deionized water. An approximately 500 mg aliquant of this solution is then sealed in a clean 2 ml polyethylene vial and irradiated together with a similarly diluted 2 ml aliquant of the REE carrier solution for 24 h on the rotating sample holder of the same reactor. 8 days after irradiation each sample is counted once and a total of six REE determined in this counting (see Table 1). The chemical yields for the other five elements can then be determined by interpolation.

Yields range from 80—98% for the lighter REE and 30—70% for the heavier REE. Experiments indicate that the heavy REE are preferentially retained by the silica gel during the chemical separation. This effect demonstrates the important point that chemical separation of the REE as a group can involve significant fractionation of them relative to one another. Thus, determining the yield of one element and assuming the yield to be the same for all the REE (as has been done in some previous studies) may cause significant errors in the results.

Following the yield counting the digital peak data, heretofore stored on paper punch tape, is read into a computer together with suitable information on sample weights, standard concentrations, etc. Peak areas are calculated at full width-half maximum or, if necessary, as full peak areas to negate the effect of peak broadening or drift. The concentrations of the individual REE are then obtained by computer comparison of the peak areas

Table 2. Comparison of REE analyses of the U.S. Geological Survey standard rock W-1 (concentrations in ppm)

Element	Range of literature values ^a	Average of literature values	Average value this study ^b
La	8.8 — 20.0	11.8	10.2 \pm 0.3
Ce	15.1 — 36.6	23.6	23.5 \pm 0.5
Nd	14.8 — 21.0	17.1	13.3 \pm 0.6
Sm	2.8 — 6.6	3.91	3.26 \pm 0.07
Eu	1.04 — 1.29	1.16	1.13 \pm 0.02
Gd	3.4 — 4.2	3.9	3.7 \pm 0.4
Tb	0.57 — 0.81	0.69	0.65 \pm 0.05
Ho	0.55 — 1.35	0.83	0.77 \pm 0.07
Tm	0.295 — 0.355	0.32	0.30 \pm 0.03
Yb	1.9 — 2.33	2.11	2.00 \pm 0.09
Lu	0.32 — 0.44	0.36	0.298 \pm 0.007

^a Data from Fleischer [2,3]; values used include only analyses by isotope dilution, spark source mass spectrometry, and neutron activation techniques.

^b For most elements averages are for six analyses of W-1. For Ho only one analysis was performed, for Tm only three. Listed uncertainties are standard deviations based on counting statistics.

of the samples and standard, corrected for interference, flux inhomogenities, radioactive decay, sample weight, and yield.

Discussion

The precision of the analyses, based on statistical counting error, is generally in the range of 5—10% for samples containing 50—100 ppm total REE. Uncertainties are consistently higher for the elements Nd, Gd, Tm, and Ho and consistently lower for Ce, Sm, Eu, and Lu. Duplicate analyses of some samples and replicate analyses of the U.S. Geological Survey standard diabase, W-1, indicate that with few exceptions the concentration values obtained are identical within statistical counting error. Comparison of the REE values obtained for W-1 with those reported in the literature is somewhat hampered by the lack of agreement over the correct values. However, comparison with the range of reported values (see Table 2) indicates that the results of the present technique are generally within the range of values obtained by other highly accurate techniques.

We now know that the abundance distribution of the REE in natural materials, with well established exceptions, is very smooth [5]. Thus it is not necessary to expend the time required to determine all fourteen of the naturally occurring REE in order to define their distribution patterns in rocks and minerals. However, some of the fine structure of the distribution is valuable. The present technique, which allows

routine determination of eleven of the REE attempts to strike an optimum compromise between these two factors.

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Instrumentelle Neutronenaktivierungsanalyse von Gesteinen am Beispiel von 7 Standardgesteinen des US Geological Survey*

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Instrumental Neutron-Activation Analysis of Rocks Demonstrated on 7 Standard Rocks of the US Geological Survey. By means of instrumental neutron-activation analysis the elements Sc, Cr, Co, Rb, Sb, Cs, La, Ce, Nd, Eu, Tb, Yb, Lu, Hf, Ta, and Th were determined in the standard rocks G-2, GSP-1, AGV-1, PCC-1, DTS-1, BCR-1, and W-1 of the US Geological Survey. The results were compared with those of other authors. These standard rocks are sufficiently homogeneous, as regards their trace element distribution, to be used as multielement standards in most analyses of geological material.

Zusammenfassung. Mit Hilfe instrumenteller Neutronenaktivierungsanalyse wurden in den Standardgesteinen G-2, GSP-1, AGV-1, PCC-1, DTS-1, BCR-1 und W-1 des US Geological Survey die Elemente Sc, Cr, Co, Rb, Sb, Cs, La, Ce, Nd, Eu, Tb, Yb, Lu, Hf, Ta und Th bestimmt und mit den Ergebnissen anderer Autoren verglichen. Die Gesteinsstandards sind bezüglich ihrer Spurenelementverteilung hinreichend homogen, um bei der Analyse von geologischem Material in den meisten Fällen als Multielementstandards verwendet werden zu können.

Analyse von Gesteinen; Aktivierungsanalyse, Neutronen; US-Standardgesteine als Multielementstandards.

Einleitung

Mit der Entwicklung und raschen Verbreitung von hochauflösenden Ge(Li)-Detektoren hat die instru-

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mentelle Neutronenaktivierungsanalyse (INAA) von komplex zusammengesetzten Substanzen in den vergangenen Jahren sprunghaft an Bedeutung gewonnen. Viele analytische Probleme können seither unter Verzicht auf aufwendige und oft zeitraubende