

Neutron Activation Analysis
For the Rare Earths in Apatite

by

James F. Barker

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Abstract

A method for the determination of low concentrations ($<10\text{PPM}$) of rare earths in minerals and rocks by neutron activation analysis is presented. A 10 min. irradiation of sample and standard required no chemical purification while a 20 hr. irradiation required an ion exchange purification before actual counting. A Li-drifted germanium detector and 1600 channel gamma spectrometer provided sufficient resolution to allow determination of La, Pr, Sm, Eu, Dy, Ho, Yb and Lu in two apatite samples.

The results are generally higher than those obtained by other neutron activation analyses. The specific causes are uncertain and can be resolved best by further study and modification of this neutron activation analysis.

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Introduction

This experimental study was undertaken to develop a method of neutron activation analysis for trace amounts of rare earth elements in minerals and rocks. This method was applied to the determination of rare earth abundances in two analysed apatite samples provided by Z. S. Altschuler, United States, Department of the Interior, Geological Survey.

The non-destructive analysis was done with a Li-drifted Ge counting crystal and a 1600 channel gamma spectrometer. It was thought that the high resolution of this equipment would be needed to separate individual rare earth gamma peaks sufficiently for accurate analysis.

Experimental Procedure

Preparation of Standard Solution:

A standard solution containing all the rare earths was prepared as follows:

- a. Milligram quantities of Johnson Matthey and Mallory specpure rare earth oxides were dried overnight at 110°C. in a drying oven, cooled in a desiccator and portions accurately weighed into a 400 ml. pyrex beaker.
- b. 200 ml. of 6M. HCl was added together with concentrated perchloric acid and the mixture heated strongly on a hot plate. In order to completely dissolve the oxides, the mixture was evaporated to perchloric acid vapours and the residue taken up in 6M. HCl.
- c. This was quantitatively transferred to a 100 ml. volumetric flask and made up to 100 ml. with 6M. HCl. This solution was diluted ten-fold and used as a standard.

Preparation of Standards and Samples for Irradiation:

- a. About 0.1 ml. of standard was introduced into a weighed quartz ampoule with a capillary pipette. The ampoule was reweighed to determine the weight of standard solution. This allowed the determination of the weight of each oxide in each ampoule as the density of the solution was taken

- as that for 6M HCl. plus the total weight of oxide added.
- b. The ampoule was placed in a drying oven at about 80°C. overnight in order to completely evaporate the liquid, and then the ampoule was sealed by fusion.
 - c. Similarly, milligram portions of powdered apatite sample were added to weighed ampoules, the ampoules reweighed and sealed by fusion. The weight of apatite used varied from about 6 mg. to 15 mg.

Irradiation

- a. Two irradiation periods were used -- 10 minutes and 20 hours -- to obtain favourable counting rates on rare earth nuclides with half lives less than 9 hours and on nuclides with half lives from about 18 hours to 4 days.
- b. For irradiations of 10 min., one standard ampoule and one sample ampoule were placed in an aluminum container and irradiated in a high flux reactor position. Triplicate irradiations of each apatite were done.
- c. For 20 hr. irradiations, one standard ampoule and one ampoule of each apatite were placed in an aluminum container and were irradiated in a high flux reactor position. Again, triplicate irradiations of each apatite were done.

Treatment of Irradiated Standards

- a. After cooling, the ampoule was opened and the standard trans-

ferred to a 1 dram pyrex vial. The ampoule was washed six times with 6M. HCl to ensure complete transfer of the residue.

b. The vial was filled to the neck with 6M, H Cl and sealed.

Treatment of Irradiated Samples

a. The apatite samples irradiated for 10 min. were transferred to a 50 ml. beaker, dissolved in 6M. HCl and a 5 ml. aliquot was added to a vial. This reduced the activity and allowed immediate counting with a geometry similar to that of the standard.

b. The samples from the 20 hr. irradiation were each transferred to a 100 ml. beaker, dissolved in about 25 ml. of 6M. HCl, and evaporated to dryness to ensure the conversion of phosphates to chlorides.

c. The residue was taken up in about 5 ml. 0.5M. HCl and loaded onto a Dowex 50 ion exchange column. The column details are included in Appendix I.

d. Most of the non-rare earth activity was eluted from the column using 200 ml. 1.5M. HCl and 50 ml 2M. HCl. The rare earth activity was then eluted in up to 800 ml. 9M HCl. The elutant was collected and counted to monitor the recovery of the rare earth activity. Ytterbium was the first rare earth eluted in 9M HCl and lanthanum the last.

Experimental Results

Table I shows the rare earths determined by this method with the gamma ray energy peak used, the calculated half life, the irradiation time, and the approximate peak to background ratio of each. As this ratio decreases, the statistical error in measuring peak count increases.

TABLE I: LANTHANIDE NUCLIDES USED IN ANALYSES

Nuclide	Energy of Gamma Peak Used(Mev)	Calculated Half Life	Irradiation Time	Peak/Bkgd Ratio
La 140	1.598	42 hr.	20 hr.	12/1
Pr 142	1.573	20 hr.	20 hr.	15/1
Sm 153	0.102	46 hr.	20 hr.	4/1
Eu 152	0.123	10 hr.	20 hr.	10/1
Dy 165	0.362	3 hr.	10 min.	6/1
Ho 166	1.385	30 hr.	20 hr.	5/1
Yb 175	0.397	4.6 d.	20 hr.	3/1
Lu 177	0.208	6.9 d.	20 hr.	3/2

The lanthanide concentrations obtained for the two apatite samples are shown in Table II and Table III. Where one element was determined from two irradiation times, the value for the peak with the highest peak/background ratio was considered more reliable. Where the rare earth was not detected, it was assumed below sensitivity limit³, the calculation of which is indicated in Appendix II.

TABLE II: LANTHANIDE ABUNDANCES (ppm) FOR APATITE MOR-9

Sample Element	MOR-9 #1	MOR-9 #2	MOR-9 #3	Average	Sensitivity Limit (ppm)	Coeff. of Variation (%)
La	35.5	40.1	41.0	38.9	0.1	6.23
P						
Pr	7.0	7.5	9.0	7.8	0.1	10.92
Sm	6.6	8.0	7.4	7.3	0.2	7.84
Eu	2.6	3.0	3.1	2.9	0.05	7.61
Dy	15.9	19.4	12.6	16.0	0.3	17.40
Ho	3.8	4.1	3.6	3.9	0.08	5.64
Yb	14.8	11.0	13.5	13.1	0.15	11.01
Lu	2.1	3.0	2.9	2.7	0.1	14.84

TABLE III: LANTHANIDE ABUNDANCES (ppm) FOR APATITE HR-8C

Sample Element	HR-8C #1	HR-8C #2	HR-8C #3	Average	Sensitivity Limit (ppm)	Coeff. of Variation (%)
La	1.8	1.4	2.8	2.0	0.1	29.50
Pr	0.3	0.1	0.5	0.3	0.08	57.07
Sm	0.8	0.4	0.7	0.6	0.15	43.55
Eu	0.7	0.2	0.9	0.6	0.05	50.31
Ho	< 0.08	< 0.08	< 0.08		0.08	
Yb	< 0.2	0.2	0.5		0.2	
Lu	< 0.1	< 0.1	< 0.1		0.1	

Discussion

Precision and Accuracy

Neutron activation analysis has the advantage of no blank contributions which reduce the precision and accuracy in most other methods. The use of a high resolution germanium detector crystal increases resolution of the individual rare earth gammas only with a corresponding loss in count rate in the peak. Mapper (1960) states that for a single determination of an adequately detectable level of trace element, the coefficient of variation should be less than 10%. However, other factors tend to reduce the reproducibility in this experiment. The physical conditions for counting, including counter behaviour and sample position on counter, cannot be held constant. Handling errors and experimental limitations in processing samples and standards all contribute to a loss in precision and accuracy.

Inhomogeneity of the small samples used could be a major cause of poor reproducibility. Also, the decrease in precision corresponds to a decrease in the peak/background ratio and indicates the need for the ratio to be at least 8/1 to reduce statistical counting errors. It is felt that the accuracy decreases as does the precision with errors probably ranging from about 10-20% in the determinations of lighter lanthanides to about 50-75% in the determinations of heavier lanthanides.

Comparison of Results with Other Analyses

The two apatite samples have been analysed by Z. S. Altschuler using neutron activation. The comparison of results is shown in Table IV and Table V. Some possible reasons for the generally higher rare earth concentrations obtained in this experiment as compared with Altschuler's results are:

1. Concentrations obtained in this experiment more closely approximate the actual concentrations in the apatites.
2. Inhomogeneity due to small sample size.
3. Contributions to the peak heights in the samples due to minor interfering gammas of similar energy.
4. Loss of rare earths in the preparation of the stock standard solution.
5. Incorrect method of determining peak heights above background.

The lack of homogeneity would be expected with the small sample size irradiated (less than 15 mg.). Its importance is at least partly indicated in the rather large coefficients of variation in the triplicate analyses. Where an element could be determined in both the 20 hr. and 10 min. irradiation, the former always gave a lower result closer to Altschuler's findings. This could be due, in part, to loss of activity in the ion exchange procedure, but could also be due to the removal of some of the elements contributing to the Compton continuum near the rare earth gamma peak. The gamma ray spectrum still

showed some non-rare earth elements to be present, so some contribution still remained in the 20 hr. irradiated samples. The preparation of the standard involved an evaporation to near dryness, and some of the rare earth oxides could have been lost due to spattering. This would lead to high determinations of rare earth abundances as appears to be the case here. The method of calculating the peak heights above background might be at fault and could be leading to a high value. However, since the same method was used for standards as well as samples, this error should be generally compensated for within a few percent.

Lanthanum was the only rare earth found to be less abundant than Altschuler indicated. This could be due to loss of La^{3+} in the ion exchange step. La was found to be the last rare earth eluted from the column in 9M. HCl, and a small amount might have remained on the resin. The last elutant was monitored and showed no rare earth activity. It seems reasonable to assume, then, that virtually all the La activity was collected.

Possible Experimental Improvements:

1. A preconcentration of the rare earths by a co-precipitation method, provided it was quantitative, would probably increase sensitivity and allow counting of samples without a time consuming ion exchange step.
2. Further spreading of the gamma ray spectrum might allow more lanthanide peaks to be resolved.

3. Various irradiation times could be employed to improve the count rates for elements of both short (1-6 hr.) and long (4-10 days) half lives.
4. Different counting conditions, such as removing the sample a fixed distance from the crystal, would reduce the flux reaching the germanium detector and allow counting of a more concentrated and hotter sample.

TABLE IV: COMPARISON OF ABUNDANCES IN MOR-9 (ppm)

	La	Pr	Sm	Eu	Dy	Ho	Yb	Lu
Barker	38.9	7.8	7.3	2.9	16.0	3.9	13.1	2.7
Altschuler	43.8	5.8	6.8	2.5	11.0	3.2	10.8	1.6
% Diff.	-	+	+	+	+	+	+	+
In Analyses*	11.2	34.5	7.3	16.3	45.3	22.2	21.3	69.3

TABLE V: COMPARISON OF ABUNDANCES IN HR-8C (ppm)

	La	Pr	Sm	Eu	Ho	Yb	Lu
Barker	3.0	0.4	0.6	0.6	<0.08	<0.3	<0.1
Altschuler	0.8	0.1	<0.33	<0.33	<0.07	0.12	<0.07
% Diff.	+	+					
In Analyses*	275.8	264.3					

* - The difference is reported as + if Barker's analysis is the higher.

Conclusions

A study of the lanthanide abundances in apatites using neutron activation analysis has suggested the following conclusions:

1. The Li-drifted germanium detector crystal provides sufficient resolution, without critical loss in sensitivity, to allow determination of individual lanthanides to sensitivity limits of less than 0.2 ppm.
2. The range for the coefficient of variation, as a measure of reproducibility, is from 4.3% to 29.5% in these analyses.
3. Generally the determined lanthanide abundances are considerably higher than those found by Altschuler. These discrepancies are most probably due to limitations in this experiment.
4. Further experimental refinements, such as a preconcentration step, combined with the germanium detector and 1600 channel gamma radiation analyser, could yield reasonably accurate and reproducible analysis of trace amounts of rare earths in apatites, other minerals and rocks.

Appendix I

Chemical Reagents:

1. HCl - C.I.L., C.P. Reagent, concentrated.
2. Lanthanide oxides - Johnson Matthey, and Mallory,
specpure.
3. Dowex 50W-X8 resin, - 50 - 100 mesh, ionic form H⁺,

J.I. Baker Chemical Company

Apparatus:

1. Counter - multichannel (1600 ch.) gamma radiation spectrometer with Li-drifted germanium detector crystal.
2. Nuclear reactor - McMaster research reactor,
light water moderated, nominal
flux = 2×10^{13} n/cm²/sec.
3. Balance - 5 - place Mettler.
4. Ion exchange columns - 2 100 ml. burettes, inside dia. 3/4",
plastic reservoir of 500 ml. capacity.
5. Hotplate - Temco type 1900.
6. Drying oven - Blue M, single wall transite oven.

Details of the Ion Exchange Columns

Two similar columns, one for each apatite sample, were constructed by sealing 400 ml. plastic reservoirs on top of 100 ml. burettes, one equipped with a stop-cock and the other with a clear plastic tube and small clamp to regulate flow. On top of a glass wool plug, about 10 gm. of Dowex 50W-X8 resin, a strongly acidic cation exchange resin, was slurried into the burette and allowed to settle. Another glass wool plug fixed the top of the bed. The columns were alternately washed with 800 ml. 6M HCl and 500 ml. distilled water, and finally prepared for loading by washing with 200 ml. 0.5M HCl.

Previous work with these columns indicated that the rare earths would be eluted in 9M HCl after 200 ml. 15 M HCl and 50 ml 2M HCl had been passed through the column at about 4 ml/min. This was the flow rate and volumes used and the collected elutant was monitored in order to ensure collection of all the rare earth activity.

Appendix II

Details of Counting and Calculations

The gamma radiation spectrum was broken into two intervals -- 0.0 Kev. to 0.55 Kev. and 0.50 Kev to 1.78 Kev. -- which were each spread across the 1600 channel analyser. The settings used for each interval are shown in Table VI below:

TABLE VI: ANALYSER SETTINGS

	Amplifier		Gain		Threshold	Sensitivity
	Coarse	Fine	Coarse	Fine		
Lower Level	2	1040	1/8	40	0	40
Upper Level	2	250	1/8	40	200	40

Each sample and standard was counted twice, one over each interval. Each spectrum was displayed on an oscilloscope and the lanthanide peaks visually checked for interference which could make a peak count incorrect.

A consistent method was adopted to obtain the counts - above- - background for a peak. An average value, per channel, of the background beneath the peak was obtained by averaging the count rate in about 10 channels sufficiently removed from either side of the gamma peak. This background was mainly due to the Compton continuum of other nuclides. The count rates in those channels

having a count rate above $1/2$ the value of peak minus background for the channel with the highest count rate were summed and divided by the number of channels summed. The average background value was then subtracted, yielding count rate for the peak.

Identification of Lanthanide Gamma Peaks.

A standard was irradiated for 10 min., all peaks counted in each interval, and then the counting was repeated three more times at 3 hr. intervals. The count rate for each peak was plotted against time on semilog paper and the half life read directly from the best-fit straight line. The gamma radiation energy and half life were compared to accepted values and peaks which did not correspond were rejected for measurement purposes.

A standard was also irradiated for 20 hr. and the counting repeated at 8 hr. intervals. In this way, the lanthanide gamma peaks were identified for both irradiation times and half lives needed in the calculations were determined.

Calculation of Sensitivity Limits

The lower limit of sensitivity depends upon element abundance, sample size, nature of gamma ray peak counted, and counter sensitivity. This limit was considered as the concentration of rare earth which would have given a count-above-background of 25 in the counting time used,

and, of course, it varied between determinations. Where no lanthanide gamma ray peak was found, the abundance of that element was considered below the determined sensitivity limit.

A calculation of the sensitivity limit in the determination of Ho in the first MOR-9 sample follows:

$$1190 \text{ counts} = 3.8 \text{ ppm.}$$

$$25 \text{ counts} = \frac{25}{1190} \times 3.8 \text{ ppm} = 0.08 \text{ ppm.}$$

Therefore, the sensitivity limit was taken as 0.1 ppm.

The limit of detection in Table II is the lowest sensitivity limit among the three samples.

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