DETERMINATION OF RARE EARTHS
IN GEOLOGICAL SAMPLES
BY NEUTRON ACTIVATION ANALYSIS

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The significance of rare earth distribution patterns in trace element geochemistry is briefly reviewed. Established methods for their determination at the Reactor Centre by instrumental and radiochemical techniques are described, and examples of recent applications discussed.

Introduction

Current interest in the distribution of the rare earths in rocks and minerals is associated with the availability of facilities for their determination by neutron activation analysis. In Britain such analyses are a significant proportion of the analytical programmes at the University Reactors at East Kilbride (Scottish Universities Research and Reactor Centre), Risley (Universities Research Reactor, Manchester and Liverpool), and Silwood Park (University of London Reactor Centre). The organisation of the work at the different reactors varies: the Radiochemistry Group at East Kilbride has worked in collaboration with Geochemists from the Scottish Universities, at Risley an activation analysis service is provided, whilst the facilities at Silwood Park are used by visiting Geochemists.

Whilst a complete separation of the rare earths was required for their determination with NaI(Tl) detectors,[1] the development of Ge(Li) detectors now enables them to be determined instrumentally or after separation as a group. Most modern instrumental procedures are derived from that described by GORDON et al.[2] Most group separations involve a hydroxide-fluoride precipitation cycle with chemical yield determined by reactivation, as described by DENECHAUD et al.[3] A significant feature of recent work is the increasing use of small computers for spectrometry and data reduction.

After a short description of the significance of the rare earths in geochemistry this paper provides details of the procedures currently in use at East Kilbride and
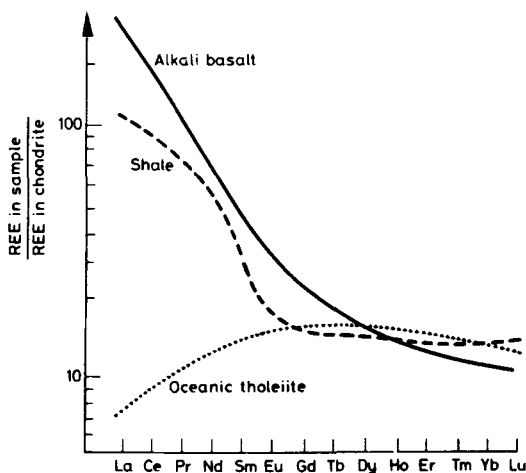
Fig. 1. Chondrite normalised rare earth abundances in sedimentary rocks (shale) and basalts

concludes with examples of recent British studies, with comments on their effects on approaches to the interpretation of rare earth patterns.

The significance of rare earth distribution patterns

The absolute abundances of the rare earths in natural materials as a function of atomic number show a characteristic saw-toothed pattern which is attributable to the favoured formation of even numbered nuclides at the time of nucleosynthesis. Modifications of this pattern by natural processes are best seen by dividing the observed abundances by abundances representative of primordeal matter. Chondritic meteorites are considered to be representative of such material, and it is now common practice to discuss rare earth abundances in terms of their chondrite normalised abundance patterns. In this paper the values used for chondritic abundances are those provided for the Leedey chondrite by NAKAMURA.[4] These values were determined by isotope dilution mass spectrometry and interpolated values have been adopted for those rare earths which cannot be determined by this technique.[5]

The rare earth patterns of a wide range of sedimentary rocks have been found to be constant, with enrichment of the light rare earths (Fig. 1).[6] This pattern is considered to represent the average crustal abundance, and the variation from chondritic abundances attributed to the selective removal of the heavy rare earths at the time of separation of the crust and mantle.

In contrast considerable variation has been found in the patterns of igneous rocks. These variations have been attributed to fractional crystallisation, partial
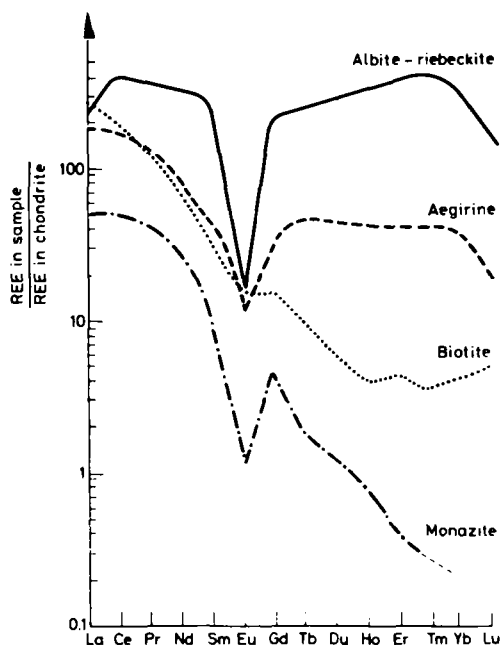
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Fig. 2. Chondrite normalised rare earth abundances in a selection of granitic rocks

melting, mixing, and fluid interactions. The establishment of such patterns and their interpretation is currently an area of considerable activity and controversy. In these rocks the rare earths occur in the major rock-forming minerals. Mineral/ whole rock distribution coefficients are frequently used in support of petrogenetic hypotheses although it has not yet been established that these are independent of bulk composition.

Two characteristic patterns have been recognised for oceanic tholeitic and alkaline basalts (Fig. 1). From a consideration of distribution coefficients these patterns have been explained by the degree of partial melting of the mantle and are used to differentiate between "hot spot" and mid-ocean-ridge material.[7]

In granitic rocks the absolute abundances are greater than in basalts and greater variety is found in the observed patterns (Fig. 2). In such patterns the anomalous behaviour or europium is often a striking feature. This has been attributed to the ease with which europium can be reduced to its divalent from when it can be removed from a melt on the separation of feldspar, and it has also been suggested that the europium anomaly can be used as a measure of oxygen fugacity.

Whilst it has been established that certain geochemical processes affect the rare earth patterns in recognisable ways, the effects of a variety of processes have yet to be adequately explained. The understanding of these latter processes requires further analyses of rocks and separated minerals from situations where the processes have been ubiquitously identified. Neutron activation analysis is the most frequently used technique for such studies.

Experimental

Analytical procedures

Both instrumental and radiochemical activation analyses are used for the determination of the rare earths at the Scottish Universities Research and Reactor Centre. Factors affecting the choice of method include the number and nature of samples to be processed for specified projects, the time and manpower available for the analyses, and the choice of determining all of the rare earths with optimum accuracy by the radiochemical approach or determining a limited number of rare earths with the potential for the determination of other elements by the instrumental approach. The instrumental method is based on the procedure of GORDON et al.[2] whilst the radiochemical method is a variation of that described by POTTS et al.[8] Since both procedures have many common features they are described together below.

Preparation of samples and standards

With the neutron fluxes available in the university reactors irradiation of a few hours produces adequate levels of activity for measurement of the rare earths in samples in the region of 0.1 g. Samples are ground to pass 200 mesh B.S.I. to ensure homogeneity, and weighed into 1 ml polyethylene vials which are then heat-sealed and identifying numbers engraved on them. In instrumental analysis the number of samples to be processed in a batch is limited to 12 by the counting programme. In radiochemical analysis the requirements of a rapid separation limits the number of samples in a batch to 8. With each batch a sample of a standard rock is included to monitor accuracy, the most frequent choice being BCR1 because of its high rare earth content and the quality of published results for this rock.[9] Whilst for many rocks only single samples are processed, an exception is made for separated minerals of potentially high rare earth content. In this case duplicates of 10 and 20 mg are processed, the constancy of induced specific activities being taken as an indication of the absence of self-shielding effects.

Basic single element standard solutions are prepared from ignited spectrographically pure rare earth oxides, to contain approximately 10 mg rare earth per ml.

and calibrated by titration with zinc-standardised EDTA. For instrumental analysis single element standards for irradiation are prepared by dispensing 20 μg quantities by micro-pipette onto 0.1 g quantities of high purity silica in 1 ml polyethylene ampoules. These standards are dried and heat sealed for irradiation. Aqueous multi-element standards are used for radiochemical analysis, to minimise the processing required to produce sources for counting comparable to those prepared from rock samples. Aqueous standards are sealed in silica for irradiation.

Irradiation

In both procedures samples and standards are irradiated together for 6 hours in the Central Vertical Stringer of the Reactor at East Kilbride, where the thermal neutron flux is $3.6 \cdot 10^{12}$ n $\cdot$ cm$^{-2} \cdot$ s^{-1}. This irradiation position is at the centre of the core of the reactor where the flux has been demonstrated to be homogeneous over the sample volume.

For the radiochemical procedure a further irradiation of 1 hour in a rabbit system is employed after the samples have decayed overnight so that 2.36 hour ^{165}Dy can be included in the analytical scheme to complete the determination of all the rare earths. Since there is a significant flux gradient along the rabbits, which terminate at the side of the core, the total flux received by samples for radiochemical processing is monitored by iron foils.

Radiochemical separation of the rare earths

When the rare earths are to be radiochemically separated (as a group) the samples are stored for one hour after the booster irradiation to permit the decay of short-lived activities. At this stage the dose rate from unshielded samples is typically 200 mr/hr at 25 cm so the processing is carried out behind shielding of 5 cm of lead. The major source of this radiation is activity induced in the major elements, which is discarded when the rare earths are first precipitated. The separation, based on the method of POTTS et al.[8] is described below. Full details are available in an S.U.R.R.C. Report.[10]

(1) Each rock sample is fused with Na_2O_2 in the presence of rare earth carriers, hold-back carriers for Cr, Co and Sc, and NaCl filler in a nickel crucible. On cooling the peroxide cake is dissolved in conc. HCl and the crucible cleaned with demineralized water to produce a solution of 150 ml.

(2) The rare earth hydroxides are precipitated by addition of NH_4OH in the presence of NH_4Cl buffer. The precipitate is separated by centrifugation and filtration and the supernate discarded.

(3) The precipitate is dissolved in conc. HCl, and silica removed by precipitation in the presence of gelatin.

(4) The hydroxide precipitation is repeated and the supernate discarded. The precipitate is dissolved in HCl and the rare earths reprecipitated by addition of HF. The supernate is discarded and the precipitate dissolved with H_3BO_3.

(5) Step (4) is repeated and the rare earth hydroxides reprecipitates. The hydroxide precipitate is dissolved with the minimum quantity of 2N HCl and the volume accurately made up to 10 ml with demineralised water. 7 ml of this solution is transferred to a counting ampoule and 0.5 ml is subsequently sealed in a polyethylene ampoule for chemical yield determination by reactivation.

The time required for the concurrent processing of eight samples is approximately 4 hours. Counting is commenced immediately on completion of the chemical separation. The fraction reserved for chemical yield determination is reactivated in a rabbit irradiation of 5 minutes, 12 weeks after the first irradiation with a standard of carrier solution, and subjected to a similar counting procedure.

Counting procedure

Two Ge(Li) detectors are employed for counting: an 80 cm^3 coaxial detector with a resolution of 2.2 keV at 1.332 MeV and a 0.5 cm^2 planar detector with a resolution of 623 eV at 122 keV. The latter detector facilitates the resolution of photopeaks in the crowded region of the spectrum below 150 keV.

The 80 cm^3 detector is used in association with a NOVA 1210 computer programmed to operate as a 4096 channel analyser with the facility for data storage on floppy magnetic discs, or direct line transfer to a NOVA 3 for processing.

The 0.5 cm^2 detector is used in association with a DEC PDP8E, utilising 2048 channels, with paper tape output for transfer to a PDP10.

It is not possible to commence counting for instrumental analysis until 4 days after irradiation, the spectra up to this time being dominated by the photopeaks and Compton continuum of ^{24}Na. Thereafter samples are counted on five occasions, with counting times of between 1 and 6 hours, the final count being 2 months after irradiation. The most useful photopeaks and optimum counting times are detailed in Table 1, where it can be seen that a number of elements, particularly amongst the heavy rare earths, are not amenable to instrumental analysis, and the number of useful photopeaks is limited by the presence of other activities.

After the group separation of the rare earths, counting is commenced immediately on completion of the separation, so that short-lived isotopes of Dy, Er, Pr and Ho can be included. Samples are counted on 4 occassions up to 1 month after irradiation, and the elimination of interferences permits the use of more photopeaks for each element.

Table 1

Photopeaks used in instrumental and radiochemical analysis

Isotope	Half-life	Instrumental analysis		Radiochemical analysis	
		Decay	Photopeaks, keV	Decay	Photopeaks, keV
^{140}La	40.2 h	4 d	1596, 816	3 d	1596, 816, 752, 487, 329
^{141}Ce	32.5 d	30 d	145		145
^{142}Pr	19.2 h			6 h	1576
^{147}Nd	11.1 d	10 d	91	12 d	531, 91
^{153}Sm	46.8 h	4 d	103	3 d	173, 103
^{152}Eu	12.7 y	60 d	1408	12 d	1408, 1112, 779, 344, 122
^{153}Gd	242 d	60 d	103	30 d	103, 97
^{160}Tb	72 d	60 d	966–963	30 d	1272, 1178, 966, 879, 299
^{165}Dy	2.4 h			6 h	95
^{166}Ho	27 h			3 d	1380, 81
^{171}Er	7.5 h			6 h	308
^{170}Tm	130 d	60 d	84	12 d	84
^{175}Yb	4.2 d	10 d	396, 283	3 d	396, 283
^{177}Lu	6.7 d	10 d	208	12 d	321, 248, 208, 113

Calculation of results

The primary programme for the calculation of photopeak areas is run on a PDP10 in the adjacent Kelvin Laboratory (Department of Natural Philosophy, Glasgow University). In this programme peak boundaries are identified in differentiation after spectrum smoothing as described by YULE.[11] This computer also accommodates a programme to calculate rare earth concentrations by a weighted comparison of up to 5 photopeaks in samples and standards. In the radiochemical procedure this latter programme is also used to calculation of chemical yields by replacing sample and standard weights by 100% for the standard carrier and unity for the sample solution.

The limited number of well-defined photopeaks obtained in instrumental analysis are conveniently processed on the NOVA 3 at the Reactor Centre. The currently limited core of this computer permits only the calculation of photopeak areas above a smoothed background.

A Calcomp plotter associated with the PDP10 is used to draw the final chondrite-normalised abundance diagrams and can also be used to plot spectra when these are required.

Table 2
Rare earths in standard basalt BCR 1

Element	Instrumental analysis		Radiochemical analysis		Literature value*
	ppm	Precision, %	ppm	Precision, %	
La	21.8	3	30.4	1.6	26[a]
Ce	53	6	53.3	2.6	53.9[r]
Pr	N.D.	–	5.6	29	7[a]
Nd	31	18	34.9	17	29[r]
Sm	7.0	2	6.5	3.4	6.6[a]
Eu	1.8	5	1.99	2.0	1.94[r]
Gd	N.D.	10	6.9	0.7	6.6[r]
Tb	1.4	–	1.0	2.9	1.0[r]
Dy	N.D.	–	6.4	8.5	6.3[r]
Ho	N.D.	–	1.1	3.5	1.2[m]
Er	N.D.	–	3.39	28	3.59[r]
Tm	N.D.	–	0.6	1.1	0.6[r]
Yb	3.7	20	3.64	4.7	3.36[a]
Lu	0.62	6	0.48	4.2	0.55[r]

*FLANAGAN.[9]
r = Recommended.
a = Average.
m = Magnitude.
N.D. = Not determined.

Results obtained for the standard rock BCR1 are given in Table 2 for instrumental and radiochemical analysis. The indicated precisions are derived from counting statistics, and for instrumental analysis are dependent on the levels of rare earths in the sample and the level of Compton continuum from other elements.

Procedures similar to the instrumental method described above are used by HENDERSON[12] and POTTS[13] after irradiations in the University of London Reactor. The radiochemical procedure employed by URR Risley is described in Ref.[17]

Discussion

Recent applications of rare earth analyses

Examples of the application of results of instrumental and radiochemical analyses are given below to illustrate current approaches to the significance of the rare earths in geochemistry.
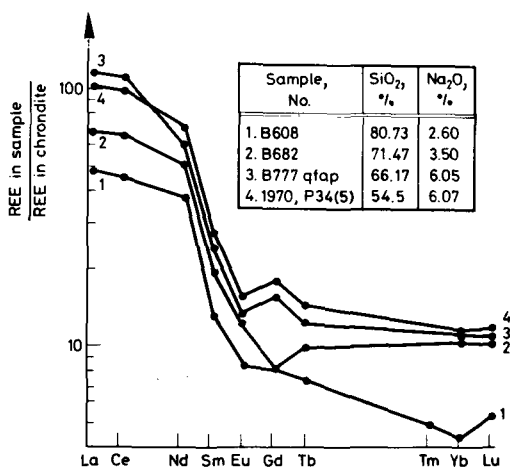
Sample, No.	SiO_2, %	Na_2O, %
1. B608	80.73	2.60
2. B682	71.47	3.50
3. B777 qfap	66.17	6.05
4. 1970, P34(5)	54.5	6.07

Fig. 3. Chondrite normalised rare earth abundances in sodic fenites, determined by instrumental analysis

Investigations of rare earth mobility

One of the major problems in the correct interpretation of distribution patterns is the extent of the mobility of the rare earths in rock-water interactions. Fenitisation is such an interaction in which silica is removed from the ground rock and other elements displaced by a peralkaline fluid. Rare earths have recently been determined by instrumental analysis in a suite of fenites from the Borralan Complex, N. W. Scotland. The fenitisation has been described by WOOLLEY et al.[14] and the rare earth investigation was suggested by MARTIN.* Both sodic and potassic trends in fenitisation were recognised. The chondrite-normalised rare earth patterns for the sodic trend are illustrated in Fig. 3, where it can be seen that the rare earth content increases with fenitisation. Whilst the trend for the light rare earths is well defined, the omission of three or four neighbouring rare earths in the instrumental approach occasionally introduces difficulties in interpreting such figures. The slight irregularities in the region of Eu and Gd are considered to be attributable to the poor precision for the determination of Gd by instrumental analysis rather than significant Eu anomalies. A similar trend is found for potassic fenitisation, and extrapolation of rare earth abundances to unaffected quartzite

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indicate that this contained insignificant quantities of rare earths. Linear correlation between several rare earths have been found in these samples. Similar trends have previously been used as evidence of fractional crystallisation in the genesis of igneous rocks. It is apparent that an alternative source of such patterns must now be considered. Similar movement of rare earths has been reported by HELLMAN and HENDERSON[15] for spilitisation, the University of London Reactor being used for activation. In spilitisation errupting basalts are considered to react with seawater, and the results suggest that the rare earths are also mobile in this situation.

The Open University also use the University of London Reactor, and have recently described the determination of 10 rare earths in Granites from Skye,[16] suggesting that they originate from fractional crystallisation of magma.

Rare earths in pantellerites

In view of the value of results for the heavy rare earths and the requirement for the determination of relatively small quantities of these elements in separated minerals the radiochemical approach has been selected for studies of the origin of peralkaline rocks at East Kilbride. A facet of this programme has involved the analysis of pantellerites, and is described below as an illustration of the use of radiochemical analysis.

Pantellerites have long attracted the attention of geologists because of their high peralkalinity. Most investigations of these rocks have been concerned with the relationship between the pantellerites and the more abundant subaluminous magmas, and particularly with the fractionation of alkali feldspar from a peralkaline quartz trachyte. In an attempt to understand the relationship between a pantelleritic liquid and the minerals which crystallise from it the rare earths have been determined in a pantellerite and separated glass and feldspar, and the results are provided in Fig. 4. The value of the radiochemical approach is particularly evident for the feldspar where the absolute abundances are relatively low, and the regularity of the curves is attributable to the complete elimination of interferences. (At the time of these analyses a Nd standard was not available.)

Both the whole rock and the glass have very high abundances of rare earths, and their similarity indicates that the majority of the rare earths are rejected by the crystallising phases and concentrated in the melt. Both patterns show enrichment of the light rare earths, with significant europium anomalies. The rare earth abundances in the feldspar are approximately two orders of magnitude less than the whole rock or the glass and a positive europium anomaly is evident. Since feldspar is the only mineral known to preferentially incorporate divalent europium the
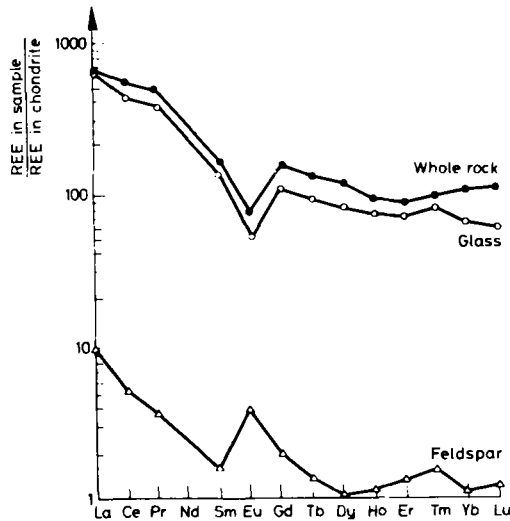
Fig. 4. Chondrite normalised rare earth abundances in a pantellerite, separated glass and feldspar

data supports the hypothesis that such a crystallising feldspar plays a dominant role in the derivation of pantelleritic liquids. This model in terms of a simple liquid-crystal equilibrium has been criticised and it has been suggested that account should also be taken of the effects of the intervention of an alkali-bearing vapour phase and of the role of water in the origin of these rocks.

Conclusion

It is apparent that rare earth studies are making a significant contribution to modern geochemistry and that a major contribution to this is their determination by neutron activation analyses. Some recent British activity has been described, and such work is expected to continue as a major aspect of the useage of the three British University Reactors.

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References

1. L. A. HASKIN, T. R. WILDEMAN, M. A. HASKIN, J. Radional. Chem., 1 (1968) 337.
2. G. E. GORDON, K. RANDLE, G. G. GOLES, J. B. CORLISS, M. H. BEESON, S. S. OXLEY, Geochim. Cosmochim. Acta, 32 (1968) 369.
3. E. B. DENECHAUD, P. A. HELMKE, L. A. HASKIN, J. Radional. Chem., 6 (1970) 97.
4. N. NAKAMURA, Geochim. Cosmochim. Acta, 38 (1974) 757.
5. N. NAKAMURA, Geochem. J., 9 (1975) 183.
6. L. A. HASKIN, F. A. FREY, Science, 152 (1966) 299.
7. J. G. SCHILLING, Nature, 242 (1973) 566.
8. M. J. POTTS, T. O. EARLY, A. G. HERMANN, Z. Anal. Chem., 263 (1973) 97.
9. F. J. FLANAGAN, Geochim. Cosmochim. Acta, 37 (1973) 1189.
10. A. B. MOYES, J. E. WHITLEY, S.U.R.R.C. Report No. 59, 1977.
11. H. P. YULE, Anal. Chem., 40 (1968) 1480.
12. J. N. WALSH, P. HENDERSON, Contrib. Mineral. Petrol., 60 (1977) 31.
13. D. K. PAUL, P. J. POTTS, I. L. GIBSON, P. G. HARRIS, Earth Planet. Sci. Lett., 25 (1975) 151.
14. A. R. WOOLLEY, R. F. SYMES, C. J. ELLIOTT, Mineral. Mag., 38 (1972) 819.
15. P. L. HELLMAN, P. HENDERSON, Nature, 267 (1977) 38.
16. R. S. THORPE, P. J. POTTS, M. B. SARRE, Earth Planet. Sci. Lett., 36 (1977) 111.
17. J. DUFFIELD, G. R. GILMORE, J. Radioanal. Chem., 48 (1979) 135.