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QUANTITATIVE ION MICROPROBE ANALYSIS OF THE
RARE EARTH ELEMENTS IN MINERALS

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Abstract

The lanthanides or rare earth elements (REE) which are present in trace concentrations in rocks are most useful for investigating the origin of these objects. Of the microbeam techniques presently used to measure the REE concentrations of individual crystals, secondary ion mass spectrometry (SIMS) is the only method sensitive enough to allow the determination of REE abundances in most natural minerals. Usually, energy filtering is applied to remove all complex molecular interferences. All the REE, down to a level of ≤ 100 ppb, can be measured in spots 5 to 20 μm in diameter. A growing number of studies involving both terrestrial and extraterrestrial materials have been undertaken.

Introduction

Petrologists have long recognized that trace elements have great potential as indicators of rock forming processes. Much of the geochemical work on these elements has probed into the origin of igneous rocks (i.e., those crystallizing from magmas or melts). Because trace elements are more strongly partitioned than major elements into either liquid or crystal phase, their study has given insights into the history of the melt sources, their compositions (and modification by assimilation), as well as the extent of the melting processes involved. In this context, the rare earth elements (REE) have been particularly useful.

The fifteen REE (with atomic numbers from 57, lanthanum, to 71, lutetium) are very similar geochemically. With the exception of Pm ($Z = 61$) which does not have any stable isotope, they are all associated in nature. The REE share a common 3+ oxidation state with different behavior occurring only under certain conditions for Eu (2+) and Ce (4+). They are comparatively refractory and, as lithophile elements, show an affinity for silicates. During igneous processes involving mafic magmas, the REE tend to remain in the liquid phase. The minerals that do take up REE in their structures will generally show a preference for either light (LREE) or heavy (HREE) REE, depending on the nature of the ionic positions available for substitutions. This is mainly a consequence of the regular decrease in ionic radii for the trivalent REE, from La to Lu (the so-called lanthanide contraction). The REE abundances in a given mineral also depend on the nature of the other phases present.

When comparing the REE contents of different rocks or minerals, one generally normalizes the concentrations of the individual REE to their abundance in ordinary or carbonaceous chondrites (the meteorites that best represent the composition of the non-volatile fraction of solar system material). This is done to take into account the fact that elements with even atomic numbers are more abundant than their neighbors with odd atomic numbers (Oddo-Harkins effect), a consequence of nuclear stability. The normalization results in REE patterns (normalized concentration vs atomic number) that are smooth, except for occasional anomalies for Eu and Ce (because of their sometimes differing oxidation states) in terrestrial samples and for a number of REE in meteorites, where these elements can be partitioned according to their relative volatilities. Chondritic normalized concentrations will be used throughout this paper to present REE abundance data. General reviews of REE geochemistry have been written by Haskin and Paster (1979), Hanson (1980) and Henderson (1984).

Key words: Rare Earth Elements, Secondary Ion Mass Spectrometry

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The bulk of REE data on geological materials that have appeared in the literature were obtained by neutron activation methods (INAA, instrumental neutron activation analysis and, less frequently, RNAA, radiochemical neutron activation analysis). Isotope dilution mass spectrometry has also been important and plasma spectrometry is being used increasingly. Neutron activation and isotope dilution are established and reliable techniques; generally, they use from a few mg to a g of rock or mineral separate. Boynton (1984) reported that new radiochemical neutron activation techniques permit studies of μg samples: Individual grains have been extracted from thin sections so that their petrogenetic setting is known; this type of analysis, however, is by no means routine. In addition, because of the small sample size, some of the REE usually measured by neutron activation cannot be detected.

In interpreting measurements of REE in bulk samples or mineral separates, it is important to determine the degree to which their abundances are influenced by minor phases, such as zircon, sphene, apatite, monazite and allanite, which can have relatively high REE concentrations (Exley, 1980; Watson et al., 1985). These accessory phases are usually present in such minor amounts that problems associated with the uncertain purity of mineral separates have to be considered. To evaluate the importance of these minor phases, it is obvious that in-situ analyses would be preferable.

In-situ measurements also allow for the interpretation of the data in their petrographic context and offer the opportunity to study crystal zoning as well as intergrain variations.

Presently, the quantitative modeling of the behavior of trace elements is limited by an imperfect knowledge of the distribution coefficients that describe, in various conditions, the partitioning of these elements between phases. To determine distribution coefficients, both natural and synthetic samples have been studied. In the latter case, 0.1 to 1% amounts of the "trace" elements studied are added so that the products can be analyzed by standard electron probe techniques. It is necessary to establish for each study whether the distribution coefficients measured at percent levels are the same as at the trace element levels characteristic of many minerals of interest. This so called "Henry's law debate" has been summarized and referenced by Shimizu and Hart (1982) and Burnett and Woolum (1983). There is thus a need to develop techniques that are sensitive enough to measure trace element concentrations in individual mineral grains.

In what follows, in-situ techniques for the measurement of REE in minerals will be compared and the SIMS techniques will be shown to be superior. Although most of the applications of these techniques to date are studies of extraterrestrial minerals, the quantitative microanalysis of the REE in terrestrial minerals should be a fertile area of study in the future.

The Measurement of REE Abundances in Individual Mineral Grains

The use of the electron microprobe for the investigation of the REE chemistry of minerals presents formidable difficulties: there is considerable overlap of the REE L series X-ray lines and the sensitivities for REE are low, setting a practical detection limit of ~ 100 ppm, adequate only to measure a few REE in REE-rich phases or REE minerals.

Because the ratio of characteristic X-ray signals to the bremsstrahlung background is much higher for heavy charged particles than for electrons, the proton-induced X-

ray emission (PIXE) method offers some promise (Burnett and Woolum, 1983). So far, however, only Ce and Nd concentrations at the level of 100 ppm (in meteoritic calcium phosphate) have been reported (Benjamin et al., 1984).

Potentially more sensitive (detection limits on the order of 1 ppm are expected for the REE) is an X-ray fluorescence technique that uses synchrotron radiation (Rivers et al., 1985). It is based on the analysis of the K spectra of the REE. However, no results obtained by this method on geological samples have yet been published and even a detection limit of 1 ppm is inadequate for many interesting samples.

In recent years, the most important advance has come from the application of ion probe techniques which made possible the quantitative determination of all the REE at the scale of a few microns with detection limits of ≤ 100 ppb.

Secondary Ion Mass Spectrometry (SIMS) methods for the measurement of REE concentrations in mineral grains.

The potential of SIMS for the analysis of geological samples has long been recognized. The review by Lovering (1975) covered the techniques then available and discussed a number of geochemical applications. Further progress was reported in reviews by Shimizu et al. (1978) and Reed (1980). A particularly useful introduction to the applications of the ion microprobe to geochemistry and cosmochemistry was written by Shimizu and Hart (1982).

The ion probe has been applied to the quantitative elemental analysis of minerals and also to the study of isotopic compositions, with work in this latter area having been particularly fruitful during the last few years. In principle, it is possible to detect certain elements present in very low concentrations (a few ppb). The measurements can be carried out in-situ, thus eliminating the need for mineral separation, and sample preparation is usually limited to the preparation of polished thin or thick sections. Sample consumption is on the order of 1 ng. Sensitivities vary greatly from element to element, most of which can in principle be detected, but are very high for REE, resulting in low detection limits. The latter also crucially depend on the size of the analyzed volume. While a spatial resolution of $\sim 0.04 \mu\text{m}$ can be achieved (Levi-Setti et al., 1985), REE analyses in practice are made in spots $\geq 5 \mu\text{m}$ in diameter.

Molecular Interferences

Not only are geological materials complex chemically, but even a chemically simple system like quartz has a very complex secondary ion mass spectrum due to the presence of molecular ions (oxides, dimers ...). Ion probe analysis thus faces the task of separating the ions of interest from molecular isobaric interferences. This problem is one of the major causes for the lack of routine application of SIMS in geochemistry. The other one is the so-called matrix effect addressed below. There are two ways to eliminate molecular interferences; the use of high mass resolution to separate atomic and molecular ions or the application of energy filtering to suppress molecular ions (whose energies are lower) relative to atomic ions. The main interferences for REE atomic peaks are complex molecules, formed from the major elements, and oxides of the light REE at the masses of the heavy ones (Reed, 1984). Separation of the REE oxides requires a mass resolving power $m/\Delta m$ of between ~ 7000 and ~ 9000 , which can be attained in modern machines such as the Cameca IMS 3f, that uses a double focussing mass spectrometer design.

In commercially available ion probes, the magnetic field control does not achieve absolute field settings which would allow high mass resolution measurements without peak clustering on calibration peaks. The method of automatic peak centering has been applied successfully to isotopic measurements at high mass resolution (Huncke et al., 1983; McKeegan et al., 1985). In the case of REE measurement, low signals would not permit peak centering for most peaks of interest. It has not been demonstrated yet that precise measurements at high mass resolution can be made at a large number of masses in an automatic peak jumping mode, if only a few mass peaks can be centered on the mass range of interest. In contrast, energy filtering allows relatively fast data acquisition and has been used, in various forms, for most REE abundance determinations. Of course, its use also inevitably results in a loss of intensity. Energy filtering can be achieved by the specimen isolation technique (Metson et al., 1983; 1984a; 1984b; 1985) or by the conventional way as described by Shimizu et al. (1978), Crozaz and Zinner (1985) and Zinner and Crozaz (1986a). Before these techniques are discussed in the next section, the approach pursued by Reed (1981; 1983; 1984; Reed et al., 1983) will be presented.

Like all other investigators analyzing the REE in minerals, Reed uses a beam, 15 to 20 μm in diameter, of O^- ions, in order to minimize sample charging in insulating minerals. The intensities of the major REE isotopes are first measured at low mass resolving power ($m/\Delta m \sim 400$) and compared with the known relative isotopic abundances for selection of the isotopes showing the least interferences (Reed et al., 1983). The selected isotopes are then inspected at a mass resolving power of $\sim 6,000$ and only retained if the level of molecular interferences is acceptable. Subsequent measurements are made at low mass resolution. Monoxides of the light REE (La through Sm) strongly interfere with the ions of the usually less abundant heavier REE and the monoxide peaks of the heavy REE have to be used (fortunately, REE dioxide peaks are found to be of very low intensity). The oxides of Ba, when present, interfere with the two Eu isotopes; in orthoclase feldspar, where both elements are usually associated with one another, Eu, the dominant REE, cannot be measured. Although this technique is not as sensitive as some of those based on energy filtering that will be described below and although the abundance patterns in the HREE region are not as smooth, it remains a good method that opened the field to a variety of geological applications.

Energy Filtering

The reason that energy filtering has been quite successful for the analysis of REE is that these elements occupy an atomic mass region in which, for most minerals of interest, the molecular interferences occur in the form of complex ions (molecules of three or more atoms) which are very effectively removed by energy filtering (see figs. 1 and 2 in Zinner and Crozaz, 1986a). Dimers in this mass region are those of rare elements (such as Ge, As, Se, Br, Kr). This is also the case for two-atom interfering molecules formed with major elements such as Mg, Si, Ca, Fe; these elements combine with elements of normally very low abundance. Hydrides are usually insignificant.

In the specimen isolation technique used by Metson and his group, the specimen is isolated from the sample holder and allowed to charge under a 200-300 nA O^- primary beam focussed into a spot 50 μm or larger. This creates an extreme kinetic energy selection (>400 eV) that leads to the suppression of practically all molecular interferences. Field and contrast apertures of the secondary ion column are kept open so that the mass

resolving power is low (~ 250) and the energy window is broad (~ 130 eV) (Metson et al., 1983). Apparently, the intensity loss of ion signal is lower than would occur with conventional energy filtering of the same energy offset, and intensities are adequate for the detection of all the REE at the 100 ppb level (MacRae and Metson, 1985).

The major drawback of this technique is that the primary beam cannot be focussed into a spot smaller than ~ 50 μm while maintaining the charging conditions necessary for the energy selection effect. In addition, the sample charging depends on primary current density and specimen conductivity, which cannot be well controlled. This creates a problem for quantitative analysis because the energy distributions of REE and standard element are different and the relative ion yields depend on the amount of energy filtering. Thus, it will be difficult to determine absolute REE concentrations by this technique, as standards will presumably be analyzed with a different (and unknown) degree of energy filtering. Metson et al. (1984b) have also assumed identical ionization efficiencies for the REE. As shown by Reed (1983) and also observed by Zinner and Crozaz (1986a), the ion yields for the various REE are not equal (extreme values differ by about a factor of two). The assumption of constant REE ion yields does not, however, affect the general shape of the REE patterns obtained; only the smoothness of the pattern is lost to a certain extent (Fig. 1, Arendal sphene, Metson et al., 1984b). In conclusion, it is apparent that while the specimen isolation technique is useful for observing REE abundance patterns in large homogeneous phases (Metson et al., 1984b), its usefulness for the quantitative analysis of REE in small grains has yet to be established.

Shimizu et al. (1978) suggested that an energy filtering that only allows ions with more than 150 eV kinetic energy to be detected was sufficient to practically eliminate the interference of molecular ions for both major and trace elements. They studied the mineral hornblende under these conditions. Ion yields of REE were assumed to be constant and the results were normalized to La. In this early work, performed on the CAMECA IMS300, minimum spot size was 20 μm . Whether an energy offset of 150 eV is sufficient to eliminate all interferences depends on the REE pattern. A voltage offset of 125 eV increases the M^+/MO^+ ratio by a factor of ~ 20 (Metson et al., 1985; Zinner and Crozaz, 1986a), apparently not sufficient to remove all oxide interferences for REE chondritic abundances which decrease steeply with increasing atomic number. In addition, such an offset usually (for ions in general, not just REE) results in at least a two orders of magnitude intensity drop. Shimizu and his collaborators have published very little concerning the techniques they use to analyze for REE, and it is hard to determine the detection limits associated with such measurements.

The method recently developed by Zinner and Crozaz (Crozaz and Zinner, 1985; Zinner and Crozaz, 1986a; 1986b) uses a more modest degree of energy filtering (~ 80 eV voltage offset). The measurements are performed with a Cameca IMS 3f ion probe (Lepareur, 1980). Polished samples coated with gold are bombarded with an O^- primary beam (typically of 3 to 20 nA) focussed into a spot 5-25 μm in diameter. The width of the energy slit is 32.5 V and the mass resolution ~ 500 . Secondary ions are counted at the isotopic masses of major and trace elements of interest as well as the atomic masses from 133 to 191 (the REE and REE monoxide mass region). A single analysis takes from 20 minutes to ~ 2 hours. All complex molecular interferences are removed effectively by the energy filtering. The remaining monoxide interferences are eliminated by deconvolution of the mass spectrum into

contributions from REE and their monoxides only (as noted by Reed, 1984, fluorides can also contribute and have to be corrected for). Details of the experimental procedures and necessary corrections are given by Zinner and Crozaz (1986a).

Secondary Ion Yields

The fact that the ion yield of different elements varies over a wide range and depends on the composition of the sample analyzed (matrix effect) is the second complication which has hampered the development of quantitative analysis by the SIMS technique. There is no sound theoretical basis for calculating differences in ion yield and their dependence on matrix composition (see Reed (1980) and Shimizu and Hart (1982) for further discussion of this subject).

In the early work on REE, it was assumed that all the REE had the same (albeit not well known) ion yield (Andersen and Hinthorne, 1972; Shimizu et al., 1978), an approximation that seemed reasonable as relatively smooth REE patterns were obtained for a variety of mineral compositions. In retrospect, this fact also suggested that relative ion intensities for the various REE are quite similar, regardless of matrix composition.

The use of standards, with uniform, known REE concentrations and the same major element compositions as the unknown samples, is presently the best way to convert relative ion intensities to elemental concentrations. It should be realized that standards with all these characteristics are hard to come by, a problem well known to electron probe users. REE concentrations of a potential standard can be measured by other techniques, such as neutron activation or isotope dilution, and homogeneity of the standard verified by repeated SIMS measurements. Few such standards presently exist. Reed et al. (1983) used the Durango apatite and Crozaz and Zinner (1985) a terrestrial apatite from a gabbro that has a less steeply sloping REE pattern than that of the Durango apatite (and is therefore preferable because of less interferences of light-REE monoxides at the masses of heavy REE). Zinner and Crozaz (1986a) found a linear relationship between REE concentrations measured in three different calcium phosphate samples by either INAA or electron probe and concentrations measured in the ion probe. Extremes in concentration ranged over more than a factor of 50 and deviations from the linear relationship were usually less than 15%.

For the determination of relative sensitivity factors in silicates, Reed (1983) and Zinner and Crozaz (1986b) have used Ca-Al-Silicate glasses prepared by Drake and Weill (1972). These contain different combinations of REE in known concentrations, at the level of several percent. The results of the two groups (in terms of ion yields of the REE relative to Ca) are compared in Fig. 2.

Ion yield ratios REE^+/Ca^+ differ in absolute magnitude by about a factor of two between the two measurements. This is not too surprising since the Reed ratios were obtained at low ion-energies (no energy filtering) and the Zinner and Crozaz values at high ion energies (with energy filtering). In order to obtain a comparison of relative ion yields among the REE, the REE^+/Ca^+ ratios of Reed (1983) plotted in Fig. 2 were multiplied by a factor 1.86 so that the Ce^+/Ca^+ ratio is the same as that measured by Zinner and Crozaz (1986b). As can be seen, the relative sensitivity factors among the different REE do not agree very well either. At present, we must attribute this disagreement to the different ion energies at which the measurements were performed.

If we restrict ourselves to the data obtained with energy filtering, there is considerable variation of the ion

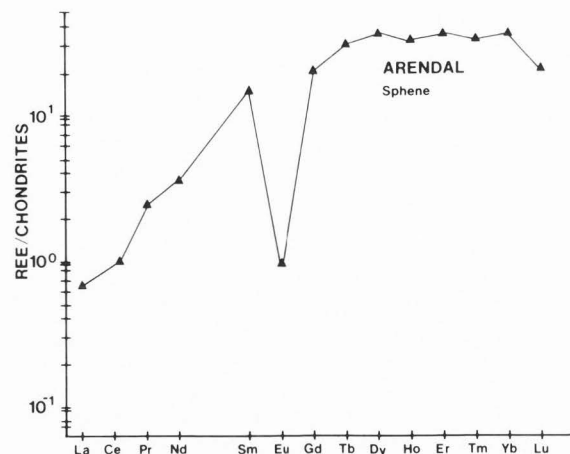


Fig. 1. Rare earth element distribution in a sphene from Arendal, Norway (Metson et al., 1984b).

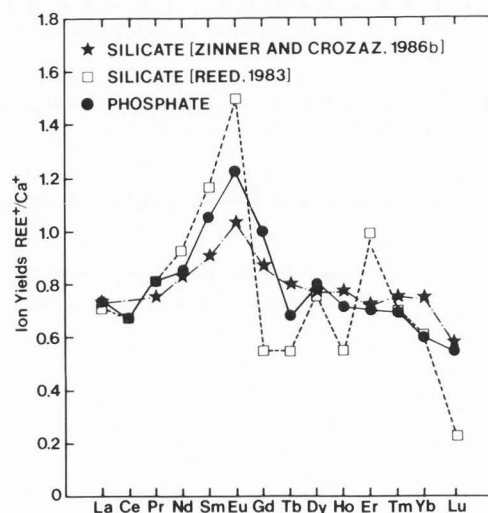


Fig. 2. Ion yields of the REE relative to Ca measured in a silicate glass standard with (Zinner and Crozaz, 1986b) and without (Reed, 1983) energy filtering. The Reed ratios were renormalized so that the Ce^+/Ca^+ ratio is the same as that of Zinner and Crozaz (1986b). Also plotted are relative ion yields measured in a phosphate standard (Zinner and Crozaz, 1986a).

yield ratios REE^+/Ca^+ , i.e., a factor of 1.80 between Eu and Lu for the Zinner and Crozaz (1986b) values. Additional measurements in pyroxene (Zinner and Crozaz, 1986b) and zircon (unpublished) show good agreement with the ion yields from the silicate glasses.

Also plotted in Fig. 2 are relative ion yields determined in terrestrial apatite (Zinner and Crozaz, 1986a). There is generally good agreement with the silicate values. Unpublished measurements on oxides (perovskite, hibonite) indicate that, while ion yield ratios REE^+/Ca^+ are higher by about 30-35% than in phosphates and silicates, the relative yields between REE are almost identical.

The important conclusion from these observations is that matrix effects which can be very large (factors of >10) are substantially reduced or practically eliminated if

only high energy secondary ions are analyzed. Thus energy filtering not only removes interferences but also reduces matrix effects.

Typical results from our laboratory, from the analysis of the two types of calcium phosphate minerals (merrillite and apatite) found in chondritic meteorites are shown in Fig. 3. Comparison with measurements by Reed et al. (1983) is provided. The results are in general agreement, but our REE patterns are much smoother than those of Reed et al. (1983). Detection limits depend on the overall REE pattern but are generally less than 50 ppb for the light REE and ~ 100 ppb for the heavy REE. All the REE can be determined.

For grains with REE concentrations on the order of chondritic abundances (i.e., 30 to 800 ppb, depending on the element), measurements with moderate precision can still be obtained in a reasonable time (less than 2 hours) if Gd, Yb, and Lu concentrations are not determined and ion signals are counted at only key masses for the other REE. Fig. 4 shows the results obtained under such conditions for a grain of merrillite from a carbonaceous chondrite. The errors from counting statistics are indicated and are largest, as expected, for the HREE. The Eu concentration is only 1.4 ppm and all the other REE concentrations are below 1 ppm (the Tm concentration is ~ 70 ppb).

The ion probe techniques have thus recently progressed to the point where REE abundances of individual grains can be determined not just in relatively REE-rich accessory phases but also in relatively REE-poor, major (silicate) phases. This should lead to a host of new studies of terrestrial as well as extraterrestrial materials.

Geological Applications

So far, measurements of REE patterns made by ion probe analysis have been reported in a variety of natural minerals: REE-rich accessory minerals in lunar material (Andersen and Hinthorne, 1972), hornblende (Shimizu et al., 1978; Metson et al., 1984b), zircon (Gaudette et al., 1981; Zinner and Crozaz, 1986b), allanite (Reed, 1985), sphene and monazite (Metson et al., 1984b), pyroxene (Zinner and Crozaz, 1986b; MacRae and Metson, 1985), plagioclase (MacRae and Metson, 1985; Zinner and Crozaz, unpublished), hibonite (Fahey et al., 1985a; Hinton et al., 1985), garnet (Hickmott et al., 1985), perovskite (Fahey et al., 1985b), melilite (this paper) and calcium phosphates (see below).

In the last 5 years, the field has moved past the stage of purely technical development and an increasing number of problem-oriented REE determinations have been published.

Terrestrial Studies

In an interesting provenance study, Gaudette et al. (1981) separated and identified (on the basis of color, morphology and crystal habit) four distinct populations of zircons in the Cambrian Potsdam sandstone of New York. The populations exhibit different degrees of erosion, have different ages, and also have distinct REE abundance patterns. The authors showed conclusively that the zircons in this sandstone are a mixture of grains from different source regions. Hickmott et al. (1985) have recently investigated trace element zoning in metamorphic garnets from New England, USA and the Alps. Such work can provide insights into the histories of these metamorphic samples.

Extraterrestrial Materials Studies

The bulk of problem-oriented REE determinations have been made on extraterrestrial samples.

Reed et al. (1983), Reed and Smith (1985), and Crozaz and Zinner (1985) measured REE abundances in the

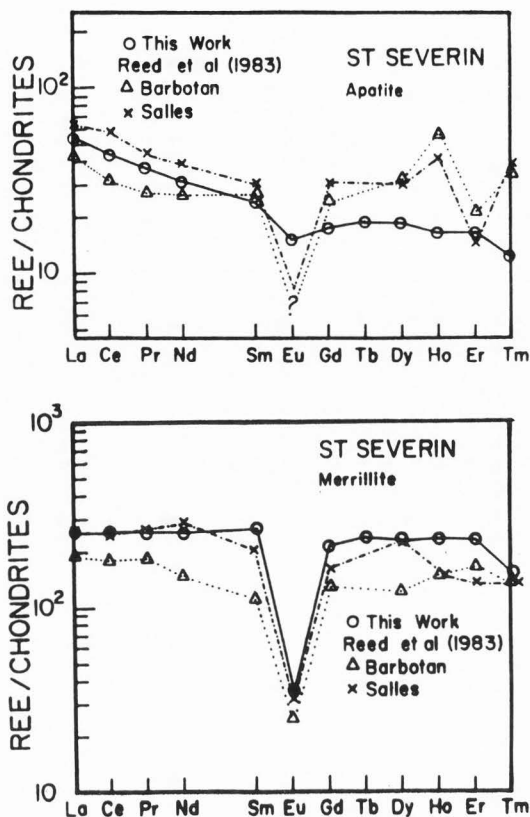


Fig. 3. Ion probe REE abundances in apatite (a) and merrillite (b) from the chondrite St. Severin. Comparison of results obtained by Crozaz and Zinner (1985) (solid line) and Reed et al. (1983).

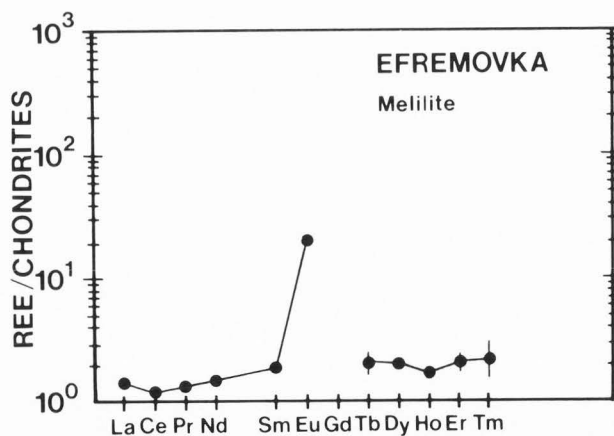


Fig. 4. REE distribution in a melilite grain from the carbonaceous chondrite Efremovka.

phosphates of chondrites and found them to be different in merrillite and apatite (see Fig. 3). This finding has renewed the hope to determine relative meteorite formation ages using ^{244}Pu , a nuclide with a half-life of 82 m.y. that was incorporated in the meteorites when they formed but has since long decayed. Reed and Smith (1985) reported only LREE data in merrillite and, in apatite, Ce was the only

REE that could easily be measured. In contrast, Crozaz and Zinner (1985) were able to measure LREE and HREE in both calcium phosphate phases.

Crozaz et al. (1985) analyzed the merrillite of mesosiderites (a type of stony meteorite). A great variety of REE patterns were observed, even within a given meteorite, indicative of the metamorphic origin of this phase. Apparently, the merrillite formed by metamorphic redox reactions between P-bearing metal and silicates.

Fahey et al. (1985b) measured REE abundances in perovskite from both core and rim of a Ca-Al-rich inclusion (CAI) in the carbonaceous chondrite Efremovka to determine whether the core and rim had a common origin. Inclusions of this type are thought by most investigators to be either early condensates from the solar nebula or incompletely vaporized residues of grains from the pre-solar cloud. These meteoritic components, in which isotopic anomalies are prevalent, have been the object of many studies in the past decade. A variety of REE patterns (for a detailed discussion, see Boynton, 1984) have been observed in CAIs and have been used to classify them. Boynton and Wark (1984) used the similarity of REE patterns in the core and rim of an inclusion as an indication of their common origin. Although Fahey et al. (1985b) also observed identical REE patterns in the core and rim of the Efremovka inclusion, Mg isotopic fractionation (data also obtained by ion probe) in these two sites are evidence against this point of view.

One of the most refractory minerals found in Ca-Al-rich inclusions, and as isolated fragments in unequilibrated chondrites, is hibonite. Two research groups (Fahey et al., 1985a; Hinton et al., 1985) have used the ion probe to measure REE patterns in this mineral and to study the isotopic compositions of a number of elements. A variety of REE patterns was observed as well as large (up to 10%) ^{50}Ti excesses (Fahey et al., 1985c). ^{26}Mg excesses (from the in-situ decay of ^{26}Al , a radionuclide with a 7.5×10^5 yrs half-life) were also observed; however, no correlation between REE patterns and ^{26}Al was found.

Finally, two similar studies (Goodrich et al., 1985; Lindstrom et al., 1985) have looked into the origins of and possible relationships between REE-rich lunar highland cumulate rocks. These rocks are of three types and have recently been identified from small clasts (<50 mg) in lunar breccias. The REE in these clasts are concentrated in phosphates, both whitlockite and apatite, although other phases (pyroxenes and plagioclase) also exhibit unusually high REE contents. REE concentrations in the two phosphate minerals (Lindstrom et al., 1985) differ by factors of 20 to 30 (see Fig. 5). The REE patterns in whitlockite from three different clasts are similar, suggesting that the whitlockites were generated from systems with similar REE concentrations, but nevertheless distinct enough to indicate that the whitlockites of these clasts did not crystallize from a single melt.

Conclusions

In summary, it is now possible to measure, by ion probe techniques, REE concentrations down to ~ 100 ppb (an improvement of at least 2 orders of magnitude over what can be analyzed in the electron probe). Measurements of individual grains are made in-situ (in polished thin or thick sections) with a spatial resolution of $\sim 10 \mu\text{m}$. A wide variety of geological applications should be forthcoming.

Acknowledgements

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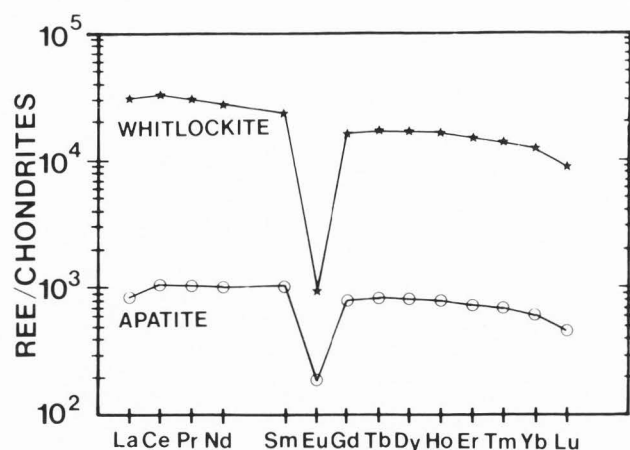


Fig. 5. REE distribution in whitlockite and apatite (both calcium phosphates) from a lunar breccia clast from lunar rock 67975.

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Discussion with Reviewers

S. J. B. Reed: What is the effect of the energy filtering used by the authors on MO^+/M^+ ratios and what is a typical M^+ count-rate per ppm?

Authors: The oxide to elemental ratios of the REE, in our experimental conditions, range from 0.06 to 0.32 and a typical elemental count-rate is 0.25 counts/sec x ppm La for 1nA primary O⁻ beam current. More details can be found in Zinner and Crozaz (1986a).

S. J. B. Reed: Energy filtering partially suppresses REE oxides, but the M^+ peaks of heavy REE presumably still suffer interference from light REE MO^+ peaks. Hence, the determination of HREE must depend essentially on their observed MO^+ intensities (especially when, as is often the case, the LREE concentrations are much higher). Does not energy filtering therefore have the drawback of decreasing the relative sensitivity for HREE by reducing their MO^+ intensities considerably more than the M^+ intensities of the LREE?

Authors: It is correct that, even with energy filtering, there are still MO^+ interferences from light REE at the masses of the heavy REE. However, as explained in detail in Zinner and Crozaz (1986a), it is possible to make a deconvolution of the spectrum and obtain the concentrations of the HREE from their M^+ peaks. This has the advantage of higher signals since, under conditions of energy filtering the MO^+/M^+ ratios are typically < 10% for the HREE. Without any energy filtering, on the other hand, the mass range of the HREE MO^+ peaks may be dominated by complex molecular interferences (depending on matrix composition and HREE concentrations) making the measurement of the HREE from their MO^+ peaks impossible.

J. B. Metson: In referring to the specimen isolation method the authors suggest the variable and "unknown" degree of charging creates problems for quantitative analysis, because of differences in rare earth energy distributions. However in this energy range (400-500 eV), relative ion yields are quite insensitive to the amount of energy filtering, particularly for the rare earths. Furthermore the degree of energy filtering is relatively easily determined by scanning of the electrostatic analyzer-see Lau et al., *Surf. Interface Anal.* **7**, 275 [1985], or MacRae and Metson, *Chem. Geol.* **53**, 325-333 [1985].

Authors: It is indeed correct that in the 400-500 eV energy range, the REE relative ion yields do not vary significantly. What is required though, to determine REE absolute abundances by the specimen isolation method, is a calibration curve for REE ion yields relative to a reference element such as Si, Ca etc. as a function of energy filtering. No such curve has yet been presented.