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Quantitative analysis of REEs by SIMS

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ABSTRACT

Accurate REE data are readily obtained by ion-microprobe analyses of bulk rock samples and of minerals in polished sections. The specimen isolation (SI) mode of kinetic energy filtering, which dramatically removes molecular species from the secondary-ion spectra, combined with a sample-dilution technique to homogenize the support matrix, decreases detection limits for REEs to levels of parts per billion. Empirical working curves produced from international geostandards quantify the bulk-sample analytical data. Working curves for in-situ mineral analysis must be constructed from previously analyzed mineral separates (or single crystals) for each mineral species. Two analyses of augite—one of a crystalline sample and one of a fused glass button—indicate that secondary-ion yields are independent of sample structure.

INTRODUCTION

Because of their distinctive response to natural processes, the abundance and distribution of the rare-earth elements (REEs) are important variables to be determined in many petrologic and geochemical investigations. Bulk rock samples may be analyzed by a variety of techniques, including X-ray fluorescence, neutron-activation analysis (NAA), mass-spectrometric isotope dilution, atomic absorption, inductively-coupled-plasma mass spectrometry (ICP–MS), and secondary-ion mass spectrometry (SIMS). Mineral analysis techniques generally fall into two categories: (1) those for which bulk mineral separates are required, essentially the same techniques as for whole rocks, and (2) those in-situ methods, including electron microprobe, proton-induced X-ray emission (PIXE), laser microprobe, and SIMS. Each technique has its particular advantages and disadvantages. SIMS analysis has the potential of extreme sensitivity, unfettered by the background noise of X-ray–based methods or by the numerous interferences of instrumental neutron-activation analysis (INAA). However, the lack of quantification of secondary-ion intensities, the generation of a multitude of molecular ions in the sputtering process, and the unknown interactions caused by matrix-composition variations have greatly slowed accumulation of geologically useful SIMS data.

The molecular ions may be largely removed from the spectra by using a technique of high mass resolution (Huneke et al., 1983; Compston et al., 1984), or by kinetic energy filtering (Huneke et al., 1983; Shimizu, 1978), a technique based upon the fact that molecular ions have a much narrower kinetic energy distribution than atomic ions. A modified form of energy filtering, termed the specimen isolation (SI) method (Metson et al., 1983; McIntyre et al., 1983), accomplishes more complete removal of molecular ions in the REE spectra while retaining excellent sensitivity.

The problems that the effect of matrix variation have upon secondary-ion intensity yields are commonly handled empirically in trace-element analysis by comparing unknowns with standards of the same major-element chemistry (Ray and Hart, 1982; MacRae and Metson, 1985). Nesbitt et al. (1986) have devised a technique, applicable to both major and trace elements in bulk samples, in which samples and standards are equally diluted in a uniform matrix of Pb_2SiO_4, each mixture is fused at high temperature, and the resultant glasses are analyzed.

Analysis of REEs poses a problem in quantification for both bulk-rock and in-situ mineral techniques that is overcome with the SIMS technique developed at the University of Western Ontario. Various preliminary developmental steps have been described in Nesbitt et al. (1986), MacRae and Metson (1985), and MacRae and Russell (1987).

TECHNIQUE

The present data, and those of all previous studies using the SI method reported on here, were obtained on a Camera IMS 3f instrument using a duoplasmatron-source primary beam of $^{16}O^-$ at an accelerating voltage of approximately 12 keV and approximately 250 nA. The sample holder was maintained at a secondary accelerating voltage of 4.5 keV. For the SI method, the uncoated (thus nonconductive) samples were mounted in a stainless-steel sample holder, fronted by a stainless steel–topped (0.15 mm thick) Teflon (0.55 mm thick) mask drilled with 15 3-mm-diameter holes. A Teflon disc behind the button insured that no part was in contact with the sample holder. The sample surface is thus allowed to charge freely under the primary beam, creating a potential well that effectively provides extreme selection, trapping ions of low kinetic energy (Lau et al., 1985; Metson et al., 1983, 1984). The spectra obtained are essentially free from molecular ions over the entire mass range. In a comparative

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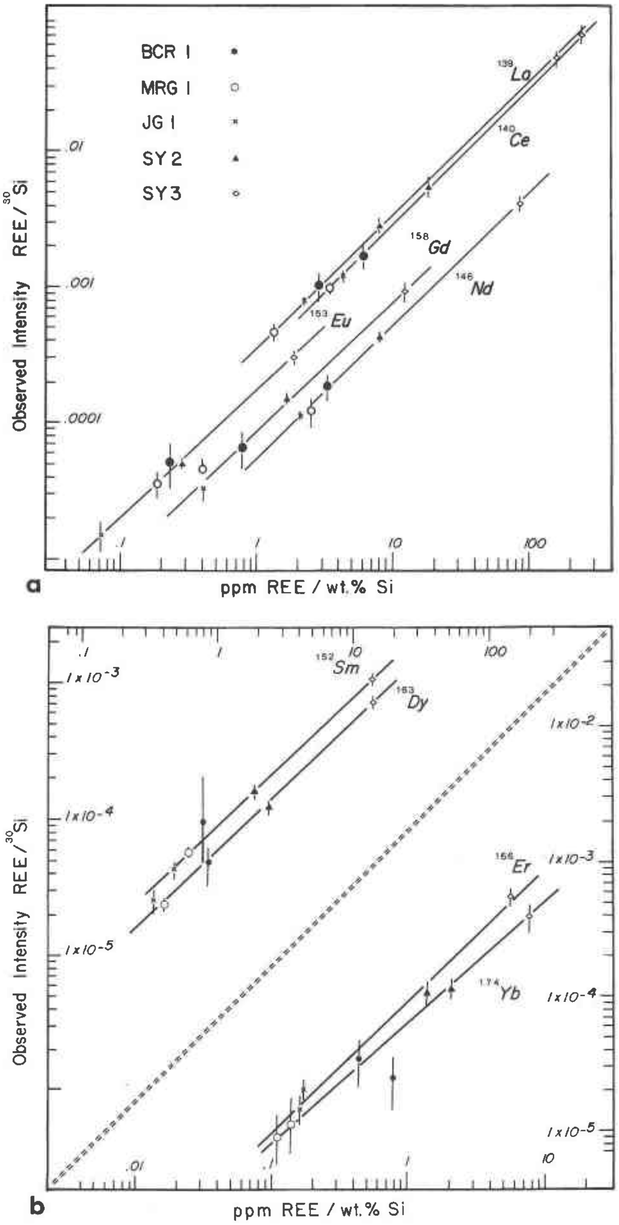

Fig. 1. Whole-rock REE calibration curves for sample-dilution method using Pb_2SiO_4. (a) La, Ce, Nd, Eu, Gd. (b) Sm, Dy, Er, Yb.

study of analyses by conventional energy filtering and SI, Muir et al. (1987) have pointed out that the heavy-REE spectra must still be corrected by a peak deconvolution method for the interference effects of light-REE oxides for the conventional method of analysis, but that molecular-ion suppression is so great by SI that no correction is required. An application by MacRae and Russell (1987) shows that for samples of lowest REE abundance, $LaO^+/La^+ < 10^{-3}$, and interference of $^{139}La^{16}O^+$ on $^{155}Gd^+$ was not detectable.

Table 1. REE abundances (ppm) of whole-rock standards

	BCR1*	MRG1**	JG1*	SY2**	SY3**
La	25	10	22	74	1350
Ce	53.7	26	43	170	2200
Nd	28.7	19	20.6	74	760
Sm	6.6	4.5	4.5	16	120
Eu	1.96	1.4	0.69	2.5	17
Gd	6.7	3?	3.9	15?	110?
Dy	6.35	3?	3.2	21?	120?
Er	3.6	1?	1.6	12?	50?
Yb	3.39	0.8	1.5	18	68

Note: Questioned values indicate fewer than recommended select results (see Abbey, 1983) and/or fewer than three analytical methods.

* Govindaraju, 1984.

** Abbey and Gladney, 1986.

As a result of using maximum primary-beam currents and wide-open energy slits, the primary-beam spot size at the sample surface for the SI mode geometry is commonly about 70–80 μm as compared to 5–20 μm for conventional mode. Secondary-ion intensities for both modes of operation in equivalent samples are virtually identical (Muir et al., 1987).

Bulk-rock analysis

Using the method of Nesbitt et al. (1986), one part by weight powdered rock sample was mixed with six parts by weight Pb_2SiO_4 (prepared from 99.999% pure SiO_2 and PbO obtained from Aldrich Chemical Company). The mixture (roughly 7 g) was fused in a Pt crucible at 1150 °C for one h and quenched by pouring into a massive stainless-steel mold; the resultant glass button (measuring ~ 14-mm diameter) was then annealed at 350 °C for at least 4 h. To avoid possible contamination, the buttons were not handled further prior to analysis.

Because the count rates for the REEs in most samples were below the level required for manual alignment, the magnet sector of the mass spectrometer was aligned for each mass before analysis using a sample of moderate REE abundance, and those values automatically used for each sample determination (details in MacRae and Metson, 1985). Computer storage limitations restricted automatic mode to determination of 10 different masses, thus 9 REEs (^{139}La, ^{140}Ce, ^{146}Nd, ^{152}Sm, ^{153}Eu, ^{158}Gd, ^{163}Dy, ^{166}Er, ^{174}Yb) and ^{30}Si were selected (^{30}Si rather than ^{28}Si was selected for these high-silica samples to avoid overloading the counting system).

The Si-normalized REE secondary-ion intensities (average ratio of REE counts per ^{30}Si counts), with standard deviations, versus Si-normalized REE abundances (ppm REE per wt% Si) for five internationally accepted rock standards (BCR1, MRG1, JG1, SY2, and SY3; abundances and references in Table 1) are plotted on a log-log scale in Figure 1. These "calibration curves" are straight lines with nearly identical slopes, indicating both that the sample-dilution method using Pb_2SiO_4 indeed eliminates matrix-variation problems (Nesbitt et al., 1986) and that the secondary-ion yield factors of all REEs measured are virtually identical. Clearly, the most poorly controlled curves are for Eu and Yb. In particular, the BCR1 plots

TABLE 2. REE abundances (ppm) of matrix Pb_2SiO_4

	Batch 1	Batch 2	Batch 3
La	0.1	0.4	0.3
Ce	0.1	0.2	0.04
Nd	0.006	0.007	0.008
Sm	n.d.	0.02	n.d.
Eu	0.01	n.d.	0.02
Gd	0.03	0.1	n.d.
Dy	0.1	0.1	n.d.
Er	0.03	0.06	n.d.
Yb	n.d.	n.d.	0.05

Note: PbO and SiO_2 of 99.999% purity from Aldrich Chemical Company. n.d. = not detected.

tend to fall off the trends established by the other points; no reason was apparent. Count rates were as low as 0.25 cps, and data accumulation times were as high as 40 s per mass, repeated over four cycles for each sample point. The sputter craters indicate a maximum of 50-ng glass removal.

The standard deviations shown (Fig. 1) are, in some cases, larger than expected. Several reasons are obvious, including some inhomogeneity of the quenched glasses, insufficient counting times for a few determinations, or some undetermined instrumental variations over the two years during which data were collected. Undoubtedly, standard deviations will improve as more data points are added to the array. Nonlinearity of sample points may, to some extent, be blamed on inhomogeneity of the glasses, but also on possible original sample-split inhomogeneities, on incorrect REE literature values, and different trace levels of REEs in the batches of Aldrich chemicals used. Three different "blank" Pb_2SiO_4 glass buttons from three different reagent mixes were examined (Table 2). The REE values shown (obtained using extensions of the working curves of Fig. 1) will be higher than the actual ones simply because of the enhancement effect of Pb_2SiO_4 on secondary-ion yields, but the differences between batches should not substantially affect rock-standard values.

In-situ mineral analysis

Secondary-ion yields are not strictly linearly related to abundance, but are significantly affected by matrix-composition variations. Until all ion interactions can be theoretically derived, it is necessary for in-situ mineral analysis to work from empirical calibration curves constructed from mineral "standards" similar in composition to the samples. For a study of REE distribution in clinopyroxene of a komatiitic flow, MacRae and Russell (1987) selected four augite samples from the University of Western Ontario mineral collections and established calibration curves for each REE, which were subsequently used for in-situ augite analyses. The quality of data obtained indicate that the same technique may be used for any mineral study.

Following selection of appropriately pure and homogeneous mineral specimens (homogeneity of major and many minor elements may be determined by electron microprobe), a portion of each specimen is coarsely ground and any foreign material removed prior to fine grinding (−325 mesh). REE abundances may be readily determined by preparing one split of each ground sample according to the bulk-rock method outlined above, obtaining Si wt% by electron microprobe, then using the bulk-rock calibration curves of Figure 1.

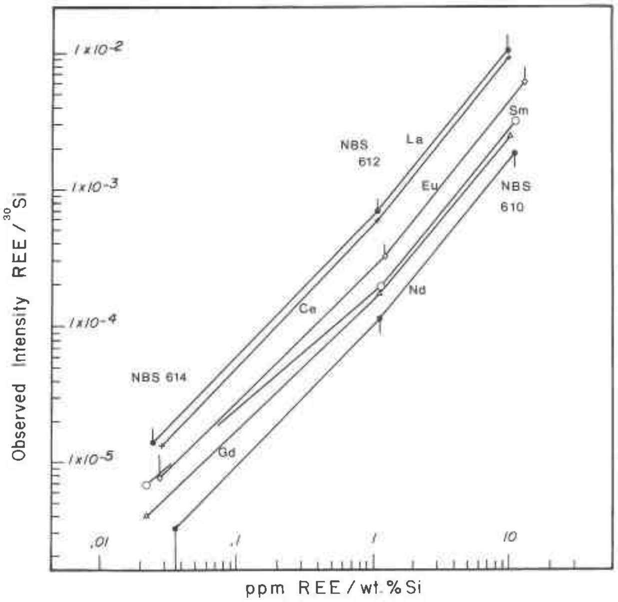

Fig. 2. REE distribution curves of NBS glasses 610, 612, and 614.

For most minerals, splits of each ground specimen may be melted in a Pt crucible [for augite, MacRae and Russell (1987) held the samples at 1450 °C for 1 h] and a glass of the pure phase produced by pouring into a stainless-steel mold, as for the bulk-rock method. For those minerals that do not melt readily, crystal faces, cleavage fragments, and polished chips may be analyzed rather than glass buttons. Because fusing tends to remove inhomogeneities, more data from the crystalline materials may be necessary to obtain true average values.

REE contents of the mineral standards may be obtained using the bulk-rock method detailed above. Exactly as for bulk rocks, calibration curves for pure minerals may then be constructed by using a plot of Si-

TABLE 3. REE content (ppm) of augite A9

	Glass bulk-rock method	Crystal in-situ method
La	0.65	0.69
Ce	2.5	2.5
Nd	3.8	4.7
Sm	1.8	2.5
Eu	0.10	0.11
Gd	1.1	1.4
Dy	0.64	1.0
Er	0.32	0.36
Yb	1.3	1.7

Table 4. REE contents (ppm) of NBS glasses

	NBS 612			NBS 610		NBS 614		
	NBS*	SIMS	INAA**	SIMS	INAA**	SIMS	INAA**	Others
La	36	36.3	41.1	330	464	0.83	1.2	0.83*
Ce	39	36.8	55	335	553	0.96	1	
Nd	36	37.3	24	377	98	1.2	<3	
Sm	39	39.1	38.0	382	361	0.73	0.73	0.68, 0.69†
Eu	36	42.1	33.0	440	384	0.92	0.69	0.99
Gd	39	37.8		354		0.74		0.8, 0.7*†
Dy	35	39.5		359		0.82		
Er	39	32.5		272		0.73		
Yb	42	45.4	38.3	442	371	0.75	0.76	

* U.S. National Bureau of Standards, 1982.
** Nuclear Activation Services Ltd., Hamilton, Ontario, Canada.
† Gladney et al., 1985.

normalized REE abundance vs. ^{30}Si-normalized REE secondary-ion intensity (ppm REE per wt% Si vs. REE counts per ^{30}Si counts) from either the fused or crystalline pure minerals.

Polished thin sections of rock on glass, about 2-cm diameter, are the most convenient sample form. In this case, the regular SI stainless steel–Teflon mask is used, but the uncoated sample is held in place by a ring of stainless steel (rather than a solid plate), with a narrow Teflon spacer ring between sample and steel ring. This backless design allows centering of specific mineral grains via transmitted light with a regular petrographic microscope prior to analysis.

MacRae and Metson (1985) and MacRae and Russell (1987) have used the method to document REE variations in augite through a differentiated igneous intrusion and through a differentiated flow, respectively. One large augite (A9) from the University of Western Ontario mineral collection was analyzed by the sample-dilution method using Pb_2SiO_4 and by the in-situ method using a mineral chip (Table 3). Considering that differences due to natural zonation in large crystals must always be expected, the results are reasonable.

Discussion

As a demonstration of the bulk-rock procedure, National Bureau of Standards glasses 610, 612, and 614 (U.S. National Bureau of Standards, 1982) were prepared and analyzed in the manner above. This set of synthetic glasses has a support-matrix composition of 72 wt% SiO_2, 12% CaO, 14% Na_2O, and 2% Al_2O_3 to which 61 different elements have been added at nominal levels of 500 ppm (NBS 610), 50 ppm (NBS 612), and 1 ppm (NBS 614). Of these, NBS has published complete REE analyses for only glass 612. Analyses from our SIMS method and from one INAA determination are recorded in Table 4 together with the NBS abundances. Three of the nine SIMS determinations vary from the NBS values by more than 10%: Eu (17%), Dy (13%), Er (17%). The Er variance could be blamed on the poorly controlled working curve for that element (Fig. 1), but no reason is readily apparent for the poor agreement of Eu and Dy analyses. The NBS 610 values obtained for all but La, Ce, and Nd involve using a long extention of the Figure 1 working curves, as do all the values for NBS 614 (Table 4). Although there are some supporting data for the NBS 614 analyses (Table 4), none were located for NBS 610; the INAA values recorded here are not considered of research quality and thus are broad indicators only.

Based on the assumption that each NBS glass contains roughly equal amounts of REE (supported by the 612 data), curves of secondary-ion intensity (expressed as REE/^{30}Si) vs. abundance (expressed as ppm REE/wt% Si) should all be approximately parallel for the pure undiluted NBS glasses. Since the support matrix is the same in all glasses, the curves should also be straight lines on log-log plots. Figure 2 shows the correlation curves to be slightly concave upward; if the abundance values of NBS 612 are correct, then those of NBS 610 and/or NBS 614 are slightly too low. It seems unlikely that the element contents in NBS 610 are high enough to produce a matrix effect. It should also be noted that the relative standard deviations for secondary-ion data points of the pure glasses were sufficiently high that straight lines could have been drawn for each element. To avoid overcrowding of the diagram, Figure 2 shows only six of the nine element curves and standard deviation bars for only La, Nd, and Eu.

Table 5. Statistical detection limits (ppm) for REE by SIMS

	MRG1	SY3
La	0.004	0.006
Ce	0.004	0.006
Nd	0.02	0.04
Sm	0.02	0.01
Eu	0.007	0.01
Gd	0.01	0.02
Dy	0.02	0.03
Er	0.02	0.02
Yb	0.04	0.04

Note: Detection limit = $(6/m)(C_b/T)^{1/2}$, where m = number of counts per unit of concentration in T seconds and C_b = background counts per second (Norrish and Chappell, 1977). Background was determined by counting for 129 min at mass 1.454.

Limits of detection for REE by SIMS are estimated by

Crozaz and Zinner (1986) at 100 ppb, but their paper does not include supporting data. Limits of detection for SIMS analyses by the SI method of lead silicate–diluted samples have been estimated using the Norrish and Chappell (1977) method (Table 5). The results were obtained during a time when samples of low REE levels were being analyzed, and ion-source memory should not be a problem. Nevertheless, the figures are based on the counting statistics only and are overly optimistic. The contents of REE in the Pb_2SiO_4 (Table 2) may provide a more realistic estimate for this method.

For silicates with low REE abundances, in-situ analysis by the SI method combined with bulk analysis after diluting the sample with Pb_2SiO_4, has already proved valuable (e.g., MacRae and Russell, 1987; MacRae and Metson, 1985). The procedure of preparing working curves for each mineral is time consuming, but avoids consideration of matrix variations on secondary-ion yields. One definite limitation of the method, as pointed out by Zinner and Crozaz (1986) and Crozaz and Zinner (1986), is the inability to do detailed single-crystal chemical-zonation studies with a primary-beam diameter of approximately 80 μm. Certainly, the diameter may be decreased, but to do so restricts sensitivity. The conventional method of Au-coated sample, moderate energy filtering, and small beam size (see Zinner and Crozaz, 1986) will allow zonation studies, but the quality of data is otherwise no better than for the SI method, and, in view of the apparently unavoidable oxide interference from light-REE at heavy-REE masses (Reed, 1986; Crozaz and Zinner, 1986), the data are considerably more cumbersome to obtain.

Finally, the possible difference in secondary-ion yield from glass or crystalline samples must be addressed. Ray and Hart (1982) found that for each of the eight elements they analyzed (Na, Mg, Al, Ca, Ti, Sr, Sc, and Cr), ions were sputtered from clinopyroxene more readily than from glass of the same composition; they concluded that glass-calibration standards would be unsuitable for the analysis of crystalline material. Muir et al. (1987), in a comparative study of ion intensities from crystal, glass, and ceramic of the same composition by both SI and conventional energy filtering, found no significant differences for the 14 different masses (no REEs measured. I have compared secondary-ion intensities of REE/^{30}Si from a polished section and a fused glass button of augite (sample A9, noted above). The average intensities from the crystalline sample are, in each case, very marginally lower than from the equivalent glass, but there is generous overlap of standard deviations for each determination. Also, in every case, standard deviations for the crystalline sample are larger than for the fused sample. Apparently, any differences in ion yields due to matrix structure are within the statistics of analysis.

SUMMARY

SIMS is a sufficiently sensitive method of analysis that even for a highly diluted sample, detection limits are at ppb levels. Using fused buttons of one part sample to six parts Pb_2SiO_4 matrix and the SI mode of instrument operation (Metson et al., 1983; McIntyre et al., 1983), the two problems of varying sample composition and molecular-ion interference are completely eliminated for the REE spectra. For any element, including REEs, calibration curves may be constructed using known geostandards that cover a wide abundance range.

Individual minerals may be analyzed in situ from polished sections if empirical working curves are established for each mineral species, thus avoiding matrix corrections. The one restriction of the SI method of single-grain analysis is spatial resolution, dictated by the primary beam of approximately 70–80 μm.

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