

# RARE EARTH ELEMENT SENSITIVITY FACTORS IN CALCIC PLAGIOCLASE (ANORTHITE)

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## 1. Introduction

The rare earth elements (REE) are sensitive indicators of the geochemical processes responsible for the evolution of differentiated rocks. Although most measurements are made on bulk samples by a variety of techniques, in recent years the ability to make in situ ion microprobe analyses of the REE on individual minerals within a petrographic context has become increasingly important for understanding the crystallization and metamorphic histories of igneous rocks. Quantitative measurement of the REE using secondary ion mass spectrometry (SIMS) requires a good knowledge of the relative sensitivity factors for the minerals of interest. Although matrix effects are an important factor governing the ion yields for different elements, it has been established that relative ion yields between REEs are almost identical for all mineral standards reported so far (apatite, perovskite, hibonite and synthetic silicate glass), and absolute ion yields for a given REE vary by less than 30% for all these phases [1].

However, recent comparisons of instrumental neutron activation analysis (INAA) and SIMS data for plagioclase in lunar anorthosites suggest that ion yields for the REE in plagioclase may be significantly lower than those determined for silicate glass. Comparison of SIMS [2] and INAA [3] REE data for Moore County (eucrite) plagioclase also indicate lower ion yields for this mineral. We have therefore initiated a study of REE concentrations in lunar anorthite (calcic plagioclase) crystals in order to determine whether revised sensitivity factors are required.

## 2. Experimental Methods

We selected two anorthite grains – 76503,7081 and 76503,7233 – from an Apollo 17 soil sample and analyzed them as individual coarse-grained crystals by INAA (see [4] for details of the procedures). Both samples were irradiated for approximately 24 hours at thermal-neutron fluxes of  $5.5$  and  $4.9 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$  for 7081 and 7233, respectively; results are listed in Table 1. Electron microprobe analyses show that both grains appear to be homogeneous at the major element level (An~96); however, they contain numerous microscopic inclusions ( $<5 \mu\text{m}$ ) of (primarily) magnesian pyroxene. These inclusions are distributed homogeneously throughout sample 7081, but form stringers along crystallographic and strain boundaries in sample 7233, in addition to occurring throughout other areas of the grain. Ion microprobe analyses were made in areas containing homogeneous distributions of inclusions; concentrations as well as areas devoid of inclusions were avoided. REE measurements were made according to the experimental procedures of [5], at primary beam ( $\text{O}^-$ ) currents of 10 – 15 nA.

Complex molecular interferences were removed by energy filtering at low mass resolution, and the resulting mass spectrum was deconvolved in the REE mass region into elemental and monoxide components. REE concentrations were calculated using the sensitivity factors listed in column 8 of Table 1 (Old  $F_i$ ) and  $\text{SiO}_2$  concentrations determined by electron microprobe analysis ( $\text{SiO}_2 = 43.84 \text{ wt.}\%$  for 7081 and  $44.11 \text{ wt.}\%$  for 7233).

### 3. Results and Discussion

We made a total of seventeen SIMS measurements on the anorthite grains. Average concentrations for each sample are listed in Table 1 and are shown in Fig. 1.

Table 1. Rare Earth Element Data (ppm) and Sensitivity Factors\*

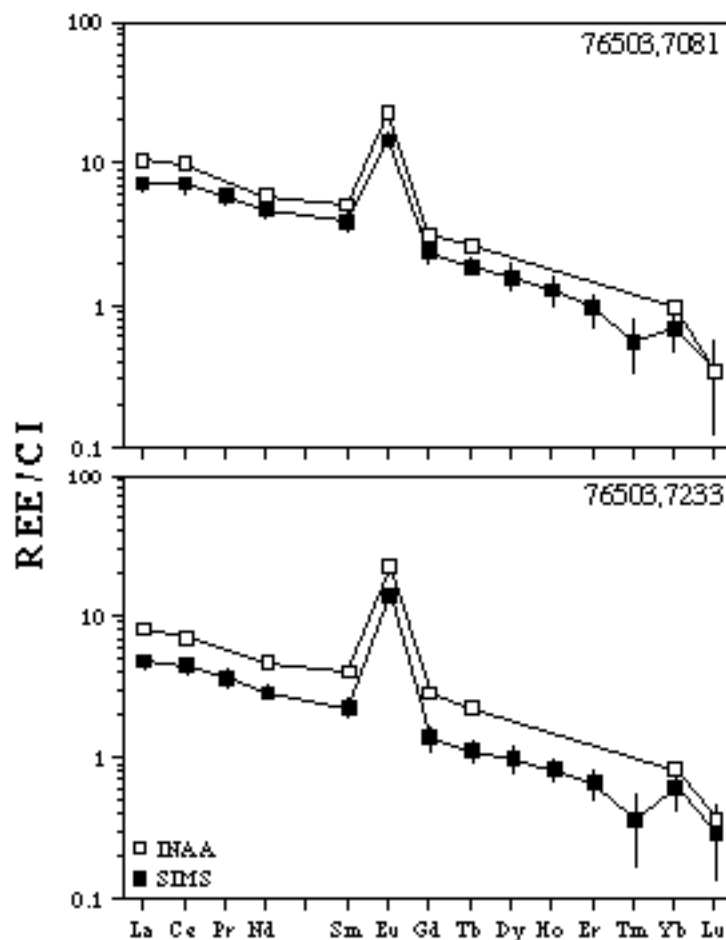
	76503,7081			76503,7233			Old $F_i$	New $F_i$	New Ion Yield $\dagger$
	INAA	SIMS	ratio $\S$	INAA	SIMS	ratio $\S$			
La	$2.58 \pm 0.02$	$1.72 \pm 0.21$	0.67	$1.921 \pm 0.019$	$1.13 \pm 0.15$	0.59	0.92	1.45	1.60
Ce	$6.07 \pm 0.06$	$4.39 \pm 0.63$	0.72	$4.38 \pm 0.09$	$2.73 \pm 0.30$	0.62	1.05	1.65	1.41
Pr		$0.54 \pm 0.06$			$0.33 \pm 0.05$		0.93	1.47	1.60
Nd	$2.7 \pm 0.5$	$2.22 \pm 0.32$	0.82	$2.1 \pm 0.6$	$1.33 \pm 0.17$	0.64	0.86	1.35	1.77
Sm	$0.767 \pm 0.007$	$0.58 \pm 0.09$	0.75	$0.606 \pm 0.006$	$0.34 \pm 0.05$	0.56	0.79	1.24	2.01
Eu	$1.309 \pm 0.012$	$0.84 \pm 0.11$	0.64	$1.255 \pm 0.015$	$0.79 \pm 0.08$	0.63	0.72	1.13	2.23
Gd		$0.47 \pm 0.08$			$0.28 \pm 0.05$		0.89	1.40	1.87
Tb	$0.098 \pm 0.003$	$0.07 \pm 0.01$	0.72	$0.082 \pm 0.006$	$0.04 \pm 0.01$	0.50	0.99	1.56	1.70
Dy		$0.40 \pm 0.08$			$0.24 \pm 0.05$		1.03	1.62	1.67
Ho		$0.07 \pm 0.02$			$0.05 \pm 0.01$		1.05	1.65	1.66
Er		$0.16 \pm 0.04$			$0.11 \pm 0.03$		1.15	1.81	1.54
Tm		n.r.			n.r.		1.10	1.73	1.62
Yb	$0.158 \pm 0.008$	$0.11 \pm 0.04$	0.71	$0.135 \pm 0.008$	$0.10 \pm 0.03$	0.76	1.15	1.81	1.59
Lu	$0.0086 \pm 0.0014$	n.r.		$0.009 \pm 0.0013$	n.r.		1.49	2.35	1.24

\* sensitivity factors are derived from the equation  $I_{\text{REE}}/I_{\text{Si}} = (1/F_i) \times (C_{\text{REE}}/C_{\text{SiO}_2})$ , where  $I$  is the ion intensity,  $F_i$  is the sensitivity factor relative to  $\text{Si}$ , and  $C$  is the concentration of the REE or  $\text{SiO}_2$ ;

$\S$ ratio = conc. SIMS / conc. INAA;  $\dagger$ ion yield =  $(W_i/W_{\text{SiO}_2}) \times (1/F_i)$ , where  $W_i$  is the atomic weight of element  $i$ , and  $W_{\text{SiO}_2}$  is the molecular weight of  $\text{SiO}_2$ ; n.r.: not reported.

Concentrations for the HREE have relatively large errors because these elements have low abundances in plagioclase, as well as significant interferences of the light REE (LREE) monoxides at the masses of the heavy REE (HREE); abundances are not reported for Tm and Lu. REE concentrations determined by ion microprobe are consistently lower than concentrations determined by INAA, with SIMS / INAA concentration ratios ranging from 0.50 to 0.82. Ratios for the trivalent REE in sample 7081 are systematically higher than those in 7233, but concentration ratios for Eu are similar in both samples (Table 1). The reason for this difference in trivalent REE concentration ratios between the two samples is not clearly understood, but it does not seem to be related to the proportion of inclusions incorporated into the ion microprobe analyses. Pyroxene inclusions are likely to be REE-enriched (particularly in the HREE) with negative Eu anomalies and, thus, one might expect trivalent REE concentrations to be positively and Eu negatively correlated with Mg and Fe abundances. We observe, however, that while HREE abundances covary to some extent with Fe and Mg, concentrations of the LREE are independent of Fe and Mg abundances, but tend to covary with Na concentrations; the best correlation is between Na and Eu.

Our data indicate that matrix effects for plagioclase are significantly different from those of other silicates and that revised sensitivity factors for the REE are required. The relatively small differences in concentration ratios between individual REE in each sample do not warrant revision of each sensitivity factor independently, particularly given the uncertainties involved and the fact that we do not clearly understand the reason for the systematic difference in concentration ratios for the trivalent REE between 7081 and 7233. Instead, we have revised old silicate sensitivity factors by a constant factor of 0.635, the mean Eu concentration ratio of the two samples, in order to calculate new sensitivity factors for plagioclase ( $\text{new } F_i = \text{old } F_i / 0.635$ ). We have noted that SIMS / INAA concentration ratios for Eu are nearly identical in the two samples and that this element shows the best correlation with plagioclase composition; in addition, Eu concentrations are less likely to be affected by the incorporation of variable proportions of pyroxene inclusions than concentrations of the trivalent REE. One potential problem with this approach is that Eu may in fact behave differently than the other REE, due to its compatibility in plagioclase in the divalent state. However, the fact that relative ion yields between individual REE have been nearly constant in other standards with highly variable REE compatibility factors suggests that this effect, if present at all, must play a minor role. We note, furthermore, that the unweighted mean concentration ratio for all



*Figure 1. CI chondrite-normalized REE concentrations in anorthite as determined by INAA and SIMS.*

the trivalent REE in plagioclase from both samples (0.65) falls near the value for Eu. New ion yields calculated for plagioclase from these data (column 10 of Table 1) are significantly lower than previous values.

We recalculated the REE concentrations of plagioclase in Moore County from [2] using the new sensitivity factors. The revised abundances (Fig. 2) show much better agreement with the INAA data of [3] than the original values, particularly for the LREE and Eu. Slightly higher HREE abundances indicated by the INAA data may reflect minor contamination of the plagioclase separate by a HREE-enriched phase, such as pyroxene. Also shown in Fig. 2 are the data of

[6], which were determined by isotope dilution and corrected for pyroxene contamination; agreement is good in the LREE, but the HREE abundances of [6] are even lower than the original concentrations reported by [2].

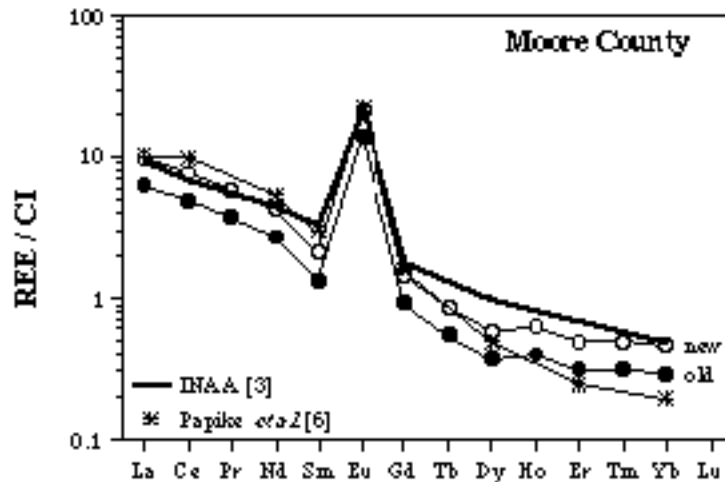


Figure 2. CI chondrite-normalized REE abundances in Moore County plagioclase, calculated using old and new sensitivity factors for plagioclase. Data from [2,3,6].

#### 4. Summary

We have compared REE concentrations obtained by INAA and SIMS in two lunar anorthite crystals and determined that matrix effects for the REE in plagioclase are significantly different from those of the silicate standard used to date. Revised sensitivity factors for plagioclase, relative to Si, are based on the mean INAA / SIMS concentration ratio for Eu and are a factor of 1.57 higher than those previously used.

#### References

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