

**MOLECULE-FREE REE ABUNDANCES IN HIBONITE BY SIMS-SSAMS.** E. E. Groopman<sup>1,2</sup>, L. Kööp<sup>3</sup>, K. S. Grabowski<sup>2</sup>, and A. J. Fahey<sup>4</sup> <sup>1</sup>National Research Council Postdoctoral Fellow, 500 Fifth Street NW, Washington, DC 20001 ([evan.groopman.ctr@nrl.navy.mil](mailto:evan.groopman.ctr@nrl.navy.mil)) at <sup>2</sup>Materials Science & Technology Division, U.S. Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC 20375. <sup>3</sup>Dept. of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637. <sup>4</sup>Microscopy & Surface Analysis, Corning, Inc., Corning, NY 14831.

**Introduction:** Rare Earth element (REE) abundances in calcium-aluminum-rich inclusions (CAIs) reflect oxygen fugacity and fractionation processes present during their formation. *In situ* analysis of REEs in small (<100  $\mu\text{m}$ ) grains is possible with Secondary Ion Mass Spectrometry (SIMS), though it is complicated by the presence of molecular isobars, especially oxides, over the heavy REEs (HREE, see Figure 1). High mass resolving power is not sufficient to separate these interferences. To achieve percent-level uncertainties in REE abundances by SIMS, time-intensive calibration of the oxide-to-atomic-ion yields ( $\text{MO}^+/\text{M}^+$ ) must be performed while biasing the sample voltage, which reduces all ion yields, but suppresses molecules more intensely than atomic ions [1–3]. Ion intensities are then measured on the tails of the energy distributions, thus the overall yield is at least one order of magnitude lower than without a bias voltage, but the interferences are minimized. Abundances are further deconvolved through a least-squares fit of some 47+ atomic and oxide masses, which relies upon knowing the isotopic abundances *a priori*. Resonance Ionization Mass Spectrometry (RIMS) can eliminate many of these issues, however only 2 to 3 elements may be typically measured in an analysis before laser retuning is required. Using a Single-Stage Accelerator Mass Spectrometer (SSAMS) connected to the output of a SIMS instrument, we are able to directly measure the REEs in standards and samples without molecular interferences.

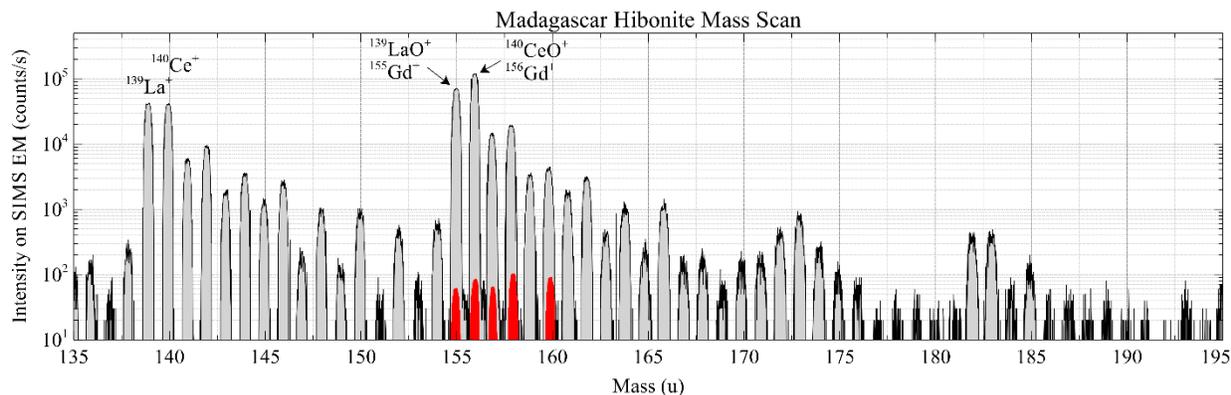
**Methods:** The NRL SIMS-SSAMS consists of a Cameca ims 4f SIMS connected to a National Electrostatics Corporation

(NEC) SSAMS, both significantly modified [4]. 4.5 keV ions from the SIMS are accelerated by 300 kV in the SSAMS and transit a gas stripping cell filled with Ar where collisions with the gas dissociate molecules. Molecular fragments or atomic ions are selected magnetically and electrostatically on the high-voltage “Deck” following the stripping cell. Electrostatic peak switching (EPS) allows for the selection of masses up to  $\pm 6.5\%$  of the Deck magnet’s central mass. An electron multiplier (EM) counts the high-energy ions.

Wavelength- & Energy-Dispersive X-Ray Spectroscopy (WDS; EDS; U. Chicago) were used to quantify the major and minor elements in polished chips of Madagascar hibonite (MH; Table 1). The NRL SIMS-SSAMS was used to measure the REEs, Ba, and Hf from chip G4 of MH, using NIST Standard Reference Material (SRM) 610 as a standard [5]. While not an ideal matrix match, the ion yields of  $\text{REE}^+$  relative to  $\text{Ca}^+$  have been found to be similar between phosphates, silicates, and hibonite [1,2]. The La abundance of MH, quantified by WDS, was used as an anchor for the REE abundances measured by SIMS-SSAMS. Four analyses each of the light REE (LREE) and HREE from two

Chip	MgO	Al <sub>2</sub> O <sub>3</sub>	CaO	TiO <sub>2</sub>	FeO	La <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>	ThO <sub>2</sub>
G1	2.46	77.40	5.58	2.92	4.85	2.14	3.45	1.20
G2	2.36	77.91	5.84	2.98	4.79	1.98	3.25	0.89
G4	2.47	77.29	5.65	3.00	4.85	2.10	3.51	1.13
Mean	2.45	77.42	5.64	2.96	4.84	2.11	3.44	1.13
1 $\sigma$	0.05	0.29	0.11	0.08	0.04	0.07	0.25	0.11

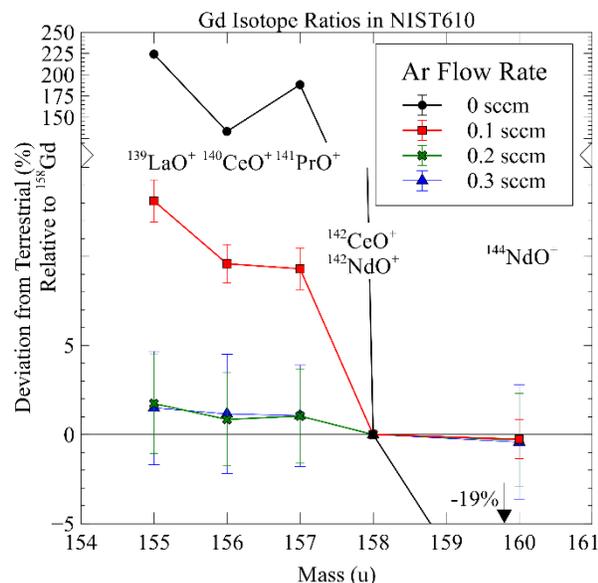
**Table 1:** WDS & EDS quantification of different MH chips (wt. %). Average for each chip shown, plus mean of all analyses.



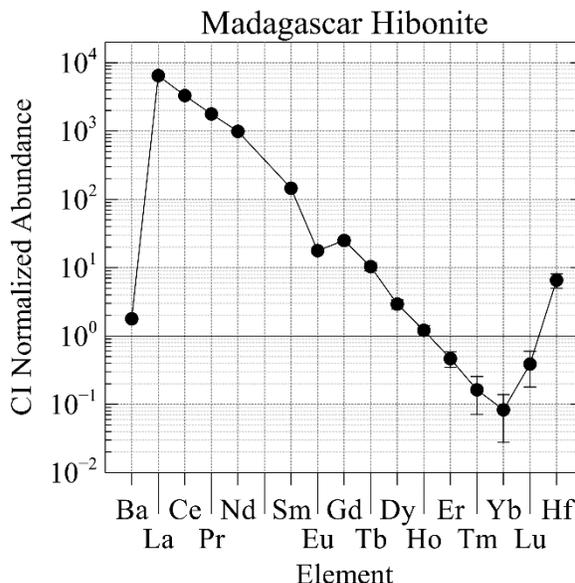
**Figure 1:** Mass scan of Madagascar hibonite on SIMS EM. Gd isotopes (measured with SSAMS) in red.

spots were performed with a 10 nA, 15 keV  $^{16}\text{O}^-$  Köhler beam focused on a 65- $\mu\text{m}$ -sized spot. From a 150  $\mu\text{m}$  imaged field, a 100  $\mu\text{m}$  aperture was used to limit the analyzed area at the crater centers to  $\sim 40 \mu\text{m}$  to avoid crater wall effects. Higher transmission would be achieved without this aperture. Two Deck magnetic fields were used to measure the REE, centered on mass  $\sim 146.5 \text{ u}$  for LREE and mass  $\sim 166.5 \text{ u}$  for HREE. EPS was used to select  $^{138}\text{Ba}^+$ ,  $^{139}\text{La}^+$ ,  $^{140}\text{Ce}^+$ ,  $^{141}\text{Pr}^+$ ,  $^{146}\text{Nd}^+$ ,  $^{147}\text{Sm}^+$ ,  $^{152}\text{Sm}^+$ ,  $^{153}\text{Eu}^+$ ,  $^{155}\text{Gd}^+$ , and  $^{156}\text{Gd}^+$  for LREE; and  $^{157}\text{Gd}^+$ ,  $^{158}\text{Gd}^+$ ,  $^{159}\text{Tb}^+$ ,  $^{163}\text{Dy}^+$ ,  $^{165}\text{Ho}^+$ ,  $^{166}\text{Er}^+$ ,  $^{169}\text{Tm}^+$ ,  $^{172}\text{Yb}^+$ ,  $^{175}\text{Lu}^+$ , and  $^{178}\text{Hf}^+$  for HREE. Gd isotopes were used to check for fractionation between the two Deck fields. Analyzed isotopes were chosen to be the most abundant species lacking or with minimal nuclear isobars. An Ar flow rate of 0.3 standard cubic centimeters per minute (SCCM) was used during the measurements, as this satisfactorily eliminated molecular isobars in NIST610 glass (Figure 2) where all elements are of roughly equal abundance. In hibonite, the oxide isobars over HREE are relatively more intense, so 0.3 SCCM was chosen over 0.2 SCCM as a precaution, even though it further lowered transmission.

**Results:** The CI chondrite-normalized [6] REE elemental abundance pattern in MH is shown in Figure 3, ranging from  $0.26 \pm 0.01 \text{ at. \% La}$  to  $6.2 \pm 3.5 \text{ at. ppm Tm}$ . Hf and Ba abundances are  $1.0 \pm 0.2$  and  $8 \pm 0.4 \text{ at. ppm}$ , respectively, though the Ba concentration in NIST610 was found to be heterogeneous spot-to-spot, limiting its usefulness in determining Ba's relative sensitivity. Our measurements qualitatively agree with those reported in [2,7] for MH determined by spark source mass spectrometry, neutron activation, and



**Figure 2:** Gd isotope ratio deviation vs. Ar flow rate. Interferences are labeled.



**Figure 3:** CI chondrite-normalized REE abundances in Madagascar hibonite chip G4 by SIMS spot analysis.

SIMS, though we have additionally directly measured Ba, Gd, Er, Tm, Lu, and Hf. Our abundances are  $\sim 5\times$  lower than previously measured for MH, either a reflection of heterogeneous concentration in different samples or our increased ability to remove molecular isobars. Lu is enhanced over Yb by  $\sim 10\times$  relative to an extrapolation from HREE, though this feature has also been observed in the meteoritic HAL hibonite [8,9]. Gd and Sm isotope ratios matched terrestrial composition, within uncertainties. Counting statistics were the largest component of the total propagated uncertainties.

**Discussion:** We have directly measured the REE abundances in MH by SIMS-SSAMS. These measurements provide high sensitivity, even to the low-abundance HREE, and enable their quantification from single analysis spots. This analysis, no more complex than a routine SIMS measurement, would facilitate greater throughput of CAIs and other samples where REEs are of interest, e.g. [8-10]. The ability to directly measured REEs free of molecules also facilitates REE imaging. These measurements allow MH to be used as a reference for REE measurements of CAIs and presolar grains.

**References:** [1] Zinner, E. & Crozaz, G. (1986) *Int J Mass Spectrom Ion Process*, 69, 17. [2] Fahey, A. J. et al. (1987) *GCA*, 51, 329. [3] Fahey, A. J. (1998) *Int J Mass Spectrom*, 176, 63. [4] Fahey et al. (2016) *Anal Chem*, 88, 7145. [5] Jochum K. P., et al. (2011) *Geostand Geoanal Res*, 35, 397. [6] Anders, E. & Grevesse, N. (1989) *GCA*, 53, 197. [7] Floss et al. (1998) *MAPS*, 33, 191. [8] Davis, A. M. et al. (1982) *GCA*, 46, 1627. [9] Hinton, R. W. et al. (1988) *GCA*, 52, 2573 [10] Ireland, T. R. et al. (1988) *GCA*, 52, 2841. \*We thank A.M. Davis for helpful comments.