

## Eu speciation in apatite at 1 bar: An experimental study of valence-state partitioning by XANES, lattice strain, and Eu/Eu\* in basaltic systems

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### ABSTRACT

Partition coefficients for rare earth elements (REEs) between apatite and basaltic melt were determined as a function of oxygen fugacity ( $f_{O_2}$ ; iron-wüstite to hematite-magnetite buffers) at 1 bar and between 1110 and 1175 °C. Apatite-melt partitioning data for REE<sup>3+</sup> (La, Sm, Gd, Lu) show near constant values at all experimental conditions, while bulk Eu becomes more incompatible (with an increasing negative anomaly) with decreasing  $f_{O_2}$ . Experiments define three apatite calibrations that can theoretically be used as redox sensors. The first, a XANES calibration that directly measures Eu valence in apatite, requires saturation at similar temperature-composition conditions to experiments and is defined by:

$$\left(\frac{\text{Eu}^{3+}}{\sum \text{Eu}}\right)_{\text{Apatite}} = \frac{1}{1 + 10^{-0.10 \pm 0.01 \times \log(f_{O_2}) - 1.63 \pm 0.16}}.$$

The second technique involves analysis of Sm, Eu, and Gd in both apatite and coexisting basaltic melt (glass), and is defined by:

$$\left(\frac{\text{Eu}}{\text{Eu}^*}\right)_D^{\sqrt{\text{Sm} \times \text{Gd}}} = \frac{1}{1 + 10^{-0.15 \pm 0.03 \times \log(f_{O_2}) - 2.46 \pm 0.41}}.$$

The third technique is based on the lattice strain model and also requires analysis of REE in both apatite and basalt. This calibration is defined by

$$\left(\frac{\text{Eu}}{\text{Eu}^*}\right)_D^{\text{lattice strain}} = \frac{1}{1 + 10^{-0.20 \pm 0.03 \times \log(f_{O_2}) - 3.03 \pm 0.42}}.$$

The Eu valence-state partitioning techniques based on ( $\sqrt{\text{Sm} \times \text{Gd}}$ ) and lattice strain are virtually indistinguishable, such that either methodology is valid. Application of any of these calibrations is best carried out in systems where both apatite and coexisting glass are present and in direct contact with one another. In holocrystalline rocks, whole rock analyses can be used as a guide to melt composition, but considerations and corrections must be made to either the lattice strain or  $\sqrt{\text{Sm} \times \text{Gd}}$  techniques to ensure that the effect of plagioclase crystallization either prior to or during apatite growth can be removed. Similarly, if the melt source has an inherited either a positive or negative Eu anomaly, appropriate corrections must also be made to lattice strain or  $\sqrt{\text{Sm} \times \text{Gd}}$  techniques that are based on whole rock analyses. This being the case, if apatite is primary and saturates from the parent melt early during the crystallization sequence, these corrections may be minimal.

The partition coefficients for the REE between apatite and melt range from a maximum  $D_{\text{Eu}^{3+}} = 1.67 \pm 0.25$  (as determined by lattice strain) to  $D_{\text{Lu}^{3+}} = 0.69 \pm 0.10$ . The REE partition coefficient pattern, as observed in the Onuma diagram, is in a fortuitous situation where the most compatible REE (Eu<sup>3+</sup>) is also the polyvalent element used to monitor  $f_{O_2}$ . These experiments provide a quantitative means of assessing Eu anomalies in apatite and how they be used to constrain the oxygen fugacity of silicate melts.

**Keywords:** Apatite, europium, Eu/Eu\*, XANES, oxygen fugacity,  $f_{O_2}$ , valence, anomaly, KREEP, basalt, lunar, merrillite; Experimental Halogens in Honor of Jim Webster

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