

Appendix OM4: calculating the influence of an initial anomaly and plagioclase fractionation

The following information is provided as a guide to evaluating how an inherited or intrinsic Eu anomaly can be corrected for a natural system where melt composition (e.g., glass) cannot be determined. Similarly, this supplement presents a simplified calculation of how plagioclase crystallization can influence a system where co-existing melt cannot be calculated. For simplicity all calculations are based on modification of $e \left[\left(\frac{\text{Eu}}{\text{Eu}^*} \right)_D^{\sqrt{\text{Sm} \times \text{Gd}}} \right]_{\text{Melt}}$, though similar corrections are required for lattice strain methods.

(i) Correcting for melts with an initial (pre-existing) Eu anomaly

For out of context apatite grains, or in systems where glass/whole rock analyses are not possible (e.g., lunar samples), it is theoretically possible to correct calibrations based on an inherited negative Eu anomaly. The classic example of an inherited anomaly can be found among the lunar mare basalts, known to have a negative Eu anomaly that is a product of lunar highland crust formation, giving rise to a situation where Eu is already fractionated from neighboring Sm and Gd in the melt source region (this process is easiest visualized when compared against a chondrite normalized whole rock projection to remove the “odd-even effect” among REE; Fig. OM4.1b).

If the partitioning values between apatite-basalt for Eu^{2+} and Eu^{3+} are fixed (i.e., unaffected by temperature over 1110-1175 °C), the $\text{Eu}^{2+}:\text{Eu}^{3+}$ in the melt is constant (i.e., fixed by f_{O_2} and defined by Eu L_3 XANES from in this work) and no other phase significantly fractionates Eu from $\sqrt{\text{Sm} \times \text{Gd}}$, the calculation (an oversimplification of natural systems) can be expressed by:

$$\left[(\text{Eu}/\text{Eu}^*)_D^{\text{Ap/melt}} \right]_{f_{\text{O}_2}} = \frac{\left[\left(C_{\Sigma \text{Eu}}^{\text{melt}} \times (X_{\text{Eu}^{2+}}^{\text{melt}})_{f_{\text{O}_2}} \right) \times D_{\text{Eu}^{2+}}^{\text{Ap/melt}} \right] + \left[\left(C_{\Sigma \text{Eu}}^{\text{melt}} \times (X_{\text{Eu}^{3+}}^{\text{melt}})_{f_{\text{O}_2}} \right) \times D_{\text{Eu}^{3+}}^{\text{Ap/melt}} \right]}{\sqrt{\left(C_{\text{Sm}}^{\text{melt}} \times D_{\text{Sm}}^{\text{Ap/melt}} \right) \left(C_{\text{Gd}}^{\text{melt}} \times D_{\text{Gd}}^{\text{Ap/melt}} \right)}}$$

Where, $(X_{\text{Eu}^{2+}}^{\text{melt}})_{f_{\text{O}_2}}$ represents the $\text{Eu}^{2+}:\text{Eu}^{3+}$ or $\text{Eu}^{3+}/\Sigma \text{Eu}$ for the melt at the f_{O_2} in question (in this example a fixed value determined from XANES analysis of basaltic glass presented in Table 6). The partition coefficients used in this calculation include $D_{\text{Eu}^{3+}}^{\text{Ap/melt}}$ from all experiments and $D_{\text{Eu}^{2+}}^{\text{Ap/melt}}$ is derived from preferred values presented in Table 6. By varying the concentration ratio of $(\sqrt{\text{Sm} \times \text{Gd}}/\text{Eu})_{\text{initial}}$, essentially a measure of the intensity of the negative anomaly, it is possible to trace how this influences $(\text{Eu}/\text{Eu}^*)_D$ at constant f_{O_2} . In the example presented in Fig. OM4.1a, this has been modelled at QFM, IW, C-CO-CO₂ with $(\sqrt{\text{Sm} \times \text{Gd}}/\text{Eu})_{\text{initial}}$ varying from 1-250. As can be seen from Fig. OM4.1a, the most notable effect of an initial Eu anomaly is to suppress the range over which variation occurs. To make the point, the variation in $(\text{Eu}/\text{Eu}^*)_D$ between the QFM and C-CO-CO₂ buffer where there is no initial anomaly is 0.29 (see a-a' in Fig. OM4.1a), but this value shrinks to 0.029 (see b-b') where of $(\sqrt{\text{Sm} \times \text{Gd}}/\text{Eu})_{\text{initial}}=10$ and

0.001 (see c-c') where of $(\sqrt{\text{Sm} \times \text{Gd}}/\text{Eu})_{\text{initial}}=100$. It should also be noted that inherited anomalies are not uncommon among basalts from many of the terrestrial bodies, with the lunar mare being the most noteworthy example. Whole rock analysis from various Apollo samples used in previous apatite research (15065, 15058, 14053, 10047; Strasheim, 1972; Wanke, 1975; Helmke et al., 1973; Goles, 1970; Rhodes, 1980; Wakita, 1970; Hubbard, 1972), show $(\sqrt{\text{Sm} \times \text{Gd}}/\text{Eu})_{\text{initial}}$ between 4-8 (corresponding to the shaded region in Fig. OM4.1b) and is an indication these melts likely formed with a notable inherited negative anomaly.

(ii) Correcting for plagioclase crystallization

Equilibrium fractionation models can be used to demonstrate the potential influence of plagioclase crystallization on $(\sqrt{\text{Sm} \times \text{Gd}}/\text{Eu})_{\text{melt}}$ or Eu/Eu^* . In this study we use plagioclase-basalt (herein referenced as plag-melt) partitioning data from Drake (1972) and for modeling purposes (where $C_l/C_l^0 = [F(1 - D) + D]^{-1}$) we assume all elements have constant partition coefficients. The work of Drake (1972) does indicate that trivalent elements are near constant over a range of temperatures and compositions, but it should be noted that Eu^{2+} partitioning does appear to be influenced by both plagioclase composition and temperature. The model also assumes plagioclase is the only crystallizing phase, and while this is clearly not a condition met by natural basaltic systems, because plagioclase is the dominant phase driving fractionation of Eu^{2+} from Eu^{3+} these calculations are still a useful indicator. This method also assumes the melt has no initial inherited Eu anomaly (see previous section of supplementary material 3), and the initial $\text{Eu}^{2+}:\text{Eu}^{3+}$ is arbitrarily set at 6.45:3.55 (noting this ratio is observed within glass of experiment ApREE-09 at the graphite-CO-CO₂ buffer). A final condition of this method is that $\text{Eu}^{2+}:\text{Eu}^{3+}$ is not fixed with fractionation but is simply a measure of partitioning and fractionation. A natural melt, by contrast, will have an $\text{Eu}^{2+}:\text{Eu}^{3+}$ proportional to the intrinsic f_{O_2} regardless of concentration.

As shown in Fig. OM4.2, the two orders of magnitude difference in partitioning between plagioclase/basalt observed among Eu valence species (particularly where one is compatible and the other highly incompatible) gives rise to a situation where even minor fractionation can result in modification of Eu/Eu^* . At $F=0.9$, the melt $\text{Eu}/\text{Eu}^*=0.95$ and by $F=0.7$ the melt $\text{Eu}/\text{Eu}^*=0.84$. It is worth noting that the $(\text{Eu}^{2+}:\text{Eu}^{3+})_{\text{initial}}$ represents a highly reduced condition, and model calculations with higher Eu^{3+} content will result in smaller changes to calculated Eu/Eu^* .

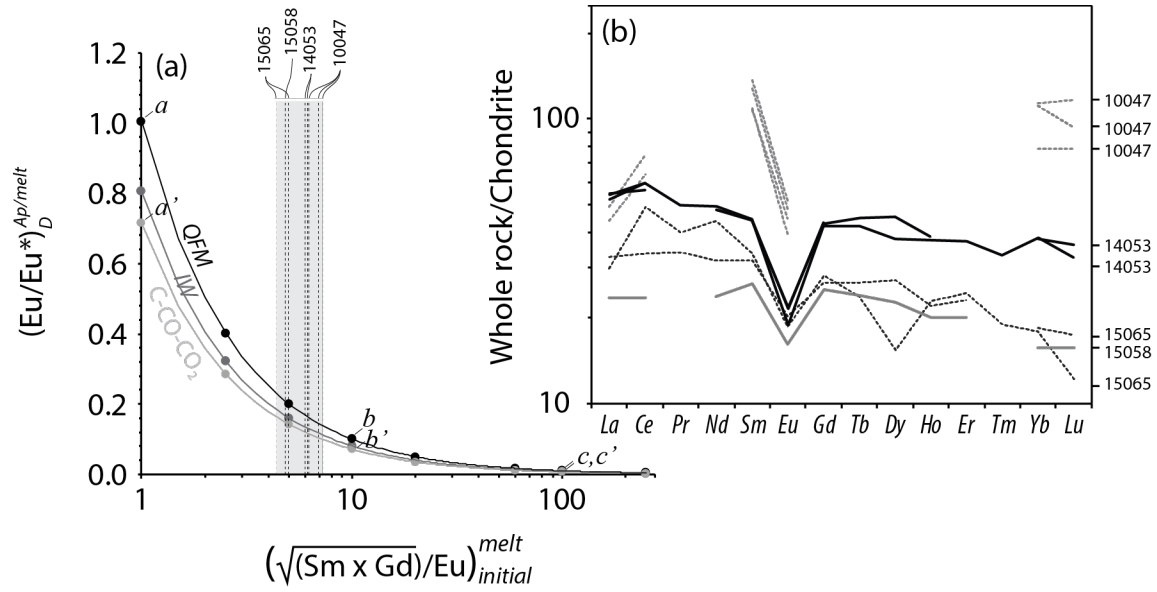


Figure OM4.1: (a) calculated effect of an inherited negative anomaly on the $(Eu/Eu^*)_D^{\sqrt{Sm \times Gd}}$ calibration assuming equilibrium and no fractionation effects. Vectors a-a', b-b' and c-c' report the variance between buffers in terms of $(Eu/Eu^*)_D^{\sqrt{Sm \times Gd}}$ and is discussed in text. Shaded region corresponds to estimated initial Eu anomalies or $(\sqrt{Sm \times Gd}/Eu)_{initial}^{melt}$ from lunar whole analyses. (b) Whole rock REE concentration for documented apatite-bearing lunar basalts obtained from the literature. Samples 14053, 15065 and 15058 use $(\sqrt{Sm \times Gd}/Eu)_{initial}^{melt}$ for anomaly intensity calculations, while sample 10047 uses Sm/Eu in the absence of Gd data.

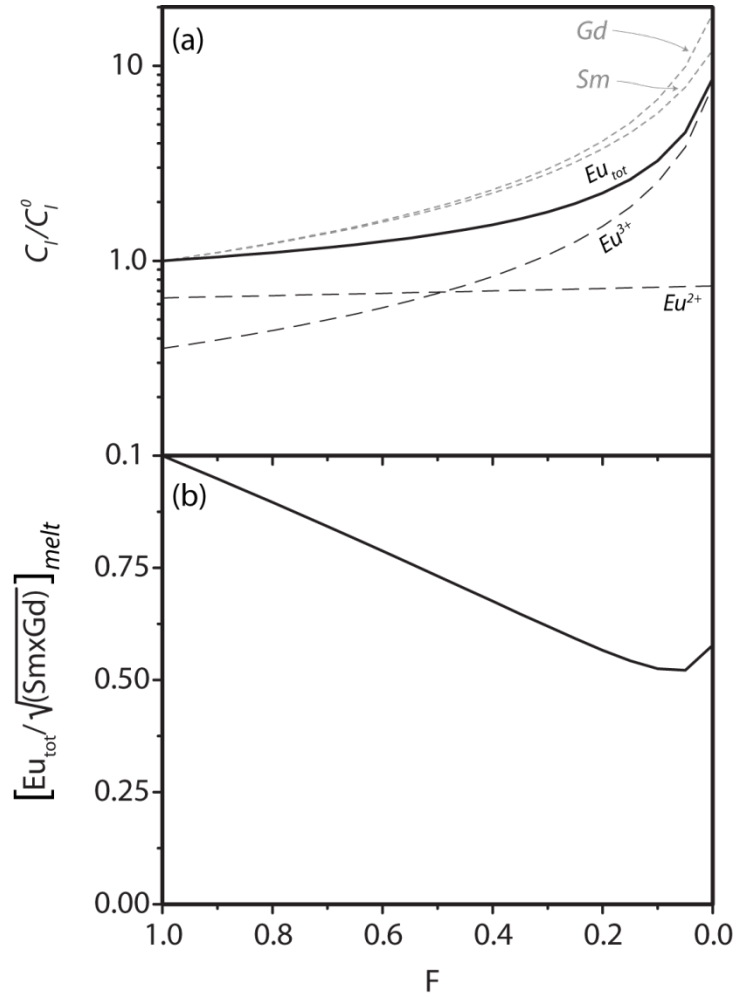


Figure OM4.2: equilibrium fractionation calculations for plagioclase-basalt system reporting total Eu (Eu_{tot}), Eu^{2+} , Eu^{3+} , Sm and Gd using partition coefficient data from Drake (1972; where $D_{Eu^{2+}}^{plag/melt} = 1.65$ and $D_{Eu^{3+}}^{plag/melt} = 0.045$). All calculations assume constant partitioning for each element and valence species (such that there is no temperature effect), an initial Sm:Eu_{tot}:Gd is 1:1:1 (i.e., no initial anomaly), the initial Eu^{2+} : Eu^{3+} is 6.45:3.55 (and arbitrary valence ratio that corresponds to the G-CO-CO₂ buffer in this experimental study), and plagioclase is the only crystallizing phase. (a) Element concentrations (C_l) relative to initial concentration (C_l^0) as a function of fraction of liquid remaining (F). (b) Calculated $[Eu_{tot} / \sqrt{Sm \times Gd}]_{melt}$ or Eu/Eu* as a function of melt fraction (F).