Europium Anomaly in Plagioclase Feldspar: Experimental Results and Semiquantitative Model

Abstract. *The partition of europium between plagioclase feldspar and magmatic liquid is considered in terms of the distribution coefficients for divalent and trivalent europium. A model equation is derived giving the europium anomaly in plagioclase as a function of temperature and oxygen fugacity. The model explains europium anomalies in plagioclase synthesized under controlled laboratory conditions as well as the variations of the anomaly observed in natural terrestrial and extraterrestrial igneous rocks.*

The rare earth elements (REE) behave during most natural processes as a coherent geochemical group, a consequence of their closely related electronic structures. Exceptional behavior is observed only for those REE which can be stabilized in an oxidation state other than the predominant trivalent one. It has long been recognized (*1*) that among the REE only Eu can be stabilized in the divalent state without resorting to extreme reducing conditions, and that this would lead to a separation of Eu from the other REE during natural processes. More recent investigations (*2–7*) have confirmed that the abundance of Eu in terrestrial and extraterrestrial rocks and minerals can depart significantly from the smooth trend established by its neighbors in the periodic table (when all abundances are normalized to the abundances in chondrites). There is general agreement that the problem of explaining the anomalous behavior of Eu is reduced to one of explaining the differences in geochemical behavior between Eu^{2+} and Eu^{3+}, but beyond this point published explanations differ. Thus, Chase *et al.* (*2*), attributed negative Eu anomalies in granites to the stabilization of Eu^{2+} by sulfate ion in the magma. Towell *et al.* (*3*) associated the Eu anomaly with the enrichment of Eu^{2+} in feldspars and tentatively suggested that magmatic systems could be sufficiently reducing to stabilize an appreciable fraction of Eu in the divalent state. Philpotts and Schnetzler (*5*) emphasized the stabilization and concentration of Eu^{2+} in feldspar (crystal chemical control) but did not believe that the magnitude of the Eu anomaly is strongly coupled to differences in Eu^{2+}/Eu^{3+} in the magmatic liquid (redox control). Towell *et al.* (*6*) held that both factors should be considered together. Subsequently, Philpotts (*7*) argued that crystal chemistry could not be all-important and that the Eu anomaly must (at least in part) be related to the magmatic oxidation potential. Much of this confusion is unnecessary and can be reconciled by an explicit consideration of the relevant chemical equilibria and a few controlled experiments.

The partition of divalent and trivalent Eu between plagioclase (s) and liquid (l) may be considered in terms of the reaction

$$\mathrm{Euo(1)} + \mathrm{SiO_2(1)} + \mathrm{EuAl_3SiO_8(s)} \rightleftharpoons \mathrm{EuAl_2Si_2O_8(s)} + \mathrm{EuO_{1.5}(l)} + \mathrm{AlO_{1.5}(l)} \quad (1)$$

The equilibrium constant for reaction 1, K_1, defined in the usual way, can be rearranged, yielding $K_1(\mathrm{SiO_2/AlO_{1.5}})_l \approx Q \equiv D_2/D_3$ where D_2 and D_3 are the distribution coefficients for divalent and trivalent Eu:

$$D_2 = \frac{(\mathrm{Eu^{2+}})_s}{(\mathrm{Eu^{2+}})_l} \qquad D_3 = \frac{(\mathrm{Eu^{3+}})_s}{(\mathrm{Eu^{3+}})_l}$$

The approximation sign is necessary because we have replaced activity ratios with concentration ratios. Equation 1 is only one out of many possible valid chemical reactions that can be written to express the exchange equilibrium of divalent and trivalent Eu in the plagioclase-liquid system. The derivation of a semiquantitative model equation for the Eu anomaly in plagioclase which follows is not critically dependent on whether the species chosen to express the equilibrium are always dominant, but only assumes that the ratios of their activities are approximated by the concentration ratios of the two ions in each phase. The formulation we have used emphasizes the fact that, if most of the Eu^{2+} and Eu^{3+} ions in plagioclase occupy large cation lattice sites, the exchange equilibrium must also involve Al^{3+} and Si^{4+} substitution. To the extent that this approximation is valid we might expect Q to be relatively constant (at a fixed temperature) in systems with a limited range of Si/Al variations in the liquid. It has not usually been recognized that Eu partition between plagioclase and liquid may depend on the ratio of silica and alumina activities in the liquid, and such a dependence may prove to be an interesting point for future study (*8*). For the present discussion we limit ourselves to systems where this effect is likely to be small.

Table 1. Experimentally observed (*11*) and calculated Eu anomalies in plagioclase feldspar–liquid systems. Each measured value of D_f/D_3 is the average for several experiments over a range of total Eu concentrations; D_3 = 0.06 (*12*).

T (°K)	$\log f_{O_2}$	D_f/D_3 Measured	D_f/D_3 Calculated
1568	− 0.68	1.0	1.2
1568	− 6.0	3.0	5.2
1568	− 9.0	12.1	13.5
1568	−12.5	19.3	21.5
1528	− 0.68	1.3	1.2
1528	−12.5	23.7	23.9
1458	− 0.68	1.2	1.1
1458	−12.5	30.6	27.4

Routine analytical methods do not distinguish the valence states of Eu, so it is convenient at this point to define the measurable or "effective" Eu distribution coefficient $D_f = (\Sigma\mathrm{Eu})_s/(\Sigma\mathrm{Eu})_l$, where ΣEu is the total concentration of Eu. We can obtain D_3 by interpolation from a smooth curve in a plot of the distribution coefficients for all the REE against ionic radius. Thus, D_f/D_3 is directly determinable from a series of partition experiments or analyses of natural materials. It is a measure of the Eu anomaly in plagioclase (*9*), and may also be used to calculate the Eu anomaly in the residual liquid if the relative amounts of plagioclase and liquid are known.

$$\frac{D_f}{D_3} = Q\left(\frac{\mathrm{Eu^{2+}}}{\Sigma\mathrm{Eu}}\right)_l + \left(\frac{\mathrm{Eu^{3+}}}{\Sigma\mathrm{Eu}}\right)_l \quad (2)$$

Equation 2 is useful for sorting out the variables that are likely to control the size of the Eu anomaly in plagioclase. The ratio Q is independent of oxidation potential and reflects the degree of crystal chemical control (*5*). The crystal chemistry of feldspar tells us that it is reasonable to expect Eu^{2+} to be preferentially incorporated in the large cation sites. Its ionic radius in eightfold coordination is identical to that of Sr^{2+} (*10*), which is known to have a distribution coefficient (plagioclase/liquid) greater than unity under magmatic conditions. The incorporation of Eu^{3+} is energetically less favorable because of local charge balance problems. This contrast is forcibly demonstrated by direct analogy with

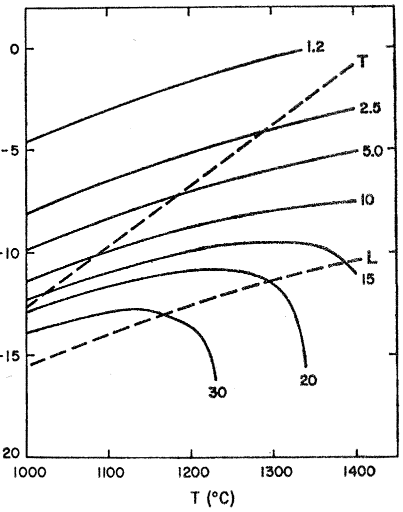

Fig. 1. The Eu anomaly, D_f/D_3, as a function of temperature and oxygen fugacity. (Solid curves) Constant D_f/D_3 contours calculated from Eq. 4. (Curve *L*) Wüstite-iron-oxygen equilibrium curve, representative of lunar oxygen fugacity during magmatic crystallization. (Curve *T*) Olivine-pyroxene-magnetite-oxygen equilibrium curve with variable solid solution compositions, representative of terrestrial oxygen fugacity during magmatic crystallization in a closed, water-poor system.

the other trivalent REE for which all distribution coefficients measured to date are appreciably less than unity. Crystal chemical control of the Eu anomaly simply means that we expect Q to be significantly greater than unity. Oxidation potential control of the Eu anomaly (*6, 7*) is reflected in the liquid phase composition terms of Eq. 2 which are related to the equilibrium

$$\mathrm{EuO(l)} + \tfrac{1}{4}\mathrm{O_2(g)} \rightleftharpoons \mathrm{EuO_{1.5}(l)} \quad (3)$$

The equilibrium constant for this reaction, K_3, may be incorporated into Eq. 2 to give

$$D_f/D_3 = \frac{(K_3 f_{O_2}^{\,1/4} + Q)}{(K_3 f_{O_2}^{\,1/4} + 1)} \quad (4)$$

If Q and K_3 can be determined as functions of temperature, Eq. 4 serves as a model for predicting the magnitude of the Eu anomaly. Distribution coefficient D_2 has never been measured directly but has sometimes been assumed to be identical to the distribution coefficient of Sr, D_{Sr}, because of the similar ionic radii of Eu^{2+} and Sr^{2+} (*1, 7*). In developing our model it will not be necessary to assume that $D_2 = D_{\mathrm{Sr}}$ but only that these two distribution coefficients have a similar temperature dependence. Values of D_{Sr} have been experimentally determined (*11*) between 1150° and 1400°C, giving us $D_2 = \exp(9489/T - B)$. Also, D_3 has been experimentally determined (*12*).

From the Van't Hoff equation $\partial \ln K_3/\partial T = \Delta H°/RT^2$ and the thermodynamic approximations of McCarthy and White (*13*), the temperature dependence of K_3 is approximated by $K_3 = \exp(26{,}000/T - A)$. The experimental results (*11*) summarized in Table 1 have been used in conjunction with Eq. 4 to solve for the constants A and B. A nonlinear least squares fit of the data in Table 1 to Eq. 4 yields the solution $A = 11.6$ and $B = 5.70$. [For comparison, the direct experimental determination of the Sr distribution between plagioclase and liquid (*11*) yielded $D_{\mathrm{Sr}} = \exp(9489/T - 5.52)$.] These values have been used to calculate the predicted Eu anomalies also listed in Table 1.

The general dependence of the Eu anomaly on temperature and oxygen fugacity can best be visualized with the aid of the Eu anomaly contours drawn in Fig. 1. The magnitude of the anomaly is strongly dependent on the oxidation potential existing in the magma system at the time of crystallization. Furthermore, the oxygen fugacities considered typical for many terrestrial as well as lunar magmas are sufficiently reducing to cause large anomalies. The line *L* represents approximately the oxygen fugacity prevalent during the crystallization of the lunar igneous rocks returned to date. The large Eu anomalies observed in lunar plagioclases are predicted by the model. The line *T* gives a general indication of the behavior of oxygen fugacity during terrestrial magmatic crystallization in closed, water-poor systems. The model predicts relatively small Eu anomalies at high crystallization temperatures and larger anomalies (D_f/D_3 = 15 to 20) at temperatures representative of more acidic magmas. Dudas *et al.* (*14*) have recently measured REE concentrations in plagioclases and their host matrix in a series of volcanic rocks. Their data can be directly converted to D_f/D_3 values and indicate a range of 5.4 to 19.7, in good agreement with the prediction of the model. A strong positive correlation between the magnitude of the Eu anomaly and the albite concentration of plagioclase has been noted (*14, 15*). This correlation also follows directly from the model of Fig. 1 if we allow that in general the albite concentration of plagioclase increases with decreasing temperature of crystallization.

In spite of the necessary approximations involved in its construction, the model presented here provides a reasonable explanation for the Eu anomaly in plagioclase, as observed in natural and experimentally controlled systems. The "anomalous" behavior of Eu is a predictable function of temperature and oxygen fugacity, and the variations of the Eu anomaly observed in natural plagioclase crystals are compatible with the conditions of temperature and oxygen fugacity generally operative during magmatic crystallization. We hope that the model will contribute quantitatively to the interpretation of the geochemical behavior of the REE which have already proven so useful in unraveling the geochemical evolution of terrestrial and extraterrestrial material.

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References and Notes

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8. L. Haskin and co-workers (private communication) are currently conducting experiments investigating the effect of compositional variations on $\mathrm{Eu}^{2+}/\mathrm{Eu}^{3+}$ in magmatic liquid.
9. The Eu anomaly in plagioclase is sometimes also defined by the concentration ratio ΣEu/Eu* in plagioclase, where Eu* is interpolated from a normalized REE concentration plot. The magnitude of the Eu anomaly defined in this manner is dependent on the previous history of the system. For example, a magmatic liquid already heir to an anomalous REE concentration pattern would crystallize phases displaying Eu concentration anomalies even under conditions such that $D_f = D_3$. Since we are primarily interested in explaining and relating the Eu anomaly to measurable thermodynamic parameters we restrict our discussion to the distribution coefficient anomaly, D_f/D_3.
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12. A value for D_3 has been obtained by interpolation between D_{Sm} and D_{Gd} in a separate series of experiments described in (*11*). The average value obtained in 12 experiments in the temperature range 1150° to 1343°C is 0.06. The temperature dependence of D_3 is negligible for the present discussion.
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