Modeling of REE Fractionation in the Acid Melt–Fluoride–Chloride Fluid System

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Modeling of REE Fractionation in the Acid Melt–Fluoride–Chloride Fluid System

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High-F silicic (HS) rocks have some characteristic geochemical features. The REE distribution, for example, is characterized by approximately equal chondrite-normalized abundances of LREE and HREE (equal-arm distribution) and a significant Eu minimum.

Strong Eu depletion in HS rocks is related to either feldspar fractionation [3] or selective fluid removal of Eu from the melt [4, 5]. Recent petrological data [6] suggest fluid–magmatic differentiation of REE in HS rocks. This work presents estimates of the effect of REE fractionation between fluid and HS melt, which confirms this viewpoint.

The problem of REE fractionation in the acid melt–fluid system has seemingly been solved for a long time, especially after the pioneer experiments of Flynn and Burnham [4]. However, later experiments [7] on REE distribution between fluid and magma were inconsistent with the earlier data. In addition, REE transfer was mainly studied for the aqueous–chloride system, whereas the fluoride mode of REE transfer by fluids dominates in HS rocks. Thermodynamic data on soluble REE fluorides and chlorides [8] make it possible to simulate the element dissolution in the chloride–fluoride solutions, i.e., to reconstruct the HS rock evolution.

Fluid and melt compositions for modeling can be taken from the available data on well-studied magmatic systems. The REE variations during differentiation (Fig. 1) are expressed in ratios of element concentrations in strongly differentiated rocks to those in weakly differentiated rocks for well-studied HS systems [9]. REE distribution correlates well with F concentration in magma: Ce/Yb and Eu/Eu* ratios are lower in high-F magmas. The LREE/HREE ratio decreases owing to HREE increase or LREE decrease. The analysis of such trends shows that the evolution of HS rocks is not accompanied by a total REE increase; therefore, such a REE distribution is mainly caused by LREE removal

from the melt and F accumulation. Unlike F, Cl is not correlated with Ce/Yb and Eu/Eu* ratios, thus indicating its subordinate role in REE redistribution. Such relations suggest that Eu and other REE are mainly redistributed in magma as fluoride compounds.

The Ln (i.e., REE) redistribution between the fluid and acid melt may be described by the following reactions:

$$12HF(fl) + 2Ln_2O_3(m) = 6H_2O(m) + 4LnF_3(fl), (1)$$

$$2YbF_3(fl) + La_2O_3(m) = Yb_2O_3(m) + 2LaF_3(fl), \quad (2)$$
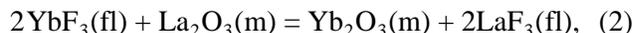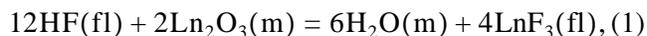
where Ln_2O_3 is referred to as species soluble in the melt, while fluorides occur in fluid. Reaction (1) reflects the REE distribution between fluid and melt, while reaction (2) records the preferential accumulation of LREE or HREE. Reactions (1) and (2) should be considered for both two- and three-valent species of Eu at variable oxygen fugacity.

The description of polyphase equilibrium requires the correct expression of REE solubility both in fluid and magma. If we accept the REE oxide concentrations to be equal, the $D_{REE1}^{fl/m} / D_{REE2}^{fl/m}$ ratio can be estimated, and difficulty related to the exact calculation of $a_{Ln_2O_3}^m$ can be avoided, because

$$\frac{D_{REE1}^{fl/m}}{D_{REE2}^{fl/m}} = \frac{C_{REE1}^{fl}}{C_{REE1}^{m}} \frac{C_{REE2}^{m}}{C_{REE2}^{fl}},$$

where $C_{REE1}^{m} = C_{REE2}^{m}$. Based on these prerequisites, the initial REE concentrations in primary melts were taken to be 0.1 mol Ln_2O_3, which corresponds to ~0.14 wt % oxide of each REE in the acid melt.

Calculations were performed using the Balans program by Akinfiev [11]. The SUPCRT92 program was used as the thermodynamic base [12]. The F concentrations in fluid were governed by variations of HF fugacities within a range of 0.5–4 bar ($\log f_{HF} = -0.5-0.5$), which corresponds to typical fluid phase values in HS rocks [10]. Cl concentrations were assumed to be constant (0.1 m NaCl). Thus, we simulated the REE distri-

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bution between the aqueous chloride–fluoride fluid and the melt.

Calculations show that, at high temperatures (800°C), REE (excluding Eu) have low solubility and fluid contains only traces of REE hydroxyls (Fig. 2). Significant REE concentrations (up to 0.015 mol/kg) are observed in the fluid phase at temperature less than 650°C. An increase of REE concentrations is related to the appearance of fluoride complexes. REE abundances in solution are comparable to those determined in magmatic fluids that are in equilibrium with topaz granitoids [13]. As seen from the results, fluoride fluid mainly contains LREE (La^{fl}/Yb^{fl} = 83, Ce^{fl}/Lu^{fl} = 9). These calculations are qualitatively consistent with experimental determinations of $D_{LREE}^{fl/m} / D_{HREE}^{fl/m} \approx$ 1.5–6 [4].

Europium differs in solubility from other REE. Within a wide range of oxygen fugacity (from QFM –2 to QFM +2), EuO was oxidized to Eu_2O_3 in end products, while Eu concentration in the solutions was several orders of magnitude higher than other REE concentrations. Calculations with variable $\log f_{O_2}$ and $\log f_{HF}$ showed that soluble species of divalent Eu dominates over the entire range of oxygen fugacity. An increase in oxygen activity results in a decrease in divalent Eu and total Eu concentration in the solution. Thus, we observe a dynamic equilibrium between Eu^{2+} in the solution and Eu^{3+} in the melt. At low $\log f_{HF}$ values (from –2 to –4), the solution mainly contains Eu chlorides, which reveals a weak negative correlation with oxygen fugacity (Fig. 3). At high HF fugacity ($\log f_{HF} \geq$ –0.5), Eu concentration increases owing to the appearance of soluble fluorides (mainly as EuF_2, aq and EuF_3^-). Fluorides account for 60–70% of the total dissolved Eu. Eu solubility in a fluoride environment is highly sensitive to variations in oxygen fugacity. In a reducing environment (QFM –2), Eu solubility is three times higher than that of QFM. Over the entire range of oxygen fugacity (from QFM –2 to QFM +2), the solubility of Eu is significantly higher than that of other REE. For example, at 600°C (f_{O_2} corresponding to QFM and $\log f_{HF}$ = 0.5), Eu concentrations are three to five orders of magnitude higher than Sm and Gd concentrations (Fig. 2).

Thus, calculations show that the percolation of fluoride fluid through a melt may significantly affect the REE distribution in the melt. Strong depletion of acid magmas in Eu can result from its selective accumulation in the fluoride fluid, which is later removed from the system (model of open degassing). Such fractionation may occur over a wide range of oxygen fugacities. This is consistent with empirical data on the appearance of Eu minimum in magmas with a wide range of f_{O_2} values [3].
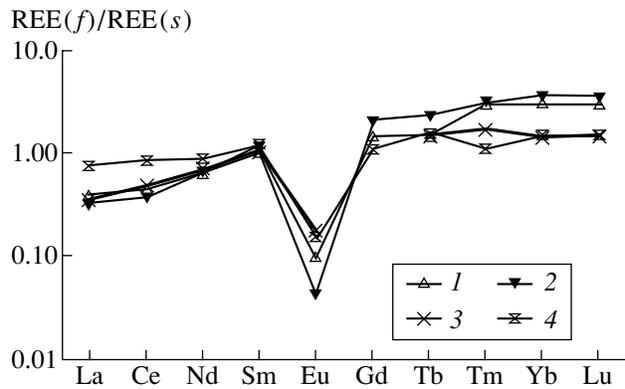
Fig. 1. Ratio of REE concentrations in strongly differentiated (*f*) HS rocks and weakly differentiated (*s*) granitoids in studied systems (after [9]). (*1*) Snake River, (*2*) SE Sitgreaves, (*3*) Long Valley, (*4*) Cerro Toledo.
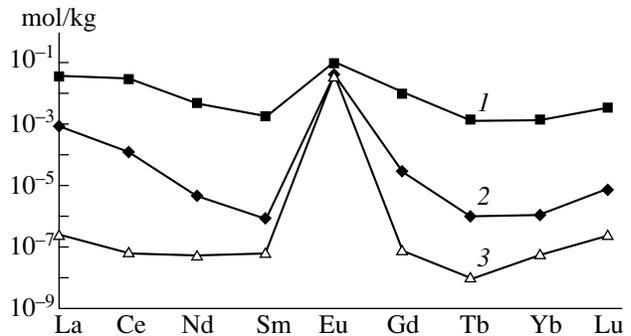

Fig. 2. Calculated REE concentrations in fluid (mol/kg) at temperatures of (*1*) 500, (*2*) 600, and (*3*) 800°C at 2 kbar, f_{O_2} = QFM, $\log f_{HF}$ = 0.5, 0.1 *m* NaCl.

Modeling also explains the redistribution of LREE and HREE in acid magmas. The calculations show that LREE and HREE concentrations in fluid are very low at high temperatures (700–800°C). At granite solidus temperatures (650–600°C), LREE solubility in fluid significantly increases. Hence, the equal-arm REE distribution may be related to the differential LREE removal from magmas within the above temperature range. This conclusion is consistent with data [8, 14] indicating that the difference in geochemical behavior of LREE and HREE in magmatic processes may be caused by different styles of REE transfer to soluble fluid forms rather than by a steric factor.

Hence, the REE distribution in HS rocks mirrors the selective redistribution of elements between magmas and high-F fluids. Strong Eu depletion in magma is not indicative of feldspar fractionation or high reducing environment of magmas. It is related to the high selective Eu solubility in fluoride solutions over a wide range of oxygen fugacities.
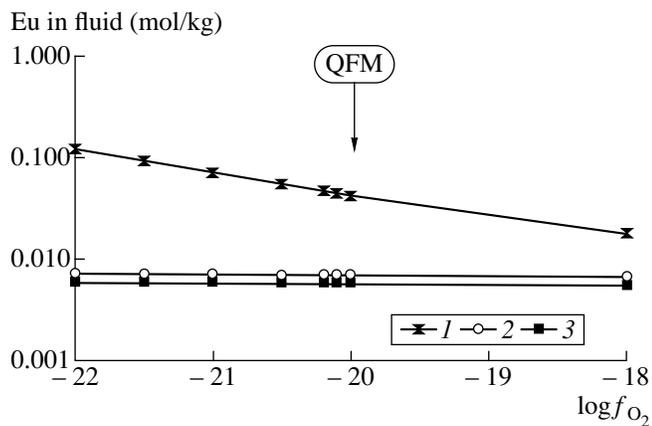
Eu in fluid (mol/kg)

Fig. 3. Calculated Eu concentrations in fluid (mol/kg) at various values of $\log f_{HF}$ and $\log f_{O_2}$ at 600°C, 2 kbar, and 0.1 m NaCl. (*1*) $\log f_{HF} = -0.5$, (*2*) $\log f_{HF} = -2$, (*3*) $\log f_{HF} = -4$.

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