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Abnormal Eu behavior at formation of H2O- and Cl-bearing fluids during degassing of granite magmas

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One of the important features of REE behavior in the process of decompression degassing of granite melts is the presence of europium anomalies in REE spectrum of forming fluid phase. Negative Eu anomaly in REE spectrum of fluids enriched by chlorine that were formed under high pressures at early stages of degassing relative to REE spectrum of granite melts may take place. Negative Eu anomaly in fluid is replaced by positive one with pressure decrease and decline of Cl concentration in fluid [1, 2]. Observable unique features of europium redistribution between fluid and melt find an explanation in such a fact that Eu in contrast to the other REE under oxidation-reduction conditions, being typical for magmatic process, is present in acidic silica-alumina melts in two valency forms Eu^{3+} and Eu^{2+} whereas the dominant form for the other REE in such a melts is $(REE)^{3+}$ [3, 4].

From the analysis of melt-fluid exchange reactions with participation of two valency forms of europium Eu^{3+} and Eu^{2+} follows that the total distribution coefficient of Eu between fluid and melt $D(Eu)^{f/m}$ is equal as a first approximation to [5, 6]:

$D(Eu)^{f/m} = a_1\alpha\,[C(Cl)^f]^3 + a_2\,(1 - \alpha)[C(Cl)^f]^2$,

where $C(Cl)^f$ – the concentration of Cl in fluid, $\alpha = Eu^{3+}/(Eu^{3+} + Eu^{2+})$, i.e. fraction of Eu^{3+} from the general amount of europium in the melt, and, a_1 and a_2 – constants that can be approximately estimated from empirical data upon Eu fluid/melt distribution.

The equation given allows to estimate the influence of oxidizing condition of europium on sign and size of Eu anomaly, which is expressed by $Eu/Eu^{\#}$ ratio, where Eu is real concentration of europium in fluid being in equilibrium with melt with constant $Eu^{3+}/(Eu^{3+} + Eu^{2+})$ ratio, and $Eu^{\#}$ is possible "virtual" concentration of europium that could be in the same fluid provided that all europium as other REE as well were exclusively present in trivalent form. The sign and size of Eu anomaly in fluid depends upon Cl concentration in fluid and Eu^{3+}/Eu^{2+} ratio in melt. The abnormal behavior of Eu shows itself the stronger, the lower fO_2 and, accordingly, the more fraction of Eu^{2+} is present in melt.

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