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The Oxidation States of Cerium and Europium in Carbonate Melts

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Natural carbonate melts, carbonatites, are the world's primary source of rare earth elements (REE), but it's currently unknown why this enrichment occurs. Ce and Eu are the only REE that occur in oxidation states other than 3+, so understanding how Ce^{3+}/Ce^{4+} and Eu^{2+}/Eu^{3+} vary in carbonate melts may help constrain the oxygen fugacity of the processes leading to REE enrichment.

The oxidation states of Ce and Eu were studied as functions of oxygen fugacity in different compositions of carbonate melts that were quenched to glasses. Ce and Eu L_{III}-edge X-ray adsorption near edge structure (XANES) spectra were recorded for three synthetic carbonate glass compositions: $MgCO_3$-$Mg_2P_2O_7$-MgO at 1400ºC and 2 GPa, $MgCO_3$-K_2CO_3-$CaCO_3$ at 1300ºC and 0.5 GPa, and $MgCO_3$-K_2CO_3 at 1000ºC and 0.5 GPa, buffered by Pt-PtO_2, Ir-IrO_2, Ru-RuO_2, Re-ReO_2, and CCO, corresponding to a range of oxygen fugacities (fO_2) of ~14 log units. The log$K$' values for the oxidation of Ce and Eu and the ratios $Ce^{4+}/\sum Ce$ and $Eu^{3+}/\sum Eu$ (where $\sum Ce = Ce^{3+} + Ce^{4+}$ and $\sum Eu = Eu^{2+} + Eu^{3+}$) were determined from the spectra allowing for the relationships between oxidation states and fO_2 and melt composition to be established.

At the fO_2 corresponding to the quartz-fayalite-magnetite buffer, QFM, $Ce^{4+}/\sum Ce$ is between 0.003-0.007 in all compositions. In silicate melts, $Ce^{4+}/\sum Ce$ is higher at QFM and around 0.03. The log$K$' values for Ce in carbonate melts are similar to those in silicate melts at around -0.5. At QFM the $Eu^{3+}/\sum Eu$ values range from 0.9 to 0.975. Compared to silicate melts where $Eu^{3+}/\sum Eu$ is around 0.88 at QFM, the carbonate melts stabilize more Eu^{2+}. The Eu log$K$' values are higher in carbonates, ranging from 2.6 to 4.3, compared with 2.5 in silicates.