The effect of CaO on the partitioning behavior of REE, Y and Sc between olivine and melt: Implications for basalt-carbonate interaction processes

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The partitioning of REE, Y and Sc (R^{3+}) between olivine and melt has been investigated during basalt-carbonate interaction experiments. Three synthetic glassy basalts ($^{melt}Mg\#_{72}$, $^{melt}Mg\#_{75}$ and $^{melt}Mg\#_{78}$) were doped with 0, 10 and 20 wt.% $CaCO_3$ and then equilibrated for 72 h at 1 atm, 1,150, 1,200 and 1,250 °C, and the QFM oxygen buffer. The thermal decomposition of $CaCO_3$ produced CaO contents in the melt up to ~22 wt.%. Regular relationships are found between the ionic radius and the partition coefficient (D_{R3+}), showing typical near-parabolic patterns. D_{R3+} is weakly dependent on temperature, but decreases with increasing $CaCO_3$ in the starting material (e.g., D_{Sc} decreases from 0.20 to 0.13). From the point of view of the lattice strain theory, D_{R3+} is described in terms of the radius of the crystal site (r_0), the Young Modulus (E) due to the elastic response of that site to lattice strain caused by cation insertion, and the strain-free partition coefficient (D_0^{3+}). The value of r_0 decreases as Ca cations are accommodated into the more distorted M2 site of olivine via progressive Ca-Fe substitutions. This mechanism is accompanied by a higher proportion of Mg cations entering into the smaller M1 site, making the optimum ionic radius smaller and favoring the crystallization of

more forsteritic olivines from decarbonated melts. The enrichment of Ca in the crystal lattice is also proportional to the number of Si and Ca cations available in the melt. This causes E to be anticorrelated either with Ca in olivine or the activity of CaO in the melt. R^{3+} cations behave as network modifiers and, during basalt-carbonate interaction, the increasing abundance of non-bridging oxygens enhances the solubility of REE, Y and Sc in the melt. As a consequence, D_0^{3+} is negatively correlated with the degree of melt depolymerization. Additionally, the strain of the crystal lattice dominates the D_{R3+} parabolic patterns and D_0^{3+} is strongly controlled by forsterite and aluminium concentrations in olivine. The accommodation of REE, Y and Sc in the crystal lattice requires maintenance of local charge-balance by the generation of vacancies, in accord with a paired substitution of R^{3+} and a vacancy for Mg in octahedral sites.