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REE partitioning between titanian clinopyroxene and alkali melts as a function of oxygen fugacity: an experimental study

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Since titanian clinopyroxene (Ti-Cpx) is one of the most distinctive phases in the mineral assemblages of mafic to intermediate alkaline rocks, it plays an important role in understanding their origin and evolution along igneous plumbing systems. This work examines the distribution of rare-earth elements (REE) between Ti-Cpx and alkali melts at one-atmosphere pressure and a wide range of temperature and oxygen fugacity conditions. We performed crystallization experiments on a basanite and a tephrite, at 1200-1000 °C with fO_2 ranging from 2 log units above and below the QFM buffer, using a high-temperature vertical furnace coupled with a CO/CO_2 gas mixing system. The Ti-Cpx is homogenous and encompasses compositions from subsilicic augite to diopside. It is the liquidus phase in the tephrite, whereas in the basanite crystallizes before olivine. From both starting compositions, the melts evolved from ultrabasic to intermediate liquids, with the liquid lines of descent strongly SiO_2-undersaturated for basanite and slightly SiO_2-undersaturated to SiO_2-saturated for tephrite. D_{REE} varies from slightly incompatible to slightly compatible (from 0.2 to 2) as a function of ionic radii with a parabolic behavior, increasing the compatibility from La to Dy or Tb. The experimental data fit well for the Lattice Strain Model [1] into the M2 clinopyroxene sites. The REEs partitioning is influenced by both compositional and physical parameters. In the first case, the crystal chemistry of the clinopyroxene (mainly Ti, Mg#, and ^{IV}Al) via Tschermakite-type substitution [2] and the melt composition expressed through the non-bridging oxygens per tetrahedral cations (NBO/T) show a strong relationship with the incorporation of REE [3]. In the second case, D_{REE} shows a systematic dependence on fO_2 over the experimental set, being higher under oxidizing conditions. Finally, the thermodynamic model based on the activity of the $Na_{0.5}(REE)_{0.5}MgSi_2O_6$ component [4] closely reproduces the observed partitioning of the REEs under 1-atm.

References: [1] Blundy and Wood (1994), *Nature* 352, 452-454. [2] Gaetani and Grove (1995), *Geochimica et Cosmochimica Acta* 59, 1951-1962. [3] Gaetani (2004), *Contributions to Mineralogy and Petrology* 147, 511-527. [4] Wood and Blundy (1997), *Contributions to Mineralogy and Petrology* 129, 166-181.

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