Trace-element partitioning between vacancy-rich eclogitic clinopyroxene and silicate melt

MAIK PERTERMANN^{1,*} AND MARC M. HIRSCHMANN¹

¹Department of Geology and Geophysics, University of Minnesota, 108 Pillsbury Hall, 310 Pillsbury Drive S.E., Minneapolis, Minnesota 55455, U.S.A.

ABSTRACT

We investigated experimentally trace-element partitioning between clinopyroxene and anhydrous silicate melt at conditions relevant to near-solidus melting of quartz eclogite in the upper mantle. Partitioning experiments were carried out at 3.0 GPa and 1335–1365 °C on a synthetic mixture similar to a low-degree melt of a quartz eclogite. Clinopyroxene is Al₂O₃-rich (~17 wt%), cation deficient (~3.92 cations per six O atoms), and coexists with andesitic melt (~57 wt% SiO₂), quartz, and traces of rutile. The clinopyroxene cation deficiency indicates a large proportion of vacant M2 sites in form of the Ca-Eskola (CaEs) component (Ca_{0.5} $\square_{0.5}$ AlSi₂O₆) Clinopyroxene-melt partition coefficients (D-values) were determined for Sr, Y, Zr, Nb, REE, Th, and U by SIMS, and for Sc, V, Cr, Mn, Co, Ni, K, and major elements by electron microprobe analysis. Compared to previous studies of clinopyroxene with >10 wt% Al₂O₃, partition coefficients in vacancy-rich aluminous clinopyroxene for elements substituting into the M2 site are elevated for monovalent cations $(D_{\text{Na}} \sim 1.0, D_{\text{K}} = 0.027)$, and reduced for trivalent cations, particularly for LREE $(D_{\text{La}} = 0.029)$. D_{Th} and $D_{\rm U}$ range from 0.0017 to 0.0037, much lower than previously assumed for clinopyroxene pertaining to partial melting of eclogite in the upper mantle, and $D_{\rm U}/D_{\rm Th}$ is apparently >1. Observed partitioning behavior of elements substituting into M2 is attributable to the low average charge (1.53-1.57) of the site. This low average charge increases the number of configurations available to charge balance 1+ cations and vacancies, and decreases the number of configurations available to charge balance cations with high valences. Stablization of low-valence species suggests that these vacancyrich clinopyroxenes may be substantial hosts of noble gases in the mantle. Partition coefficients for cations substituting into the M1 site show relatively little effect from the high vacancy concentrations of M2, but partitioning systematics may be obscured by strong crystal field stabilization of some cations in the M1 site, notably Ni²⁺ and Cr³⁺. Application of the measured D-values of this study to partial-melting calculations results in small increases in the Sm/Yb of liquids produced by modest extents of melting of quartz eclogite. Significant enrichments in (230Th)/(238U) activity ratios (>1.21) are expected for decompression melting of quartz eclogite at upwelling rates below 5 cm/ year, but enrichments would be small (<1.11) above 10 cm/year.