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

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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 (Ca0.5■0.5AlSi2O6). 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 ($D_{Na} \sim 1.0$, $D_K = 0.027$), and reduced for trivalent cations, particularly for LREE ($D_{La} = 0.029$). $D_{Th}$ and $D_{U}$ 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 $D_{U}/D_{Th}$ 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. Stabilization of low-valence species suggests that these vacancy-rich 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 $^{230}Th/^{238}U$ 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.

INTRODUCTION

Clinopyroxene (cpx) is a principal host of trace elements in likely ultramafic and mafic sources of mantle-derived magmas, and partitioning between cpx and coexisting magma depends on cpx composition (e.g., McKay 1986; Lundstrom et al. 1994, 1998; Gaetani and Grove 1995; Wood and Blundy 1997; Blundy et al. 1998; Hill et al. 2000). Liquid composition may also be important (e.g., Salters and Longhi 1999; Gaetani and Watson 2000), but this is less well-established. One application of cpx/melt partition coefficients ($D_{melt}$) is evaluating the possible role of lithologic heterogeneities such as pyroxenite or eclogite in basal source regions (e.g., Hirschmann and Stolper 1996; Stracke et al. 1999; Eiler et al. 2000). However, the cpx compositions for pyroxenite or eclogite undergoing partial melting are not well-documented, and so it has not been clear which $D_{melt}$ values are most appropriate for such calculations.

Phase-equilibria studies of natural basaltic compositions between 2 and 7.5 GPa indicate that the pyroxene present during nominally anhydrous partial melting of quartz or coesite eclogite is Al-rich (up to 17 wt% Al2O3) and cation deficient (down to 3.94 cations per six O atoms) (Johnston 1986; Yasuda et al. 1994; Yaxley and Green 1998; Pertermann and Hirschmann 2002). Although cation deficiencies are greatest when a silica phase is present, they also occur in cpx from eclogite partial-melting experiments that are not silica-saturated (Takahashi et al. 1998; Pertermann and Hirschmann 2002), presumably because a high silica activity is imposed by coexisting silica-rich liquid. Vacancy-rich pyroxenes also have been described in high-pressure synthetic-system experiments in which a silica phase is present (Wood and Henderson 1978; Gasparik 1986; Milholland and Presnall 1998). To date, pyroxenes with appreciable cation deficiencies have not been reported from partial melting of eclogite under hydrous conditions.