High-pressure phase transitions of clinoenstatite

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ABSTRACT

Clinoenstatite (Mg,Si2O6) undergoes a well-known phase transition from a low-pressure form (LPCEN, space group P21/c) to a high-pressure form (HPCEN, space group C2/c) at ~6 GPa. High-pressure structure refinements of HPCEN were carried out based on single-crystal X-ray diffraction experiments between 9.5 and 35.5 GPa to determine its P-V equation of state and structural evolution over an expanded pressure range relevant to pyroxene metastability. The best-fit isothermal equation of state to our data combined with the five data points between 5.34 and 7.93 GPa from Angel and Hugh-Jones (1994) yields a second-order Birch-Murnaghan equation with K0 = 121(2) GPa and V0 = 403.9(5) Å3 (with K′0 = 4 implied). Further reduction of misfit upon fitting a third-order Birch-Murnaghan equation is not significant at the 90% confidence level. At ~45 GPa, a transition from HPCEN to a P21/c-structured polymorph (HPCEN2) was observed, which is isostructural to the P21/c phase recently observed in diopside (CaMgSi2O6) at 50 GPa (Plonka et al. 2012) and in clinoferrasilite (Fe2SiO4) at 30–36 GPa (Pakhomova et al. 2017). Observation of HPCEN2 in Mg,Si2O6 completes the third apex of the pyroxene quadrilateral wherein HPCEN2 is found, facilitating a broader view of clinopyroxene crystal chemistry at conditions relevant to metastability in the Earth’s mantle along cold subduction geotherms.

Keywords: MgSiO3, clinoenstatite, enstatite, pyroxene, single-crystal X-ray diffraction

INTRODUCTION

Pyroxenes are a major component of the Earth’s crust and upper mantle, constituting around 25% by volume of the pyrolite model from 100–400 km depth (Ringwood 1976; Akaogi and Akimoto 1977). The components of both orthopyroxene (Mg,Fe)SiO3 and clinopyroxene-CaMgSi2O6 are incorporated into pyrope and majoritic garnet at depths from 300–500 km, however under the colder conditions along subducting slabs it is possible for metastable pyroxenes to persist deep in the upper mantle (e.g., Hogrefe et al. 1994; Bina 2013; Nishi et al. 2013; Van Mierlo et al. 2013; Agusta et al. 2014; Finkelstein et al. 2015; King et al. 2015). Pyroxenes penetrating the mantle to such depths could potentially undergo further phase transitions impacting subducting slab mineralogy and mantle dynamics.

The major pyroxenes relevant to mafic-ultramafic rocks and the Earth’s upper mantle are characterized by single chains of corner-sharing SiO4 tetrahedra interconnected by MO6 octahedra containing M cations Mg, Fe, or Ca forming the pyroxene compositional quadrilateral with end-members enstatite (En, Mg2SiO4), ferrosilite (Fs, Fe2SiO4), diopside (Di, MgCaSi2O6), and hedenbergite (Hd, CaFeSi2O6) (Morimoto et al. 1989). Pyroxenes along the En-Fs join are orthorhombic (Pnma), and hence known as orthopyroxenes, whereas Ca-bearing pyroxenes in the quadrilateral are monoclinic and hence called clinopyroxenes (Cpx). Ca-rich Cpx crystallizes in C2/c (augite) while Ca-poor Cpx crystallizes in P21/c (pigeonite).

Orthoenstatite-Mg2SiO4 (OEN) is a major phase of peridotite and was found to transform to a monoclinic, high-pressure clinoenstatite (HPCEN) with space group C2/c along a phase boundary corresponding to ~200–250 km depth (e.g., Pacalo and Gasparik 1990; Angel et al. 1992), suggesting that the transformation might be associated with upper-mantle seismic discontinuities, namely the Lehman discontinuity or the X-discontinuity (e.g., Revenaugh and Jordan 1991; Angel et al. 1992; Deuss and Woodhouse 2004; Kung et al. 2004; Ferot et al. 2012). In experiments, the HPCEN phase quenches to the monoclinic, low-pressure clinoenstatite (LPCEN) with space group P21/c, which is however rare in nature (e.g., Poldervaart and Hess 1951; Shiraki et al. 1980).

On compression, the transformation from LPCEN to HPCEN at 300 K varies from 6 to 8 GPa, depending on Fe-content, water content, and stress (e.g., Ross and Reynard 1999; Jacobsen et al. 2010). With both OEN and LPCEN transforming to HPCEN at pressures below 10 GPa, it has been presumed that HPCEN is the stable phase of (Mg,Fe)Si2O6 below ~250 km depth. The reference physical properties of HPCEN are not well constrained because it is not a quenchable phase, however, in situ sound velocity measurements by Kung et al. (2004) were used to determine its adiabatic elastic moduli at a reference pressure of 6.5 GPa, with K0 = 156.7(8) GPa and G0 = 98.5(4) GPa. Previous volume-compression studies