INTRODUCTION

Water is perhaps the most important unconstrained compositional variable in the Earth’s interior. Nominally anhydrous phases in the mantle are likely to compose a significant reservoir of water in the planet’s interior (Bell and Rossman 1992; Hirschmann et al. 2005). Water incorporation into the nominally anhydrous phases of the mantle has a major effect on their physical properties such as density, seismic velocities, electrical conductivity, strength, and rheology. Water in these phases also controls the temperature of the onset of melting and so controls igneous activity and geochemical differentiation. Relative water solubility in these phases can also shift phase boundaries and thus depths of discontinuities (Wood 1995; Smyth and Frost 2002; Frost and Dolejs 2007).

The pyroxene minerals are major constituents of mafic and ultramafic rocks of the upper mantle. Orthopyroxene, $Pbca$, coexists with clinopyroxene in lherzolites, peridotites, and pyroxenites to depths of about 150 km. The common orthopyroxene is usually $En_{90}Fs_{10}$ in composition with 2 to 3 mol% wollastonite component and coexists with olivine of about $Fo_{90}Fa_{10}$ composition and a clinopyroxene of about $Di_{80}Hd_{10}En_{10}$ composition. Orthopyroxenes from mantle xenoliths containing spinel or garnet are also typically quite aluminous with 2 to 11 wt% $Al_2O_3$ (Takeda 1972; Arai and Abe 1995). Orthopyroxene typically constitutes 10 to 25 modal percent of such rocks. At temperatures and pressures higher than 7 GPa and 800 °C, the orthorhombic pyroxene transforms to a high-pressure clinoenstatite (Angel and Hugh-Jones 1994), which, like orthopyroxene, forms a phase distinct from the calcic clinopyroxene. The high-pressure clinoenstatite is space group $C2/c$ at mantle conditions but quenches to $P2_1/c$ (e.g., Smyth 1995; Smyth and Frost 2002; Frost and Dolejs 2007).

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Natural clinopyroxenes from high-pressure rocks can also contain a significant hydrous component, with H contents correlating with the so-called Ca-Eskola component, $CaAl_2SiO_7$.