HIGH-PRESSURE PHASE TRANSITIONS AND HYDROGEN INCORPORATION INTO MgSiO3 ENSTATITE

GEOFFREY DAVID BROMILEY1,2,* AND FIONA ANNE BROMILEY1

1Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany
2Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.

ABSTRACT

Hydrogen incorporation into orthoenstatite (Pbca), low-clinoenstatite (P21/c), and high-pressure clinoenstatite (C2/c) has been investigated using polarized and unpolarized infrared spectroscopy. Using shifts in OH stretching frequencies between the spectra and data from different crystal models, we test various models for hydrogen incorporation. The only significant differences between orthoenstatite and low-clinoenstatite spectra relate to anisotropy of the higher wavenumber bands, which implies a change in orientation of longer OH dipoles between the two structures. High-pressure clinoenstatite reverts to low-clinoenstatite during depressurization, but subtle differences are noted between IR spectra of samples synthesized in the high-pressure clinoenstatite and low-clinoenstatite stability fields. Differences probably relate to the splitting of oxygen sites into two sets of non-equivalent sites during transformation of high-pressure clinoenstatite. The most realistic models for hydrogen incorporation into all three polymorphs involve association of hydrogen with the underbonded O2a and O2b sites. However, changes in OH dipole orientation between the different polymorphs and the effects of phase transitions on water solubility in the system MgSiO3 mean the effects and implications of hydrogen incorporation into the three polymorphs may differ considerably.

Keywords: Enstatite, transition, hydrogen, water, mantle

INTRODUCTION

Over the last few decades, numerous investigations have demonstrated that significant amounts of “water” may be stored in nominally anhydrous minerals (NAMs) and phases that constitute the Earth’s mantle (Bell and Rossman 1992; Bolfan-Casanova et al. 2000; Ingrin and Skogby 2000). Water is stored in such phases as hydrogen structurally bound to specific oxygen sites, forming spectroscopically active OH groups. Hydrogen contents of NAMs vary from a few tens of parts per million to several weight percent H2O, and NAMs provide a mechanism for storing significant amounts of water in different parts of the Earth’s mantle. Hydrogen incorporation into NAMs may play an important role in many mantle processes (e.g., Bercovici and Karato 2003), and may influence a range of mineral and bulk mantle properties as diverse as electrical conductivity and rheology (e.g., Huang et al. 2005; Mackwell et al. 1985).

Orthopyroxenes are major constituents of the upper mantle, and investigations of mantle xenoliths demonstrate that natural pyroxenes can contain up to thousands ppm H2O wt (Ingrin and Skogby 2000). Numerous experimental investigations have focused on determining mechanisms for hydrogen incorporation into pure MgSiO3 orthoenstatite, orthoenstatite doped with Al2O3, Fe2O3, and Cr2O3, and natural orthopyroxene annealed at high-pressure (Mierdel and Keppler 2004; Rauch and Keppler 2002; Stalder and Skogby 2002; Stalder 2004). These studies demonstrate that hydrogen incorporation into MgSiO3 enstatite is charge-balanced by Mg2+ vacancies. In more complex systems, hydrogen incorporation may also be connected to coupled substitutions involving trivalent cations, and hydrogen solubility in pyroxene is greatly enhanced by the presence of Al3+. However, precise information on hydrogen positions in orthopyroxenes is lacking. Near-infrared spectra (NIR) from hydrogen-bearing orthopyroxenes are characterized by the presence of a significant number of OH stretching bands at frequencies ranging from 2800 to 4000 cm–1, implying the presence of hydrogen in several non-equivalent sites. The difficulty of assigning OH absorption bands in NIR spectra from pyroxenes is further compounded by many potential hydrogen sites in pyroxene structures, and sometimes also from a lack of good quality polarized infrared absorption data.

Over the variable P-T conditions of the upper mantle the occurrence of several polymorphs of MgSiO3 has been demonstrated [see Ulmer and Stalder (2001) for a recent review]. Over a broad range of temperatures up to pressures of between 6 and 10 GPa, MgSiO3 has an orthorhombic Pbca structure (orthoenstatite). Toward lower temperatures, orthoenstatite transforms to P21/c clinoenstatite (low-clinoenstatite). With increasing pressure, both low-clinoenstatite and orthoenstatite transform to C2/c clinoenstatite (high-pressure clinoenstatite). This high-pressure structure is non-quenchable, and reverts to low-clinoenstatite. The orthoenstatite and low-clinoenstatite structures can be derived from each other by displacing alternating octahedral and tetrahedral layers along [001]. Differences between the high-pressure clinoenstatite and low-clinoenstatite structures mainly relate to configurations of the silicate tet-