A synchrotron Mössbauer spectroscopy study of (Mg,Fe)SiO₃ perovskite up to 120 GPa

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ABSTRACT

The electronic environment of the Fe nuclei in two silicate perovskite samples, Fe₀.₀₅Mg₀.₉₅SiO₃ (Pv05) and Fe₀.₉Mg₀.₁SiO₃ (Pv10), have been measured to 120 GPa and 75 GPa, respectively, at room temperature using diamond anvil cells and synchrotron Mössbauer spectroscopy (SMS). Such investigations of extremely small and dilute ⁵⁷Fe-bearing samples have become possible through the development of SMS. Our results are explained in the framework of the “three-doublet” model, which assumes two Fe⁸⁺-like sites and one Fe⁷⁺-like site that are well distinguishable by the hyperfine fields at the location of the Fe nuclei. At low pressures, Fe⁷⁺/₂Fe is about 0.40 for both samples. Our results show that at pressures extending into the lowermost mantle the fraction of Fe⁷⁺ remains essentially unchanged, indicating that pressure alone does not alter the valence states of iron in (Mg,Fe)SiO₃ perovskite. The quadrupole splittings of all Fe sites first increase with increasing pressure, which suggests an increasingly distorted (noncubic) local iron environment. Above pressures of 40 GPa for Pv10 and 80 GPa for Pv05, the quadrupole splittings are relatively constant, suggesting an increasing resistance of the lattice against further distortion. Around 70 GPa, a change in the volume dependence of the isomer shift could be indicative of the endpoint of a continuous transition of Fe⁷⁺ from a high-spin to a low-spin state.

INTRODUCTION

Iron-bearing magnesium silicate perovskite, coexisting with small amounts of (Mg,Fe)O ferropericlase and CaSiO₃ perovskite, is thought to be the most abundant phase in Earth’s lower mantle (e.g., Liu 1974; Jeanloz and Thompson 1983; Anderson and Bass 1986; Ito 1989; Fiquet et al. 2000; Weidner and Wang 2000). Knowledge of the physical and chemical properties of such phases under conditions approaching those of the lower mantle is therefore essential to our understanding of the deep mantle. Of particular importance is the electronic state of iron-bearing magnesium silicate perovskite, because it can affect electrostatic charge balance and equilibrium defect concentrations. Properties highly sensitive to such effects include rheology, transport properties, solubility of volatiles, and partitioning of major and trace elements in the lower mantle (e.g., McCammon 1998a). For example, the electrical conductivity of lower mantle phases is strongly influenced by the valence state of iron (Li and Jeanloz 1990; Li et al. 1993; Xu et al. 1998; Katsura et al. 1998). X-ray emission spectroscopic (XES) data recently demonstrated a pressure-induced gradual loss of magnetic moment of the iron component in iron-bearing MgSiO₃ perovskite (Li et al. 2003). Experiments on lower mantle phases suggest that iron-bearing magnesium silicate perovskite is the principal sink for ferric iron in the Earth’s lower mantle (McCammon 1997, 1998a; McCammon et al. 1998). Therefore, knowledge of the behavior of iron in perovskite under the pressure conditions of the lower mantle is necessary for our understanding of this region within the Earth.

There have been numerous studies performed on the crystal chemistry of (Mg,Fe)SiO₃ perovskite, including extended X-ray absorption fine structure (EXAFS) (Jackson et al. 1987; Farges et al. 1994), optical absorption spectroscopy (Shen et al. 1994; Keppler et al. 1994), single-crystal X-ray diffraction (e.g., Kudoh et al. 1990; Ross and Hazen 1990), electron microscopy (Wang et al. 1992), high-resolution powder X-ray diffraction (e.g., Paris et al. 1990; Mao et al. 1991; Jephcoat et al. 1999), atomistic simulations (Richmond and Brodholt 1998), XES (Li et al. 2003), and ⁵⁷Fe Mössbauer spectroscopy (MBS) under ambient conditions (e.g., Jeanloz et al. 1992; Lauterbach et al. 2000) and at a range of temperatures (McCammon et al. 1992; Fei et al. 1994; McCammon 1998b). Nevertheless, in situ measurements of the pressure dependence of the proportion of Fe⁷⁺ and Fe⁸⁺ in (Mg,Fe)SiO₃ perovskite have not been performed.

Direct information on the electronic behavior of iron can be obtained by using Mössbauer spectroscopy. Conventional Mössbauer spectroscopy has been performed up to Mbar pressures in a diamond anvil cell using iron-concentrated samples (Pasternak et al. 1997). However, experiments under very high pressure using small samples (<50 μm) containing dilute iron concentrations (≤10 mol% iron) have not been performed with conventional