Local structure in $C2/c$ clinopyroxenes on the hedenbergite (CaFeSi$_2$O$_6$)–ferrosilite (Fe$_2$Si$_2$O$_6$) join: A new interpretation for the Mössbauer spectra of Ca-rich $C2/c$ clinopyroxenes and implications for pyroxene exsolution

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ABSTRACT

Three synthetic Ca-rich clinopyroxenes on the hedenbergite-ferrosilite join, with compositions (Hd$_{50}$Fs$_{50}$), (Hd$_{30}$Fs$_{70}$), and (Hd$_{10}$Fs$_{90}$), were investigated by single-crystal X-ray diffraction and Mössbauer spectroscopy at room temperature. For all samples, there is no evidence for the presence of phases with symmetry other than $C2/c$. Structure refinement, using a split-atom model, shows the existence of two different local configurations in the M2 cavity, a hedenbergite-like arrangement and a $C2/c$ clinoferrosilite-like arrangement that are centered by Ca and Fe$^{2+}$, respectively. The Mössbauer spectra were analyzed by a quadrupole-splitting distribution (QSD) method, and the hyperfine parameters of the QSD fit indicate the presence of Fe$^{2+}$ in three local environments that are similar to those of Fe$^{2+}$ at the M1 site in hedenbergite, and the M1 and M2 sites in $C2/c$ clinoferrosilite, in agreement with the structure-refinement results. Our results are consistent with the calculated phase diagram for hedenbergite-ferrosilite, where a miscibility gap and a two-phase field of metastable hedenbergite and metastable pigeonite occur at low temperature. The coexistence of a hedenbergite-like configuration around Ca and a $C2/c$ clinoferrosilite-like configuration around Fe can be considered as a precursor for pyroxene exsolution at low temperature. Our results support previous structure-refinement work on Ca-rich clinopyroxenes along the diopside-enstatite joins, and provide a new insight in the interpretation of Mössbauer spectra of Ca-rich $C2/c$ clinopyroxenes.

Keywords: Clinopyroxene, hedenbergite-ferrosilite, crystal structure, local structure, Mössbauer spectroscopy, X-ray diffraction

INTRODUCTION

Pyroxene is an important rock-forming mineral in the Earth’s upper mantle and one of the major constituents of stony meteorites. The study of pyroxenes and their chemistry is essential for determining the petrogenesis of their host rocks. Calcium pyroxenes along or near the join diopside (CaMgSi$_2$O$_6$)–hedenbergite (CaFe$^{2+}$Si$_2$O$_6$) are monoclinic and have space-group symmetry $C2/c$. The larger and the more distorted M2 polyhedron is usually occupied by Ca, and the M1 polyhedron contains Mg, Fe$^{2+}$, trivalent, and tetravalent cations (Cameron and Papike 1980).

Mössbauer spectroscopy is one of the techniques that has been used extensively in the study of pyroxenes, with emphasis on Mg-Fe$^{2+}$ order-disorder over the non-equivalent M1 and M2 sites (e.g., Dundon and Hafner 1971; Skogby et al. 1992; Domenechetti and Steffen 1992; Dyar et al. 2007). The Mössbauer spectra of orthopyroxenes are generally simple, and consist of two overlapping doublets at room temperature (RT) due to Fe$^{2+}$ at the M1 (outer doublet) and M2 (inner doublet) sites. However, the spectra of Ca-rich clinopyroxenes (space group $C2/c$) are more complicated, and their interpretation is more difficult. For example, where the RT spectra of Ca-rich $C2/c$ clinopyroxenes, with a small Ca-deficiency at the M2 site, are fit with two doublets and assignment is made as above, the relative area of the M2 doublet is anomalously larger than that expected from stoichiometry (Williams et al. 1971), which results in overestima-

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