Single-crystal thermometric calibration of Fe-Mg order-disorder in pigeonites

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ABSTRACT

The single-crystal X-ray technique was used to calibrate a new intracrystalline geothermometer based on equilibrium Mg-Fe* fractionation (Fe* = Fe2+ + Mn2+) between M1 and M2 sites of natural P21/c pigeonite. Suitable crystals free of exsolution textures and sharp diffraction maxima were selected by careful TEM and XRD investigations from a large number of samples. Two single crystals, PCA82506-3 (Wo30En43Fs17) from the Pecora Escarpment 82506 Antarctic ureilite, and BTS308-2 (Wo30En43Fs17) from the BTS308 Paraná rhyodacite, were annealed at temperatures ranging from 600 to 1000 °C. The TEM investigation, carried out on fragments of selected single crystals both before and after thermal treatment, shows heating-induced texture modifications preliminary to spinodal decomposition in both crystals and a size increase in antiphase domains in BTS308-2. The two geothermometric equations calculated by linear regression of ln K‡ vs. 1/T are:

\[
\ln K_f^\alpha = -3291(\pm 269)/T(K) + 0.971(\pm 0.253); \ (r^2 = 0.974)
\]

\[
\ln K_f^\beta = -2816(\pm 83)/T(K) + 0.542(\pm 0.083); \ (r^2 = 0.995)
\]

respectively for PCA82506-3 (XFe2 += 0.20) and BTS308-2 (XFe2 += 0.49) [XFe2+ = Fe*/(Fe* + Mg)]. These results imply negligible compositional effects on Mg-Fe* site partitioning within the range of compositions encompassed by the samples. Comparison of the intracrystalline fractionation data of pigeonite with those of Phca orthopyroxenes shows a similar degree of ordering for both at a given temperature. This result suggests only a small effect of Ca on Fe*-Mg ordering in pyroxene with Ca content up to Wo10.

INTRODUCTION

The order-disorder Mg-Fe2+ exchange reaction between M1 and M2 sites in pyroxenes has been the subject of several investigations, as it provides a tool to determine the thermal history of pyroxene-bearing rocks. The intracrystalline partitioning coefficient (K) of Mg-Fe2+ depends on the closure temperature of the exchange, which in turn is affected by the sample cooling rate. Several studies have been devoted to developing a reliable thermodynamic model to account for Mg-Fe2+ partitioning, both according to the Mueller model (Ganguly 1982) and to the Landau theory for non-convergent ordering (Carpenter and Salje 1994; Kroll et al. 1994). Regardless of the kinetic model, retrieval of the cooling rate of natural samples from their Fe2+-Mg ordering states requires experimental calibration of the equilibrium K vs. T relationship and of kinetic partitioning coefficients. Major experimental work has focused on Phca orthopyroxenes (Saxena and Ghose 1971; Smyth 1973; Sueno et al. 1976; Ganguly 1982; Molin et al. 1991; Sykes-Nord and Molin 1993; Ganguly et al. 1994; Ganguly and Domeneghetti 1996; Stimpfl et al. 1999) and, to a lesser extent, on C2/c Ca-rich clinopyroxenes (McCallister et al. 1976; Molin and Zanazzi 1991). The above studies showed significant differences in Fe2+-Mg ordering between C2/c clino- and Phca orthopyroxenes, as expected in an intracrystalline reaction that strongly depends on crystal structure. These calibrations cannot, therefore, be extended to other structural varieties of pyroxene, such as P21/c pigeonite. For the latter, the only available calibration is that of Saxena et al. (1974), using Mössbauer spectroscopy to determine site partitioning. Their results suggest that ordering of Fe in the M2 site increases with increasing Ca content. However, this calibration is limited only to pyroxenes with Fe/(Fe + Mg) = 0.5 and is not supported by equilibrium reversals. Furthermore, it has been demonstrated that Ca in the M2 site interferes with the Mössbauer spectrum of Fe (Dowty and Lindsley 1973). Smyth (1974) showed a significant increase in Fe2+ ordering in the M2 site of a clinoferrasilite inverted from an orthopyroxene of the same composition.

The aim of the present work was to study the temperature dependence of the intracrystalline exchange reaction FeM1 + MgM2 ↔ FeM2 + MgM1 under equilibrium conditions in P21/c pigeonites with differing Mg/Fe ratios and Ca contents, enabling us to extend application of the intracrystalline geothermometer to pigeonite-bearing rocks. A detailed study of relationships between P21/c pigeonite structure and composition, particularly for the samples investigated in this work, will be the subject of a forthcoming publication.