Ordering kinetics of Mg-Fe$^{2+}$ exchange in a Wo$_{43}$En$_{46}$Fs$_{11$} augite

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**ABSTRACT**

The kinetics of Fe$^{2+}$-Mg exchange between the M1 and M2 sites (Fe$^{2+}_{\text{M1}}$ + Mg$_{\text{M1}}$ = Fe$^{2+}_{\text{M2}}$ + Mg$_{\text{M2}}$) were followed by ordering experiments in an augitic clinopyroxene (Ca$_{0.841}$Na$_{0.019}$Mg$_{0.888}$Fe$^{2+}_{0.151}$Ti$_{0.011}$Al$_{0.025}$Cr$_{0.006}$Si$_{1.914}$Al$_{0.086}$) from a dike on Alicudi (Aeolian Islands, Italy). The same single crystal was annealed in silica tubes in an iron-wüstite buffered Ar atmosphere, at 700, 750, 800, 850, and 950 °C, followed by quenching after each thermal treatment, and was used for the collection of X-ray diffraction data and for microprobe analysis.

Kinetic constants (K) for each isotherm were calculated from the distribution coefficient $K_{\text{D}} = (\text{Fe}^{2+}/\text{Mg})_{\text{M1}}/(\text{Fe}^{2+}/\text{Mg})_{\text{M2}}$ measured during a series of experiments carried out by increasing annealing times until exchange equilibrium was achieved. Calculations of K were performed using the Ginzburg-Landau equation, the kinetic model of Mueller, and the mathematical formulation proposed by Sha and Chappell (1996) to check the responses of various kinetic models for a Ca-rich pyroxene on the same data set. The activation energy of the Fe$^{2+}$-Mg exchange spans a narrow range, yielding values of 200 (±28) kJ/mol, independent of the method used to calculate K.

**INTRODUCTION**

The study of intracrystalline Fe$^{2+}$-Mg exchange between the two crystallographically non-equivalent octahedral M1 and M2 sites in pyroxenes is a powerful tool for modeling the thermal history of the host rocks. The thermodynamics and kinetics of the Fe$^{2+}$-Mg exchange reaction have been extensively investigated in Pbca orthopyroxenes (Virgo and Hafner 1970; Saxena and Ghose 1971; Besancon 1981; Ganguly 1982; Saxena et al. 1987, 1989; Anovitz et al. 1988; Skogby 1992; Sykes-Nord and Molin 1993). A more general approach to calculate the kinetic constants of sub-solidus reactions is the Ginzburg-Landau theory, which describes quite complex transition behavior over remarkably wide ranges of temperature and composition (Salje 1988; Carpenter and Salje 1988; Carpenter et al. 1990a, 1990b; Salje and Kroll 1991; Redfern et al. 1996). Carpenter and Salje (1989) demonstrated that application of the Landau and associated Ginzburg-Landau kinetic theory has practical implications in the treatment of cation ordering transitions. Sha and Chappell (1996) proposed another kinetic model and stressed that caution must be used when applying Mueller’s model to multi-component solid systems, which cannot be simplified as binary solid solutions in a general sense. They also presented an explicit form of the order-disorder kinetic equations required for multi-cation ordering-disordering in minerals with two non-equivalent sites and for two-cation ordering-disordering in multicomponent solid solution.

All three methods mentioned above were used to compute the transition kinetic constants in an augitic clinopyroxene from an andesitic dike on Alicudi (Aeolian Islands, Sicily). The principal aim of the present work was to determine the kinetic constants of the Fe$^{2+}$-Mg exchange reaction in the M1 and M2 sites at various temperatures, namely, the activation energy of the process, to improve the application of clinopyroxene as a