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Kinetics of Fe^{2+}-Mg order-disorder in $P2_1/c$ pigeonite

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Abstract

The kinetics of the Fe-Mg intracrystalline exchange reaction in $P2_1/c$ pigeonite ($Wo_{10}En_{47}Fs_{43}$) free of exsolved augite, from the Paraná rhyodacite sample BTS308, was studied by single-crystal X-ray diffraction (XRD). Isothermal disordering annealing experiments, with oxygen fugacity controlled at the IW buffer, were performed on two crystals at 650, 700, 750, and 800 °C until the Fe-Mg exchange equilibrium was reached. The XRD data were collected from the two untreated crystals and after each annealing experiment. Structure refinements were carried out taking into account the recently discovered stronger preference of Mn for the M2 site compared to Fe^{2+}. The linear regression of $\ln k_D^*$ vs. $1/T$ yielded the following equation:

$$\ln k_D^* = -2925(\pm 110)/T(\mathrm{K}) + 0.574(\pm 0.111); (R^2 = 0.997)$$

The T_c values calculated using this equation were 566 (±6) and 571 (±6) °C for the two crystals. Analysis of the kinetic data was performed according to Mueller's model, which allowed retrieval of the disordering rate constants $C_0K_{dis}^+$ for all four temperatures. The Arrhenius relation:

$$\ln K_{dis}^+ = \ln K_0 - Q/(\mathrm{R}T) = 20.45(\pm 1.91) - 25191\ (\pm 1900)/T(\mathrm{K}); (R^2 = 0.989)$$

yielded an activation energy of 50.03 (±3) kcal/mol for the Fe-Mg exchange process. Cooling time constants, calculated at the QMF buffer conditions of the host rock were, for the two crystals, $\eta = 0.94 \times 10^{-1}\ \mathrm{K^{-1}year^{-1}}$ and $\eta = 1.10 \times 10^{-1}\ \mathrm{K^{-1}year^{-1}}$, and gave cooling rates on the order of 10 °C/h consistent with very fast lava cooling.