The role of Fe content on the Fe-Mg exchange reaction in augite

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ABSTRACT

The study of the intracrystalline Fe-Mg exchange between M1 and M2 crystallographic sites in clinopyroxene on samples a variety of geological settings has provided a framework to understand the thermal history of pyroxene-bearing rocks. The Fe-Mg exchange reaction has successfully been exploited as a geothermometric tool in the study of orthopyroxene and pigeonite-bearing rocks, but relatively few data are available for clinopyroxene. A strong correlation between total iron content and the slope of the Fe$^{2+}$-Mg equilibrium distribution coefficient ($k_D$) as a function of temperature has been found for orthopyroxene and pigeonite, and we investigate this relationship in augite.

We carried out new equilibrium annealing experiments at 800, 900, and 1000 °C followed by single-crystal X-ray diffraction and structural refinement to obtain a new geothermometric calibration for augite from a 120 m thick lava flow from Ontario, Canada [Theo’s Flow, En$_{36}$Fs$_{24}$Wo$_{40}$] hereafter also referred as Fs$_b$, where Fs = 100 \Sigma Fe/(\Sigma Fe+Mg+Ca) with \Sigma Fe = Fe$^{2+}$+Fe$^{3+}$+Mn]. This new calibration enabled us to evaluate the compositional effects (mainly Fe content) by comparison with the data previously obtained on augite from MIL 03346 martian sample (En$_{49}$Fs$_{24}$Wo$_{40}$ hereafter referred to as Fs$_{24}$).

The extremely good agreement observed between the data obtained on Theo’s Flow and Miller Range (MIL 03346) augite demonstrate that for the range of compositions between Fs$_b$ and Fs$_{24}$, total iron content has a negligible or null influence on equilibrium behavior. Furthermore, linear regression of data from Theo’s Flow and MIL 03346 gave a single calibration equation:

$$\ln k_D = -4040(\pm180)/T(K) + 1.12(\pm0.17) \quad (R^2 = 0.988).$$

This new calibration describes the equilibrium behavior of augite and can be reliably used to determine the closure temperature ($T_c$) of augite with composition ranging between Fs$_b$ and Fs$_{24}$.

Keywords: Augite, geothermometer, single-crystal X-ray diffraction, Fe-Mg exchange reaction

INTRODUCTION

Several methods are commonly used to determine the exchange equilibrium temperature of minerals to infer the thermal history of their host rocks (e.g., Ghose and Ganguly 1982; Ganguly and Saxena 1987). Among these, the intracrystalline Fe-Mg exchange between M1 and M2 crystallographic sites in clinopyroxenes has been successfully applied to samples from different geological settings (e.g., Dal Negro et al. 1982; Ghose and Ganguly 1982; Molin and Zanazzi 1991; Brizi et al. 2000). More recently, the same method has also been applied to clinopyroxenes from extraterrestrial samples, in particular to pigeonite from ureilite (Alvaro et al. 2011) and to augite from martian nakhlites (Alvaro et al. 2015).

Alvaro et al. (2011) highlighted a possible correlation between total iron content [hereafter referred as X$_{Fe}$, or X$_{Fe} = Fe^{2+}/(Fe^{2+}+Mg)$] and equilibrium behavior (see Fig. 4 of Alvaro et al. 2011). However, these authors could only account for the data already available: their own results obtained on natural pigeonite and Brizi et al. (2000) data on natural augite. The slope of the arrhenian calibration equation appeared to decrease with increasing Fe content of the pyroxene. Domeneghetti et al. (2013) and Alvaro et al. (2015) suggested that this change in slope was the possible cause of the discrepancy between the closure temperatures ($T_c$) of the augite from martian nakhlite Miller Range 03346 [MIL 03346, $T_c = 600 \degree C, \quad (En_{49}Fs_{24}Wo_{40})$] and the corresponding terrestrial Theo’s Flow (TS, $T_c = 720 \degree C, \quad En_{36}Fs_{24}Wo_{40}$), both calculated using the calibration equation obtained on MIL 03346 samples. However, the lack of data on equilibrium behavior ($k_D$) as a function of Fe content of augite does not allow confirmation of the abovementioned correlation observed for pigeonite.

Here we report the results of a study of the dependence of $k_D$ on temperature, carried out on Theo’s Flow augite (En$_{49}$Fs$_{24}$Wo$_{40}$) samples using the same approach as in MIL 03346, which allows the influence of iron content on the degree of ordering ($k_D$) to be evaluated as a function of temperature and to provide a reliable means of comparison with the data obtained by Alvaro et al. (2015) on MIL 03346 (En$_{49}$Fs$_{24}$Wo$_{40}$).