Fe-Mg exchange reaction in clinopyroxene and its application to the thermal history of planetary bodies M. Murri[1], L. Scandolo[1], A.M. Fioretti[2], M. Alvaro[1*], F. Nestola[3], M.C. Domeneghetti[1]. [1]Dept. Of Earth and Environmental Sciences, University of Pavia, Italy (mara.murri01@universitadipavia.it; lorenzo.scandolo@unipv.it; chiara.domeneghetti@unipv.it; matteo.alvaro@unipv.it), [2]CNR-IGG U.O. Padua, Italy, [3]Dept. of Geosciences University of Padua, Italy.

Introduction: The broadest application of intracrystalline Fe^{2+}-Mg partitioning between the *M*1 and *M*2 crystallographic sites in the pyroxene structure is the determination of the closure temperature (T_c) of the Fe^{2+}-Mg exchange reaction that provides important constraint on the cooling rate of the pyroxene-bearing host rocks (eg. [*1*]). Although this approach has been successfully developed and applied for orthopyroxene and pigeonite-bearing rocks, relatively few data are available for clinopyroxenes (cpxs). The most recent calibration for cpxs has been obtained by [*2*]. Calculations performed for cpxs in some Earth and planetary contexts, provided (i) T_c consistent among different samples and coherent with their respective geological setting; (ii) cooling rates for different samples from the same context in significant disagreement one to another. [*3*] showed that the relative low T_c calculated for augite from Miller Range nakhlite (MIL 03346) using the available geothermometers would correspond to a slow cooling rate inconsistent with the petrologic evidence for an origin from a fast-cooled lava flow.

In order to account for these discrepancies [*4*] performed an *ex situ* equilibrium annealing study on augite crystals from Miller Range 03346 nakhlite (MIL 03346, Fs_{24}). This calibration has been then applied also to the augite from Theo's Flow always regarded as the terrestrial analogue for MIL03346. With the new calibration it is clear that the nakhlites T_c is about 600°C thus lower than that of 720°C for TS7 sample, which was supposed to be cooled at a burial depth of 85m. However, despite the similar geological setting, the difference in T_c could be just ascribed to the differences in Fe content that may affect the Mg-Fe equilibrium behaviour.

Aim: Therefore, we have carried out a new equilibrium annealing experiments at 800, 900 and 1000°C in order to obtain a new geothermometric calibration for the Fe-poor augite from Theo's Flow (Fs_9). This new calibration will enable us to evaluate the compositional effects (mainly Fe content) by comparison with the data previously obtained on augite from MIL 03346 sample.

Experimental: The annealing experiments have been carried out at 800, 900 and 1000°C using TS7 N.16 crystal until the equilibrium in the Fe^{2+}-Mg exchange reaction was reached. The crystal was sealed into a silica vial, after alternate flushing with nitrogen and evacuating, together with an iron-wustite buffer to control the oxygen fugacity fO_2. Inside the silica tube, the crystal and the buffer were put into two small separate Pt crucibles to avoid contact between them. After equilibrium in the Fe-Mg exchange reaction was reached, quenching was performed by dropping the tubes into cold water. Further details on the annealing protocol used are given in [*3*, *5*]. HR-SC-XRD data (i.e. up to 0.434 $Å^{-1}$) were collected on crystal TS7 N. 16 before and after each annealing experiment using a three-circle Bruker AXS SMART APEX diffractometer, equipped with a CCD detector and 0.3 mm MonoCap collimator (graphite-monochromatized MoKa radiation, λ = 0.71073Å operating 55 kV, 30 mA) following the same procedure described in [*3*]. After the annealing experiments Electron Microprobe Analysis (EMPA) have been carried out on the same crystal.

Results: The Fe^{2+}-Mg ordering state was estimated from the site population determined as in [3]. The intracrystalline distribution coefficient (k_D), was calculated using the same expression adopted by [*2*]: $k_D = ([Fe^{2+}\ M1][MgM2]/\ [Fe^{2+}\ M2][MgM1])$. The obtained k_D values are 0.052, 0.071, 0.096, 0.120 for the natural sample and the three temperatures (800, 900 and 1000°C) respectively. These results are represented together with those obtained on MIL 03346 in Figure 1.

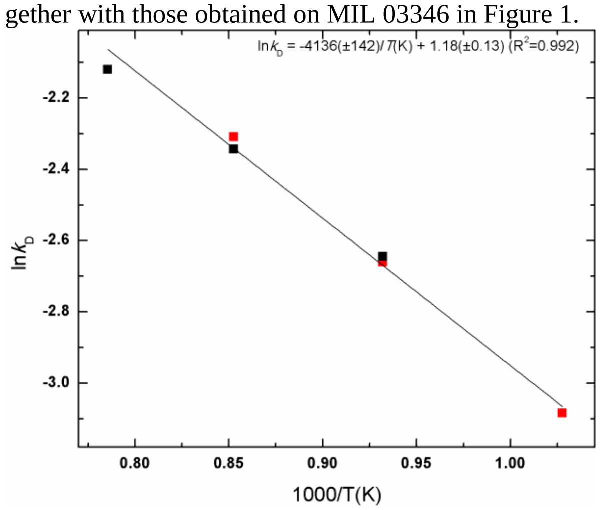

Figure 1. Lnk_D versus 1000/T (K) for the augite samples considered in this work together with those by [4, 5]. Solid line represent geothermometer equation calibrated by linear fitting of MIL N.19 data (red squares) together with those obtained in this work (black squares).

Conclusions: It is clear from Figure 1 that there is no effect on the equilibrium behavior (i.e. closure temperature) arising from the different Fe contents. Therefore it has been possible to calculate a single calibration equation valid for augites with composition ranging between Fs_9 and Fs_{24}. The resulting equation is:
$\ln k_D = -4136(\pm 142)/T(K) + 1.18(\pm 0.13)$ (R^2=0.992). However, it cannot be excluded the possible role of Fe content on the kinetic behavior. Therefore, while the closure temperature can be reliably determined using the geothermometer here reported the cooling rate calculation still require new kinetic data for clinopyroxenes.

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