Fe-Mg exchange reaction in clinopyroxene and its application to the thermal history of planetary bodies

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Introduction

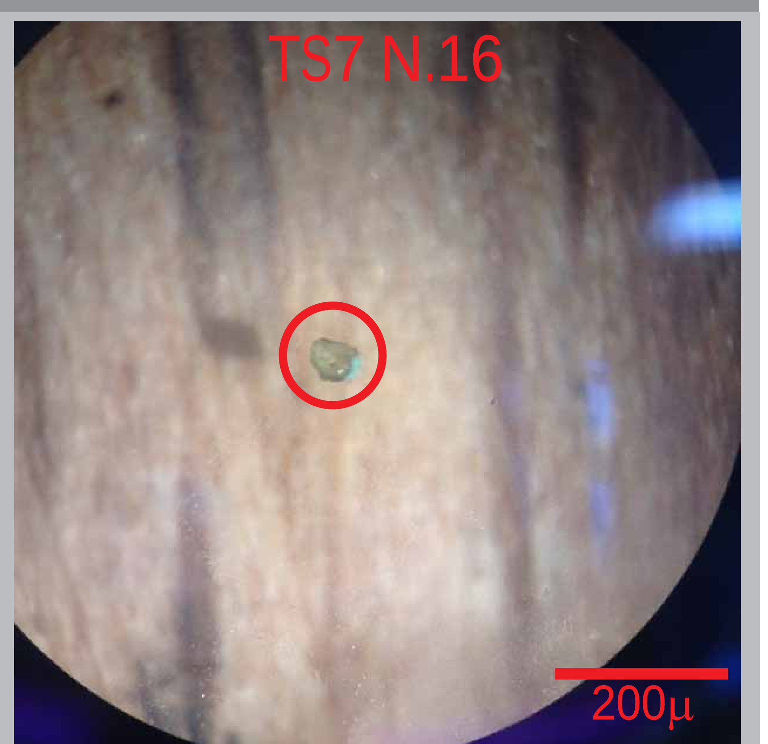
Several methods are commonly used to determine equilibrium temperature in minerals to infer the thermal history of their host rocks. Among these, the intracrystalline Fe-Mg exchange between M1 and M2 crystallographic sites in orthopyroxenes (opxs) has been successfully applied to samples retrieved from different terrestrial geological settings (e.g. 1). More recently, the same method has been applied also to clinopyroxenes (cpxs) from extraterrestrial samples, in particular to pigeonites from ureilite [2] and to augites from Martian nakhlites [3].

Equilibrium behaviour and exchange reaction

The most recent calibration (for both kinetic and equilibrium) for clinopyroxenes has been provided by [4] and [5] respectively. Calculations performed for cpxs in some Earth and planetary contexts (e.g., [6,7]), provided (i)closure temperature (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. Investigation of samples with different composition may clarify the compositional effects on such discrepancies.

Samples

A small chip (0.10 g) from the pyroxenite sample TS7 from Theo's flow was obtained at location 85 m below the cooling surface of the 120-m-thick lava flow (Ontario, Canada, sample provided by A.H. Treiman). Theo's Flow has always been regarded as the terrestrial analogue of Miller Range (MIL 03346) sample. One pyroxene crystal (sizes 0.300 x 0.260 x 0.170 mm), labelled TS7 N.16 was carefully selected for high-resolution X-ray single crystal diffraction analysis on the basis of the quality of the diffraction peaks and absence of twinning. Furthermore a new ex situ annealing experiment was performed.



Experimental methods

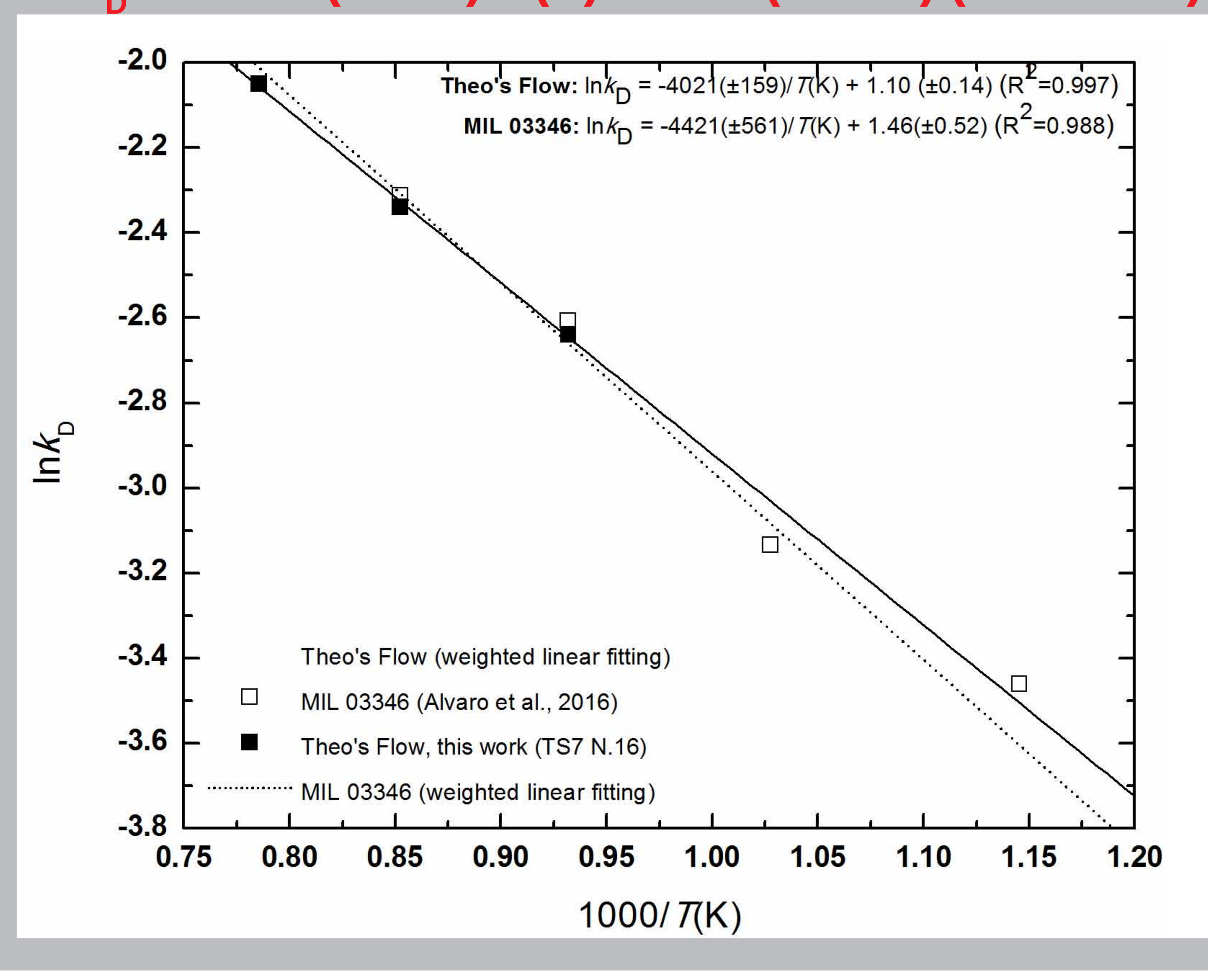
In order to assess the role of Fe content on T_c we performed a new series of equilibrium experiments at 800, 900 and 1000°C (much higher temperature than those reached in previous experiements) thus obtaining a new geothermometric calibration on a Fe-poor augite from Theo's Flow (Fs_9).

Results and discussion

The results of our new calibration performed on Fe-poor augite enabled us to evaluate the compositional effects (i.e. Fe content) by comparison with the data previously obtained on Fe-rich augite composition (e.g. Miller Range nakhlite MIL03346 samples).

The Fe^{2+}-Mg ordering state was estimated from the site population determined as in [8]. The intracrystalline distribution coefficient (k_D), was calculated using the same expression adopted by [8] as 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. In Figure 3 our results are represented together with those obtained on MIL03346.

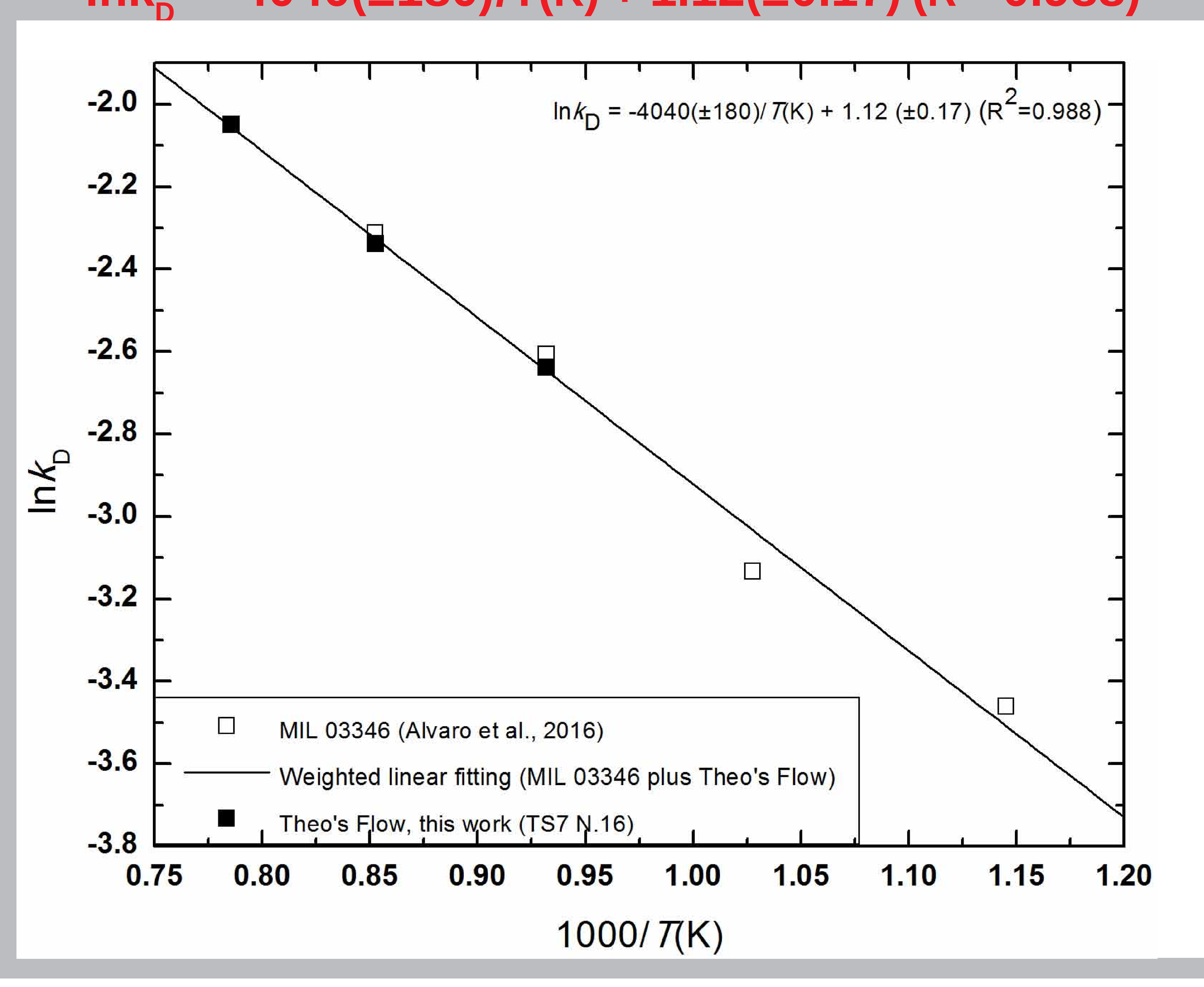
$$\ln k_D = -4021(\pm159)/T(K) + 1.10(\pm0.14)\ (R^2=0.997)$$



Conclusions

It is clear from Figure 4 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}. However, it cannot be excluded the possible role of Fe content on the kinetic behavior. Moreover, while the closure temperature can be reliably determined using the geothermometer here reported the cooling rate calculation still require new kinetic data for clinopyroxenes.

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



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