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

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15 **ABSTRACT**

16 The study of the intracrystalline Fe-Mg exchange between *M1* and *M2* crystallographic sites in clinopyroxene on
17 samples from a variety of geological settings has provided a framework to understand the thermal history of
18 pyroxene-bearing rocks. The Fe-Mg exchange reaction has successfully been exploited as a geothermometric tool in
19 the study of orthopyroxene and pigeonite-bearing rocks, but relatively few data are available for clinopyroxene. A
20 strong correlation between total iron content and the slope of the Fe²⁺-Mg equilibrium distribution coefficient (k_D) as
21 a function of temperature has been found for orthopyroxene and pigeonite, and we investigate this relationship in
22 augite.

23 We carried out new equilibrium annealing experiments at 800, 900 and 1000°C followed by single-crystal X-ray
24 diffraction and structural refinement in order to obtain a new geothermometric calibration for augite from a 120-m-
25 thick lava flow from Ontario, Canada [Theo's Flow, $En_{49}Fs_9Wo_{42}$ hereafter also referred as Fs_9 , where
26 $Fs=100*\Sigma Fe/(\Sigma Fe+Mg+Ca)$ with $\Sigma Fe=Fe^{2+}+Fe^{3+}+Mn$]. This new calibration enabled us to evaluate the
27 compositional effects (mainly Fe content) by comparison with the data previously obtained on augite from MIL
28 03346 Martian sample ($En_{36}Fs_{24}Wo_{40}$ hereafter referred to as Fs_{24}).

29 The extremely good agreement observed between the data obtained on Theo's Flow and Miller Range (MIL
30 03346) augite demonstrate that for the range of compositions between Fs_9 and Fs_{24} , total iron content has a negligible
31 or null influence on equilibrium behavior. Furthermore, linear regression of data from Theo's Flow and MIL 03346
32 gave a single calibration equation:

33
$$\ln(k_D) = -4040(\pm 180)/T(K) + 1.12(\pm 0.17) (R^2 = 0.988).$$

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34 This new calibration describes the equilibrium behavior of augite and can be reliably used to determine the closure
35 temperature (T_c) of augite with composition ranging between Fs_9 and Fs_{24} .

36 **Keywords:** augite; geothermometer; single-crystal X-ray diffraction; Fe-Mg exchange reaction.

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INTRODUCTION

39 Several methods are commonly used to determine the exchange equilibrium temperature of
40 minerals to infer the thermal history of their host rocks (e.g. Ghose and Ganguly 1982; Ganguly
41 and Saxena 1987). Among these, the intracrystalline Fe-Mg exchange between $M1$ and $M2$
42 crystallographic sites in clinopyroxenes has been successfully applied to samples from different
43 geological settings (e.g. Dal Negro et al. 1982; Ghose and Ganguly 1982; Molin and Zanazzi
44 1991; Brizi et al. 2000). More recently, the same method has also been applied to clinopyroxenes
45 from extraterrestrial samples, in particular to pigeonite from ureilite (Alvaro et al. 2011) and to
46 augite from Martian nakhlites (Alvaro et al. 2015).

47 Alvaro et al. (2011) highlighted a possible correlation between total iron content (hereafter
48 referred as $X_{Fe} = Fe^{2+}/Fe^{2+}+Mg$ or Fs) and equilibrium behavior [see Figure 4 of Alvaro et al.
49 2011]. However, these authors could only account for the data already available: their own
50 results obtained on natural pigeonite and Brizi et al.'s (2000) data on natural augite. The slope of
51 the arrhenian calibration equation appeared to decrease with increasing Fe content of the
52 pyroxene. Domeneghetti et al. (2013) and Alvaro et al. (2015) suggested that this change in slope
53 was the possible cause of the discrepancy between the closure temperatures (T_c) of the augite
54 from Martian nakhlite Miller Range 03346 (MIL 03346, $T_c=600^\circ C$, $(En_{36}Fs_{24}Wo_{40})$) and the
55 corresponding terrestrial Theo's Flow (TS, $T_c=720^\circ C$, $En_{49}Fs_9Wo_{42}$), both calculated using the
56 calibration equation obtained on MIL 03346 samples. However, the lack of data on equilibrium
57 behavior (k_D) as a function of Fe content of augite does not allow confirmation of the
58 abovementioned correlation observed for pigeonite.

59 Here we report the results of a study of the dependence of k_D on temperature, carried out on
60 Theo's Flow augite ($En_{49}Fs_9Wo_{42}$) samples using the same approach as in MIL 03346, which
61 allows the influence of iron content on the degree of ordering (k_D) to be evaluated as a function
62 of temperature and to provide a reliable means of comparison with the data obtained by Alvaro et
63 al. (2015) on MIL 03346 ($En_{36}Fs_{24}Wo_{40}$).

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EXPERIMENTAL METHODS

66 *Samples*

67 A small chip (0.10 g) of the pyroxenite sample TS7 from Theo's flow (Lentz et al. 2011),
68 obtained at 85 m below the cooling surface of the 120-m-thick lava flow [Ontario, Canada; Pyke
69 et al. (1973)] was kindly provided by Dr. A.H. Treiman. One pyroxene crystal (size 0.300 x
70 0.260 x 0.170 mm), labelled TS7 N.16 (where 16 refers to the progressive numbering of
71 samples) was carefully selected for high-resolution X-ray single crystal diffraction analysis on
72 the basis of the quality of the diffraction peaks and absence of twinning.

73 *Annealing experiments*

74 After alternate flushing with nitrogen and evacuation, augite crystal TS7 N.16 was sealed
75 into a silica vial together with an iron-wüstite buffer to control oxygen fugacity fO_2 . The crystal
76 and the buffer were placed in two small separate Pt crucibles to avoid contact between them. The
77 annealing experiments were carried out at 800, 900 and 1000°C on the same augite crystal until
78 equilibrium in the Fe^{2+} -Mg exchange reaction was reached. Quenching was performed by
79 dropping the tubes into cold water. Further details on the annealing protocol used are given in
80 Alvaro et al. (2011), Alvaro et al. (2015) and Domeneghetti et al. (2013). Two
81 annealing/quenching experiments of different durations were performed at each temperature to
82 ascertain that equilibrium was reached.

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84 *Single-crystal X-ray diffraction*

85 High resolution single-crystal X-ray diffraction data (HR-SC-XRD) up to 0.434 \AA^{-1} were
86 collected on crystal TS7 N.16 before (referred to as "untreated") and after each annealing
87 experiment. A three-circle Bruker AXS SMART APEX diffractometer (graphite-
88 monochromatized $MoK\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ operating 55 kV, 30 mA), equipped with a
89 CCD detector was used. Because of the small size of the crystals, a 0.3mm MonoCap collimator
90 was used to collect the data.

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91 Data up to 9000 frames (frame resolution 512×512 pixels) were gathered using the Bruker
92 SMART software package (Bruker-AXS ©) at ten different goniometer settings, using the ω -scan
93 mode (scan width: $0.2^\circ \omega$; exposure time: 10 second/frame; detector-sample distance: 5.02 cm).
94 About 13900 reflections ($\sim 99\%$ of the measured data) were collected up to $2\theta = 110^\circ$.

95 RESULTS AND DISCUSSION

96 *Data reduction and structural refinement*

97 Data reductions, including intensity integration and background, and Lorentz-polarization
98 corrections, were carried out using the Bruker SAINT+ software v6.45A (Bruker-AXS©). The
99 semi-empirical absorption correction of Blessing (1995), based on the determination of
100 transmission factors for equivalent reflections in the monoclinic Laue group $2/m$ was applied using
101 the program SADABS (Sheldrick 1996). Table 1 shows the unit-cell parameters, obtained by a
102 least-squares procedure to refine the position of about 7000 reflections in the $6 - 110^\circ 2\theta$ range,
103 for the untreated crystal and after each disordering experiment. It also shows the value of the
104 discrepancy factor R_{int} calculated from the average of the $[F_o]^2$ values for equivalent pairs in $2/m$
105 Laue symmetry. The observed F_o^2 values were then treated with a full-matrix least-squares
106 refinement in the $C2/c$ space group by SHELX-97 (Sheldrick 2008) starting from the atomic
107 coordinates reported by Domeneghetti et al. (2013) for sample TS7 N.2, and taking into account
108 the $M21$ and $O2B1$ split sites that had been refined with isotropic displacement parameters [for a
109 detailed description of the $M21$ and $O2B1$ split sites see Rossi et al. (1987)]. The atomic scattering
110 curves were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton
111 1970). Neutral vs. ionized scattering factors were refined for all sites not involved in chemical
112 substitutions (Hawthorne et al. 1995) and complete ionization was assumed for Mg and Fe in the
113 $M1$ site, for Ca and Mg in the $M2$ site and for Fe in the $M21$ site [see Domeneghetti et al. (2013)
114 for further details on the refinement strategies adopted here]. Individual weights and the weighting
115 scheme suggested by the program were used. The extinction correction was applied with the
116 procedures of the SHELX-97 program. Table 1 reports the mean atomic numbers (m.a.n.) in
117 electrons per formula unit (e.p.f.u.) at the $M1$ and ($M2 + M21$) sites obtained when the structure
118 refinement reached convergence, before introducing the chemical constraints. The average of the
119 atomic numbers of 33.74 e.p.f.u., obtained from the sum of $M1 + M2 + M21$ for each structural

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120 refinement, did not show variations greater than 0.1 e.p.f.u. with respect to the m.a.n. of the
121 untreated sample (see Table 1).

122 This mean atomic number is in good agreement with those obtained from the Electron
123 Microprobe analysis (EMPA) by Domeneghetti et al., (2013) for crystal TS7 N.2 [33.62(14)
124 e.p.f.u.- here and in the remaining of the text the numbers in parenthesis are 1 standard deviation
125 of our determined values]. The good agreement (less than 1 standard deviation) allowed us to use
126 the EMPA data reported for this crystal (Table 2 of Domeneghetti et al. 2013) for our subsequent
127 structure refinements with chemical constraints, following the same procedure as in Domeneghetti
128 et al. (2013) and Nestola et al. (2007). The site populations obtained from the structural
129 refinements with chemical constraints are reported in Table 2.

130 *Dependence of the closure temperature of augite on iron content*

131 The site population reported in Table 2 was determined as in Domeneghetti et al.
132 (2013). Fe²⁺-Mg ordering was estimated from site population by means of the intracrystalline
133 distribution coefficient k_D , using the same expression adopted by Brizi et al. (2000): $k_D =$
134 $[(Fe^{2+}_{M1})(Mg_{M2})/(Fe^{2+}_{M2})(Mg_{M1})]$. The obtained k_D values and relative propagated errors are also
135 reported in Table 2. As expected, the intracrystalline distribution coefficient increased with
136 temperature.

137 For the untreated TS7 N.16 crystal a k_D of 0.052(3) was obtained. This value is identical,
138 within error, with those measured for the other two TS7 samples (N.1 and N.2) of 0.052(4) and
139 0.048(3) respectively, reported by Domeneghetti et al. (2013), confirming the nearly identical
140 cation distribution and closure temperature (T_c) of these crystals.

141 In Figure 1 plots the $\ln k_D$ against $1/T$ for our TS7 N.16 along with those by Alvaro et al.
142 (2015) on the MIL 03346 crystal (N.19), and that of Domeneghetti et al. (2013) on the MIL
143 03346 crystal (N.14) . The weighted linear regression of $\ln k_D$ versus $1/T$ yielded the following
144 equation:

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$$\ln(k_D) = -4021(\pm 159)/T(K) + 1.18(\pm 0.14) \quad (R^2 = 0.997) \quad (1)$$

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147 which agrees extremely well with that of Alvaro et al. (2015):

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$$\ln(k_D) = -4421(\pm 561)/T(K) + 1.46(\pm 0.52) \quad (R^2=0.988) \quad (2)$$

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151 The closure temperatures obtained using our new geothermometer and that by Alvaro et
152 al. (2015) for our sample TS7 N.16 together with those for MIL03346 N.14, N.19 and TS7 N.1
153 and N.2 (Domeneghetti et al. 2013) are reported in Table 3. As seen in Table 3, and as expected
154 from the similar k_D values, the T_c calculated for the three samples were identical within one
155 standard deviation, once again confirming the good agreement between the two calibration
156 equations. Therefore, a new single calibration equation was obtained using our data together with
157 those reported by Alvaro et al. (2015):

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$$\ln(k_D) = -4040(\pm 180)/T(K) + 1.12(\pm 0.17) \quad (R^2=0.988) \quad (3)$$

159

160 This equation can be used with confidence to retrieve the closure temperature (T_c) for terrestrial
161 and extraterrestrial augite with composition ranging between Fs_9 and Fs_{24} . Furthermore, these
162 results confirmed once again that the use of the older and erroneous calibration by Brizi et al.
163 (2000) should be abandoned.

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IMPLICATIONS

165 In this study we have shown that at least for the range of compositions between Fs_9 and
166 Fs_{24} , total iron content has no influence on the Fe^{2+} -Mg exchange equilibrium (Figure 2),
167 although the role of Fe content in kinetic behavior cannot be excluded until a broader range of
168 compositions is investigated. Our newly determined calibration allows the calculation of closure
169 temperatures and a preliminary estimation of the cooling rates using the method of Ghose and
170 Ganguly (1982) for diopside from the Lesotho Kimberlite pipe and used in Alvaro et al. (2015).
171 This procedure will enable, for instance, calculation of the burial depth for samples from
172 different overlapping magmatic units as in Theo's flow (work in progress).

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Tables and Figures

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Table 1. Unit cell parameters and information on data collection and structure refinement for untreated TS7 N.16. Data for TS7 N.16 obtained after each annealing temperature are also reported.

	Untreated	72 h 800°C	120 h 800°C	73 h 900°C	166 h 900°C	15 h 1000°C	30 h 1000°C
	kcs	kda	kdg	kdu	kdw	kdx	kdz
a (Å)	9.7401 (4)	9.7356 (5)	9.7393 (4)	9.7353 (4)	9.7430 (4)	9.7480 (4)	9.7424 (5)
b (Å)	8.9195 (3)	8.9237 (4)	8.9255 (4)	8.9185 (3)	8.9269 (4)	8.9307 (4)	8.9286 (5)
c (Å)	5.2513 (2)	5.2515 (2)	5.2524 (2)	5.2510 (2)	5.2542 (2)	5.2577 (2)	5.2552 (3)
	106.2619	106.2279	106.2341	106.2670	106.2690	106.2734	106.2759
β (°)	(12)	(16)	(13)	(11)	(11)	(12)	(16)
V(Å ³)	437.96 (3)	438.06 (3)	438.38 (3)	437.66 (3)	438.68 (3)	439.38 (3)	438.81 (4)
μ (mm ⁻¹)	0.19	0.19	0.19	0.19	0.19	0.19	0.19
I_{ind}	2704	2766	2779	2738	2775	2788	2784
R_{int}	0.022	0.026	0.026	0.013	0.029	0.038	0.034
R_{all}	0.023	0.028	0.027	0.023	0.028	0.029	0.030
R_w	0.061	0.077	0.073	0.062	0.073	0.080	0.079
S	1.19	1.13	1.17	1.16	1.18	1.14	1.14
m.a.n	33.78	33.74	33.79	33.74	33.68	33.76	33.71

Standard deviations are given in parentheses. I_{ind} is the number of independent reflections used for structure refinement; $R_{int} = \sum |F_o^2 - F_c^2(\text{mean})| / \sum [F_o^2]$ where F_o and F_c are the observed and calculated structure factors; $R_{all} = \sum ||F_o^2| - |F_c^2|| / \sum [F_o^2]$; $R_w = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{0.5}$, where n is the number of reflections and p is the total number of parameters refined. ^(a) m.a.n. is the mean atomic number (in electrons per formula unit) before introducing the chemical constraints. Crystal system monoclinic C2/c; radiation type MoK α . Standard deviations are given in parentheses.

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Table 2. Site population and distribution coefficients (k_D) for TS7 N.16 untreated sample together with those obtained on the same crystal at different annealing temperatures.

		Untreated	72 h	120 h	73 h	166 h	15 h	30 h
		d	800°C	800°C	900°C	900°C	1000°C	1000°C
		kcs	kda	kdg	kdu	kdw	kdx	kdz
T	Si	1.948	1.948	1.948	1.948	1.948	1.949	1.949
	Al	0.052	0.052	0.052	0.052	0.052	0.051	0.051
M1	Mg	0.869(2)	0.860(2)	0.860(3)	0.855(2)	0.854(2)	0.847(2)	0.848(2)
	Fe	0.070(3)	0.079(3)	0.079(3)	0.083(3)	0.085(3)	0.092(3)	0.091(3)
	Fe³⁺	0.042	0.042	0.042	0.043	0.041	0.041	0.042
	Al	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Cr	0.009	0.010	0.010	0.010	0.010	0.010	0.010
	Ti	0.007	0.007	0.007	0.007	0.007	0.007	0.007
	Mn	0.002	0.002	0.002	0.003	0.003	0.003	0.003
M2	Mg	0.065(3)	0.076(3)	0.072(3)	0.079(3)	0.080(3)	0.089(3)	0.086(3)
	Fe	0.101(2)	0.092(2)	0.093(2)	0.086(2)	0.083(2)	0.075(2)	0.077(2)
	Ca	0.817	0.815	0.819	0.816	0.819	0.820	0.819
	Mn	0.003	0.003	0.003	0.003	0.003	0.002	0.003
	Na	0.015	0.014	0.014	0.015	0.014	0.014	0.014
	k_D	0.052(3)	0.076(4)	0.071(4)	0.089(4)	0.096(4)	0.129(5)	0.120(5)
	$\ln k_D$	-2.96(6)	-2.58(5)	-2.64(5)	-2.42(5)	-2.34(5)	-2.05(4)	-2.12(4)

Note: $k_D = [(Fe^{2+}_{M1})(Mg_{M2})/(Fe^{2+}_{M2})(Mg_{M1})]$. The site occupancy values represent atoms per six oxygen atoms. (a) Chemical constraints introduced are based on the chemical analysis provided by Alvaro et al. (2015). Standard deviations are given in parentheses.

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Table 3. Closure temperature calculated with different calibration equations.

T_c (°C)	T_c (°C)	references
Brizi et al. (2000)	Alvaro et al. (2015)	T_c (°C)
		This study

MIL 03346	Untreated (N.1)	533	640	624	a
	Untreated (N.2)	496	611	593	a
	Untreated (N.14)	499	612	582	b
	600°C (N.14)	515	625	609	b
	Untreated (N.19)	479	597	579	b
	700°C (N.19)	597	689	677	b
	800°C (N.19)	773	814	811	b
	900°C (N.19)	906	899	904	b
	Theo's Flow	Untreated (N.1)	649	728	718
Untreated (N.2)		625	710	698	a
Untreated (N.16)		648	727	726	c
800°C (N.16)		758	804	809	c
900°C (N.16)		890	889	901	c
1000°C (N.16)		1012	961	980	c

Note: (1) Brizi et al. (2000); (2) Alvaro et al. (2015); (3) This study. References: (a) Domeneghetti et al. (2013); (b) Alvaro et al. (2015); (c) This study.

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258 **Figure 1.** $\ln k_D$ versus $1/T$ (K^{-1}) for the augite samples considered in this work (Theo's Flow
 259 TS7 N.16, solid squares) together with those reported by Alvaro et al. (2015) for MIL 03346 and
 260 our data (open square). (a) Dashed and dotted lines represent the linear regression of the $\ln k_D$ vs
 261 $1/T$ for our sample and for those published by Alvaro et al. (2015), respectively. (b) Solid line
 262 represents a single linear regression of the $\ln k_D$ vs $1/T$ for our sample together with those
 263 published by Alvaro et al. (2015).

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