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THERMAL HISTORY OF NAKHLITES: A COMPARISON BETWEEN MIL03346 AND ITS TERRESTRIAL ANALOGUE THEO'S FLOW

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ABSTRACT

High resolution single-crystal X-ray diffraction (HR-SCXRD) and Mössbauer spectroscopy of the intracrystalline cation distribution have been performed on augitic core-crystals from a Miller Range nakhlite (sample MIL 03346,13) with approximate composition of $\text{En}_{36}\text{Fs}_{24}\text{Wo}_{40}$. The Mössbauer data on the single-crystal yielded a very low Fe^{3+} content [$\text{Fe}^{3+}/\text{Fe}_{\text{total}} \sim 0.033(23)$ a.p.f.u.] that, together with the Electron Microprobe Analysis (EMPA) and the X-ray structural data allowed us to obtain the accurate cation site distribution and the Fe^{2+} -Mg degree of order. This leads to a closure temperature (T_c) of 500 with a standard deviation of $\pm 100^\circ\text{C}$ that would correspond to a slow cooling rate, which is in disagreement with petrologic evidence that indicates that this sample originates from a fast cooled ($\sim 3\text{-}6^\circ\text{C/h}$) lava flow.

In order to clarify this discrepancy we undertook (i) a SC-XRD study of an augite ($\sim \text{En}_{49}\text{Fs}_9 \text{Wo}_{42}$) from a pyroxenite (TS7) of Theo's flow, a 120-m-thick lava flow regarded as a terrestrial analogue of MIL 03346; (ii) an annealing experiment at 600°C on a crystal from exactly the same fragment of MIL 03346. SC-XRD data from TS7 augite yields a $T_c = 600(20)^\circ\text{C}$, consistent with the cooling rate expected at 85m below the surface. This T_c is higher, although similar within error, to the $T_c = 500(100)^\circ\text{C}$ obtained for MIL03346; thus suggesting relatively slower cooling for MIL 03346 with respect to TS7. The annealing experiment on the MIL 03346 crystal clearly showed that the degree of order remained unchanged, further confirming that the actual T_c is close to 600°C .

This result appears inconsistent with the shallow depth of origin ($\sim <2\text{m}$) assumed for MIL 03346, further supporting the discrepancy between MIL 03346 textural and petrologic evidence of fast cooling and the abovementioned T_c results obtained for augite. Therefore, a tentative scenario is that, soon after eruption and initial quench and while still at relatively high- T ($\sim 600^\circ\text{C}$), MIL 03346 was blanketed with subsequent lava flows that slowed down the cooling rate and allowed the augite Fe^{2+} -Mg exchange reaction to proceed.

Keywords: augite, closure temperature, nakhlite, single crystal, X-ray diffraction, thermal history, cooling rate.

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1. INTRODUCTION

Miller Range sample MIL03346 is a nakhlite ("SNC" type meteorite, composed of 79% clinopyroxene, ~ 1% olivine, and 20% vitrophyric intercumulus material) that was found in Antarctica (McBride et al. 2005; Day et al. 2006; Treiman 2005). The clinopyroxene is augite with a homogeneous core (with composition of $\sim\text{En}_{36}\text{Fs}_{24}\text{Wo}_{40}$) and an iron-enriched rim. Since the first modern petrologic studies of Nakhla (Reid and Bunch 1975; Bunch and Reid 1975), the nakhlite group of meteorites has been interpreted as igneous cumulate rocks, 'sediments' of augite and olivine crystals accumulated from basaltic magma that erupted onto the surface of Mars (Bunch and Reid 1975; Reid and Bunch 1975). In the subsequent 25 years of study, all analyzed characteristics of many nakhlites have confirmed their igneous origin: mineralogy, petrography, chemical composition, chronology, and petrology (e.g., Stolper and McSween Jr 1979; McSween 1985; McSween 1994; Treiman 1986; Treiman 1993; Longhi and Pan 1989; McSween and Treiman 1998; Treiman 2003). However, many details of some of the nakhlites' history have been disputed (e.g., the composition of its parental magma, whether it has been affected by infiltration metasomatism, and the importance of crystal-liquid re-equilibration). Among those open questions, a reliable evaluation of the oxidation state and the thermal history are still critical issues under discussion. In particular Mössbauer spectra of MIL 03346 whole-rock samples and clinopyroxene separates showed a significantly higher Fe^{3+} content compared to the other SNCs (Dyar et al. 2005). Furthermore, MIL 03346 has always been considered the

most rapidly cooled nakhlite on the basis of petrological and textural evidence (see Treiman 2005 and Hammer 2009).

The intracrystalline Fe^{2+} -Mg partitioning between the M1 and M2 sites in clinopyroxene can be used to determine the closure temperature (T_c) of the Fe^{2+} -Mg exchange through the relationship between distribution coefficient (k_D) and T_c (Ganguly and Domeneghetti 1996). In our study we calculated T_c using the equation by Brizi et al. (2000) that improved the experimental calibration by Molin and Zanazzi (1991) by taking into account the dependence of the k_D on the composition, in particular on the (Ca + Na) and R^{3+} cation content of the pyroxene.

We have investigated augite core crystals from the MIL 03346 meteorite using high-resolution single crystal X-ray diffraction (HR-SCXRD) and electron microprobe analysis (EMPA) in order to obtain an accurate site partitioning that, together with the $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratio measured on exactly the same crystal by Mössbauer spectroscopy, enables us to constrain the Fe^{2+} -Mg order degree between M1 and M2 sites (Domeneghetti et al. 2006). Our preliminary data (ibid) showed a high degree of order in the Fe^{2+} -Mg distribution corresponding to a T_c value of $\sim 450^\circ\text{C}$ that suggested a cooling rate much slower than the one indicated by petrological and textural evidence. Righter et al. (2008) reported structural refinement data for two MIL 03346 clinopyroxene crystals, which confirmed the degree of order that we had previously obtained. In the present study we report data obtained on the two MIL 03346 clinopyroxene crystals together with those obtained on a third crystal from the same rock sample that provide a more accurate estimated standard deviations (e.s.d.'s) on the closure temperature. In addition, this work presents (i) comparison of data obtained by HR-SCXRD and EMPA on two augite crystals (with composition $\sim \text{En}_{49}\text{Fs}_9\text{Wo}_{42}$) from a pyroxenite (TS7, Lentz et al. (2011) of Theo's flow (Ontario, Canada, Pyke et al. 1973) regarded as a terrestrial analogue of MIL03346 (Lentz et al. 1999;

Mikouchi et al. 2000; Mikouchi and Miyamoto 2001; Treiman 2003); and (ii) data obtained before and after an annealing experiment at 600°C on an augite crystal from MIL 03346.

2. EXPERIMENTAL

2.1 Samples

A small fragment (0.10 g) of MIL 03346,13 nakhlite was obtained from the meteorite sample curator of NASA Johnson Space Center. A careful selection of pyroxene single crystals under the polarizing microscope was performed and three relatively small (sizes are reported in Table 1) core single crystals were obtained by cutting off the zoned rims. These core crystals, labelled N.1, N.2 and N.14 showed sharp extinction and sharp diffraction profiles and were, therefore, considered suitable for X-ray data collection. After the diffraction work was performed, crystal N.1 was analyzed by electron microprobe, crystal N.2 was analyzed by Mössbauer spectroscopy, and crystal N.14 was used for the annealing experiment.

A small chip (0.10 g) from the pyroxenite sample TS7 from Theo's Flow obtained at location 85 m below the cooling surface of the 120-m-thick lava flow (Ontario, Canada; Pyke et al. 1973) was provided by A. H. Treiman. Two pyroxene crystals, labelled TS7 N.1 and N.2 were carefully selected for high-resolution X-ray single crystal diffraction analysis. The same crystals were then analyzed by EMPA.

2.2 X-ray single-crystal diffraction and structure refinement

Intensity data were collected on a three-circle Bruker AXS SMART APEX diffractometer, equipped with a CCD detector (graphite-monochromatized MoK α radiation, $\lambda = 0.71073$ Å, 55 kV, 30 mA). Because of their small size, a MonoCap collimator was used to collect the data on the crystals from MIL 03346. The Bruker SMART software (Bruker-AXS ©) package was used. A total of 9000 frames (frame resolution 512×512 pixels) were collected with ten different goniometer settings using the ω -scan mode (scan width: $0.2^\circ \omega$; exposure time: 10-20 s-frame⁻¹ depending on size of the crystals; detector-sample distance: 5.02 cm). About 13900 reflections were collected for each crystal. A completeness of $\sim 99\%$ on the measured data was achieved up to $\theta = 55^\circ$. The Bruker SAINT+ software v6.45A (Bruker-AXS ©) was used for data reduction, including intensity integration and background and Lorentz-polarization corrections. The semi-empirical absorption correction of Blessing (1995), based on the determination of transmission factors for equivalent reflections, was applied using the program SADABS (Sheldrick 1996) and the monoclinic Laue group $2/m$. The unit-cell parameters of the five crystals, obtained by a least-squares procedure that refines the position of about 7000 reflections in the range $6 - 110^\circ 2\theta$, are reported in Table 1. In the same table the value of the discrepancy factor R_{int} calculated from the average of the $[F_o]^2$ values of equivalent pairs in $2/m$ Laue symmetry is also reported. The observed F_o^2 values were then treated with a full-matrix least-squares refinement in the $C2/c$ space group by SHELX-97 (Sheldrick 2008) starting from the atomic coordinates reported by Brizi et al. (2000) for sample FON39, excluding their $M21$ site. Individual weights and the weighting scheme suggested by the program were used. The extinction correction was applied with the procedures of program SHELX-97. The structure refinement of the data obtained from pyroxene crystals from samples MIL 03346 and TS7 showed two significant residual electron-density maxima in the difference-Fourier map: the first maxima of $14.6 \text{ e}\text{\AA}^{-3}$ and $13.3 \text{ e}\text{\AA}^{-3}$ for samples MIL 03346 and

TS7, respectively, were located at $\sim 0.46 \text{ \AA}$ from the *M2* site; the second maxima of $2.2 \text{ e\AA}^{-3}$ and $2.0 \text{ e\AA}^{-3}$ for samples MIL 03346 and TS7, respectively, were located at about $0.44 \text{ \AA}$ from the O2 site. The first feature had been already observed by Rossi et al. (1987), and was added to the model as a split position (*M21*), with the atomic coordinates of the residual (ca. $x = 0$, $y = 0.26$, $z = \frac{1}{2}$). The second feature, although already observed by Rossi et al. (1987) but not included in their model, was therefore considered and added to our model as the O2B split position with atomic coordinates of the residual (ca. $x = 0.38$, $y = 0.24$, $z = 0.37$). Both split positions (*M21* and O2B) were refined with isotropic displacement parameters for MIL 03346, whilst for TS7 only the split position of the *M21* site was refined with isotropic displacement parameters. The occupancies of both split positions were constrained to sum to 1 with the occupancies of their relative atom non-split positions. Structure refinements carried out with the split model produced an improvement in the agreement factor with respect to the non-split model. In addition, the occupancy at the split oxygen site was equivalent to the occupancy at the *M21* site, confirming the robustness of the model. The atomic scattering curves were taken from the *International Tables for X-ray Crystallography* (Ibers and Hamilton 1970). Neutral vs. ionized scattering factors were refined in all sites that are not involved in chemical substitutions (Hawthorne et al. 1995) and complete ionization was assumed for Mg and Fe in *M1* site, for Ca and Mg in *M2* site and for Fe in *M21* site. At convergence of the model and before applying chemical constraints, the site occupancies refined for the O2B1 site were 0.152(9) and 0.13(1) for sample MIL 03346 and TS7, respectively, whilst occupancies refined for the *M21* site were 0.177(2) and 0.129(2) for sample MIL 03346 and TS7, respectively. This result suggests the presence of $\sim 15\%$ and 13% of local configurations for the MIL 03346 and TS7 samples, respectively, with the cation at the *M21* site bonded to the oxygen at the O2B1 position. Following Rossi et al. (1987) the splitting of the underbonded O2

oxygen shifting towards the small divalent cation at the *M21* site would improve the charge balance of this oxygen atom. The unit-cell parameters and information on the data collection and structure refinements are reported in Table 1. This table also reports the mean atomic numbers (m.a.n.) in electrons per formula unit (e.p.f.u.) at the *M1* and (*M2* + *M21*) sites obtained when the structure refinement reached convergence, before introducing the chemical constraints.

2.3 Electron microprobe analysis

After SC-XRD study the crystals MIL 03346 N.1 and TS7 N.1 and N.2 were embedded in epoxy and polished for electron microprobe analysis. A Cameca-SX50 electron microprobe with a fine-focused beam (1 μm diameter) operating in the wavelength-dispersive (WDS) mode was used. Operating conditions were 15 kV accelerating voltage and 15 nA beam current; counting times were 20 s at the peak and 20 s at the background. The following synthetic end-member mineral standards were used: diopside for Mg, ferrosilite for Fe, wollastonite for Si and Ca, chromite for Cr, corundum for Al, MnTiO_3 for Mn and Ti, and a natural albite (Amelia albite) for Na. X-ray counts were converted into oxide weight percentages using the PAP correction program (as in Fioretti et al. 2007). Analyses are precise to within 1% for major elements and 3-5% for minor elements. The results of the chemical analysis are reported in Table 2. The crystal chemical formula was calculated on the basis of six oxygen atoms, following Papike (1969). Only those spot analyses with total cation contents of 4.000 ± 0.005 atoms on the basis of six oxygen atoms and charge balance $3^{[4]}\text{Al} + \text{Na} - 3^{[6]}\text{Al} - 4\text{Ti} - 3\text{Cr} - 3\text{Fe}^{3+} \leq |0.005|$ were selected and averaged. The Fe^{3+} content was calculated by stoichiometry following Droop (1987).

For sample MIL 03346 the clinopyroxene core composition is similar to that reported by Dyar et al. (2005). Calculation of its crystal-chemical formula after Papike et al. (1974) provides for sample N.1 a Fe^{3+} content of 0.022(1) atoms per formula unit (Table 2), corresponding to $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of 4.7 %. Table 2 also reports the calculated total mean atomic number for the *M1* and *M2* sites, in electrons per formula unit, for the analyzed crystal. The value of 37.09(14) e.p.f.u. calculated from the analysis of crystal MIL 03346 N.1 is in very good agreement with the sum of the observed m.a.n.s for the *M1* and *M2* sites obtained from the structure refinement, before introducing chemical constraints, i.e. 37.09(5), 37.03(7) and 37.07(6) e.p.f.u. for crystals N.1, N.2, and N.14, respectively (see Table 1).

For sample TS7 the values of 33.56(10) and 33.62(14) e.p.f.u. obtained for crystals TS7 N.1 and TS7 N.2, respectively, are in good agreement with those of 33.39(6) and 33.57(6) calculated from the refinement without chemical constraints.

2.4 Mössbauer analysis

Room temperature Mössbauer spectra were collected for the single crystal MIL 03346 N.2 using a conventional transmission Mössbauer spectrometer fitted with a point source at the Bayerisches Geoinstitut in Bayreuth. While determination of Fe^{3+} concentration from relative areas is straightforward in polycrystalline samples because the areas of component doublets can be assumed to be equal, it is more challenging for single crystals because the component doublet areas are orientation dependent. We, therefore, recorded Mössbauer spectra of the crystal at two different orientations (see Fig. 1) and fitted the spectra simultaneously with the hyperfine parameters of each subspectrum (center shift, quadrupole splitting, line width) constrained to be

equal between different orientations. In addition, the ratio of component areas for Fe^{2+} in each site ($M1$ and $M2$) were constrained to be equal. In this way we were able to extract a robust determination of $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ of 7%, with an estimated uncertainty of plus or minus 5%.

2.5 Annealing experiment

For the annealing experiment at 600°C, crystal N.14 was sealed into a silica vial, after alternate flushing with nitrogen and evacuating, together with an iron-wüstite buffer to control the oxygen fugacity $f\text{O}_2$. Inside the silica tube, the crystal and the buffer were placed into two small separate Pt crucibles to avoid contact between them. Heating experiments were terminated by quenching after 2 weeks by dropping the tubes into cold water. Further details on the annealing protocol used are given in Alvaro et al. 2011). HR-SC-XRD data were collected on crystal N.14 before and after the annealing experiment following the same procedure used for collecting data on all the other samples of this study (see above section 2.2).

2.6 Determination of the Fe^{2+} -Mg ordering state

To obtain the pyroxene site distribution, full-matrix least-squares refinements were carried out using the chemical constraints taken from the microprobe analysis, assuming 1σ as the error. For crystals MIL 03346 N.2 and N.14 the microprobe analysis of crystal N.1 was used. For crystal N.2 we found the calculated Fe^{3+} site occupancy at the $M1$ site, i.e. 0.025 a.p.f.u., to be in good agreement with that measured by Mössbauer spectroscopy. The final least-squares

refinements were then performed using the chemical constraints and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ taken from the Mössbauer analysis, and yielded the same agreement factors reported in Table 1.

For both MIL 03346 and TS7 crystals the following constraints were also introduced into the refinement:

- i) all structural sites were considered fully occupied;
- ii) Al was distributed between the *T* and *M1* sites;
- iii) Fe^{3+} , Cr^{3+} and Ti^{4+} were considered fully ordered at the *M1* site;
- iv) Mg and Fe^{2+} were allowed to fractionate between the *M1* and *M2*, *M21* sites and Mn partitioned in the same way as Fe^{2+} (Hawthorne and Ito 1978);
- v) Ca and Na were assumed to occupy the *M2* site;
- vi) the charge balance equation for isomorphous replacements was taken to be

$$X_{[6]_{\text{Al}}} + 2X_{\text{Ti}^{4+}} + X_{\text{Cr}} + X_{\text{Fe}^{3+}} = X_{\text{Na}} + X_{[4]_{\text{Al}}}$$

The discrepancy indices R_{all} and R_{w} based on all the F_o^2 , the goodness of fit (S), and the observed mean bond distances for the *M1* and *M2* sites (<M1-O> and <M2-O>) are reported in Table 1. The site populations are reported in Table 3. The positional and atomic displacement parameters are reported in Table 4, and lists of the observed and calculated structure factors are available as Electronic Annexes.

The Fe^{2+} -Mg ordering state was estimated by means of the intracrystalline distribution coefficient k_{D} , using the same expression adopted by Brizi et al. (2000), as follows:

$k_{\text{D}} = [(\text{Fe}^{2+}_{\text{M1}})(\text{Mg}_{\text{M2}})/(\text{Fe}^{2+}_{\text{M2}})(\text{Mg}_{\text{M1}})]$. The k_{D} values are reported in Table 3. For the three MIL 03346 crystals k_{D} ranges from 0.028(5) to 0.034(5), whereas for the two TS7 crystals k_{D} values are 0.052(4) and 0.048(3) for TS7 N.1 and N.2, respectively.

3. RESULTS AND DISCUSSION

Mössbauer analyses on a clinopyroxene separate from MIL03346 (Dyar et al. 2005) yielded a $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratio of 24%. Because clinopyroxene in MIL03346 is significantly zoned and the analyses by Dyar et al. (2005) were performed on a separate, we could not use this result to constrain the Fe^{3+} site occupancy at the *M1* site. Therefore, we carried out a Mössbauer investigation on the core single-crystal MIL 03346 N.2. Results of our Mössbauer measurement yielded a $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ of $7 \pm 5\%$, which is in agreement with the EMP analysis carried out in the present study on the same crystal. The corresponding Fe^{3+} content in the clinopyroxene formula, i.e. 0.033(23) a.p.f.u., is about five times lower than that measured by Dyar et al. (2005) on clinopyroxene separates, suggesting a significant increase of the Fe^{3+} proportion from core to rim, possibly reflecting increasing oxygen fugacity during pyroxene crystallization.

Oxygen fugacity ($f\text{O}_2$) recorded in nakhlites ranges from IW+1.1 (NWA 998) to IW+3.2 (MIL 03346) (McCanta et al. 2009; Righter et al. 2008, and references therein). Using the relation between Fe^{3+} content in clinopyroxene and $f\text{O}_2$ of the crystallizing magma proposed by McCanta et al. 2004), Dyar et al. (2005) derived a crystallization $f\text{O}_2$ of IW+5 (QFM+1.5) from the clinopyroxene separate. Using the same method we derived a crystallization $f\text{O}_2$ of IW+2.65 for the MIL 03346 clinopyroxene core, with an approximate error of +0.8 / -1.1 graphically estimated taking into account only the $\pm 5\%$ uncertainty of the Mössbauer measurement (Fig. 2). This result is significantly lower than the crystallization $f\text{O}_2$ obtained from the MIL 03346 clinopyroxene separate, and also lower than, although within error with, the crystallization $f\text{O}_2$ of IW + 3.2 (± 0.6) value derived from Eu-oxybarometer in MIL 03346 (McCanta et al. 2009).

Our result is very similar to fO_2 values reported for the Governador Valadares and Lafayette nakhlites (McCanta et al. 2009).

These data together all indicate that the earliest fO_2 crystallization conditions of MIL 03346 were within the same crystallization range of most of the other nakhlites, and less oxidizing than previously reported (McCanta et al. 2009 and references therein). The difference observed between fO_2 estimated from our new data on a crystal core and that estimated from bulk clinopyroxene (Dyar et al. 2005), if confirmed, would be consistent with magma oxidation during crystallization, similarly to what was reported for LAK 06319 shergottite (Peslier et al. 2010).

The closure temperature T_c of the Fe^{2+} -Mg ordering process was calculated for all crystals using the following equation:

$$T(K) = [12100(750) - 27700(1700) (Ca+Na+R^{3+}) + 20400(1000) (Ca+Na+R^{3+})^2] / [-\ln k_D + 7.1(0.6) - 20.3(1.4) (Ca+Na+R^{3+}) + 15.2(0.8) (Ca+Na+R^{3+})^2] \quad (1)$$

obtained by Brizi et al. (2000) from three geothermometric equations experimentally determined on three terrestrial augite natural volcanic samples with compositions (En₃₆Fs₂₇Wo₃₇), (En₄₆Fs₁₁Wo₄₃), and (En₄₂Fs₁₂Wo₄₆). These crystals were annealed until equilibrium was reached in a temperature range between 700 and 1100 °C through both disordering and ordering experiments, and the Fe^{2+} -Mg order degree was measured by single-crystal XRD. Equation (1) allows to take into account the effects of trivalent cations R^{3+} and (Ca+Na) on the geothermometric calibration of the Mg/ Fe^{2+} ratio. The T_c values for the samples of our study were calculated using the abovementioned equation (1) and are

reported in Table 3. The errors on k_D were calculated by standard error propagation, whilst the errors on the T_c were estimated on the basis of 99% confidence from the error of k_D (i.e., 3σ of k_D). It is then apparent that even for the most pessimistic estimation for which T_c ranges between 469(91) and 500(76) °C for MIL 03346 and between 617(45)°C and 604(39) for TS7, the temperatures estimated for each sample are still different within errors.

The observed differences of the σk_D can be explained on the basis of the particular compositions of the augites, which have $M2$ site mainly occupied by Ca. As already discussed in the "X-ray single-crystal diffraction and structure refinement" section 2.2 above, in MIL 03346 augite the $M2$ site population is obtained by combining the anisotropic refinement of a non-split $M2$ position (occupied by Ca, Mg, Mn and Na) with the isotropic refinement of a $M21$ split position (occupied by Fe). In the presence of very low Mg contents at $M2$ site (~ 0.015 a.p.f.u.), as in MIL 03346 crystals, the uncertainty in the Fe site occupancy determination, through the isotropic refinement of the $M21$ split position, can strongly affect the evaluation of k_D . Otherwise for TS7 the $M2$ site population is obtained by combining the anisotropic refinement of a non-split $M2$ position (with Ca, Mn, Na; without Mg) with the isotropic refinement of a $M21$ split position occupied by both Fe and Mg. In fact, whilst for TS7 the observed atomic fraction of Mg at the $M2$ sites is 22 times the observed error, for MIL 03346 it is just 4 times. The structural refinement data for two MIL 03346 clinopyroxenes by Righter et al. (2008) support this observation.

The closure temperature of the ordering process depends both on the kinetics of the Fe^{2+} -Mg exchange reaction and on the cooling rate of the host rock. The comparison of T_c values of different samples allows the retrieval of information on the relevant rate at which the samples cooled: lower T_c would correspond to slower cooling rates. Therefore, the T_c value

of ≈ 500 °C measured on MIL 03346 augite core-crystals together with $T_c \sim 600$ °C measured on TS7 augite using the same geothermometer allows a reconsideration of the previous interpretations given in the literature for the thermal history of nakhlite rocks.

Lenaz and Princivalle (2007) reported clinopyroxene T_c values in the range from 555 to 673 °C for rocks crystallized at pressures from about 4.5 to 1.5 kbar, and T_c in the range of 602 to 700 °C for samples crystallized at shallower depth, at pressures below 1 kbar. Malgarotto et al. 1993 reported T_c of 850°C at the margins and 630°C close to the middle section of a 2.8-m-thick andesitic dyke on Alicudi (Aeolian Islands, Sicily) that allowed a calculation of the cooling rates across the dyke section: from 8 and 34°C/h near the boundaries to 1°C/h in the middle. The T_c of ~ 611 °C measured on TS7 augite from Theo's flow is consistent with its stratigraphic position, at 85 m below the top, and with data from analogous geological settings reported in the literature (Friedman et al. 1995; Lentz et al. 1999).

The $T_c \approx 500$ °C value obtained from MIL 03346 augite indicates that this sample experienced a cooling rate at about the T_c that is slower than that of the Theo's flow TS7 sample, and therefore appears inconsistent with the petrographic and mineralogical evidence of fast cooling.

It is important to emphasise that petrographic texture necessarily provides an indication of the cooling rate at temperatures above (or near) the solidus, i.e., $> 950^\circ\text{C}$ (Sautter et al. 2012). Likewise, the fast cooling rate retrieved from Ca and Mg-Fe zoning in olivine applies to the cooling rate experienced above ~ 700 °C (Mikouchi and Miyamoto 2002), and the closure temperatures of the Fe,Ti-oxides (Szymanski et al. 2010) provide information on the equilibration at temperatures above 600° (Ghiorso and Sack 1991).

The intracrystalline Fe²⁺-Mg partitioning between the *M1* and *M2* sites in pyroxene can proceed well below these temperatures. The degree of Fe²⁺-Mg order achieved provides information on the cooling rate at temperature near the T_c and is, therefore, unique in detecting thermal events at temperatures where most inter-crystalline thermometers are no longer sensitive.

The results of the annealing experiment (see Table 5) showed that after 2 weeks at 600°C the Fe²⁺-Mg order degree remained practically unchanged, as is evident from the comparison of the k_D values before and after heating of crystal N.14 [0.028(5) and 0.031(6), respectively]. In terms of T_c , this proves that the actual closure temperature for the MIL 03346 sample should be very close to 600°C and that the T_c value calculated using the equation by Brizi et al. (2000) could be underestimated by ~ 100°C. This inconsistency appears to suggest that the Brizi et al. (2000) equations cannot fully account for the dependence of the geothermometer on compositional and/or other thermodynamic parameters and calls for further investigation (work in progress). The low T_c value recorded by MIL 03346 clinopyroxene suggests that, following the initial fast cooling documented by petrographic texture and mineral geothermometers, an event occurred that either slowed down the ongoing cooling or caused a reheating at temperatures higher than the clinopyroxene T_c , followed by a relatively slow cooling. Thermochronologic studies show that, since they formed, nakhlites were never reheated to more than 350° (Shuster and Weiss 2005) and MIL 03346 experienced no significant shock heating (Cassata et al. 2010). Taken together, these data appear to indicate that MIL 03346 experienced variable cooling rates during and after its solidification, and exclude the possibility that the rock was reheated after its cooling. Therefore, a possible scenario to account for a fast cooling rate at high

temperature, followed by a much slower rate at around 500 °C, is that, while still cooling, additional lava flowed on top of the nakhlite pile, blanketing the whole sequence and delaying heat dispersion. Repeated emplacement of magma in a cooling sill would have the same effect.

The occurrence of a secondary thermal event in the history of nakhlites has been recently proposed (Korochantseva et al. 2011) based on ^{40}Ar - ^{39}Ar dating of mineral separates from Lafayette. According to these authors, an “unspecified secondary medium-grade, protracted thermal event” would be responsible for complications in radiometric chronological studies of many nakhlites, often ascribed to weathering effects.

The low T_c ($\approx 500^\circ\text{C}$) recorded by MIL 03346 would confirm the Korochantseva et al. (2011) observation, suggesting that the thick nakhlite sequence may be the result of repeated episodes of magma emplacement in a restricted time interval.

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FIGURES & TABLES

Fig. 1. Room temperature Mössbauer spectra collected at two different orientations (a and b) of the single crystal MIL03346 N.2. The relative Fe^{3+} concentration was uniquely determined by simultaneous fitting the two spectra assuming equal hyperfine parameters (center shift,

quadrupole splitting, line width) between each spectrum. Fe^{3+} absorption is shaded red, Fe^{2+} absorption is outlined in blue, and the residual is shown in purple.

Fig. 2. Diagram of variation of augite Fe^{3+} content with experimental f_{O_2} (triangles) and best-fit line redrawn from McCanta et al. (2004). The 7% ferric iron content of the clinopyroxene (cpx) core from MIL 03346 (full star) corresponds to a f_{O_2} of $\text{IW} + 2.65$. Error bar in the Mössbauer measurement is 5% (absolute); the horizontal error bar represents the respective variation in f_{O_2} . Ferric iron content of bulk cpx separate and corresponding f_{O_2} (empty star) is from Dyar et al. (2005). The f_{O_2} value of $\text{IW} + 3.2 (\pm 0.6)$, calculated using the Eu-Oxybarometer on MIL 03346 cpx core (McCanta et al., 2009), is reported at the bottom of the diagram.

Table 1. Unit cell parameters and information on data collection and structure refinement.

	Cpx MIL 03346 N.1		Cpx MIL 03346 N.2		Cpx MIL 03346 N.14		Cpx TS7 N.1		Cpx TS7 N.2	
Size (mm) of the crystal	0.090	x	0.080	x	0.150	x	0.140	x	0.090	x
	0.100	x	0.120	x	0.110	x	0.150	x	0.150	x
	0.125		0.170		0.090		0.300,		0.350	
<i>a</i> (Å)	9.7502(5)		9.7528(4)		9.7537(5)		9.7373(4)		9.7388(3)	
<i>b</i> (Å)	8.9430(5)		8.9423(4)		8.9444(5)		8.9194(4)		8.9178(3)	
<i>c</i> (Å)	5.2487(3)		5.2510(2)		5.2508(3)		5.2522(2)		5.2502(2)	
β (°)	106.207(2)		106.244(1)		106.196(2)		106.265(1)		106.252(1)	
<i>V</i> (Å ³)	439.48(6)		439.68(4)		439.90(4)		437.92(4)		437.75(4)	
<i>I</i> _{ind.}	2695		2769		2727		2741		2741	
<i>R</i> _{int} (%)	1.28		1.81		1.78		1.39		1.45	
<i>R</i> _{all} (%)	2.26		3.22		3.28		2.78		2.58	
<i>R</i> _w (%)	5.02		7.27		8.33		6.08		5.76	
<i>S</i>	1.036		1.244		1.076		1.266		1.284	
m.a.n. M1	16.19(2)		16.18(3)		16.19(2)		13.57(3)		13.70(3)	
m.a.n. (M2+M21)	20.90(4)		20.85(6)		20.88(5)		19.82(5)		19.87(5)	
m.a.n. (M1+M2+M21)	37.09(5)		37.03(7)		37.07(6)		33.39(6)		33.57(6)	

Note: Standard deviations are given in parentheses. *I*_{ind} is the number of independent reflections used for structure refinement; $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$ where *F*_o and *F*_c are the observed and calculated structure factors; $R_{\text{all}} = \sum |F_o^2 - F_c^2| / \sum [F_o^2]$; $R_w = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $S = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{0.5}$, where *n* is the number of reflections and *p* is the total number of parameters refined; m.a.n. is the mean atomic number (in electrons per formula unit) before introducing the chemical constraints.

Table 2. Electron microprobe analysis and formula in atoms per formula unit (apfu) based on six oxygen atoms.

	Cpx MIL 03346 N.1 (averaged spots 10)	Cpx TS7 N.1	Cpx TS7 N.2
wt %			
SiO ₂	52.15(24)	53.27(29)	53.22(21)
TiO ₂	0.30(2)	0.28(3)	0.26(3)
Al ₂ O ₃	0.90(3)	1.18(17)	1.13(20)
Cr ₂ O ₃	0.24(5)	0.42(10)	0.33(14)
FeO	14.80(34)	6.45(51)	6.42(37)
MnO	0.43(5)	0.18(3)	0.17(3)
MgO	12.48(9)	17.30(26)	17.56(26)
CaO	19.27(15)	20.70(62)	20.84(41)
Na ₂ O	0.25(3)	0.19(2)	0.19(3)
K ₂ O	0.01(1)	0.00(0)	0.00(0)
Total	100.82(40)	99.95(30)	100.12(25)
a.p.f.u.			
Si	1.966(7)	1.954(7)	1.948(5)
Ti	0.008(1)	0.008(1)	0.007(1)
Al	0.040(1)	0.051(7)	0.049(9)
Cr	0.007(2)	0.012(3)	0.010(4)
Fe ²⁺	0.444(9)	0.169(19)	0.158(8)
Fe ³⁺	0.022(1)	0.029(11)	0.038(6)
Mn	0.014(2)	0.006(1)	0.005(1)
Mg	0.701(4)	0.946(14)	0.958(14)
Ca	0.778(6)	0.813(24)	0.817(16)
Na	0.018(2)	0.014(2)	0.014(2)
K	0.000(4)	0.000(0)	0.000(0)
Total	4.000(2)	4.000(4)	4.004(3)
m.a.n.*	37.09(14)	33.56(10)	33.62(14)

m.a.n.*: calculated total mean atomic number for M1 and M2 sites, in electrons per formula unit. Standard deviations are given in parentheses.

Table 3. Site populations obtained from structure refinements using chemical constraints.

Site		Cpx MIL 03346 N.1	Cpx MIL 03346 N.2*	Cpx MIL 03346 N.14*	TS7 N.1	TS7 N.2
<i>T</i>	Si	1.964	1.964	1.964	1.952	1.948
	Al	0.036	0.036	0.036	0.048	0.052
<i>M1</i>	Mg	0.687(3)	0.689(3)	0.688(3)	0.877(3)	0.874(2)
	Fe	0.257(3)	0.255(4)	0.256(4)	0.065(4)	0.064(3)
	Fe ³⁺	0.024	0.025	0.026	0.032	0.043
	Al	0.009	0.007	0.007	0.004	0
	Cr	0.007	0.007	0.007	0.011	0.01
	Ti	0.008	0.008	0.008	0.008	0.007
	Mn	0.008	0.008	0.008	0.002	0.002
<i>M2</i>	Mg	0.018(3)	0.015(3)	0.015(3)	0.068(3)	0.066(3)
	Fe	0.192(3)	0.192(3)	0.191(4)	0.098(2)	0.101(2)
	Ca	0.764	0.767	0.768	0.815	0.814
	Mn	0.006	0.006	0.006	0.004	0.004
	Na	0.020	0.020	0.020	0.015	0.016
	<i>k_D</i>	0.034(5)	0.029(6)	0.028(5)	0.052(4)	0.048(3)
	<i>R³⁺</i>	0.048	0.048	0.047	0.055	0.060
Ca + Na		0.784	0.787	0.788	0.830	0.829
<i>T_c</i> (°C)		500 (76)	472(91)	469(91)	617(45)	604(39)

Note: $k_D = [(Fe^{2+}_{M1})(Mg_{M2})/(Fe^{2+}_{M2})(Mg_{M1})]$, $R^{3+} = Fe^{3+} + Al + Cr + Ti$. The site occupancy values represent atoms per six oxygen atoms. *Site population obtained by using the average microprobe analysis of crystal N.1

Table 4. Fractional atomic coordinates, equivalent isotropic displacement parameters, and anisotropic displacement parameters ($\text{\AA}^2$) of crystals MIL 03346 N.1, N.2, N.14 (natural and heated) and TS7 N.1 and TS7 N.2.

N.1 MIL 03346 N.1	x/a	y/b	z/c	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
T	0.2886(1)	0.0922(1)	0.2343(1)	0.006(1)	0.006(1)	0.006(1)	0.007(1)	- 0.001(1)	0.003(1)	-0.001(1)
O1	0.1173(1)	0.0879(1)	0.1448(1)	0.008(1)	0.006(1)	0.010(1)	0.008(1)	0.000(1)	0.002(1)	0.001(1)
O2	0.3616(1)	0.2498(1)	0.3208(1)	0.009(1)	0.011(1)	0.007(1)	0.010(1)	- 0.001(1)	0.003(1)	-0.003(1)
O2B	0.3805(3)	0.2380(3)	0.3728(6)	0.008(1)						
O3	0.3512(1)	0.0196(1)	- 0.0022(1)	0.010(1)	0.007(1)	0.014(1)	0.008(1)	- 0.003(1)	0.002(1)	0.000(1)
M1	0	0.9067(1)	1/2	0.007(1)	0.007(1)	0.007(1)	0.006(1)	0	0.002(1)	0
M2	0	0.3003(1)	1/2	0.009(1)	0.011(1)	0.008(1)	0.007(1)	0	0.000(1)	0
M21	0	0.2636(2)	1/2	0.010(1)						
N.2 MIL 03346 N.2										
T	0.2886(1)	0.0922(1)	0.2344(1)	0.006(1)	0.006(1)	0.006(1)	0.007(1)	- 0.001(1)	0.003(1)	-0.001(1)
O1	0.1173(1)	0.0878(1)	0.1449(1)	0.008(1)	0.006(1)	0.010(1)	0.009(1)	0.000(1)	0.003(1)	0.001(1)
O2	0.3615(1)	0.2498(1)	0.3209(4)	0.010(1)	0.011(1)	0.008(1)	0.010(1)	0.000(1)	0.003(1)	-0.003(1)
O2B	0.3812(4)	0.2381(4)	0.3733(8)	0.009(1)						
O3	0.3512(1)	0.0197(1)	- 0.0022(1)	0.010(1)	0.008(1)	0.015(1)	0.009(1)	- 0.004(1)	0.003(1)	0.000(1)
M1	0	0.9068(1)	1/2	0.007(1)	0.008(1)	0.007(1)	0.007(1)	0	0.002(1)	0
M2	0	0.3005(1)	1/2	0.009(1)	0.011(1)	0.007(1)	0.007(1)	0	0(1)	0
M21	0	0.2642(2)	1/2	0.011(1)						
N.14 MIL 03346 N.14										
T	0.2887(1)	0.0923(1)	0.2344(1)	0.008(1)	0.007(1)	0.007(1)	0.008(1)	- 0.001(1)	0.003(1)	-0.001
O1	0.1173(1)	0.0878(1)	0.1449(1)	0.010(1)	0.008(1)	0.011(1)	0.010(1)	0.001(1)	0.003(1)	0.001(1)
O2	0.3616(1)	0.2499(1)	0.3210(1)	0.011(1)	0.013(1)	0.008(1)	0.012(1)	- 0.003(1)	0.003(1)	-0.001(1)
O2B	0.3809(8)	0.2372(6)	0.3720(2)	0.010(1)						
O3	0.3512(1)	0.0196(1)	- 0.0021(1)	0.011(1)	0.009(1)	0.015(1)	0.009(1)	0.000(1)	0.003(1)	-0.003
M1	0	0.9067(1)	1/2	0.009(1)	0.009(1)	0.008(1)	0.008(1)	0	0.002(1)	0
M2	0	0.3003(1)	1/2	0.011(1)	0.012(1)	0.009(1)	0.009(1)	0	0.000(1)	0
M21	0	0.2640(1)	1/2	0.011(1)						
N.14 Heate d MIL 03346 N.14										
T	0.2887(1)	0.0923(1)	0.2344(1)	0.008(1)	0.008(1)	0.007(1)	0.009(1)	- 0.001(1)	0.003(1)	-0.001
O1	0.1173(1)	0.0879(1)	0.1448(1)	0.010(1)	0.008(1)	0.011(1)	0.010(1)	0.001(1)	0.003(1)	0.001(1)
O2	0.3616(1)	0.2498(1)	0.3207(1)	0.011(1)	0.013(1)	0.008(1)	0.012(1)	-	0.003(1)	-0.001(1)

								0.003(1)		
O2B	0.3809(8)	0.2374(6)	0.3720(2)	0.010(1)						
O3	0.3512(1)	0.0196(1)	-	0.011(1)	0.009(1)	0.015(1)	0.010(1)	0.000(1)	0.003(1)	-0.003
			0.0023(1)							
M1	0	0.9067(1)	1/2	0.008(1)	0.009(1)	0.008(1)	0.008(1)	0	0.002(1)	0
M2	0	0.3005(1)	1/2	0.011(1)	0.013(1)	0.008(1)	0.009(1)	0	0.000(1)	0
M21	0	0.2647(1)	1/2	0.011(1)						
<hr/>										
TS7										
N.1										
T	0.2880(1)	0.0927(1)	0.2330(1)	0.006(1)	0.006(1)	0.006(1)	0.007(1)	-	0.003(1)	0.000(1)
								0.001(1)		
O1	0.1165(1)	0.0878(1)	0.1432(1)	0.008(1)	0.006(1)	0.009(1)	0.008(1)	0.000(1)	0.002(1)	0.001(1)
O2	0.3614(1)	0.2502(1)	0.3198(1)	0.009(1)	0.011(1)	0.007(1)	0.009(1)	-	0.002(1)	-0.002(1)
								0.001(1)		
O2B	0.3804(1)	0.2416(1)	0.3719(1)	0.008(1)	0.007(1)	0.011(1)	0.006(1)	-	0.000(1)	-0.003(1)
								0.002(1)		
O3	0.3512(1)	0.0193(1)	-	10(1)	0.008(1)	0.013(9)	0.008(1)	-	0.002(1)	0.000(1)
			0.0027(1)					0.003(1)		
M1	0	0.9072(1)	1/2	0.007(1)	0.008(1)	0.007(1)	0.006(1)	0	0.002(1)	0
M2	0	0.3010(1)	1/2	0.009(1)	0.011(1)	0.007(1)	0.007(1)	0	0.000(1)	0
M21	0	0.2638(3)	1/2	0.011(1)						
<hr/>										
TS7										
N.2										
T	0.2880(1)	0.0927(1)	0.2330(1)	0.006(1)	0.006(1)	0.006(1)	0.007(1)	-	0.002(1)	0.000(1)
								0.001(1)		
O1	0.1165(1)	0.0877(1)	0.1432(1)	0.008(1)	0.006(1)	0.009(1)	0.008(1)	0.000(1)	0.002(1)	0.001(1)
O2	0.3613(1)	0.2501(1)	0.3195(1)	0.009(1)	11(1)	0.007(1)	0.009(1)	-	0.002(1)	-0.003(1)
								0.001(1)		
O2B	0.3793(1)	0.2418(1)	0.3706(1)	0.009(1)	0.009(1)	0.012(1)	0.006(1)	-	0.001(1)	-0.003(1)
								0.002(1)		
O3	0.3511(1)	0.0192(1)	-	0.010(1)	0.008(1)	0.013(1)	0.008(1)	-	0.002(1)	0.000(1)
			0.0027(1)					0.003(1)		
M1	0	0.9071(1)	1/2	0.007(1)	0.008(1)	0.007(1)	0.007(1)	0	0.002(1)	0
M2	0	0.3010(1)	1/2	0.009(1)	0.011(1)	0.007(1)	0.007(1)	0	0.000(1)	0
M21	0	0.2641(3)	1/2	0.011(1)						

The equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) are defined as one third of the trace of the orthogonalized U_{ij} tensor).
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$ (Sheldrick, 2008).

Table 5a. Unit cell parameters and information on data collection and structure refinement for crystal N.14 after 2 weeks annealing at 600°C

	Cpx MIL 03346 N.14 heated
Size (mm) of the crystal	0.150 x 0.110 x 0.090
a (Å)	9.7514(10)
b (Å)	8.9419(9)
c (Å)	5.2494(5)
β (°)	106.207(2)
V (Å ³)	439.48(6)
I_{ind}	2750
R_{int} (%)	1.86
R_{all} (%)	3.13
R_w (%)	8.07
S	1.10
m.a.n. M1	16.08(2)
m.a.n. (M2+M21)	20.78(4)
m.a.n. (M1+M2+M21)	36.86(5)

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

Table 5b. Site populations obtained from structure refinements using chemical constraints for crystal N.14 after 2 weeks annealing at 600°C.

Sit		Cpx MIL
		03346 N.14
<i>T</i>	Si	1.964
	Al	0.036
<i>M</i>	Mg	0.689(3)
	Fe	0.256(4)
	Fe ³⁺	0.023
	Al	0.009
	Cr	0.007
	Ti	0.008
	Mn	0.008
<i>M</i>	Mg	0.016(3)
	Fe	0.190(3)
	Ca	0.768
	Mn	0.006
	Na	0.020
	<i>k_D</i>	0.031(6)
	<i>R</i> ³⁺	0.047
	Ca + Na	0.788

Note: $k_D = \frac{[(Fe^{2+}_{M1})(Mg_{M2})/(Fe^{2+}_{M2})(Mg_{M1})]}{R^{3+}=Fe^{3+} + Al + Cr + Ti}$. The site occupancy values represent atoms per six oxygen atoms. *Site population obtained by using the average microprobe analysis of crystal N.1

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