

## COMPLEX COOLING HISTORIES OF LUNAR TROCTOLITE 76535 AND STILLWATER

**ORTHOPIYROXENITE SC-936** M. Chiara Domeneghetti<sup>(1)</sup>, I. S. McCallum<sup>(2)</sup>, J.M. Schwartz<sup>(2)</sup>, F. Camara<sup>(1)</sup>, M. Zema<sup>(3)</sup>, C. McCammon<sup>(4)</sup>, and J. Ganguly<sup>(5)</sup>, <sup>(1)</sup> Dipartimento di Scienze della Terra, Università di Pavia, 27100 Pavia, Italy, <sup>(2)</sup> Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, <sup>(3)</sup> Centro Grandi Strumenti, Università di Pavia, 27100 Pavia, Italy, <sup>(4)</sup> Bayrisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany, <sup>(5)</sup> Department of Geosciences, University of Arizona, Tucson, AZ 85721

**Introduction:** Data from the Clementine and Prospector missions have shown that a simple model of lunar crustal stratigraphy in which an upper crust of ferroan anorthosite is underlain by a noritic lower crust is inadequate. The Moon shows a strong asymmetry in crustal thickness, composition, and distribution of KREEP and mare basalt. Some asymmetry may be primary, some may be a consequence of impacts focused on the nearside that have redistributed the upper layers, and some may be related to mantle overturn. In an effort to reconstruct the primary lunar stratigraphy, we are examining mineral and rock fragments in a subset of relatively unshocked pristine crustal samples to deduce thermal histories from which we can compute depths of burial. In this study we have applied the “orthopyroxene chronometer” to calculate the cooling rate from the Fe-Mg ordering states of the orthopyroxene crystals [1, 8, 10].

Sample 76535 is a large, texturally and compositionally pristine, coarse-grained olivine-plagioclase cumulate that shows evidence of extensive annealing and recrystallization. The sample contains roughly equal modal volumes of olivine and plagioclase while orthopyroxene makes up ~4% of the rock. McCallum and Schwartz [2] have recently determined that this sample equilibrated at a depth of ~40 kilometers at T~800-900°C. Sample SC-936 (a pristine orthopyroxenite from the Stillwater Complex) was used as a control since it has virtually the same  $X_{Fe}$  and its thermal history is reasonably well known.

**Experimental and Analytical Methods:** Two orthopyroxene crystals from 76535 and one from SC-936 were studied by single crystal x-ray diffraction. Intensity data were collected up to  $2\theta = 70^\circ$  using a conventional Philips PW 1100 four-circle automated diffractometer using  $MoK_\alpha$  radiation. Since in all three crystals several ( $0kl$ ) reflections with  $k = 2n+1$  and  $l = 4n+2$ , “forbidden” in the  $Pbca$  space group, showed  $I > 3\sigma(I)$ , the structure refinements were done following the procedure of Domeneghetti et al. [3] for a  $Pbca$  phase coexisting with a  $C2/c$  exsolved phase. The calculated fraction of  $C2/c$  phase in opx was ~1% for 76535 and ~3% for SC-936, confirming that the violations of  $Pbca$  extinction conditions are due to (100) exsolved augite and not to a lower symmetry  $P2_1ca$  as Smyth [4] had suggested for sample 76535. The observed  $F_o^2$  values, “cleaned” of the contribution from

the augite, were then treated with a full-matrix least-squares refinement by SHELX-97 [5], using individual weights and, for every crystal, the weighting scheme suggested by the program.

To ensure high accuracy of the site occupancy determinations, the compositions of all x-rayed crystals were determined by averaging the results of a large number of electron probe spot analyses. To determine the statistically most probable composition, the average compositions were mathematically projected on to a surface that satisfies the crystal chemical constraints for orthopyroxene [1]. In the case of SC-936 special care was taken to analyze areas free from clinopyroxene lamellae.  $Fe^{3+}/Fe^T$  of orthopyroxene from 76535 and SC-936 were determined by Mössbauer analysis. Mössbauer spectra were recorded at room temperature in transmission mode on a constant acceleration spectrometer using a 10 mCi  $^{57}Co$  point source. Spectra were fitted using the NORMOS program.

Since Guinier-Preston Zones (GPZ) are known to occur in some natural orthopyroxenes [6], crystals from 76535 and SC-936 were examined by TEM on a JEOL 200 kV with  $LaB_6$  electron source equipped with an Oxford ISIS system for microanalysis. In  $b$ -axis images, all crystals show (100) augite exsolution lamellae and the ubiquitous presence of GPZ. In SC-936, GPZ are one opx  $a$ -lattice wide with a variable  $c$ -lattice length (~100nm) while in 76535 GPZ are several opx  $a$ -lattice wide and shorter along  $c$  with a characteristic oblique termination and strong strain contrast. High resolution TEM images show a slight  $a$ -lattice variation in the GPZ and microanalysis shows a higher Ca content in the GPZ ( $W_{O_{5\pm 1.5}}$ ). If the analysis is representative, GPZ represent a Ca-rich opx phase as previously suggested by Nord [6].

**Determination of site distribution:** The bulk compositions of the individual grains, together with their standard deviations, were used as linear restraints in the final least squares cycles of the structure refinement by SHELX-97. The M1 site population was then checked by comparing the value of the observed M1-O mean bond distance obtained by the structure refinement and that calculated by using equation (21) in Domeneghetti et al. [7]. For all three crystals the agreement was within the e.s.d.'s (0.001) (Table 1).

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Table 1. Site Occupancies, distribution coefficients and closure temperatures of orthopyroxenes

	$X_{Fe}(M1)$	$\sigma M1$	$X_{Fe}(M2)$	$\sigma M2$	$K_D$	$\sigma K_D$	$T_C(K)$	$T_C(^{\circ}C)$	$\sigma(T_C)$
76535-1 <sup>(1)</sup>	0.0152	0.0017	0.2171	0.0015	0.0557	0.0070	818	545	29
76535-1 <sup>(2)</sup>	0.0152	0.0017	0.2171	0.0015	0.0557	0.0070	818	545	29
76535-1 <sup>(3)</sup>	0.0119	0.0018	0.2191	0.0014	0.0430	0.0068	761	488	32
76535-2 <sup>(1)</sup>	0.0165	0.0018	0.2183	0.0015	0.0599	0.0074	835	562	30
76535-2 <sup>(2)</sup>	0.0165	0.0018	0.2183	0.0015	0.0599	0.0074	835	562	30
76535-2 <sup>(3)</sup>	0.0127	0.0019	0.2198	0.0014	0.0458	0.0071	774	501	33
SC-936-1 <sup>(1)</sup>	0.0073	0.0032	0.2954	0.0020	0.0176	0.0081	615	342	61
SC-936-1 <sup>(2)</sup>	0.0073	0.0032	0.2954	0.0020	0.0176	0.0081	615	342	61
SC-936-1 <sup>(3)</sup>	0.0065	0.0032	0.2968	0.0020	0.0155	0.0080	598	325	65

<sup>(1)</sup> Averaged    <sup>(2)</sup> Optimized    <sup>(3)</sup> with Ca reduction of 40%

**Results:** The site occupancy results yield  $\ln K_D$  values of  $-2.888$  and  $-2.815$  for 76535 crystals 1 and 2, respectively, and  $-4.040$  for SC-936 crystal, where  $K_D$  is defined as  $(Fe^*/Mg)_{M1}/(Fe^*/Mg)_{M2}$  with  $Fe^*=Fe^{2+}+Mn$  (Table 1). According to the calibration of Stimpfl et al. [1] for samples with  $X_{Fe^*} = 0.11-0.17$  the  $K_D$  values correspond to closure temperatures of cation ordering of  $545\pm 29^{\circ}C$  and  $562\pm 30^{\circ}C$  for the two orthopyroxenes from 76535 and  $342\pm 61^{\circ}C$  for the orthopyroxene from SC-936. The  $\ln K_D$  values obtained using the ‘‘Ca-reduced’’ compositions were  $-3.147$ ,  $-3.083$  for lunar orthopyroxene and  $-4.167$  for Stillwater orthopyroxene, giving lower  $T_C$  values of  $488\pm 32^{\circ}C$ ,  $501\pm 33^{\circ}C$  and  $325\pm 65^{\circ}C$ , respectively.

**Cooling Rates:** The cooling rates of the crystals were determined using the updated version of the program CRATE of Ganguly [10]. The lunar samples show a very rapid cooling rate,  $\sim 1$  to  $10^{\circ}C/yr$  near the  $T_C$ , corresponding to a burial depth of  $< 50$  m. On the other hand, the Stillwater orthopyroxene data give a cooling rate of  $\sim 2-50^{\circ}C/Ma$ , for  $fO_2 \sim QFM$  buffer, and  $(fO_2)^{1/6}$  dependence of the rate constant. The latter result is consistent with estimates of the cooling time for this mid-crustal terrestrial intrusion, confirming that the chronometer gives realistic cooling rates.

**Discussion:** Thermobarometric and textural studies of 76535 [2] clearly show this sample to be of plutonic origin, derived from the lower/middle lunar crust. How then to explain the apparent very rapid cooling around  $500^{\circ}C$ ? There are two possibilities: (1) The sample was rapidly heated to a temperature around  $600^{\circ}C$ , for a time insufficient to affect the intercrystalline equilibria to any significant degree but sufficient to disorder the Fe and Mg on the M1 and M2 sites. This heating was followed

by a rapid cooling to ambient lunar surface temperatures. This scenario is consistent with excavation of this sample by impact and deposition on the lunar surface in a hot ejecta blanket. (2) Alternatively, the sample may have been excavated from deep in the lunar crust by a basin-forming impact before the troctolites cooled to the  $T_C$  ( $\sim 500-550^{\circ}C$ ) of Fe-Mg ordering in orthopyroxene. This scenario is consistent with the observations [9] that the anti-phase domains formed in 76535 anorthite during the  $\bar{1}1$  to  $P\bar{1}$  transition are comparable in size ( $\sim 100$  nm) to those observed in rapidly cooled basalts. This model is also consistent with the ‘‘ages’’ of 76535. Sm-Nd, U-Pb and Pb-Pb ages of 4.26 Ga represent the time of closure of these systems, most likely when the sample was excavated. The Rb-Sr age of 4.51 Ga (based largely on inclusions in olivine) may represent the original crystallization age.

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**References:** [1] Stimpfl M et al. (1999) *CMP*, **136**, 297-309; [2] McCallum IS & Schwartz JM (2000) *JGR*, in review; [3] Domeneghetti MC et al. (1996) *Am. Min.*, **81**, 842-846; [4] Smyth JR (1975) *Geophys. Res. Lett.*, **1**, 27-29; [5] Sheldrick GM (1998) *Univ. of Gottingen, Germany*; [6] Nord GL (1980) *Phys. Chem. Min.*, **6**, 109-128; [7] Domeneghetti MC (1995) *Am. Min.*, **80**, 253-267; [8] Ganguly J (1982) *Adv. Phys. Geochem.*, **2**, 58-99; [9] Nord GL (1976) *PLSC 7<sup>th</sup>*, 1875-1888. (10) Ganguly J & Stimpfl M (2000) *GCA*, **64**, 1291-1297.