

Intracrystalline cation order in a lunar crustal troctolite

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Abstract—Lunar rock 76535 appears to be one of the most slowly cooled bits of silicate material yet studied. The crystal structures of its three major phases, anorthite, olivine, and bronzite have been refined from three-dimensional X-ray intensity data in order to characterize the well-equilibrated specimens of these minerals and to further characterize the thermal history of this rock. The structure of the anorthite has been refined from 9393 symmetry-independent intensities with a minimum R of 0.042. Direct site occupancy refinements of the A sites indicate significant ordering of Na and possibly of vacancy on the basis of $P\bar{1}$ symmetry which would require slow equilibration below 300°C. Two of the four A sites appear to each occupy nearly equally two distinct locations up to 0.2 Å apart indicating that the true local symmetry of each cell is $P1$ rather than $P\bar{1}$. The crystal structure of the olivine (FO_{88}) has been refined from 1101 symmetry independent intensity observations with a minimum R of 0.042. The Fe and Mg appear to be only slightly ordered ($K_D = 1.10$) as is consistent with terrestrial metamorphic olivines. The bronzite in this rock has previously been recognized as a new pyroxene polymorph, and refinement of its crystal structure indicates that the intensities of diffractions violating the b -glide can be accounted for by differences in the location and scattering power of two different M2 sites. It is inferred that the lower symmetry space group arises on slow cooling because of cation order on the basis of four distinct M sites instead of two as in $Pbca$. The degree of cation order in each of these three phases is consistent with extreme slow cooling without reheating above about 300°C.

I. INTRODUCTION

LUNAR SAMPLE # 76535 is a coarse-grained troctolitic granulite containing homogeneous crystals of plagioclase (58% An_{94}), olivine (37% FO_{88}) and bronzite (4% En_{86}). Chromian spinel-bronzite-diopside intergrowths occurring along olivine-plagioclase boundaries indicate an equilibration temperature of about 1000°C at 0.6-kbar pressure (Gooley *et al.*, 1974). These authors have inferred from the coarse grain size, annealed texture and the sharpness of X-ray diffractions in the plagioclase, that the rock has undergone extremely slow cooling, and they have estimated from the phase relations of accessory metal grains that the cooling rate was a few tens of degrees per million years. Smyth (1974) reported that the bronzite exhibits diffractions of a new lower symmetry space group, $P_{2_1}ca$, consistent with extremely slow cooling.

Trace-element studies (Haskin *et al.*, 1974) suggest a cumulate origin for this rock. Age dates of between 4.1 and 4.4 b.y. have been obtained for this rock (Bogard *et al.*, 1974; Huneke and Wasserburg, 1975; Hinthorne *et al.*, 1975). Stewart (1975) has inferred that this rock represents a cumulate formed during the original crystallization of the lunar crust and underwent reequilibration during the slow cooling of the primordial crust which he has termed the Apollonian metamorphic event. Because this sample appears to be one of the most slowly

cooled bits of silicate material yet studied, it provides a unique opportunity for the study of ordering processes in the minerals present. A better understanding of these processes may permit better characterization of the thermal history of this and similar rocks.

II. CATION ORDER IN ANORTHITE

Mineralogical background

Structural studies of plagioclase feldspars have been meticulously reviewed by Smith (1974). Briefly pure anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) has a 14-Å c -axis $P\bar{1}$ triclinic cell with a framework of alumino-silicate tetrahedra ordered such that no two tetrahedra containing Al are adjacent. Low albite ($\text{NaAlSi}_3\text{O}_8$) also has an ordered alumino-silicate framework, but the two ordering schemes are incompatible resulting in miscibility gaps at An_{2-16} , An_{47-58} , An_{67-88} characterized by coherent spinodal decomposition, but anorthites in the range An_{88-100} appear to be structurally homogeneous. Pure anorthite undergoes an apparent transformation from $P\bar{1}$ to $I\bar{1}$ at 300°C above which temperature the class c and d diffractions ($h + k$ odd; l even, and l odd) become extremely diffuse. Laves and Goldsmith (1954) observed that the relative difference of the c and d diffractions was related to cooling rate and also to Na content in the range An_{95-100} such that sharp c and d diffractions could not be obtained for compositions more sodic than An_{95} . There have been several refinements of the anorthite structure (Kempster *et al.*, 1962; Wainwright and Starkey, 1971; Czank *et al.*, 1973) but very little is known about how Na is taken into the 14-Å anorthite cell.

There have been numerous reports of chemical anomalies in lunar plagioclases (Weill *et al.*, 1970a,b; Drake *et al.*, 1970, 1971; Grieve *et al.*, 1972; Trzcieski and Kulick, 1972). Various mechanisms which may account for the observed anomalies were proposed and discussed in detail by Wenk and Wilde (1973).

The composition of 76535 plagioclase given in Table 1 was determined from the same crystal used for X-ray data collection. There is very little Fe and no detectable Mg in this plagioclase, and there appears to be a significant chemical anomaly consisting of a Na deficiency or Si excess, although it is smaller than those observed for volcanic lunar plagioclases. The An content calculated on the basis of the Al/Si ratio is An_{95} while that calculated on the basis of $\text{Ca}/(\text{Ca} + \text{Na} + \text{K})$ is An_{97} . Long exposure X-ray precession photographs show no evidence of shock, and all four classes of diffractions (a , b , c , and d) are present and of equal sharpness consistent with extremely slow cooling for a plagioclase of this composition (Laves and Goldsmith, 1954). Cell dimensions (Table 2) plot along the $\beta^*-\gamma^*$ curve for low plagioclase (Smith, 1972) at about An_{95} . A complete refinement of the crystal structure was undertaken in order to obtain better understanding of how Na is incorporated into a well-ordered 14-Å anorthite structure; of chemical anomalies in lunar plagioclases; and, hopefully, of the thermal history of the rock.

Table 1. Compositions of the major phases of rock 76535 reported in oxide weight percents and cations per 24 oxygens.

	Anorthite ^a	Olivine ^b	Bronzite ^b
SiO ₂	44.70	39.9	55.9
TiO ₂		0.03	0.4
Al ₂ O ₃	36.17		1.5
Cr ₂ O ₃		< 0.02	0.6
FeO	0.03	12.0	7.4
MnO		0.1	0.1
MgO		47.1	32.7
CaO	19.06	< 0.02	1.5
Na ₂ O	0.33		
K ₂ O	0.07		
Total	100.36	99.2	100.1
Si	6.160	5.966	7.782
Ti		0.004	0.042
Al	5.875		0.243
Cr		0.002	0.067
Fe	0.003	1.500	0.862
Mn		0.009	0.008
Mg		10.503	6.787
Ca	2.814	0.002	0.226
Na	0.087		
K	0.012		
Total	14.952	17.986	16.017

^aStandards used: Hakone volcanic anorthite (An₉₈); Hawk Mtn., N.C. oligoclase (An₃₁) and Itrongay orthoclase (Or₉₈). R. Gooley, analyst. Analysis from actual crystal and for data collection.

^bValues from Gooley *et al.* (1974).

Table 2. Space group and cell parameters of principal phases of lunar rock 76535.

	Anorthite	Olivine	Bronzite
<i>a</i> (Å)	8.173(2) ^a	4.761(2)	18.235(4)
<i>b</i> (Å)	12.858(3)	10.233(6)	8.831(2)
<i>c</i> (Å)	14.170(3)	5.990(4)	5.189(1)
α (°)	93°10'(1)		
β (°)	115°57'(1)		
γ (°)	91°13'(1)		
Vol.	1335.3(3)	291.8(2)	835.6(2)
Space Group	<i>P</i> $\bar{1}$	<i>Pbnm</i>	<i>P2₁ca</i>

^aFigures in parentheses are the estimated standard deviation in terms of the last decimal place cited. This convention is followed throughout this work.

Results and discussion

Because of space limitations and the potential significance for feldspar crystal chemistry in general, the full details of the anorthite refinement will be published separately. Briefly reviewed, the atomic coordinates of the T (Si and Al) and O sites are quite similar to those determined for anorthite (Megaw *et al.*, 1962, Wainwright and Starkey, 1971), however several distinctive types of cation order are evident. The Si–O distances do not differ appreciably from those obtained by previous workers and indicate very little occupancy of Al in the Si sites. Seven of the eight mean Al–O distances are all $1.738(3) \pm .002 \text{ \AA}$ except for Tl(0zi0) which is $1.757(3) \text{ \AA}$ indicating that the latter site is nearly completely occupied by Al while the other seven may contain up to 10% Si.

The A (Na and Ca) sites also exhibit a degree of order not previously reported. Site occupancy refinements of the A sites indicate that the A(000) and A(0i0) (related by *I*-centering operation in the high temperatures $I\bar{1}$ structure) show significantly less scattering power than do A(z00) and (zi0) which appear to be fully occupied by Ca. Of the two former sites which may contain Na, A(000) has a significantly larger total scattering power deficiency. The total scattering power deficiency (compared to full Ca occupancy) for these two sites appears to be too large to be accounted for by the amount of Na reported in the chemical analysis raising the possibility that there may be some vacancy in either of these two sites. Unfortunately, there are strong correlations between temperature factors and occupancy so it cannot be stated categorically that all vacancy occurs in A(000). But it can be stated that if vacancy does occur, it occurs in A(000) because the occupancies of these two sites differ by 10σ when modeled with Ca only.

An additional complexity to the anorthite structure was also observed in this refinement. Two of the A sites, A(000) and A(zi0), appear to each occupy two well-defined positions within the alumino-silicate framework, the occupancies of which are equal within two standard deviations. It is therefore possible that the true local symmetry of each cell is *P*1 rather than $P\bar{1}$.

The existence of Na ordering on the 14-Å anorthite cell was suggested by Wainwright and Starkey (1969) and has been confirmed in this anorthite. This raises some interesting possibilities for feldspar crystal chemistry. First, if Na has a strong site preference in the 14-Å cell, the amount of Na order–disorder may strongly affect the “handedness” of the $I\bar{1} \rightarrow P\bar{1}$ transition, hence control the *c*-domain size and relative diffuseness of the *c* and *d* diffractions. If Na ordering is the rate-controlling process for domain size development in anorthites An_{90} – An_{98} , it may be possible to estimate diffusion coefficients for Na from domain size determination as a function of temperature. In this anorthite, A(z00) and A(zi0) both appear to be completely occupied by Ca, and all Na appears to be in A(000) and A(0i0). This difference indicates Na ordering on the basis of $I\bar{1}$ symmetry. Unfortunately, it is difficult to estimate the relative amounts of Na in A(000) versus A(0i0) because of the possibility of A-site vacancy, however the two sites do appear to differ significantly in scattering power. Such a difference indicates an ordering on the basis of $P\bar{1}$ symmetry which is presumably only possible below 300°C when the *c* domains become fixed. Unfortunately too little

is known about Na diffusion in ordered versus disordered states of anorthite to make a precise estimate of the amount of time required to order Na below 300°C. However, judging from the structural similarity of the two sites, and the activation energy for Na diffusion in feldspar (0.7–0.9 eV; Maury, 1968) it seems unlikely that this rock was heated above 300°C since its original equilibration.

III. CATION ORDER IN OLIVINE

Mineralogical background

In the past few years, a considerable effort has been devoted to the study of iron–magnesium ordering in the olivines. Unfortunately, there has developed no clear relationship between cation ordering and temperature of equilibration as has been established for orthopyroxenes (Virgo and Hafner, 1969, 1970). The degree of ordering is much less than for the orthopyroxenes as has been evidenced by Mössbauer studies (Bush *et al.*, 1970; Virgo and Hafner, 1972; Shinno *et al.*, 1974). Recent crystallographic studies (Finger, 1970; Finger and Virgo, 1971; Brown and Prewitt, 1973; Smyth and Hazen, 1973; Smyth, 1975) indicate a general preference of Fe for the smaller, but more distorted, M1 site. However Shinno *et al.* (1974) report several specimens showing the reverse preference and indicate that the preference of Fe for M1 may increase with increasing temperature, Finger and Virgo (1971) find the greatest amount of order (57% of Fe in M1) in a lunar volcanic olivine, while more slowly cooled terrestrial metamorphic olivines (Brown and Prewitt, 1973; Smyth and Hazen, 1973) are essentially disordered. Brown and Prewitt (1973) suggest that the amount of ordering in olivines may increase with increasing temperature because of a greater increase in distortion in M1 than in M2 with increasing temperature. This effect is also seen as an increase in quadripole splitting of Fe²⁺ in the two M sites with increasing temperature (Eibschütz and Ganiel, 1967; Virgo and Hafner, 1972). Because lunar rock 76535 shows evidence for such extreme slow cooling and equilibration, the crystal structure of its olivine has been refined and its Fe/Mg ordering determined for comparison with other olivine structures.

Data collection and structure refinement

The composition of olivine from lunar sample 76535 was presented in Table 1. A single anhedral crystal fragment approximately 200 × 100 × 250 μm in size and free of visible inclusions was selected for study. The space group was determined to be *Pbnm* from long-exposure X-ray precession photography. The crystal was then mounted in the four-circle goniostat of a Picker FACS-1 automated diffractometer. Cell edges determined from least-squares refinement of the centering parameters of 12 strong diffractions with 2θ (MoKα) greater than 45° are presented in Table 2. Using monochromatized MoKα radiation and a constant 2θ scan rate of 0.5 degrees per minute, 1101 symmetry-independent X-ray intensities were measured automatically representing all intensities of 2θ less than 80°.

All intensities were corrected for Lorentz and polarization effects. Based on a

linear absorption coefficient of 22.14 cm^{-1} , transmission factors varying from 0.68 to 0.77 were calculated using a routine written by Burnham (1966). All observations were weighted according to $1/\sigma_F^2$, where σ_F is the estimated standard deviation (Burnham *et al.*, 1971). Intensities of less than 3σ were rejected from the normal equations matrix during all stages of refinement, leaving 845 intensities greater than 3σ . Atomic scattering factors calculated for fully ionized cations and O^{-1} from Hartree–Fock wave functions neglecting relativistic effects (Cromer and Mann, 1968), and real and imaginary anomalous dispersion terms (Cromer and Liberman, 1968) were used for all stages of refinement.

The initial structural model used atomic coordinates and equivalent isotropic thermal parameters for $\text{Fe}_{0.89}$ (Wenk and Raymond, 1973) and fully disordered Fe and Mg. Throughout refinement, the chemistry was constrained to that given in Table 1. Using a slightly modified version of RFINE (Finger and Prince, 1975), four cycles of refinement with isotropic thermal parameters followed by four cycles of refinement with anisotropic thermal parameters yielded a final weighted R of 0.042. Final positional, occupancy, and thermal parameters are presented in Table 3. Magnitude and orientation of thermal vibration ellipsoids are presented in Table 4. Cation–oxygen bond distances and selected bond angles are presented in Table 5.

Discussion

This olivine shows significantly less order of Fe and Mg ($K_D = 1.10$) than lunar and terrestrial volcanic olivines ($K_D = 1.15\text{--}1.75$, Finger and Virgo, 1971; Virgo and Hafner, 1972; Brown and Prewitt, 1973) and similar to terrestrial metamorphic olivines ($K_D = 1.02\text{--}1.13$, Brown and Prewitt, 1973; Finger, 1970; Smyth and Hazen, 1973). The amount of ordering in this specimen is consistent with slow cooling of rock 76535 without significant reheating. This assumes that ordering in

Table 3. Olivine: Occupancy, positional, and thermal parameters.

	M1	M2	Si	O1	O2	O3
Occ _(Mg)	0.851(2)	0.862(2)				
Occ _(Fe)	0.149(2)	0.137(2)				
X	0	0.9895(2)	0.4261(2)	0.7666(5)	0.2204(5)	0.2788(4)
Y	0	0.2779(1)	0.0942(1)	0.0916(3)	0.4478(3)	0.1626(2)
Z	0	1/4	1/4	1/4	1/4	0.0346(3)
β_{11}	0.0058(4)	0.0070(4)	0.0036(3)	0.0046(9)	0.0047(9)	0.0046(6)
β_{22}	0.00182(9)	0.00136(9)	0.00122(7)	0.0017(2)	0.0015(2)	0.0016(1)
β_{33}	0.0030(2)	0.0026(2)	0.0020(2)	0.0021(5)	0.0022(5)	0.0032(4)
β_{12}	0.0000(1)	0.0001(1)	0.0000(1)	0.0001(4)	0.0002(4)	0.0005(2)
β_{13}	0.0004(3)	0	0	0	0	0.0001(4)
β_{23}	0.0003(1)	0	0	0	0	0.0006(2)
Beq.	0.57	0.52	0.37	0.46	0.46	0.51

Table 4. Olivine: Magnitude and orientation of major axes of thermal vibration ellipsoids.

Atom	Axis	Ampl. (Å)	Angle (°) with			Atom	Axis	Ampl. (Å)	Angle (°) with		
			<i>a</i>	<i>b</i>	<i>c</i>				<i>a</i>	<i>b</i>	<i>c</i>
M1	1	0.071	72	79	21	01	1	0.061	90	90	0
	2	0.083	19	96	107		2	0.072	176	86	90
	3	0.099	93	168	78		3	0.094	86	4	90
M2	1	0.068	90	90	0	02	1	0.063	90	90	0
	2	0.085	103	13	90		2	0.072	168	78	90
	3	0.090	13	77	90		3	0.090	78	12	90
Si	1	0.060	90	90	0	03	1	0.066	54	121	51
	2	0.064	178	88	90		2	0.072	41	85	130
	3	0.080	88	2	90		3	0.098	74	31	64

Table 5. Olivine: Cation–oxygen distances and selected bond angles.

Distances (Å)			Angles (°)		
<i>M1 Octahedron</i>					
M1–O1[2] ^a	2.087(3)		O1–M1–O3	[2]	84.92(9)
O2[2]	2.074(3)		O1–M1–O3'	[2]	95.08(9)
O3[2]	2.139(3)		O1–M1–O2	[2]	86.52(10)
			O1–M1–O2'	[2]	93.48(10)
Mean M1–O	2.100		O2–M1–O3	[2]	74.45(9)
			O2–M1–O3'	[2]	105.55(9)
			σ^2 ^b		101.72
<i>M2 Octahedron</i>					
M2–O1[1]	2.182(3)		O1–M2–O3	[2]	80.68(9)
O2[1]	2.057(3)		O1–M2–O3''	[2]	91.21(9)
O3[2]	2.069(3)		O2–M2–O3	[2]	96.74(9)
O3[2]	2.226(3)		O2–M2–O3'''	[2]	90.60(9)
			O3–M2–O3'	[1]	70.86(8)
Mean M2–O	2.138		O3–M2–O3''	[2]	88.75(8)
			O3–M2–O3'''	[1]	110.93(8)
			σ^2		97.79
<i>Si Tetrahedron</i>					
Si–O1[1]	1.621		O1–Si–O2	[1]	114.78(10)
O2[1]	1.652		O1–Si–O3	[2]	115.97(9)
O3[2]	1.627		O2–Si–O3	[2]	102.01(9)
Mean Si–O	1.632		O3–Si–O3'	[1]	104.96(8)

^aFigures in brackets are multiplicity of angle in polyhedron.

^bOctahedral angle variance $\sigma^2 = \sum_{i=1}^{12} \frac{(\theta_i - 90^\circ)^2}{11}$ (Robinson *et al.*, 1971).

olivines increases with increasing temperature in the range 500°–900° due to increasing distortion of the M1 site as was suggested by Brown and Prewitt (1973). The data of Shinno (1974) indicate that the relationship of ordering may not be quite this simple and further high temperature crystallographic and Mössbauer studies of olivines are required to fully understand the relationship of Fe–Mg ordering with temperature in olivines.

IV. CATION ORDER IN LOW BRONZITE

Mineralogical background

Lunar rock 76535 consists of about four percent bronzite (En_{86}). The composition of this phase is somewhat aluminous (Table 1), but well within the range of compositions previously reported for orthopyroxenes. Cell edges (Table 2) are not unusual for orthopyroxenes of this composition. What is remarkable about this bronzite are the diffractions which violate the b -glide symmetry element of $Pbca$ making the space group $P2_1ca$ as reported by Smyth (1974). This report was based upon long-exposure a -axis precession photographs in which diffractions of indices 011, 051, 071, 091, 072, 053, 014, 015, 016, and 056 ($0kl$, k odd) appeared and could not be accounted for by exsolved augite or upper levels in the precession photograph. These diffractions were observed further on the four circle diffractometer at several rotations of ψ (axis normal to plane of diffraction) eliminating the possibility that they are caused by double diffraction (Renninger effect).

The diffractions violating the b -glide extinction conditions are considerably weaker than most of the other points in the reciprocal lattice and might easily be overlooked if a crystal is not specifically examined for them by taking long-exposure zero-level a -axis photographs. In order to determine to what extent other bronzites might show such diffractions, several orthopyroxenes were examined. Bronzites, En_{88} from a kimberlite, En_{75} from the Stillwater Complex, and En_{86} from the Steinbach meteorite, were each examined. Of these, only the Steinbach bronzite showed any evidence of these diffractions, and these were relatively much weaker than those of the 76535 bronzite. The author has learned that Dr. Ian Steele of the University of Chicago has also found pyroxenes of this space group in Apollo 17 Station 8 soil samples and has inferred that these pyroxenes and those of sample 78235 have had a similar cooling history to those of 76535 (Steele, 1975). So far, pyroxenes of this space group have only been found in extraterrestrial samples in which other evidence indicates extremely slow cooling. It may be that $P2_1ca$ is the true stable space group of orthopyroxenes, but that diffractions violating the b -glide only become evident with extremely slow cooling. Many more samples should be carefully examined before such a statement can be made with confidence.

Smyth (1974) discussed several possible causes for diffraction in violation of the b -glide of orthopyroxenes. Thompson (1970) predicated that $P2_1ca$ should be the true space group of pyroxenes based upon the topology of structure models.

Such a structure would have three O-rotated and one S-rotated silicate chains.* Long-range disorder might make evidence for such a structure difficult to detect in all but the most slowly cooled specimens. A second possible cause for such diffractions is cation order on the basis of four M sites rather than two as in *Pbca*. In order to evaluate these possibilities, the structure of this unusual pyroxene has been determined from three-dimensional X-ray intensity data. A full report of this structure determination is being prepared for separate publication.

Results and discussion

The structure was first refined in space group *Pbca* using anisotropic thermal parameters for all atoms yielding a residual of 0.07. Removing the *b*-glide symmetry constraints, the structure was refined in *P2₁ca* using only isotropic thermal parameters yielding an *R* of 0.06 in the lower symmetry space group, the greatest differences between the pseudosymmetric halves of the structure occurred in the occupancy and positional parameters of the two M2 sites and the oxygens which coordinate them. This indicates that the lower symmetry arises on cooling because of Fe–Mg and possibly Ca ordering on the basis of four M sites rather than two as in *Pbca*.

Even though comparable *R* factors are obtained from refinements in *Pbca* using anisotropic temperature factors and in *P2₁ca* using isotropic thermal parameters, there are several reasons to prefer the refinement in the lower symmetry space group. First, the *R* for the latter is less, even though the number of parameters is less than the former. Second, and perhaps most important, the lower symmetry refinement is able to account for the observed intensities of the diffractions violating the *b*-glide. Third, the results are reasonable in the light of crystal–chemical principles. That is, the M–O distances are longer for the M sites with the greater amounts of Fe and the greatest differences (up to 10 σ) and lowest correlation coefficients (0.6–0.8) between the pseudosymmetric halves of the structure occur in the position and occupancy of the M2 sites and the oxygens which coordinate them.

Dr. Gordon Nord (USGS, Reston, Va.) has generously shared some preliminary results of an electron microscopic study of this pyroxene. His results of direct lattice imaging indicate, in addition to augite lamellae, numerous defects in the crystal which may be stacking faults (9-Å repeat) or Guinier–Preston (G–P) zones which are Ca-rich but maintain the 18-Å repeat. If the latter is true and the G–P zones scatter in phase with the rest of the structure, then it is possible that this structure refinement in *P2₁ca* represents an average of the normal orthopyroxene (*Pbca*) structure and that of the G–P zones, and the violating diffractions might then result only from the G–P zones. However it seems unlikely to this author that a few percent by volume of G–P zones would modify the X-ray-apparent structure in such a way as to result in reasonable occupancy,

*For a discussion of pyroxene structure topologies and nomenclature see Thompson (1970) and Papike *et al.* (1973).

temperature factors, and interatomic distances. A crucial test will be to image the lattice using the diffractions which violate the *b*-glide.

The structure analysis has demonstrated that the observed intensities of diffractions violating the *b* glide extinction conditions can be accounted for by differences in location and scattering power of the M cation sites in violation of the *b*-glide. All silicate chains appear to be O-rotated as they are in *Pbca*, so it does not appear that an ordered reverse kinking of one of the silicate chains is the cause of the lower symmetry as was predicted by Thompson (1970). In this refinement, the difference in scattering power between the four M sites was modeled using only Mg and Fe. It is possible that Ca may play a crucial role in this cation ordering. Without direct lattice imaging by electron diffraction, it is difficult to estimate the relative abundance of augite lamellae, and hence to know how much Ca is in the orthorhombic structure, however some approximation can be made. The chemical analysis in Table 1 indicates about 5.6% augite ($W_{O_{2.8}}$) while long-exposure *b*-axis precession photographs indicate an estimated 3% augite, leaving about 2.5% augite still in solid solution. If all of the Ca were concentrated in one of the two M2 sites it does not seem sufficient to account for the differences in scattering power of the two sites, however a coordinated preference of Ca and Fe might be.

V. CONCLUSIONS

There are several conclusions that can be drawn from this work about ordering processes in lunar mineral systems and about the thermal history of this rock. The scattering powers of the four A sites in $P\bar{1}$ anorthite appear to be significantly different indicating ordering of Na and possibly of vacancy in these sites. The apparent scattering power difference between A(000) and A(0i0) indicates that significant ordering took place below 300°C. Two of the A sites appear to be split into nearly equal fractions raising the possibility that the true local symmetry is $P1$ rather than $P\bar{1}$. The cation ordering in the olivine is consistent with terrestrial olivines favoring the interpretation that ordering in olivines increases with increasing temperature. In low bronzite, the deviations from the common orthopyroxene space group appear to be caused by cation order on the basis of four M sites instead of two. The degree of cation order in each of these minerals is consistent with this rock having been excavated from its depth of formation by tectonic or impact processes without being reheated above 300°C. The relative perfection of the crystals and their suitability for single-crystal X-ray studies indicates the absence of severe shock.

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