The Origin of Space Group Violations in a Lunar Orthopyroxene

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Abstract. The space group of an orthopyroxene (En88) from a deep crustal lunar rock (sample 76535) that was previously reported as having space group P21/ca has been re-examined on an automated X-ray diffractometer. In addition to diffractions violating the b-glide of the conventional space group, Pnca (0klk-odd) reported in the earlier study, diffractions violating the a-glide of Pnca are also present. Careful examination of both the a-glide- and b-glide-violations shows them to be sharp, with no evidence of diffuse streaks parallel to a*, and with consistent intensities at several rotations about a. Diffractions violating the b-glide are in registry with the host, however, those violating the a-glide appear to be out of registry and result from a cell with a slightly longer a of about 18.4 Å, consistent with previous electron diffraction studies.

The most reasonable explanation for the observed space group violations is that both the a- and b-glide violations result from ordering of Ca into (100) Guinier-Preston (G-P) zones that possess orthopyroxene topology, but have space group P21/c and a cell of a=18.4 Å, b=8.83 Å, c=5.18 Å, and β=90.0°; whereas the Ca-depleted host has space group Pnca and a cell of a=18.230(6) Å, b=8.828(2) Å, and c=5.1946(9) Å. In addition to the G-P zones which may compose 12% or more of the sample, the crystal contains (100) lamellae of pigeonite, and other samples from the same rock contain lamellae of augite.

1. Introduction

Orthopyroxene is an abundant rock-forming mineral in mafic and ultramafic igneous and metamorphic rocks of terrestrial, lunar, and meteoritic origin. It occurs with compositions ranging from nearly pure MgSiO3 (En100) to (Mg0.5Fe0.5)SiO3 (Fs88) and typically contains 2 to 3 mole percent wollastonite (CaSiO3). The crystal structure was determined by Warren and Modell (1930). The space group was found to be Pnca, and the structures of several compositions have been refined in this space group (Morimoto and Kato 1960; Burnham et al. 1971; Smyth 1973; Sueno et al. 1976; Hawthorne and Ito 1977; Sasaki et al. 1982; Ghose et al. 1986).

Based on topologic considerations, Thompson (1970) suggested that the true space group of orthopyroxene might be P21/ca. Smyth (1974) reported that the space group of a lunar orthopyroxene from a slowly-cooled, deep crustal troctolite (sample 76535) was indeed P21/ca. The occurrence of P21/ca orthopyroxene in other lunar and meteoritic samples was subsequently reported by several investigators (Steele 1975; Harlow 1980). However, this work and the existence of P21/ca orthopyroxene was called into question when Sasaki et al. (1981, 1984) reported that many of the X-ray diffractions violating Pnca in orthopyroxene could be accounted for by 1) double diffraction, 2) exsolution of small amounts of augite on (100), or 3) diffuse streaks parallel to a*.

Smyth (1974) discussed the first two of these three possibilities and eliminated them as possibly contributing to the observed (0kl, k-odd and l-odd) diffractions and could easily distinguish the (0kl, k-odd, l-odd) from the nearby augite diffractions. Also, in the published precession photograph (Smyth 1974), all violating diffractions appeared sharp, effectively eliminating the possibility of these diffractions resulting from diffuse streaks parallel to a*.

Nord (1980) reported TEM results using electron diffraction, high resolution lattice imaging, and bright and dark-field imaging of lunar sample 76535 orthopyroxene. He noted electron diffraction maxima violating the a-glide of Pnca and that these were out of registry with the host orthopyroxene reciprocal lattice. He found that the sample contained two different types of (100) lamellae, one set of small lenticular lamellae and another set of Guinier-Preston (G-P) zones that showed 10 Å lattice fringes in high-resolution photographs. The G-P zones were much more abundant composing 12% or more of the sample. He succeeded in imaging the lattice using the a-glide violation diffractions (dark-field) and found
that the a-glide violations were produced by the G-P zones. He concluded that their space group was Pbca, and that they had a larger a-axis (18.53 Å) and similar b- and c-axes. He noted that (0kl) diffraction pattern contained diffractions violating the b-glide of Pbca, and that these were near perfect registry, but did not determine if they were from the host, from the lamellae, from nearby upper levels (HOLZ) or due to double diffraction.

The results, then, of the three published studies of low-symmetry orthopyroxene have produced three different and conflicting conclusions. The crystallography of orthopyroxene exsolution and precipitate textures has become an important tool for estimating cooling rates of particularly extraterrestrial igneous rocks (Miyamoto et al. 1975; Takeda et al. 1976; Takeda 1979; Harlow et al. 1979; Mori and Takeda 1981), so resolution of the ambiguities surrounding the low-symmetry orthopyroxene may have implications for these studies. We have therefore undertaken to carefully examine the nature of the diffractions in violation of Pbca in 76535 orthopyroxene.

2. Space Group Determination

2.1. Precession Photography

The X-ray diffractions violating the a- and b-glides of Pbca were first examined using long-exposure precession photography. Although precession photography is a non-digital technique, it is a very effective and sensitive method of examining two-dimensional slices of reciprocal space, and some information about the third dimension is available as well. After carefully orienting a crystal of the 76535 orthopyroxene, a 240-hour exposure on (0kl) was taken with a precession angle of 30°. One quadrant of this photo appears as Fig. 1. Clearly visible in this photograph are following diffractions that violate the b-glide of Pbca: (011), (031), (051), (071), (091), (012), (032), (052), (072), (011 2), (033), (053), (073), (01 3), (014), (015), (016), and (056). Similar precession photographs of this crystal were also taken using precession angles of 25° and 20°, and similar intensities of these diffractions were observed.

Because a different precession angle results in a slightly different θ angle, observation of similar intensities for these diffractions at different precession angles effectively eliminates the possibility of these intensities arising from double diffraction. The (00l) augite lamellae nearly overlap the orthopyroxene reciprocal lattice at l-even diffractions in this layer, but are distinctly out of registry. The augite diffractions are visible in Fig. 1 at positions (016), (056), and (072) and are distinct from the orthopyroxene diffractions. Finally, the sharpness of the observed k-odd diffractions eliminates the possibility that they might be due to diffuse streaks parallel to a*. A diffuse streak parallel to a*, if sufficiently strong, would appear as a diffuse double tail in this photograph. We are therefore able to conclude that the diffractions of the type (0kl, k-odd) observed in this photograph result from violations of the b-glide in at least some portion of the structure of this orthopyroxene.

Fig. 1. Zero-level, a-axis precession photograph 240 h exposure using Zr-filtered-Mo radiation (40 kV, 18 mA) and a crystal approximately 100 × 100 × 200 μm in size. Clearly visible in this photograph are following reflections that violate the b-glide of Pbca: (011), (031), (051), (071), (091), (012), (032), (052), (072), (011 2), (033), (053), (073), (01 3), (014), (015), (016), and (056).

2.2. Diffractometry

These diffractions violating the b- and a-glides of Pbca were then examined using an automated diffractometer. The four-circle automated X-ray diffractometer allows us to digitally examine the shapes and intensities of these diffractions in reciprocal space. A crystal of the 76535 orthopyroxene was mounted and oriented on a Picker diffractometer equipped with Krisel automation. The unit cell was refined from centering parameters of eight strong diffractions of 2θ > 45° in each of eight octants. The parameters thus obtained are a = 18.230(6) Å, b = 8.828(2) Å, and c = 5.1946(9) Å. The integrated intensities of six diffractions of the type (0kl, k-odd) were measured at various angles of θ, and these intensities are plotted as a function of θ in Fig. 2. The consistent intensity of these diffractions observed at different θ-angles confirms our finding from the precession study that double diffraction does not make a significant contribution to the observed intensities of the b-glide violations.

Several (0kl, k-odd, l-odd) diffractions were then examined for the presence of diffuse streaks parallel to a*, by measuring the integrated intensity as a function
Fig. 2. Integrated intensity of the (091) reflection as a function of ψ-rotation. Integrated intensity scans were measured every 0.25° on ψ. With a constant intensity of 5 to 6 times background, this reflection that violates the b-glide of $Pbca$ cannot be the result of double diffraction.

Fig. 3. Integrated intensity scans taken at fractional $h$ values every 0.1 $h$ along $a^*$ between $h=0$ and $h=1$ for six reflections violating the b-glide of $Pbca$. This figure shows discrete maxima at $h=0$ that the intensities observed in the precession photograph are in registry with the host orthopyroxene and are not the result of upper levels or diffuse streaks along $a^*$ due to stacking disorder in the a direction.

Fig. 4. Integrated intensity scans taken at fractional $h$ values along $a^*$ in the vicinity of two reflections violating the a-glide of $Pbca$: (910) and (160). The discrete maxima in this figure show that these intensities are not the result of upper levels or diffuse streaks along $a^*$ due to stacking disorder in the a-direction. However, unlike the b-glide violations in Fig. 3, these reflections are slightly out of registry with the host. We infer that these reflections result from Ca-rich G-P zones on (100) that have orthopyroxene topology, but a slightly longer a-axis of 18.4 Å and space group $P2_1/c$.
of 9.1 Å. We are therefore able to confirm Nord's observation of diffractions violating the a-glide of Pbcn and that these diffractions are slightly out of registry with the orthopyroxene host. We conclude that these violations result from some portion of the structure that has an a-axis slightly larger than the host, probably near 18.4 Å, i.e. the G-P zones observed by Nord (1980).

Although diffraction photographs of some orthopyroxene crystals from this rock clearly indicate the presence of augite, diffraction photographs of the crystal studied on the automated diffractometer did not. The (560) diffraction was carefully step-scanned along 2θ, and no evidence of diffracted intensity from augite was observed. However, fractional-h scans between the (120 2) and (11 0 2) positions of the orthopyroxene host clearly show the presence of intensity attributable to the (702) of pigeonite lamellae on (100). These diffractions have nearly the same c dimension as the host (unlike augite), and the (702) would be absent in augite, so the lamellae are clearly pigeonite rather than augite.

In summary, we conclude that diffractions that violate both the a-glide and the b-glide of Pbcn are neither due to double diffraction, overlap of adjacent layers on h, diffuse streaks along a*, nor to augite or pigeonite exsolution. They must originate either from the orthopyroxene host itself or from some coherent precipitate with an 18 Å repeat on a. The b-glide violations are in registry with the b and c axes of the host, but the a-glide violations indicate an a-axis repeat of 18.4 Å, slightly larger than the a of the host. Because of the different a, it is likely that the a-glide violations are produced by the Ca-rich G-P zones as suggested by Nord (1980). On heating his sample, Nord observed that the a-glide violations disappeared but the b-glide violations did not, and inferred that the former were from the G-P zones which have space group Pbc21, and the b-glide violations were from the host which might have space group Pbcn or P21ca. From our observations we can conclude that either the a-glide violations are from the G-P zones (Pbc21) and the b-glide violations are from the host (space group P21ca), or both are from the G-P zones which have space group Pbc21 (but with a = 18.4 Å and β = 90°), and the host is normal orthopyroxene (space group Pbcn). Whereas we cannot distinguish between these two interpretations based on our observations and those of Nord (1980), crystal-chemical arguments presented below strongly favor the latter interpretation.

3. Discussion

Lunar sample 7635 is one of the few coarse-grained lunar rocks that does not show abundant evidence of shock metamorphism and has been studied carefully using numerous analytical techniques. The rock is a troctolitic granulate composed of 58% plagioclase (An87), 37% olivine (Fo89), and 4% orthopyroxene (En84). Trace element studies (Haskin et al. 1974) indicate a cumulate igneous origin for this rock, and textural evidence and crystal homogeneity suggest extensive subsolidus recrystallization (Gooley et al. 1974). Bronzite-diopside-spinel intergrowths occurring along olivine-plagioclase boundaries indicate an equilibration temperature above 1000°C at about 0.6 kbar (60 MPa) pressure (Gooley et al. 1974). These authors have further estimated the cooling rates on the order of a few tens of degrees per million years based on diffusion gradients in coexisting accessory kamackite-taenite pairs. Similar cooling rates were deduced by Nord (1976). Age dates between 4.1 and 4.4 billion years have been obtained for this rock (Bogard et al. 1974; Huneke and Wasserberg 1973; Hinson et al. 1975). Stewart (1975) has inferred that the rock represents a cumulate formed during the original crystallization of the lunar crust and underwent re-equilibration during the slow cooling of the primordial crust. It is the large bronzite grains, comprising about 4% of this rock, in which the lower-symmetry space group, P21ca was first reported (Smyth 1974).

Subsequently, several authors have reported the occurrence of orthopyroxene of space group, P21ca mostly from extra-terrestrial sources. Steele et al. (1975) reported a second occurrence in lunar sample 78235, and Smyth (1975) reported an occurrence in the Steinbach meteorite, a basaltic achondrite. Harlow (1980) reported several occurrences in achondrite meteorites. To date, all observations of b-glide violations, other than the double-diffraction phenomena reported by Sasaki et al. (1981), have been from very slowly cooled samples of extra-terrestrial origin. And it is only in the very slowly cooled specimens that the G-P zones are well-developed (Nord 1980; Mori and Takeda 1981).

As mentioned above we cannot distinguish whether the b-glide violations are from the host or the G-P zones because they are in perfect registry with the host, and the (100) orientation would constrain the b and c axes of the G-P zones to those of the host. Further, it would be nearly impossible to produce a dark-field image of the (100) G-P zones in the necessary (100) section using the (00l, l odd) diffractions. Although we cannot absolutely rule out the possibility that the host is P21ca as suggested by Smyth (1974), and the G-P zones Pbc21 as suggested by Nord (1980), this appears highly unlikely.

Nord (1980) estimated the Ca-content of the G-P zones in this orthopyroxene at Wo25, based on the a cell. If the G-P zones are calcic, the host must be essentially completely depleted in Ca. There would then be no topo-chemical reason for the host to order into a space group lower than Pbcn, because there is not enough Ca to fill a unique site, whereas there would be enough Ca in the G-P zones to fill one of the two different M2 sites in a lower-symmetry structure. In Fig. 5 are "l-beam" diagrams of the structures of orthopyroxene in space groups Pbcn, P21ca, Pbc21, and P21/c showing the arrangement of unique sites. In Pbcn, there are two types of six-fold sites, M1 and M2, and two different types of silicate chain, A and B. Each of the lower symmetry space groups is a subgroup of Pbcn, and each has the same cell. In each of the lower-symmetry structures, there are two different M1 sites, two different M2 sites and four distinct silicate chains arranged
as shown. \( P_2_{1} \text{ca} \) and \( Pbc2_1 \) are acentric orthorhombic whereas \( P2_1/c \) is centric and monoclinic.

If both the \( a \)- and \( b \)-glide violations are from the G–P zones, then the space group of the G–P zones would be \( P2_1/c \) with an 18.4 Å \( a \)-axis, orthopyroxene topology, and a pseudo-orthorhombic unit cell with \( \beta \) of 90.0°, that is, a new pyroxene structure type, not pigeonite. Note that no diffractions of type \( (0k0, k \text{-odd}) \) were observed. These diffractions are allowed in \( P2_{1}\text{ca} \) and \( Pbc2_1 \), but not in \( P2_1/c \). The host would then be a Ca-depleted normal orthopyroxene with space group \( Pbca \). This interpretation is preferable to the possibility of \( Pbc2_1 \) G–P zones in a \( P2_{1}\text{ca} \) host because only the high-Ca G–P zones would be in a lower symmetry due to ordering of Ca. Further, both structures, \( Pbca \) and \( P2_1/c \), are centric and chemical ordering into acentric space groups is very rare in natural systems.

The observation of (100) pigeonite lamellae is relatively uncommon in orthopyroxene. The presence of augite in some crystals but not in others, is also unusual.

The presence of pigeonite lamellae in orthopyroxene has been interpreted as evidence of shock or very-high-strain-rate deformation, or alternatively that the orthopyroxene is the product of auto-epitaxial inversion from precursor pigeonite. Sample 76535 is believed to have equilibrated at some depth in the lunar crust and to have been excavated by the Imbrium impact event (Goo-ley et al. 1974). The pigeonite lamellae may be the result of shock deformation of this event.

Another possible, albeit speculative, explanation is that the G–P zones with space group \( P2_1/c \) and orthopyroxene topology are thermodynamically more stable than augite and are drawing Ca from both the orthopyroxene host and early-formed augite lamellae, leaving pigeonite in place of the precursor augite. This might be a means of reducing the strain energy of coherence between orthopyroxene and augite. If the minimization of coherency strain were a major factor in the stability of the G–P zones, it would be unlikely that the \( P2_1/c \) "orthopyroxene" that we infer to be the structure of
the G-P zones would ever be a stable phase capable of existing without its orthopyroxene host.

Whatever the relative stability relations of the various precipitates in this crystal, it is likely that the topological ordering responsible for the space group symmetry violations can only be produced by extremely slow cooling. This means that the presence of diffractions violating the a- and b-axes of Pnca-orthopyroxene, which are diagnostic of this structure, can be taken as evidence of extremely slow-cooling.

4. Conclusions

The space group of a lunar orthopyroxene (En₄₆₄) previously reported as P2₁ca has been re-examined. Diffractions of the type (h 0 l, k odd) violating the b-glide of space group Pnca are sharp, present at several rotations about \( \psi \), and not due to augite, pigeonite, or adjacent orthopyroxene diffractions. Diffractions of the type (h k 0, b odd) violating the a-glide of space group Pnca are also sharp, present at several rotations about \( \psi \), and not due to augite, pigeonite, or adjacent orthopyroxene diffractions, but they are out of perfect registry with the orthopyroxene host. Ordering of Ca to give rise to the low-symmetry structure requires diffusion across a layer of silicate chains so that the extra X-ray diffractions only become observable with very slow cooling. Observation of these diffractions may be characteristic of slowly cooled samples. Conversely, disordering of Ca on heating of natural samples is likely to be slow, so that the low-symmetry form may survive moderate reheating.

We therefore conclude that the most reasonable explanation consistent with both the X-ray and electron diffraction evidence is a Ca-depleted host with space group Pnca and cell dimensions \( a=18.230(6) \ \text{Å}, \ b=8.828(3) \ \text{Å}, \ c=5.158(3) \ \text{Å}, \ \beta=90.0^\circ; \) together with a small proportion of pigeonite lamellae and occasional augite lamellae.

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