Diffraction and Mössbauer Studies of Minerals from Lunar Soils and Rocks

Abstract. *Constituents of lunar soils and rocks were studied by powder and single-crystal x-ray diffraction. In addition to identification of minerals, including rare amphibole, mica, and aragonite, a detailed study of the important rock-forming minerals of the plagioclase, pyroxene, and olivine groups has begun. Mössbauer spectra were recorded from lunar soils, ground rock samples, and separates of iron-bearing minerals. The proportions of iron-bearing minerals were estimated from computer-fitted areas for the bulk samples. The* Fe^{2+} *in the lower-density fraction of pyroxene was ordered, whereas that of the higher-density fraction was disordered.*

Powder and single-crystal x-ray diffraction procedures permit not only the identification of the components of lunar soils and rocks but also detailed study of the structural state, exsolution, alteration, and so forth, of individual minerals to provide data on the conditions of formation. Some qualitative observations are reported on plagioclases, pyroxenes, and olivines; the main work is still in progress.

Plagioclase, clinopyroxene, olivine, and ilmenite were identified as the predominant minerals in fines 84-11 and 85-30; various forms of glassy material, including spherules, are also present. A diffraction pattern from one of these spheres showed very weak powder rings superposed upon scattered isolated maxima. Devitrification appears to have produced at least two crystalline components of different grain size; there are similarities between the weak powder pattern and that of a sphene-like structure, though the identification is unproven. Small amounts of native iron were also present in these fines, very occasionally with apparently crystalline faces; the only specimen of this kind examined proved to be a fine aggregate with a poor degree of preferred orientation. During the preliminary optical examination, two small crystals of micaceous appearance were selected for further examination; initial single-crystal study of one of these is consistent with a mica, but the polymorphic type has not yet been established.

Single crystals of the plagioclases, pyroxenes, and olivines were examined in detail. Two plagioclase crystals were examined to ascertain the structural type and, if possible, the structural state. Both showed transitional anorthite structures (*1*) with slight differences in the intensities and diffuseness of type (*c*) reflections; without detailed analytical data on the crystals, it is impossible to assess the structural state for either. Three pyroxene crystals were studied by the methods of Bown and Gay (*2*) for submicroscopic exsolution; all three were unmixed with a host augite structure, and variable proportions of an exsolved pigeonite structure sharing the (001) plane. There is some variation in the angular separation of the augite and pigeonite components, and in all three patterns weak streaks join augite and pigeonite spots; these features suggest that the exsolution process may be incomplete. In one crystal there is a second orientation of exsolved pigeonite with the *c* axis of the pigeonite almost parallel to that of the augite, similar to that described for the pyroxene from the gabbro-picrite 4526 from the Skaergaard intrusion (*3*); for all three specimens, class (*b*) reflections with $h + k$ odd for the pigeonite structures are slightly diffuse (*4*). Single-crystal patterns from three olivine crystals are typical of forsteritic specimens with no evidence of oxidation, alteration, or other such effects.

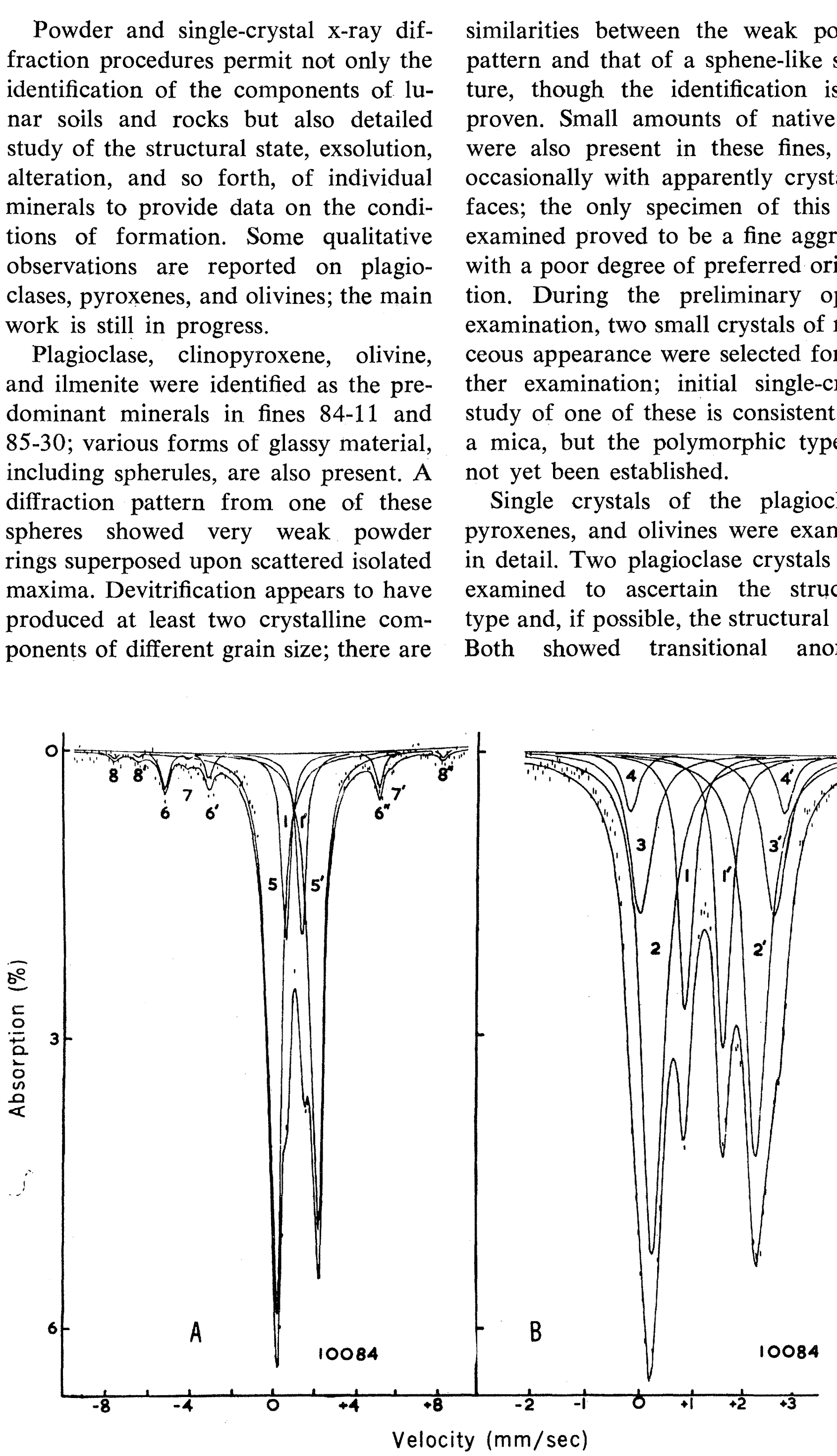

Fig. 1. Mössbauer spectra of 84-14 at room temperature. (A) High-velocity scan; (B) low-velocity scan. The numbering of peaks 1, 2, and so forth, is explained in the text.

Material from four rocks described as type A (*5*) is under investigation; plagioclase, pyroxene, ilmenite, and olivine have been identified together with small amounts of native iron and a fragment (from 17-50) of what appears to be a metallic alloy (cubic, F-lattice, $a \sim 3.68$ Å).

Detailed studies of three plagioclase crystals from two of these rocks reveal interesting variations in the subsidiary reflections. Very weak and diffuse type (*c*) reflections were detected for only one crystal (from 45-24), and this reflection class was apparently absent from both the other crystals (from 45-35). For 45-24, type (*b*) reflections are weak and diffuse and apparently split; the separation of these type (*e*) reflections for this unusual intermediate plagioclase structure was measured to give δ_c as approximately 166°, corresponding to a composition of about An_{72-73} (*6*). For one of the crystals from 45-35, very weak diffuse single type (*b*) reflections were just visible, but they could not be observed on normal exposures for the other crystal. Type (*f*) reflections were not present on the patterns from any of the crystals. These plagioclase crystals must be in an intermediate-high structural state.

All four pyroxene crystals so far examined from this rock type have shown predominantly pigeonite structures [twinned on (100) for one crystal] with class (*b*) reflections slightly diffuse. Three of them have indications of incipient augite exsolution in weak streaks associated with pigeonite spots, whereas the fourth also has weak maxima showing augite sharing (001) planes and possibly a second orientation almost parellel to the *c* axis of the host pigeonite; again the angular separation of the *z* axes for the pigeonite host and the (001) augite lamellae is less than that usually observed for intergrowths of this kind. Three olivine crystals (from 45-24, 45-35, and 72-47) give simple forsteritic patterns.

Crystals from two rocks described as type B (*5*) are under examination. Troilite and crystals of a yellow mineral thought to be a pyroxenoid comparable to pyroxmangite have been identified in 44-43; investigations of this material are incomplete, but some crystals show effects that may be associated with exsolution phenomena. In 58-23, a rare crystal of an amphibole from a vug (approximately $a = 9.85$ Å, $b = 18.20$ Å, $c = 5.30$ Å, and $\beta = 104\frac{1}{2}°$) has been studied, and a pink lath-like fragment showed a random aggregate of aragonite crystallites.

Three plagioclase crystals from 58-23 show transitional anorthite structures with some variation in the diffuseness and intensity of type (*c*) reflections; there may be some slight differences in the single type (*b*) maximums, but it is not possible to assess the structural states of these feldspars. Two pyroxene crystals from the same rock show pigeonite exsolving on (001) planes from an augite host structure; the amount of pigeonite is different in the two crystals, but both have a slight diffuseness of the class (*b*) reflections. The angular separation of augite and pigeonite is that normally observed in such intergrowths, but there are still weak streaks joining augite and pigeonite maximums.

Iron-bearing minerals have been found to give characteristic Mössbauer spectra (*7*) which make it possible to identify such minerals in a bulk rock sample; semiquantitative estimates of the relative proportions of these minerals can be made from the areas of peaks (*8*). Furthermore, since the parameters are sensitive to small differences in cation site symmetry, the Mössbauer effect has been widely used to measure accurately intracrystalline site populations in amphiboles and pyroxenes (*9*). Studies of this kind have been carried out on the fines 84-14 and 85-4, ground rock from 44-39 and 45-24, and mineral separates (olivine, ilmenite, and pyroxene) from 44-43.

Table 1. Percentages of iron-bearing minerals. These preliminary percentages are calculated on the assumption that olivine contains 20.0 percent Fe^{2+} by weight, that pyroxene contains 10 percent Fe^{2+}, and that the other minerals correspond to their ideal chemical formulas. The percentage of non-iron-bearing components is taken from the C.I.P.W. norm derived from chemical analysis by J. H. Scoon. These final values are expected to have semiquantitative significance, despite these and other assumptions.

Mineral	Percent of total Mössbauer area		Weight percent of total sample	
	84–14	45–24	84–14	45–24
Ilmenite	19.7	26.9	4.2	7.4
Pyroxenes	67.6	60.8	53.1	60.6
Olivine	4.4	6.1	1.8	3.0
Iron	5.8	2.1	0.6	0.2
Troilite	⩽1.1	⩽2.0	⩽0.1	⩽0.2
Magnetite	1.4	2.1	0.2	0.2
Noniron			40.0	28.4

Typical room temperature spectra of 84-14 at high and low velocity scans are shown in Fig. 1; qualitatively similar spectra were obtained for the other three bulk samples. Computed peaks have been assigned as follows (*10*): 1 and 1′ as ilmenite; 2, 2′, 3, and 3′ as pyroxene (mainly augite and subcalcic augite); 4 and 4′ as olivine; 5 and 5′ as an overlap of pyroxene and olivine peaks; 6, 6′, and 6″ as metallic iron; 7 and 7′ as troilite; 8, 8′, and 8″ as magnetite (with some Ti). Center shifts (C.S.), quadrupole splittings (Q.S.), and the magnetic peak positions are generally in good agreement with those of corresponding terrestrial minerals, and these parameters are consistent for all samples. Ilmenite peaks (Q.S. = 0.70 mm/sec and C.S. = 1.17 mm/sec) are in excellent agreement with those reported previously (*11*), whereas the Q.S. value (2.86 mm/sec) for olivine is slightly lower than that obtained in earlier work (*7*) for similar compositions. The Q.S. parameters for augite at 295°K are 2.00 mm/sec (inner lines) and 2.50 mm/sec (outer lines); these are similar to values for synthetic and natural terrestrial augites (*12*). Resolution of the pyroxene peaks is markedly improved at 80°K; parameters for the disordered pyroxene (Fig. 2B; see final paragraph) are very similar to those for the augite. The iron peak positions are in excellent agreement with the well-known peak positions for pure iron and indicate that there is little, if any, replacement of iron by nickel (*13*).

Ilmenite peaks (1 and 1′) are distinctly asymmetric, suggesting that there are appreciable quantities of another iron-bearing mineral present, one peak of which strongly overlaps 1′. The line widths of the pyroxene peaks for 85-4 and 84-14 are much greater than those from the rock samples; this broadening probably reflects a wider variation in chemical content for the soil pyroxene.

Table 1 lists the calculated percent-

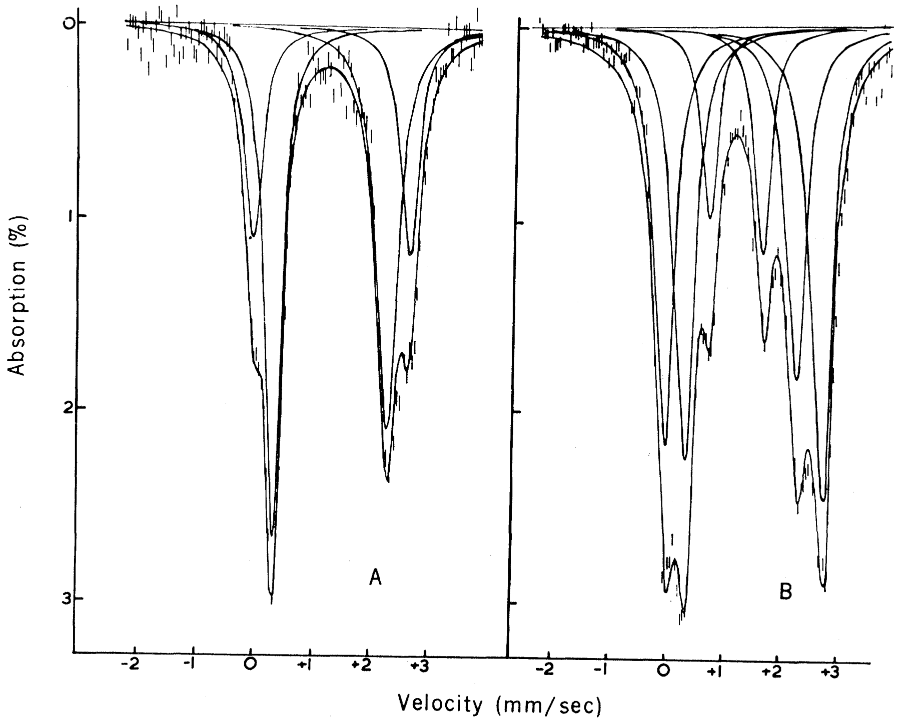

Fig. 2. Mössbauer spectra of two pyroxene fractions from 44-43 at 80°K. (A) Lower-density fraction; (B) higher-density fraction.

ages of iron-bearing minerals derived from the Mössbauer areas for 84-14 and 45-24; the assumptions and possible errors in these values will be discussed elsewhere. However, it is apparent that the iron content of 84-14 is much greater than that for 45-24, whereas 45-24 has appreciably more ilmenite, pyroxene, and olivine than 84-14.

Mössbauer spectra at 80°K of two pyroxene separates from 44-43 are shown in Fig. 2; the inner peaks in B are due to ilmenite. Fraction A (density 2.85 to 3.50) is ordered ($\text{area}_{\text{inner}}/\text{area}_{\text{total}} = 0.67$), whereas fraction B (density 3.70 to 3.90) is essentially disordered ($\text{area}_{\text{inner}}/\text{area}_{\text{total}} = 0.52$). This surprising result agrees with the optical, x-ray, and microprobe work reported here and elsewhere that this rock contains both a clinopyroxene (A) and a pyroxenoid (B) of the pyroxmangite type. For B, the line widths of the inner peaks are greater than those of the outer peaks (0.48 and 0.40 mm/sec, respectively), and the room-temperature areas are not consistent with those obtained at 80°K. Although this evidence could be interpreted as implying there are more than two cation sites with appreciably different Q.S. values, it could also be due to a lack of homogeneity caused by exsolution.

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Lunar Clinopyroxenes: Chemical Composition, Structural State, and Texture

Abstract. *Single-crystal x-ray diffraction, microprobe, optical and electron optical examinations of clinopyroxenes from Apollo 11 lunar samples 10003, 10047, 10050, and 10084 show that generally the crystals are composed of (001) augite-pigeonite intergrowths in varying ratios. Transmission electron micrographs reveal abundant exsolution lamellae, many only 60 Å thick. In addition to the phase inhomogeneities, primary chemical inhomogeneities are clearly demonstrated. There are reciprocal relationships between calcium and iron and between* $Ti^{4+} + 2Al$ *and* $R^{2+} + 2Si$*. Our evidence suggests that a chemically inhomogeneous subcalcic C2/c augite was the only primary pyroxene from which pigeonite later exsolved.*

The lunar clinopyroxenes, augite and pigeonite, from rocks 10003,38 10047,27, 10050,32, and soil 10084,100 collected by the Apollo 11 astronauts were examined by standard petrographic microscopy, by the Buerger single-crystal x-ray precession technique, by transmission and scanning electron microscopy, and by electron-microprobe analyses of single crystals mounted in epoxy cement and polished to expose a plane surface.

Examination of the clinopyroxenes with the petrographic microscope shows intercumulus textures and, within the grains, complex patterns of color varying from very light pink to fairly dark reddish brown. The characteristic properties of the lunar clinopyroxenes are the "sectorial" extinction and the apparent warping or bending of the (110) cleavage planes. These effects are caused by lattice rotation of two or more blocky, sometimes pie-shaped, "domains" contained within a crystal. Precession photographs of crystals containing such domains reveal that they are offset from one another by rotation about a common *b* axis (*1*). The rotation is generally 1° to 5°, and often a one-to-one correlation can be made between the number of domains seen optically in a crystal and the number observed in its *h0l* diffraction pattern. Color variations occur across the domain boundaries. The "sectorial" extinction so commonly displayed by the pyroxenes when examined in plane polarized light is caused by this offset domain structure.

Single-crystal x-ray diffraction patterns were made of 25 crystals or crystal chips. Almost all the crystals consisted of augite plus pigeonite oriented on (001). The approximate amount of pigeonite contained in the host augite was determined by comparing the relative intensities of the *h0l* reflections (*2*). The ratios of augite to pigeonite in some of these single crystals are as follows: rock 10003, 4 : 1, 7 : 3, 1 : 1, 1 : 1, 2 : 3, 1 : 4; rock 10047, 17 : 3, 13 : 7, 1 : 0, 7 : 3; rock 10050, 19 : 1, 19 : 1, 3 : 7, 17 : 3, 1 : 0, 17 : 3, 3 : 2, 50 : 1; rock 10072, 17 : 3; soil 10084, 13 : 5, 17 : 3, 17 : 3.

Cell parameters obtained from measurements of precession patterns can be summarized as follows: augites, *a* 9.68 to 9.76 Å, *b* 8.90 to 8.95 Å, *c* 5.25 to 5.28 Å, β 105.8° to 106.8°; pigeonites, *a* 9.68 to 9.76 Å, *b* 8.90 to 8.94 Å, *c* 5.21 to 5.24 Å, β 108.8° to 109.1°. The augites have space group *C2/c*, and the pigeonites, $P2_1/c$. The reflections violating *C2/c* symmetry in a crystal

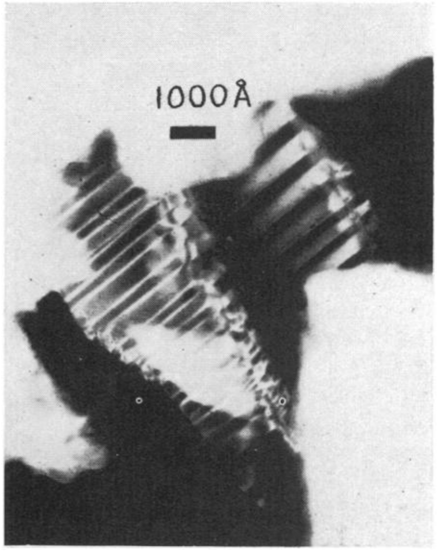

Fig. 1. Transmission electron photomicrograph of a small crystal fragment of clinopyroxene from rock 10047. The narrow lamellae to the left of the photograph (thin white bands) vary in thickness from 60 to 100 Å and are interpreted as being pigeonite unmixed on (001) from augite host (wide, dark bands 200 to 500 Å thick). Coalescence of the thin pigeonite lamellae into much thicker lamellae may be occurring to the right of the photograph (light bands approximately 400 Å thick). The discontinuity in the center of the grain trending 11 to 5 o'clock may be a domain boundary with the left domain becoming more augitic, the right, more pigeonitic.