examined. The silicate phases contribute wide lines, indicating that this rock contains iron-bearing glasses in addition to pyroxenes, which is compatible with its volcanic character (*4*).

Initial scattering measurements on breccia 10065 produced spectra somewhat similar to those of the fines, as would be expected in view of the probable origin of lunar breccia as shock lithified fines (*4*); spectral differences include considerably reduced intensity in the ilmenite regions. Magnetically ordered material is present in this breccia and it seems to be primarily metallic iron (*3, 7*).

Ferric iron is largely absent from the lunar material. At most a few percent of the iron is in the Fe^{3+} state. All of the rocks and fines from Apollo 11 which we have examined appear to have an appreciable iron content and grossly similar chemical and mineralogical compositions with the individual differences as remarked upon, as evidenced by their Mössbauer spectra.

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Mössbauer Effect and High-Voltage Electron Microscopy of Pyroxenes in Type B Samples

Abstract. *Site occupancy numbers for ferrous iron, magnesium, and calcium at the M1 and M2 sites in lunar clinopyroxenes are estimated from nuclear gamma-ray resonant absorption spectra of* ^{57}Fe. *The cation distribution is ordered; calcium and magnesium prefer M2 and M1, respectively. The distribution corresponds to an equilibrium at a temperature lower than 680°C. Crystals cleaved and sectioned by diamond-knife ultramicrotomy were examined by high-voltage (200 kv) electron microscopy and diffraction. Uniform 300- to 600-Å-wide bands that correspond to single crystal domains were found. Correlation of the bands with magnetic ordering at low temperatures is considered.*

The crystallization and subsequent cooling history of pyroxenes is reflected in their exsolution phenomenon and in the cation distribution over structural sites. Therefore, studies of the domain structure in pyroxene crystals and of the intrinsic site occupancy in the distinct phases are important (*1*).

Clinopyroxenes separated from the type B specimens 10003 and 10044 were crushed to a grain size of approximately 50 μm and further separated into fractions of different Mg,Fe,Ca compositions by means of heavy liquids. Each fraction yields a distinct resonant absorption spectrum (Fig. 1). The nuclear quadrupole doublets due to Fe^{2+} at the M1 and M2 sites are generally well resolved. The spectra of two fractions from 10044 are shown in Fig. 1. Isomer shifts and nuclear quadrupole splittings (peak to peak separation) of the clinopyroxene from rock 10044 and those of a terrestrial augite with similar chemical composition and an iron-rich orthopyroxene are given in Table 1. The widths at half peak height are approximately 0.36 mm/sec.

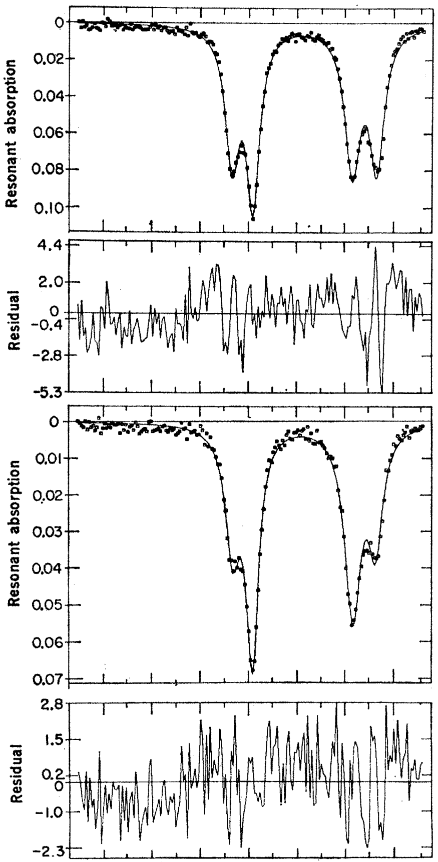

Fig. 1. Resonant absorption spectra of ^{57}Fe in clinopyroxene from specimen 10044. Upper spectrum: iron-rich fraction 10044-P3. Lower spectrum: magnesium-rich fraction 10044-P2. The solid line is a least squares fit (13 variables) to the uncorrected data. Absorbers were held at 77°K. Outer peaks: Fe^{2+} at M1; inner peaks: Fe^{2+} at M2.

The x-ray diffraction powder data indicate that the 10044 pyroxene consists almost exclusively of augite, whereas some fractions from 10003 also include pigeonite. However, measurements of isomer shifts and quadrupole splittings at 77°K in terrestrial pyroxenes with compositions within the enstatite-diopside-hedenbergite-ferrosilite quadrilateral show that the shifts and splittings are only slightly affected by small changes in Mg,Fe,Ca composition or by changes in crystal symmetry, for instance from space group $C2/c$ to $P2_1/c$. The data of Table 1 are consistent with those observations. Therefore, the resolution of the M1 and M2 doublets, for instance in the case of separates from rock 10003, is not surprising, and the hyperfine data of ^{57}Fe can be interpreted in terms of average occupancy numbers.

Average compositions and site occupancy numbers of the two chemically distinct 10044 fractions are shown in Table 2. The Mg,Fe,Ca distribution is principally an ordered one, M2 being almost exclusively occupied by Ca and Fe^{2+}, M1 being occupied by Mg and excess Fe^{2+} (Table 2). No significant Fe^{3+} peaks could be detected.

Estimates of the stability field of the observed cation distribution can be made from heating experiments. Specimens of clinopyroxene 10044-P2 were heated at 675°C for 76 hours and at 1000°C for 17 hours. A significant change in the relative doublet intensities was observed (Table 2). Therefore, the cation distribution in the natural 10044 clinopyroxene corresponds to an equilibrium temperature lower than 675°C.

Studies of the cation distribution in rapidly cooled volcanic orthopyroxenes (*2*) and kinetic studies of the cation exchange process (*3*) suggest that partial ordering of cations in lunar clinopyroxenes may proceed rapidly during initial quenching from a high temperature but complete order is only attained after significantly long geological times at low temperatures. Disordered cation distributions are attained by initial rapid cooling. For comparison some data on the terrestrial Kakanui augite (*4*) are given in Table 2. The site occupancy for this volcanic sample is considerably complicated by the presence of other cations (*5*) but the significantly higher relative proportions of Mg in the M2 sites is consistent with a more rapid cooling history in comparison with the augite from rock 10044. The change of site occupancy in lunar augite is comparable to the change in ordered orthopyroxenes heated at the same temperature. The slightly smaller change in the lunar specimen is indicative of a somewhat larger Gibbs free energy difference for the Mg,Fe^{2+}-exchange reaction between M1 and M2 at 1000°C.

Table 1. Nuclear quadrupole splittings and isomer shifts of Fe^{2+} in lunar and terrestrial pyroxenes at 77°K.

Sample	Quadrupole splitting (mm/sec)		Isomer shift referred to metallic iron (mm/sec)	
	M1	M2	M1	M2
10044-P2	2.92	2.06	1.29	1.26
10044-P3	2.96	2.03	1.29	1.26
10044-P2 heated 675°C	2.91	2.04	1.28	1.26
10044-P2 heated 1000°C	2.92	2.05	1.28	1.26
Kakanui-Augite	2.80	2.09	1.26	1.25
Orthopyroxene XYZ	3.10	2.04	1.29	1.26

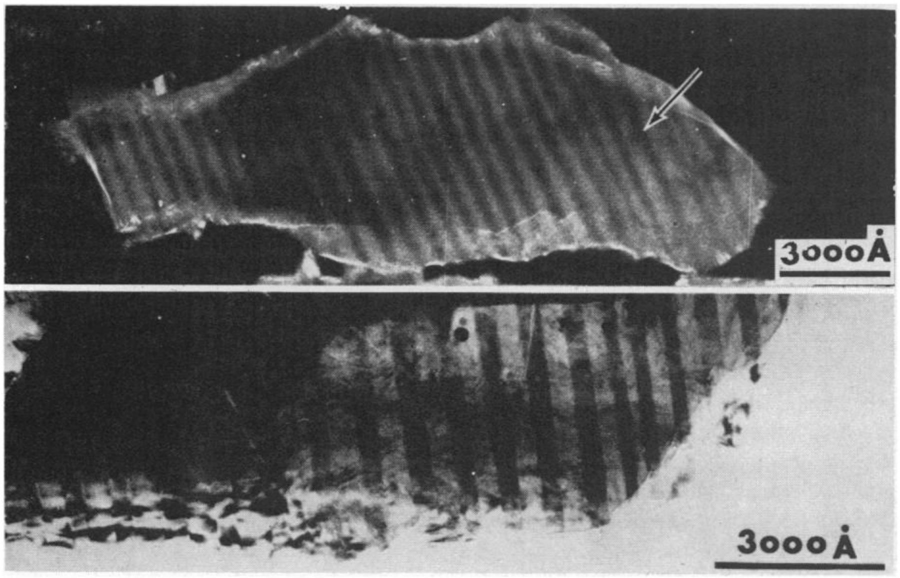

Fig. 2. High-voltage, dark field electron micrograph of cleaved clinopyroxene 10044 (above) and high-voltage electron micrograph of iron-rich clinopyroxene 10044-P3 showing uniform dense bands which are parallel (001) and irregular granules (below).

Pyroxenes cleaved and sectioned by diamond knife ultramicrotomy (*6*) and mounted directly on thin film specimen grids were examined by high voltage (200 kv) electron microscopy under conditions of increased penetration power and decreased specimen damage (*7*).

In crystals from fraction 10044-P3, regularly spaced, dense bands (Fig. 2, dark areas) with widths of 300 to 600 Å were recorded in approximately 2000 plates. These uniform bands appear to be single crystal domains and are oriented with their long axis in the plane of the crystalline layers, approximately normal to crystallographic *c*. Intrinsic lattice spacings of 2.5 Å (probably d_{002}) can be detected within the bands parallel to their long axis.

The bands resemble electron-optical images of magnetic domain walls as seen in thin layers of magnetic materials (*8*). They are predominantly seen in iron-rich (10044-P3) crystals but are absent in magnesium-rich (10044-P2) crystals and in the terrestrial orthopyroxene XYZ. In this connection resonant absorption spectra of specimen 10044-P3 taken at low temperatures do reveal magnetic ordering, below a Néel point of approximately 20 to 30°K. However, it is interesting to note that iron-bearing chain silicates are generally not mag-

Table 2. The Fe^{2+} distribution data over M1 and M2 sites in lunar and terrestrial pyroxenes. The Fe^{2+} distribution numbers were determined from the ^{57}Fe resonant absorption spectrums. The site occupancy was calculated from the distribution numbers assuming a preference of Ca for M2. Al, Ti, and Mn are ignored; suggested values are Al = 0.03, Ti = 0.03 and Mn = 0.02 (*10*). En, enstatite; Fs, ferrosilite; Wo: wollastonite.

Sample	Molecular composition	Fe^{2+} distribution numbers		Site occupancy					
				M1			M2		
		M1	M2	Mg	Fe	Ca	Mg	Fe	Ca
10044-P2	$En_{0.44}Fs_{0.20}Wo_{0.36}$	0.36	0.64	0.86	0.14	0	0.02	0.26	0.72
10044-P3	$En_{0.36}Fs_{0.34}Wo_{0.30}$	0.46	0.54	0.68	0.32	0	0.03	0.37	0.60
10044-P2 heated to 675°C		0.38	0.62	0.85	0.15	0	0.03	0.25	0.72
10044-P2 heated to 1000°C		0.40	0.60	0.84	0.16	0	0.04	0.24	0.72
Kakanui-augite*		0.34	0.66	0.72	0.06	0	0.19	0.12	0.62
Orthopyroxene XYZ	$En_{0.12}Fs_{0.85}Wo_{0.02}$	0.447	0.534	0.24	0.76	0	0.02	0.94	0.02

*0.90 Mg, 0.21 Fe, 0.61 Ca, 0.33 Al, 0.09 Na, 0.02 Ti per six oxygen atoms (*5*).

netically ordered, even at very low temperatures, especially if the amount of diamagnetic cations (magnesium, calcium) substituting for iron at the octahedrally coordinated positions is larger than 25 percent as in the 10044-P3 augite (*9*). We believe that the observed ordering is due to iron-iron clustering in the single crystal domain bands as revealed by electron microscopy (Fig. 2). In the domains between the bands, clustering of Mg,Ca seems likely. A statistical estimate shows that the total volume of the bands and interband domains within each crystal is about the same. Thus, a speculation on their respective chemical compositions can be made. If one assumes the extreme case that the ferrous ions are entirely located within the bands one is led to the pigeonite composition $\mathrm{En}_{0.19}\mathrm{Fs}_{0.68}\mathrm{Wo}_{0.13}$ for the bands and an almost pure diopside of the composition $\mathrm{En}_{0.53}\mathrm{Wo}_{0.47}$ for the interband domains (molecular percent). The speculated band composition is consistent with the Fe^{2+} distribution data for 10044-P3 in Table 2. If one assumes complete ordering of Mg and Ca in the bands, the Fe^{2+} site occupancy in M1,M2 is 0.62, 0.73, respectively. This occupancy could certainly produce magnetic ordering at low temperature due to M1-oxygen-M2 superexchange.

The electron microscopic studies suggest an unexpected complexity in the intrinsic atomic organization of the clinopyroxenes from sample 10044. While these may indicate implications on the history of the crystals with respect to temperature and pressure, more detailed investigations will be needed for definite conclusions and their relevance.

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Mössbauer Spectroscopy of Moon Samples

Abstract. *Lunar bulk sample 10084,85 (< 1 mm size dust), and samples from rocks 10017,17 (fine grained, vesicular), 10046,17 (breccia), 10057,59 (fine grained, vesicular, top surface), 10057,60 (fine grained, vesicular, interior), and 10058,24 (medium grained, not vesicular) have been investigated by* $^{57}\mathrm{Fe}$ *Mössbauer spectroscopy. Iron metal and the* Fe^{2+} *minerals ilmenite, pyroxene, troilite, and iron containing glass have been identified. An iron line of sample 10084,85 (originally sealed in nitrogen) showed no significant intensity change when the sample was exposed to air. The antiferromagnetic transition in several lunar ilmenites at* $57° \pm 2°K$ *corresponds to stoichiometric* FeTiO_3. *Magnetically separated 10057 showed troilite and some metallic iron.*

Mössbauer spectroscopy has been used to investigate the iron-containing phases in lunar bulk and rock samples. In addition to identifying and analyzing the iron-containing minerals, we looked for reactions with air and made a more detailed study of the magnetically ordered minerals. A search for unusual charge states of Fe which might be expected to be unstable in air was given first priority, followed by a test of the reactivity of the lunar material with air.

The Mössbauer apparatus included two electromechanical systems and a constant velocity mechanical system. The sources were $^{57}\mathrm{Co}$ in Cu. All spectra are shown relative to zero velocity at the center of the metallic iron spectrum. The samples were received (from NASA) sealed in nitrogen in nesting plastic containers.

The initial material, designated 10084, 85 was from the < 1 mm size fraction of the bulk sample. Immediately upon receipt, it was placed in a glove box which was flushed with nitrogen 3 times before the sample was opened and sieved. A portion (approximately 40 mg/cm^2) of the fraction < 74 μm was loaded into a vacuum cryostat (Dewar) also in the glove box.

Using an electromechanical system, we obtained spectra with $\sim 10^6$ count/channel for the velocity ranges $\pm$ 11 and $\pm$ 3.4 mm/sec at room temperature, 80°K and 5°K. All high-velocity scans showed weak lines of Fe metal. The rest of the absorption could in all cases be accounted for by Fe^{2+} in ilmenite, in pyroxene M1 and M2 sites (*1*), and in glass. A low-velocity scan at room temperature is shown in Fig. 1*a*. There was no indication either of unusual Fe charge states or of Fe^{3+} ions.

The intensity of one of the outer iron lines was then monitored with the constant-velocity spectrometer. After counting for 1 day to establish a reference, we exposed the sample to air. Counting continued for 4 days with no observable change, and we concluded that no significant reaction of the metallic phase with air occurred at room temperature. Subsequently all samples were handled in air. Measurements repeated on this sample after about 2 months exposure to air still indicate no reaction.

Approximately 330 mg of the < 74-μm dust from sample 10084 was separated into three fractions with heavy liquids (specific gravity, 3.3 and 4.25). Under a microscope the light fraction (about 250 mg) appeared to contain most of the glass and less than or about 10 percent pyroxene. The medium fraction (about 65 mg) appeared to be enriched in pyroxene, but ilmenite and some glass were also apparent. The heavy fraction (about 15 mg) was enriched in ilmenite, and considerable pyroxene was apparent.

Examination of the fractions with a magnet showed that most of the glassy material was strongly attracted, while less than half the material in either of the two heavier fractions was attracted. Mössbauer spectra showed that the Fe metal lines were relatively enhanced for the light glassy material compared with those in the spectra of the two heavier fractions. Therefore, we find a strong tendency for the Fe metal in the dust