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 $En_{0.19}Fs_{0.68}Wo_{0.13}$ for the bands and an almost pure diopside of the composition $En_{0.53}Wo_{0.47}$ 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}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}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 $< 74\ \mu$m 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

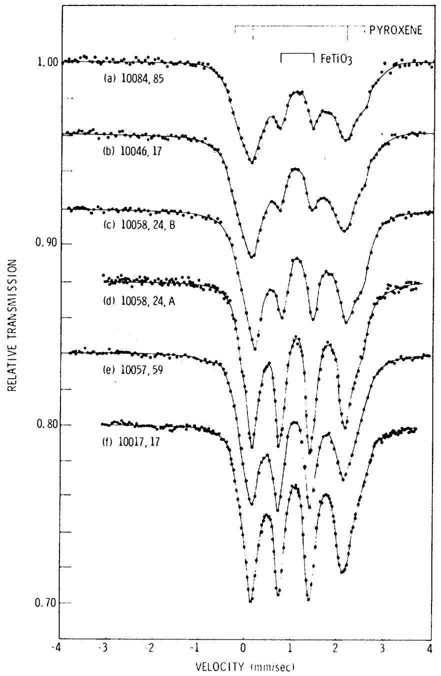


Fig. 1. Room-temperature Mössbauer spectra of lunar dust (*a*) and rock samples (*b–f*). Curves *b–f* have been displaced for clarity.

to be intimately associated with glass.

Approximately 100-mg portions of chips from four rocks, Nos. 10017,17 (fine grained, vesicular), 10058,24 (medium grained, not vesicular), 10057, 59 (fine grained, vesicular), and 10046, 17 (breccia), were crushed to fine powders. Mössbauer spectra were taken at room temperature with both wide and narrow velocity scans on the electromechanical systems. The narrow velocity spectra are shown in Fig. 1, curves *b–f*. Sample 10058 consisted of two fragments, and separate absorbers were made from parts of each. As indicated by Fig. 1, curves *c* and *d*, sampling differences within a given rock (medium grained) can be important. A few grains from each rock also were mounted for microscopic examination.

The Mössbauer spectra of the breccia 10046 were almost identical with those of the bulk material 10084. In the case of rock 10057, we had both a surface piece 10057,59 and an interior piece 10057,60. Although the top of the surface piece had visible glazing of glass, finely fractured "sugary" feldspar, and other physical differences showing surface damage, the absorber prepared by grinding up a fragment about 2 mm thick gave a Mössbauer spectrum indistinguishable from that of the interior piece, thus indicating negligible penetration of surface damage.

The central parts of the spectra of the rocks, excluding the breccia 10046, show mainly ilmenite lines and pyroxene M1 and M2 site lines. However, preliminary spectrum-stripping analysis (*2*) also suggests the presence of small amounts of glass. Again there is no evidence of unusual charge states or of Fe^{3+} ions. Only a very small amount of olivine could be present in any of these rocks.

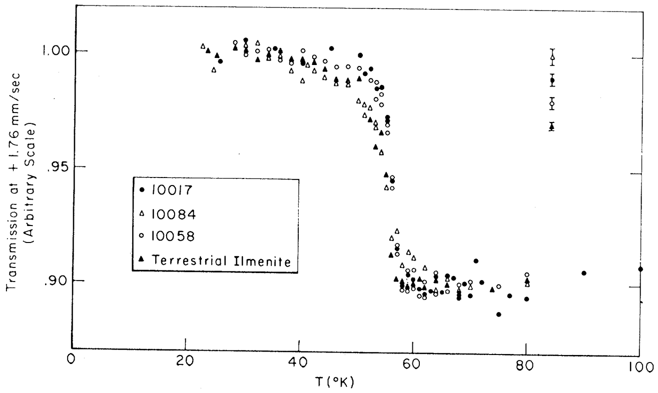
Although the pyroxene M1 and M2 site lines are not well resolved at room temperature, differences between the various rocks are apparent (especially after spectrum stripping). This may indicate chemical differences between the rocks and also provide information about the thermal or shock histories.

In the wide velocity scans of the rocks, metallic Fe was observed only in the breccia. However, weak absorption at the troilite FeS positions was definitely seen in the rocks 10017 and 10057 and possibly in 10058. The presence of pyrrhotite could not be ruled out on the basis of these data alone.

Relevant information was obtained from microscopic examination of the grain mounts. The breccia 10046 and the dust contained Fe metal (i) enclosed in glass spheres, (ii) associated with troilite blebs, (iii) as occasional irregular subangular grains, and (iv) as very fine (micrometer size) particles throughout the fine breccia matrix. Rocks 10017, 10058, and 10057 all contained troilite blebs often enclosing blebs of metallic iron. Metallic Fe was occasionally seen lining cracks in ilmenite and silicates. In sample 10058 and within rock fragments in the breccia, occasional exsolution lamellae of a phase more reflective and lighter in color were seen in the ilmenite.

On the basis of the above results we decided to investigate the stoichiometry and homogeneity of the ilmenite and to clarify the nature and association of the magnetically ordered phases. The temperature and sharpness of the antiferromagnetic transition in ilmenite of rocks 10017 and 10058 and the heavy fraction of the bulk sample 10084 were measured by the following technique. The constant-velocity spectrometer was set at the position of the higher energy line of the ilmenite quadrupole split doublet, and the counting rate was monitored as a function of temperature from about 20°K to about 80°K. Normalized results are shown in Fig. 2, together with data for a reference sample of terrestrial ilmenite (*3*) from Ashe County, North Carolina.

Approximately 500 mg of the interior portion of rock 10057 was finely powdered and forced to flow in an acetone suspension past a magnet (about 1 kilogauss). A total of 7.4



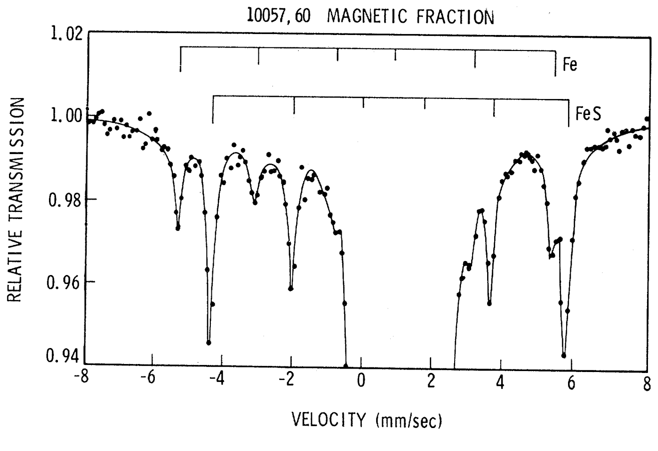


Fig. 2 (left). Normalized curves of counting rate plotted against temperature at + 1.76 mm/sec, from which the antiferromagnetic transition temperature of ilmenite is inferred. Fig. 3 (right). Room-temperature Mössbauer spectrum of magnetically separated material from lunar rock 10057.

mg of magnetic material was recovered. A spectrum of this material at room temperature is shown in Fig. 3. Relatively strong troilite lines and weaker Fe metal lines are easily visible. There is no evidence for pyrrhotite. The complete spectrum (untruncated) indicates an increase in the ratio of ilmenite to pyroxene but is otherwise similar to the spectrum of the unseparated rock.

To see whether the Fe metal plus FeS in the rock could possibly be sufficient to account for the Fe in the dust we obtained ratios of Fe metal and FeS to total Fe by summing the areas in appropriate groups of channels in the spectra. Metallic Fe plus FeS constitute about 11 percent of the total Fe in the dust and only about 5 percent of the total Fe in the rocks. On rock 10057 we found Fe metal and FeS individually to be about 1 and 4 percent of the total Fe. In the dust Fe metal is greater than or about 7 percent of the total Fe.

Assuming our samples are representative, we summarize our present conclusions as follows.

1) The original magma from which the rocks (at least 10057) crystallized was in a net-reduced state so that the assemblage of Fe metal + troilite formed on solidification with no pyrrhotite. The Fe metal lining cracks in ilmenite and silicates can be accounted for by the low temperature of the eutectic in the Fe-FeS system. It can be assumed that the major constituents of the rock were solid and that the ilmenite had already cracked because of contraction stresses before this Fe-FeS solution froze, causing some of the excess Fe to diffuse into the cracks in the ilmenite.

2) There is considerable excess of Fe metal in the dust over that in the rock or over that which could be formed by reducing all the FeS in the rocks. Therefore, a large fraction of the Fe metal in the dust must either result from reduction of Fe in the silicates during formation of the glass or be of meteoritic origin or perhaps both. Reduction of the silicates is possible with the right temperature-time relationship and could be enhanced if the surface being melted has been saturated with solar-wind hydrogen. If the different density fractions of the dust were analyzed for total Ni and the results compared with the Fe metal determined by the Mössbauer measurements, a semiquantitative estimate of the relative importance of the processes could be made.

3) The ilmenite of all samples seems to be homogeneous, well ordered, and very nearly stoichiometric $FeTiO_3$. The magnetic transition of rocks 10017 and 10058 is very sharp, and within the temperature accuracy of ± 2°K it corresponds to the values reported for synthetic $FeTiO_3$ (*5*). The transition for the dust is slightly broadened on the low-temperature side, perhaps because of disorder induced either by shock or by quenching from a high temperature. On the basis of available data (*5*), hematite (Fe_2O_3) in solution is expected to lower the magnetic transition temperature of ilmenite at a rate of about 2.8°K per mole percent. Therefore, we conclude that the ilmenite in our samples must contain less than 0.5 mole percent Fe_2O_3, and, since considerably more than this is soluble, the observed exsolution lamellae must not be Fe_2O_3. Since the original magma appears to have been highly reduced, we suggest the possibility that the lamellae might even be a phase containing Ti_2O_3.

4) As determined from bulk sample measurements, there appears to be no significant reaction of the metallic iron with laboratory air at room temperature over the time scale of about 2 months. Also, no other time-dependent spectrum changes were observed. There is no evidence for Fe^{3+} or unusual charge states.

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