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An assessment of results obtained from Mössbauer spectra of lunar samples

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Most of the minerals on the Moon's surface contain iron as a major constituent, and this enables them to be examined by Mössbauer spectroscopy. The advantages and limitations of this technique for examining lunar samples will be briefly mentioned, before reviewing the results so far obtained on material returned by the Apollo and Luna missions. By far the greatest proportion of iron is present as Fe(II) or Fe(0), and no appreciable concentration of Fe(III) has been observed. The relative amounts of iron-containing minerals at the various lunar sites have been determined and related to the lunar geological features. The more detailed determination of the distribution of iron between the M1 and M2 sites in pyroxene minerals leads to information on the thermal history of the rocks. Likewise the presence of superparamagnetic iron particles within the surface layers of some of the soil particles provides significant evidence concerning their origin and subsequent history.

Mössbauer spectroscopy is particularly valuable in providing detailed information on the chemical state of a specific element in any given sample. The high proportion of iron-containing phases in the lunar regolith has resulted in the extensive use of the ^{57}Fe resonance for non-destructive measurements, and data are available for Apollo 11, 12, 14–17 and Luna 16, 20 material. The concentration of other Mössbauer-active elements in lunar samples is too low to enable spectra to be obtained. This paper presents a brief review of some of the major results which have been obtained by using ^{57}Fe , but does not attempt to be comprehensive.

1. THE DISTRIBUTION OF IRON IN THE LUNAR REGOLITH

The Mössbauer measurement is normally made on a quantity of material sufficiently large for the spectrum of any sample of lunar fines to be truly representative of the bulk fines at that location, and enables a ready comparison of the chemical distribution of iron at different geographical locations on the lunar regolith (see for example Gibb, Greatrex & Greenwood 1974). In all cases the great majority of the iron is present as Fe^{2+} cations or as metallic iron (Fe^0), thus demonstrating that the lunar materials were formed under strongly reducing conditions. The Fe^{3+} state has not been positively identified in any significant quantity, but as detailed in §3 there is evidence that it can exist as an impurity cation.

The dominant paramagnetic materials containing iron (olivine, orthopyroxenes, clinopyroxenes, ilmenite, ulvospinel and vitreous phases) produce a complex absorption envelope which resembles three overlapping Fe^{2+} quadrupole doublets (see figure 1). An accurate estimate of the ilmenite (FeTiO_3) content may be obtained, and major variations are found in the fraction of iron present in this form. In the mare regions the ilmenite content is high ($\sim 20\%$ of total iron in Apollo 11, $\sim 8\%$ Apollo 12 and Luna 16), while in the highland regions it is generally lower, and is $< 0.5\%$ in Luna 20 fines. Measurements of the Néel temperature of the ilmenite from several Apollo 11 samples (Housley *et al.* 1970) were within 2 K of that for

synthetic FeTiO_3 , showing that the bulk of the ilmenite inclusions are close to stoichiometry with less than 2 at. % of Fe^{3+} or Mg^{2+} as substitutional impurities.

It is extremely difficult to determine the proportions of iron in the different silicate phases in a heterogeneous sample. This problem has been discussed at length elsewhere (Gibb *et al.* 1974), and we believe that the only realistic interpretation is a subdivision into the fraction of iron in olivine + M1 pyroxene sites and in M2 pyroxene sites + vitreous phases. Alternative methods of analysis have been described (e.g. Huffman *et al.* 1974; Malysheva 1973; Malysheva & Kurash 1973), but where a separate assignment of the olivine and pyroxene content is made, these figures are unlikely to be accurate unless there is a low degree of vitrification and a restricted range of composition (i.e. in homogeneous rock samples). The divergence of opinions and the dependence of the numerical data upon the model adopted complicates any correlation of data from different sources.

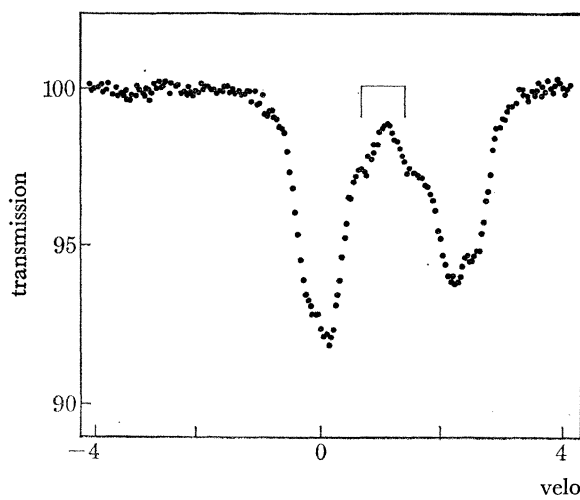


FIGURE 1

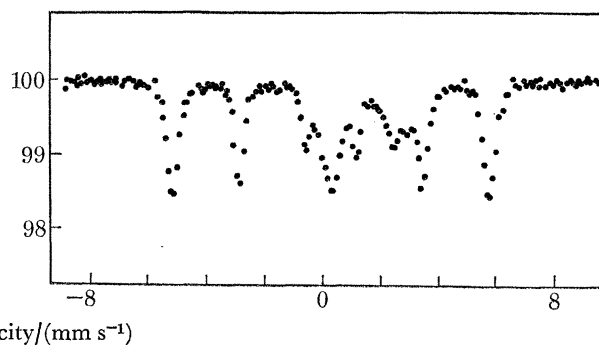


FIGURE 2

FIGURE 1. The Mössbauer spectrum at 292 K of sample L1627, 2 from the Luna 16 fines. Only the central absorption region from the silicate phases and ilmenite is shown. The ilmenite lines are indicated, but the individual silicates overlap too strongly for positive identification at this temperature.

FIGURE 2. The Mössbauer spectrum at 78 K of a magnetic concentrate from sample 14259, 17 from the Apollo 14 fines. The six-line magnetic hyperfine splitting from the ferromagnetic iron corresponds to an average nickel content of 3 at. %. The additional components in the central region are from residual silicate phases.

The dominant magnetic phase has been iron metal in all instances, and the fraction of the total iron is reasonably constant in the range 2–6 at. %, being generally higher in the more mature soils which have a higher proportion of glass-bonded agglutinates. The internal magnetic field in the metal often deviates slightly from that expected for the pure ferromagnetic iron metal as a result of alloying with nickel, and can be used to obtain an average value for the Ni content. For example, the spectrum in figure 2 was obtained from a magnetic concentrate extracted from the fines 14259. The average nickel content was estimated to be 3 at. % (Gibb *et al.* 1972). This figure may be compared with an estimate of 4.5 at. % from X-ray fluorescence measurements on the same sample, and an average of 5.4 at. % from microprobe measurements on 25 of the larger fragments.

The comparatively high proportion of iron in troilite (FeS) at the Apollo 11 site (~ 1 at. %) has not been found elsewhere. There are a few reports of unidentified magnetic phases in very low concentration which are probably Cr-spinels (e.g. Huffman *et al.* 1974).

The same minerals are found in the rocks and breccias, although the range of variation in composition is much greater. The relative proportions of iron present as iron(II) in different phases can be linked to the crystallization from the original magma. For example the Apollo 16 and 17 rocks and breccias have been shown to contain a significantly larger proportion of iron(II) as olivines, which is consistent with a higher temperature of crystallization for the material in the lunar highlands (Huffman *et al.* 1974).

2. GEOTHERMOMETRY

It is of particular interest to ascertain the subsolidus cooling rates of individual rocks, and information on this can be obtained from separates of pyroxenes or olivines by coupling Mössbauer measurements with supporting petrological and microprobe data.

The equilibrium distribution of Mg^{2+} and Fe^{2+} cations between the M1 and M2 sites in pyroxenes is significantly temperature dependent. However, the rate of redistribution as the temperature changes is comparatively slow, so that a moderately rapid cooling of the matrix results in the preservation of the high-temperature distribution and hence of a thermal record which can be detected by the Mössbauer spectrum.

The thermodynamics of the redistribution in orthopyroxenes is particularly well understood, and it has been possible to obtain for example the thermal record of rock 14310 from orthopyroxene separates (Schürmann & Hafner 1972; Ghose *et al.* 1972; Gibb *et al.* 1972). This rock has a cation distribution corresponding to an equilibrium at ~ 600 °C, consistent with a fairly slow rate of subsolidus cooling as part of a large mass at least several metres below the surface. It therefore follows that the sample was subsequently excavated to the surface without substantial reheating.

In principle the same argument can be applied to the lunar clinopyroxenes, but in practice the method is less easy to apply for two reasons. First, the determination of the M1/M2 site occupation by Mössbauer spectroscopy is not as reliable as in the orthopyroxenes (Dowty *et al.* 1972). Secondly, the occurrence of exsolution of augite from a pigeonite matrix means that an analysis by microprobe methods is averaged and cannot be related directly to the M1/M2 site occupation of the pigeonite. A detailed study of this phenomenon has been carried out for a clinopyroxene separate from rock 15065 (Yajima & Hafner 1974). The Mössbauer results are not entirely consistent with parallel measurements by X-ray methods for individual crystals of the pigeonite; the larger sample used for a Mössbauer measurement may have been inhomogeneous, whereas the X-ray data are affected by the composition assumed for the exsolved augite. A much more effective approach is to anneal the clinopyroxene separate at successively higher temperatures and observe the 'apparent' changes in cation distribution. In this way the separate from 15065 was found to have a cation distribution corresponding to a comparatively low temperature of the order of 600 °C. Whether this occurred after crystallization in a deep lava flow or in a subsequent annealing process is uncertain. However, the distinction should be drawn between the initial subsolidus cooling, which from the nature of the augite exsolution appears to have been rapid in the case of 15065, and the cooling rate at lower temperatures where the cation redistribution process is finally frozen. This is illustrated by rock 14053 which has a grain size and texture indicative of slow subsolidus cooling, but a cation disorder indicating equilibration at ~ 840 °C by rapid cooling (Schürmann & Hafner 1972). One may therefore conclude that this particular rock was reheated by an impact event and then re-cooled quickly.

The olivine minerals can similarly show ordering of the Mg^{2+} and Fe^{2+} cations on the M1 and M2 sites. However, the redistribution process is slower at any given temperature than in the pyroxenes, and in consequence is sensitive to a different rate of cooling. The ordered cation distribution for an olivine of composition $Fa_{36}Fo_{64}$ in lunar basalt 12018 is consistent with a very slow cooling during crystallization (Virgo & Hafner 1972). However, an independent X-ray study of the site population of an olivine also from rock 12018 but with a composition $Fa_{18}Fo_{82}$ has revealed a much more disordered state (Brown & Prewitt 1973). This anomalous result suggests that the early-crystallizing Mg-rich crystals are less ordered than the late-crystallizing Fe-rich crystals.

With the recent discovery of other geothermometric methods such as the partitioning of zirconium between coexisting ilmenite and ilvospinel, or of titanium between coexisting troilite and ilmenite (Taylor & Williams 1974), it should be possible to combine several different measurements on any given lunar rock to determine the subsolidus cooling history over a wider range of temperatures.

3. IMPURITY Fe^{3+} CATIONS

Although lunar material in general is in a highly reduced state, there is widespread evidence that small amounts of Fe^{3+} can be stabilized as a substitutional impurity. In two instances the chemical state of iron impurity atoms in plagioclase separates from lunar basalts has been determined (Appleman *et al.* 1971; Hafner *et al.* 1971). Over 95% of the iron occurs as high-spin Fe^{2+} ions in at least two distinct environments, one being a substituted Ca^{2+} site, the other possibly a defect site coupled with oxygen vacancies. A minor part of the resonance (< 5%) may be attributed to an unresolved Fe^{3+} component, this being in agreement with electron paramagnetic resonance data on similar types of rock. This behaviour contrasts with the terrestrial feldspars where extensive Fe^{3+} substitution at Al^{3+} sites occurs, and provides further evidence of the highly reduced state of the rocks.

4. SOLAR-WIND REDUCTION

A major feature of the Mössbauer resonance from any bulk sample of fines is an additional absorption at the centroid of the ferromagnetic iron metal components which can be attributed to superparamagnetic ultra-fine particles (< 10 nm in diameter) of iron metal. This can be seen for example in figure 1 as a more intense absorption near zero velocity in what should be a symmetrical spectrum. Measurements on size, density, and magnetic fractions from a range of samples from all the Apollo and Luna sites (e.g. Housley *et al.* 1971, 1972, 1973, 1974; Gibb *et al.* 1972, 1974, 1976; Malysheva 1973) show conclusively that the proportion of iron in this form increases with decreasing particle size, and with decreasing particle density, thus suggesting that the iron metal is contained in the surface of glass-welded aggregates. Housley *et al.* (1973*a*) have proposed a model for the surface reduction of Fe^{2+} to give Fe^0 by a combination of solar wind bombardment (by hydrogen, carbon and nitrogen atoms) and micro-meteorite impact. This model has been convincingly verified by Forester (1973): a conversion electron Mössbauer scattering experiment which records selectively those iron atoms within *ca.* 0.1 μm of the particle surface showed that the relative proportion of superparamagnetic iron is much greater in the surface layers than in the bulk of the particles.

It is not certain as to what fraction of the larger particles of ferromagnetic Fe metal were formed by agglomeration of reduced iron. Forester showed that this process is probably significant by demonstrating a rapid aggregation into ferromagnetic particles upon mild thermal annealing, and it seems likely that this origin is more probable than a purely internal chemical reduction or a direct introduction via meteoritic impact. This is supported by scanning electron microscopy measurements which have shown the presence of submicron metal balls on glass-welded aggregates (Housley *et al.* 1974). Similar balls are not found on mineral grains or fracture surfaces in the glass.

However, it is not uncommon to find large iron particles with a nickel concentration in the range 18–30 at.%, and it is probable that alloys in this composition range are paramagnetic and may be confused with the contribution from superparamagnetic small particles (Gibb *et al.* 1972). It may be significant that, although there is a linear correlation between the carbon present as carbide (normalized by using the ^{36}Ar content as a measure of total solar-wind exposure) and the total iron content, the correlation with the fraction of Fe^0 indicated by Mössbauer data is not yet clear (Pillinger *et al.* 1974). It would be instructive to draw a similar comparison with nitrogen present as nitride, as the lower tendency to lose ammonia rather than methane may result in a better monitor of surface exposure (Müller 1974). Nevertheless, the use of the $\text{Fe}^0/\text{Fe}^{2+}$ ratio as an indication of relative soil maturity is evident. Moreover, it seems that in cases where the proportion of iron in olivine is high, the Mössbauer data provide a better estimate of the proportion of ferromagnetic iron than conventional magnetic measurements, because the latter are influenced by strong antiferromagnetic interactions in the olivine (Huffman *et al.* 1974).

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