Mossbauer Studies of Luna 16 and 20 Lunar Soils

T. C. Gibb, R. Greatrex and N. N. Greenwood

Phil. Trans. R. Soc. Lond. A 1977 **284**, 157-165
doi: 10.1098/rsta.1977.0006

Phil. Trans. R. Soc. Lond. A. **284**, 157–165 (1977) [157]
Printed in Great Britain

MÖSSBAUER STUDIES OF LUNA 16 AND 20 LUNAR SOILS

By T. C. GIBB, R. GREATREX, and N. N. GREENWOOD
Department of Inorganic and Structural Chemistry, University of Leeds,
Leeds LS2 9JT

(*Communicated by Sir Harrie Massey, Sec.R.S. – Submitted* 2 *February* 1975 –
Received 5 *September* 1975)

CONTENTS

Samples of lunar soil returned by Luna 16 from Mare Fecunditatis and by Luna 20 from the highlands near the crater Appolonius C have been studied by ^{57}Fe Mössbauer spectroscopy. This enables the distribution of the total iron content between the various mineral phases to be determined. No troilite, magnetite or Fe^{3+} was detected and the suggestion that ulvospinel (Fe_2TiO_4) is present in substantial amounts in the fine-particle separates is discounted. The spectra were shown to arise from a metallic iron phase, and from Fe^{2+} in olivine, in the M1 and M2 sites of pyroxene, in ilmenite and in glasses. The slight asymmetry of the spectra is ascribed to superparamagnetic iron in the finest particles and it is considered that this is formed by solar-wind reduction. The ilmenite content of the Luna 16 soil is higher than for Apollo 12, 14 and 15 soils but less than for Apollo 11 soil; the ilmenite content of the Luna 20 soil is exceptionally low. The soils from both Luna missions show an increased amount of iron in olivine and M1 pyroxene sites comparable with that found for Apollo 15 soils from the edge of Hadley Rille. The narrower linewidths in the Mössbauer spectra of the Luna 20 soil suggest that the proportion of iron-containing glassy phases in this sample is lower than for the Luna 16 soil.

Introduction

This paper describes the results of an investigation by Mössbauer spectroscopy of samples of lunar soils collected by Luna 16 from the north eastern region of Mare Fecunditatis (Vinogradov 1971) and by Luna 20 from a highland region near the crater Appolonius C (Vinogradov 1972). Many of the component minerals contain a substantial proportion of iron, and can therefore be studied without degradation using the ^{57}Fe Mössbauer resonance. The heterogeneous nature of the soils results in this being the only experimental method which can give an estimate of the distribution of iron between different mineral phases. The data are correlated with our earlier observations on Apollo 11 (Greenwood & Howe 1970), Apollo 14

Gibb, Greatrex & Greenwood 1972) and Apollo 15 soils (Gibb, Greatrex & Greenwood 1974), and with other independent investigations of Apollo and Luna soils.

The samples made available to us comprised (1) 40 mg of unseparated material from the 27 cm level of the Luna 16 core sample (L1627,2); (2) 2 mg of the finest fines separated from the same sample (L1627,9); and (3) 40 mg of unseparated material from the 27–32 cm level of the Luna 20 core sample (L2015,2).

Preliminary investigations of the Luna 16 soil (Vinogradov 1971; Grieve, McKay & Weill 1972; Keil *et al.* 1972; Jakes *et al.* 1972) have revealed that the major silicate components are plagioclases and clinopyroxenes, with some olivines and only traces of orthopyroxenes. The major opaque mineral is ilmenite, with some iron metal, troilite, and spinel phases containing mainly Mg, Al, Ti, Cr and Fe. Glassy particles are abundant, particularly among the very fine particles. The overall composition is thus similar to those of the other mare areas. The Luna 16 soil is more closely related to the Apollo 11 soils except that the titanium and hence the ilmenite content are lower and more comparable to the Apollo 12 soils.

The Luna 20 soil (Vinogradov 1972; Tarasov *et al.* 1973; Brett *et al.* 1973) contains essentially the same minerals but with an increase in anorthositic plagioclase, clinopyroxene subordinated to orthopyroxene, a large decrease in ilmenite content, and an increase in iron-deficient spinel phases. The glass content is also unusually low.

Experimental

The Mössbauer spectra were recorded using a conventional spectrometer which has been described previously (Gibb *et al.* 1970). The 40 mg samples of the bulk fines (L1627,2 and L2015,2) were placed in small Perspex mounts designed to produce a uniform absorber of optimum thickness without degrading the sample. The 2 mg sample of the finest fines (L1627,9) was placed in a perspex mount having a small internal diameter such that a collimated beam of γ-rays could be passed through the sample in a vertical direction. The resulting absorber was not of uniform thickness. A 25 mCi source of ^{57}Co/Rh was used, and the γ-detection system was optimized by using a high-efficiency gas-proportional counter supplied by the A.E.R.E., Harwell. The small size of the absorbers necessitated longer counting times than normal to obtain 10^6 counts per channel. Even in the most difficult case of L1627,9 an absorption of 1.4 % with 8×10^6 counts per channel was obtained after counting for 10 days.

The samples L1627,2 and L2015,2 were examined at 295 K with a velocity scan of ± 10 mm s^{-1} to detect any ferromagnetic component, and then at both 295 and 78 K with a velocity scan of ± 4 mm s^{-1} to study the paramagnetic phases in more detail. The small sample L1627,9 was examined only at 295 K using a velocity scan of ± 10 mm s^{-1}. The spectra were calibrated using an iron foil enriched in ^{57}Fe and, in the diagrams, the absorption is expressed as a percentage of the total baseline count.

The data were analysed by least-squares curve-fitting methods. The central portions of the spectra obtained with a scan of ± 4 mm s^{-1} were fitted with six Lorentzian lines following the rationale given in the next section. It was found necessary to constrain the component lines from each quadrupole doublet to have equal widths, and in the case of the central ilmenite doublet the intensities of the two lines were also constrained to be equal. Various alternative procedures were also evaluated. The final figures quoted in table 1 are believed to represent the most reliable values which can be extracted from the data.

Results and discussion

The Mössbauer spectra of L1627,2, L1627,9 and L2015,2 at 295 K with a velocity scan of ± 10 mm s^{-1} are shown in figure 1. The spectra of L1627,2 and L2015,2 at 295 and 78 K with a velocity scan of ± 4 mm s^{-1} are shown in figures 2 and 3 respectively, together with the equivalent spectrum from an Apollo 15 soil from sample 15601,104 for comparison. Although the Mössbauer data obtained in the present work are visually similar to those recorded by the Russian workers (Malysheva 1972, 1973; Malysheva & Kurash 1973), there are a number of fundamental differences in our interpretation of the data which arise primarily from a different assignment of the resonance lines. For this reason the detailed arguments behind the present interpretation, which draws heavily on experience in the interpretation of the data from Apollo 14 and 15 soils, soil separates, and rocks, will be given.

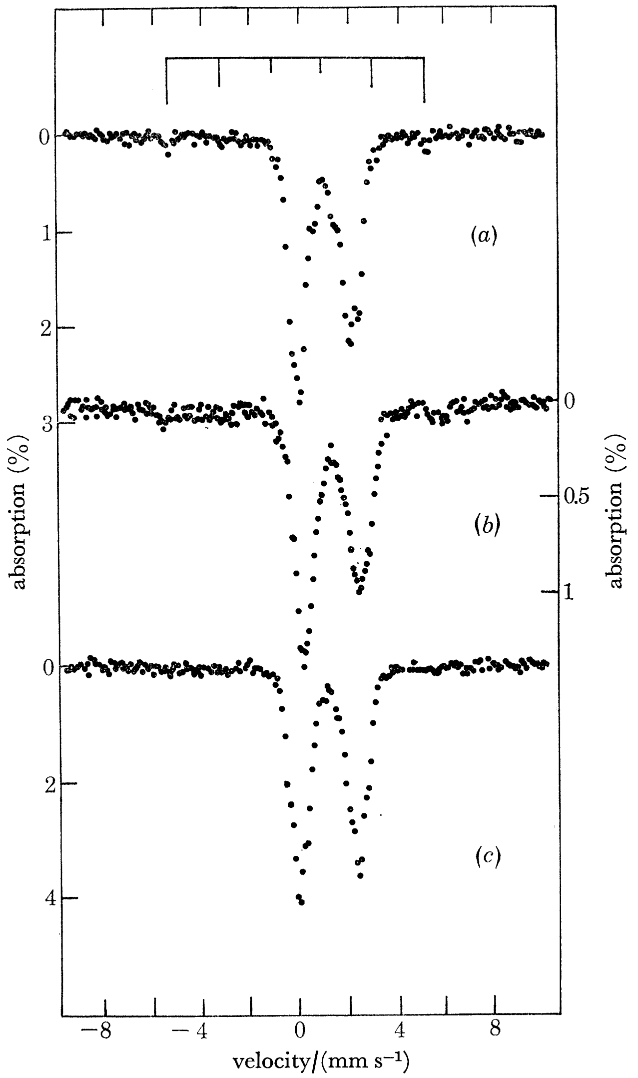

Figure 1. The Mössbauer spectra at 295 K of (*a*) L1627,2 (*b*) L1627,9 and (*c*) L2015,2. Note the increased excess area at zero velocity in L1627,9, and the apparent absence of magnetic iron in L2015,2. The known line positions for pure iron metal are indicated by the bars.

The presence of a ferromagnetic iron–nickel alloy in L1627,2 and L1627,9 can be seen by comparing the spectra in figure 1 with the stick diagram which shows the expected positions for pure iron metal. The value of the average magnetic flux density in L1627,2 is 33.0 ± 0.5 T, but unfortunately it was not possible to ascertain a more accurate value in order to determine the nickel content. However, metallic iron is clearly the dominant magnetic phase, and there is no evidence for a substantial proportion of troilite, FeS, or of any oxidized species such as magnetite, Fe_3O_4.

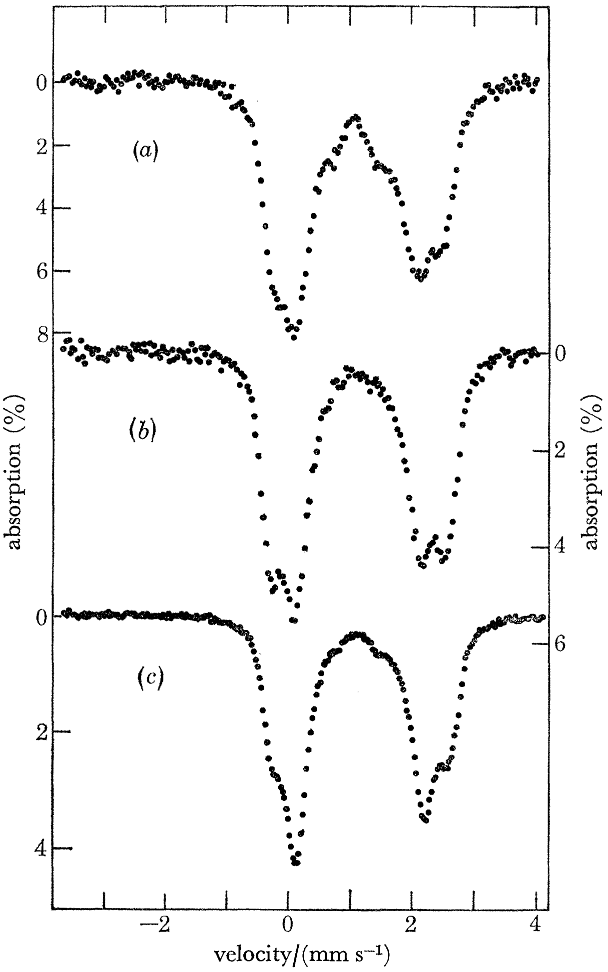

FIGURE 2. The Mössbauer spectra at 295 K of (a) L1627,2 (b) L2015,2 and (c) Apollo 15 soil 15601,104. Note the very low ilmenite content in 15601,104, and its apparent absence in L2015,2.

By way of contrast the spectrum of L2015,2 shows no evidence of a magnetic component, and it is concluded that less than 2 % of the total iron is present as a ferromagnetic iron–nickel alloy.

The central intense portion of the resonance from nearly all the Apollo and Luna soils has the appearance of three superimposed quadrupole doublets of different intensity but with similar chemical isomer shifts characteristic of the reduced Fe^{2+} species. This can be seen for example in figure 2. This part of the spectrum contains contributions primarily from the orthopyroxenes, clinopyroxenes, olivine, ilmenite, glassy phases, and superparamagnetic iron. No evidence was found for any Fe^{3+} species to within the experimental accuracy of < 0.5

mass % of total iron. The lunar ilmenite is generally close to the stoichiometry $FeTiO_3$ (see for example, Brett *et al.* 1973), and as such should have Mössbauer parameters close to those of terrestrial samples (Gibb, Greenwood & Twist 1969). For example, the parameters expected at 295 K are a quadrupole splitting of 1.06 mm s^{-1} and a chemical isomer shift of +0.70 mm s^{-1} (relative to iron metal at the same temperature). These parameters are unlikely to be drastically affected by small deviations from stoichiometry so that the linewidths of the ilmenite resonance should be comparatively narrow, and this is observed experimentally. The quadrupole splitting increases rapidly with decreasing temperature so that the ilmenite lines are most clearly resolved from the silicate components at room temperature.

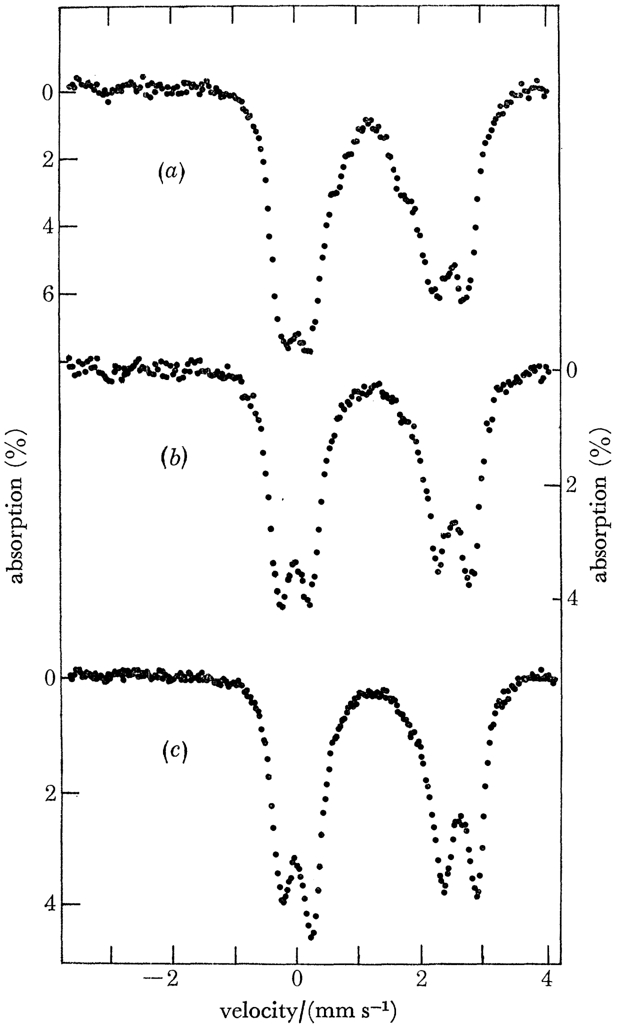

FIGURE 3. The Mössbauer spectra at 78 K of (*a*) L1627,2 (*b*) L2015,2 and (*c*) 15601,104.

Few data are available for separated lunar olivines, but in a sample of average composition $Fo_{67\cdot3}Fa_{32\cdot7}$ from Apollo 12 rock 12018, the iron atoms occupying M1 and M2 sites could not be distinguished in the Mössbauer spectrum except at temperatures well above 295 K (Virgo & Hafner 1972). More extensive data for terrestrial olivines (Virgo & Hafner 1972; Bush, Hafner & Virgo 1970) reveal no significant dependence on composition, with a quadrupole splitting at 295 K of about 2.9 mm s^{-1}.

The orthopyroxenes and clinopyroxenes both contain iron at two sites designated M1 and M2, and these give distinct quadrupole splittings at all temperatures up to and above 300 K. From an extensive study of terrestrial orthopyroxenes (Virgo & Hafner 1968, 1970) it is known that the quadrupole splittings of the M1 and M2 site Fe^{2+} cations are *ca.* 2.5 mm s^{-1} and *ca.* 2.1 mm s^{-1} respectively at room temperature and *ca.* 3.0 mm s^{-1} and *ca.* 2.1 mm s^{-1} respectively at 77 K. These values change slightly with change in the overall composition, but otherwise are not sensitive to the degree of cation order–disorder on the M1/M2 sites. However, the latter does result in significant changes in the relative absorption intensity from the two sites since this absorption intensity is approximately proportional to the Fe^{2+} populations on each site. The clinopyroxenes including pigeonite and augite are basically similar to the orthopyroxenes, and a number of lunar mineral separates have been characterized (Hafner, Virgo & Warburton 1971*a*; Ghose, Ng & Walter 1972). However, the fractional area of the outer doublet in the spectrum from a C2/c clinopyroxene (augite) as obtained by fitting four peaks to the spectrum decreases with increasing temperature (Williams *et al.* 1971; Dowty, Ross & Cuttita 1972). This is because the quadrupole splitting from cations on the M1 sites is not unique, and part of this component shows a different temperature dependence which results in it apparently merging with the M2 components at higher temperatures. The quadrupole splitting of the M1 site cations is such that this component is almost superimposed on the olivine resonance at 80 K.

The fourth major component is that originating from the glassy phases. A partial separate of glass from Apollo 11 sample 10084 has been reported to give the basic pyroxene spectrum but with much broader lines (Hafner *et al.* 1971) and a larger splitting from the M1 site cations. In one instance a large glass bubble from Apollo 12 rock 12057,10 has been found to show a broad doublet spectrum at room temperature with a quadrupole splitting of 2.08 mm s^{-1} similar to that from M2 sites in pyroxenes (Sullivan *et al.* 1971). In general the presence of glassy phases results in a broadening of the resonance lines.

In order to obtain semi-quantitative figures for the relative proportion of different minerals in the fines it is necessary, in the absence of any standardizing data, to assume that the concentration of iron is linearly proportional to the spectrum area. This assumes that the recoilless fraction is the same in each phase and that saturation effects can be ignored. Because of the difficulties discussed above, the best compromise is to estimate the fraction of iron contained in olivine + M1 pyroxene sites from the relative area of the outside pair of peaks at *ca.* 80 K, and the fraction in ilmenite from the area of the inner pair of peaks at *ca.* 295 K. The balance is then assigned to the M2 pyroxene sites + glass. This method allows a meaningful comparison of the fines from different lunar areas, but unfortunately is unable to determine the relative quantities of iron in olivine or glass. However, the apparent reduction in the olivine + M1 content at 295 K when compared to 80 K will be much greater when the clinopyroxene content is increased relative to the orthopyroxene.

One additional feature which must also be taken into account is a tendency for the component in the M2 pyroxene spectrum near zero velocity to be more intense than its twin at higher velocity. It has been proposed that this is due to superparamagnetic iron metal in the very fine particles (Housley *et al.* 1971; Housley, Grant & Abdel-Gawad 1972). Current evidence is consistent with the hypothesis that iron metal is produced in the surface layers of the particles following reduction by protons or carbon atoms in the solar-wind bombardment (Housley, Grant & Paton 1973*a*). In our earlier work on Apollo 14 fines (Gibb *et al.* 1974) the ultra-fine washings from sample 14259,17 were found to have a significantly higher excess area in this component (9.3 %) than in the bulk fines (7.8 %) or the rocks (e.g. 5.2 % in 14310,66). More recently a fourfold increase in excess area has been recorded in the < 20 μm size-fraction of Apollo 16 fines 67001,26 compared to the 75–150 μm fraction (Housley, Cirlin & Grant 1973). Both observations are consistent with an inverse dependence on particle size, and imply that the metallic iron content is related to the surface area of the soil sample. A direct confirmation of this is provided by a conversion-electron back-scattering experiment on Apollo 15 soil 15021,118 which shows a very large excess area (Forester 1973). This type of experiment only records iron atoms within less than 0.25 μm of the surface of the particles, and thus shows convincingly that the excess area results from iron in the surface as opposed to the bulk of the particles. The excess area in the spectrum of a sample of soil is therefore a function of the particle size and the total exposure to the solar wind.

TABLE 1. THE DISTRIBUTION OF IRON AMONG VARIOUS PHASES EXPRESSED AS A PERCENTAGE OF THE TOTAL IRON CONTENT

sample	M1+olivine	M2+glass	ilmenite	magnetic iron	superpara-magnetic iron
Luna L1627,2	32	53	6.9	≈ 5	3.9
Luna L1627,9	—	—	—	≈ 8	≈ 7
Luna L2015,2	41	52	< 0.2	< 2	4.2
Apollo 14 (average of 4)	17	64	8	≈ 4	6
Apollo 14259,17 fine washings	17	—	—	≈ 8	9
Apollo 15 (mare and front)	26	63	2.4	4.1	4
Apollo 15 (Rille edge)	36	57	1.3	< 2	3

The distribution of iron among the various phases which was finally deduced for Luna 16, Luna 20 and some of the Apollo 14 and 15 data are given in table 1. The spectra from sample L1627,2 are most closely comparable visually to some of the Apollo 12 soils (e.g. 12042,38 Housley *et al.* 1971), although the ilmenite content is slightly higher, but still less than in Apollo 11. The olivine + M1 pyroxene content is much higher than in any of the Apollo 14 or 15 soils with the exception of Apollo 15 soils from the edge of Hadley Rille. The large increase in the superparamagnetic iron content of the separated L1627,9 and the fine washings from 14259,17 are fully consistent with the origins of this phase in solar-wind damage.

The Luna 20 sample is unusual in that ilmenite is absent to within our limits of detection (i.e. < 0.2 % of the iron as ilmenite; an ilmenite content of only 1.3 % is clearly visible in the spectrum of 15601,104 at 295 K). This is probably the lowest ilmenite content yet recorded in a bulk sample. Here again the olivine + M1 pyroxene content is higher than usual, and the low clinopyroxene content results in a smaller temperature-dependent anomaly in the line intensities. The resonance is significantly sharper than L1627,2, and this is consistent with the lower glass content of L2015,2.

The alternative interpretation adopted by Malysheva & Kurash (1973) was to assign the three apparent quadrupole doublets in order of decreasing quadrupole splitting to olivine, pyroxene + glass, and ilmenite. For the reasons outlined above this procedure ignores many of the inherent complexities of the system. Furthermore, the area of the outer doublet as measured at room temperature is likely to be too low because of the temperature anomaly of the C2/c clinopyroxenes.

It has been suggested that the data from a fine-particle separate from Luna 20 soil (Malysheva 1973) indicate that about 6% of the iron is in the form of ulvospinel (Fe_2TiO_4). This seems surprising in view of the fact that ulvospinel is not common in the Luna 20 soil, the majority of the spinels being Al/Mg phases with a low iron content (Brett *et al.* 1973). Our earlier measurements on the Fe_3O_4-Fe_2TiO_4 solid solution (Banerjee *et al.* 1967) imply that it would be difficult to distinguish such a spinel phase from the M2 pyroxene + glass sites. Moreover, if there were a major contribution to the spectrum from Fe_2TiO_4, the fact that this phase is magnetic at 78 K should cause major changes in the spectrum, but this is not observed with the bulk sample L2015,2. It is known that the finest particles tend to contain a higher proportion of glass, and any deviations in the central region of the spectrum could quite easily originate in these phases.

CONCLUSIONS

The following conclusions can be drawn:

(1) The bulk soils returned by Luna 16 and Luna 20 show a number of significant differences from those returned by Apollo 11, 12, 14 and 15.

(2) The ilmenite content of the Luna 16 soil is higher than for Apollo 12, 14 and 15, but less than for Apollo 11 soil. The ilmenite content of Luna 20 soil is exceptionally low – less than 0.2% of the total iron content being in this form.

(3) Both the Luna 16 and 20 soils show an increased distribution of iron in olivine + M1 pyroxene sites, comparable to the Apollo 15 soils from the edge of Hadley Rille.

(4) The Luna 20 soil shows narrower linewidths, and therefore contains less glass than the Luna 16 soil.

(5) The finest particles of the Luna 16 soil contain a higher proportion of superparamagnetic iron than does the bulk soil. This iron probably results from chemical reduction caused by solar-wind bombardment.

(6) No troilite, magnetite, or any oxidized Fe^{3+} species have been detected in these samples.

We thank the Soviet Academy of Sciences for providing the samples of Luna 16 and Luna 20 material, the Royal Society for sponsorship, and the Science Research Council for financial support.

REFERENCES

Banerjee, S. K., O'Reilly, W., Gibb, T. C. & Greenwood, N. N. 1967 *J. Phys. Chem. Solids* **28**, 1323–1335.
Brett, R., Gooley, R. C., Dowty, E., Prinz, M. & Keil, K. 1973 *Geochim. Cosmochim. Acta* **37**, 761–773.
Bush, W. R., Hafner, S. S. & Virgo, D. 1970 *Nature, Lond.* **227**, 1339–1341.
Dowty, E., Ross, M. & Cuttita, F. 1972 Proc. 3rd Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 3, vol. 1, pp. 481–492.
Forester, D. W. 1973 Proc. 4th Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 4, vol. 3, pp. 2697–2707.
Ghose, S., Ng, G. & Walter, L. S. 1972 Proc. 3rd Lunar Sci. Conf., *Geochim. Cosmochim. Acta*, Suppl. 3, vol. 1, pp. 507–531.
Gibb, T. C., Greatrex, R. & Greenwood, N. N. 1972 Proc. 3rd Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 3, vol. 3, pp. 2479–2493.
Gibb, T. C., Greatrex, R. & Greenwood, N. N. 1974 *J. Chem. Soc. Dalton* pp. 1148–1156.
Gibb, T. C., Greatrex, R., Greenwood, N. N. & Sarma, A. C. 1970 *J. Chem. Soc.* A, pp. 212–217.

Gibb, T. C., Greenwood, N. N. & Twist, W. 1969 *J. inorg. nucl. Chem.* **31**, 947–954.

Greenwood, N. N. & Howe, A. T. 1970 Proc. Apollo 11 Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 1, vol. 3, pp. 2163–2169.

Grieve, R. A. F., McKay, G. A. & Weill, D. F. 1972 *Earth planet. Sci. Lett.* **13**, 233–242.

Hafner, S. S., Janik, B. & Virgo, D. 1971 *Mössbauer effect methodology* (ed. I. J. Gruverman), vol. 6, p. 193. New York: Plenum Press.

Hafner, S. S., Virgo, D. & Warburton, D. 1971*a* Proc. 2nd Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 2, vol. 1, pp. 91–108.

Housley, R. M., Grant, R. W., Muir, A. H., Blander, M. & Abdel-Gawad, M. 1971 Proc. 2nd Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 2, vol. 3, pp. 2125–2136.

Housley, R. M., Grant, R. W. & Abdel-Gawad, M. 1972 Proc. 3rd Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 3, vol., 1, pp. 1065–1076.

Housley, R. M., Cirlin, E. H. & Grant, R. W. 1973 Proc. 4th Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 4, vol. 3, pp. 2729–2735.

Housley, R. M., Grant, R. W. & Paton, N. E. 1973*a* Proc. 4th Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 4, vol. 3, pp. 2737–2749.

Jakes, P., Warner, J., Ridley, W. I., Reid, A. M., Harmon, R. S., Brett, R. & Brown, R. W. 1972 *Earth planet. Sci. Lett.* **13**, 257–271.

Keil, K., Kurat, G., Prinz, M. & Green, J. A. 1972 *Earth Planet. Sci. Lett.* **13**, 243–256.

Malysheva, T. V. 1972 Proc. 3rd Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, Suppl. 3, vol. 1, pp. 105–114.

Malysheva, T. V. 1973 *Geokhimiya*, pp. 1079–1084.

Malysheva, T. V. & Kurash, V. V. 1973 *Geokhimiya*, pp. 120–125.

Sullivan, S., Thorpe, A. N., Alexander, C. C., Senftle, F. E. & Dwornik, E. 1971 Proc. 2nd Lunar Sci. Conf. *Geochim. Cosmochim. Acta*, suppl. 2, vol. 3, pp. 2433–2449.

Tarasov, L. S., Florensky, K. P., Ivanov, A. V. & Rhode, O. D. 1973 *Geokhimiya*, pp. 1275–1286.

Vinogradov, A. P. 1971 *Geokhimya*, pp. 8–15.

Vinogradov, A. P. 1972 *Geokhimiya*, pp. 763–774.

Virgo, D. & Hafner, S. S. 1968 *Earth planet. Sci. Lett.* **4**, 265–269.

Virgo, D. & Hafner, S. S. 1970 *Am. Mineral* **55**, 201–223.

Virgo, D. & Hafner, S. S. 1972 *Earth planet. Sci. Lett.* **14**, 305–312.

Williams, P. G. L., Bancroft, G. M., Brown, M. G. & Turnock, A. C. 1971 *Nature, Phys. Sci.* **230**, 159–151.