Mössbauer Studies of Apollo 14 and Apollo 15 Lunar Soils

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Four soil samples from the Lunar regolith at Fra Mauro and five from Hadley Rille have been examined by Mössbauer spectroscopy. The proportions of the total iron content in different minerals have been established. Measurements on a series of mineral concentrates from one of the Fra Mauro soils show that the dense opaque minerals occur as inclusions in the lighter silicates and glasses, and that some of the iron–nickel alloy inclusions are apparently 'paramagnetic' in behaviour. The soils from the rim of Hadley Rille prove to be characteristically different from those of the mare basin and the Appenine front. The degree of vitrification is much less than in soils from Fra Mauro.

LUNAR material has been returned by six manned and two instrumented expeditions to the moon. These returns encompass a selection of rocks, soils (or fines), and core-samples from Mare Tranquillitatis (Apollo 11), Oceanus Procellarum (Apollo 12), and Mare Fecunditatis (Luna 16) which are all low-lying Mare areas; Fra Mauro (Apollo 14) which is believed to be an ejecta blanket of pre-mare crust from the Imbrium basin; Hadley Rille (Apollo 15) which is in a Mare area at the foot of the Appenine mountains; and Descartes (Apollo 16), Taurus-Littrow on the rim of Mare Serenitatis (Apollo 17), and a site near the edge of Mare Fecunditatis (Luna 20) which are all highland regions. In addition, crude *in situ* chemical analyses were made earlier by automatic probes at Mare Tranquillitatis (Surveyor 5), Sinus Medii (Surveyor 6), Mare Imbrium (Luna 17), and in the lunar highlands near the crater Tycho (Surveyor 7).

The preliminary work on the Apollo 11, 12, and 14 samples is now well documented,[1-3] but very little has yet been published on the later returns. The intensiveness of the parallel scientific investigation in many laboratories causes difficulties in assessing the data collected. In this paper our results on lunar soils from Apollo 15 are presented and correlated with our earlier observations on Apollo 11 [4] and Apollo 14 soils.[5]

The major constituents of both the soils and rocks at all sites have been silicate minerals (clinopyroxenes usually with orthopyroxenes, olivine, and plagioclase), opaque minerals (mainly ilmenite, troilite, and metallic iron with trace quantities of spinel oxides and other phases), and glassy material. The soils have proved to be finely powdered and almost invariant in average composition at several sites, with mineral fragments and glassy globules representing the entire suite of local surface minerals. The degree of glassification in general and the brecciation of the rocks are related to the time of surface exposure and to the local severity of catastrophic events such as meteorite impacts by which the fragments were generated. Thus these features are most severe at the Apollo 14 site which is consistent with its origin as ejected material from Mare Imbrium.

TABLE 1

Major element analyses (as wt. % of oxide)

	SiO_2	TiO_2	Al_2O_3	MgO	CaO	FeO	Na_2O	K_2O	Ni (p.p.m.)	Atomic ratios Ti : Fe	Mg : Fe	Ref.
Surveyor 5	45·9	[7·1]	14·6	5·0	[13·8]	[12·2]	0·65					6
Surveyor 6	49·1	[3·5]	14·7	6·6	[12·9]	[12·4]	0·8					6
Surveyor 7	45·3	[0]	21·7	6·7	[17·9]	[5·3]	0·7					6
Apollo 11 (average)	42·04	7·48	13·92	7·90	12·01	15·74	0·44	0·14	185	0·43	0·89	7
Apollo 12 (average)	46·40	2·66	13·50	9·73	10·50	15·50	0·59	0·32	195	0·154	1·12	7
Apollo 14 (average)	47·93	1·74	17·60	9·24	11·19	10·37	0·68	0·55	370	0·151	1·59	7
Apollo 15 (average Mare)	45·98	1·78	12·26	10·79	10·27	16·99	0·35	0·15		0·094	1·13	8
(average Front)	46·19	1·30	16·14	11·01	11·17	12·62	0·39	0·18	264	0·093	1·55	8
Apollo 16 (average)	45·12	0·56	27·25	5·66	6·20	5·26	0·42	0·10	258	0·095	1·92	9
Apollo 17 (' orange soil ')	38·98	9·23	5·67	14·47	7·3	22·44	0·43	0·04	65	0·37	1·15	10
Luna 16 (average)	41·7	3·39	15·33	8·78	12·49	16·64	0·34	0·15	190	0·18	0·94	11
Luna 20 (average)	44·40	0·56	22·90	9·70	15·20	7·03	0·55	0·10		0·071	2·46	12
14003	48·08	1·77	17·59	9·27	11·12	10·45	0·65	0·54	430	0·152	1·58	7
14163	47·97	1·77	17·57	9·18	11·15	10·41	0·68	0·58	400	0·153	1·57	7
14259	48·16	1·73	17·60	9·26	11·25	10·41	0·61	0·51	440	0·149	1·58	7
15021	46·56	1·75	13·73	10·37	10·54	15·21	0·41	0·20	288	0·103	1·21	8
15101	45·95	1·27	17·38	10·36	11·52	11·65	0·39	0·17	260	0·109	1·58	8
15601	45·05	1·98	10·20	10·89	9·87	19·79	0·29	0·10		0·090	0·98	8

Significant information can be gleaned from a comparison of the major element analyses summarized in Table 1. Typical averaged figures are given for each location (with the exception of Apollo 17 for which data are not yet available)*. The original Surveyor results [6] were more tentative as ' TiO_2 ', ' CaO ', and ' FeO ' were applied to a possible range of elements, but they follow the general trends remarkably well. Individual analyses for some of the soil samples which were also in our consignment are listed.[6-12]

Mare Tranquillitatis (Surveyor 5 and Apollo 11) is atypical of the mare areas in having an exceptionally high titanium content (mainly as ilmenite). The high aluminium–calcium and low iron–magnesium content of Surveyor 7, Apollo 16, and Luna 20 analyses confirm that the lunar highlands contain a much higher proportion of anorthositic plagioclase. Apollo 15 soils from the front of the Appenine mountains also show this feature and are distinct from samples collected on the Mare surface.

With the exception of plagioclase, all the major lunar materials contain a substantial proportion of iron, and can be studied by Mössbauer spectroscopy with the minimum of degradation. The experimental techniques used in the present work have already been described.[5]

RESULTS AND DISCUSSION

Fines from Fra Mauro.—Four samples of fines returned by Apollo 14 from the Fra Mauro formation were released to us: **14003,20** from the contingency fines, particle size <1 mm; **14162,48** (1—2 mm) and **14163,50** (<1 mm) from the bulk fines collected at the end of the first EVA from an average depth of several cm; **14259,17** from the comprehensive fines scooped from the upper 1 cm of the regolith and also <1 mm particle size. All four were collected within a 100 m radius of the lunar module. Both **14163** and **14259** were reported on preliminary examination to have about 45% glassy

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* *Added at proof:* These data have now been published in *Science*, 1973, **182**, 659.

[1] Proc. Apollo 11 Lunar Sci. Conf., *Geochim. Cosmochim. Acta*, 1970, Suppl. 1, **1—3**.

[2] Proc. Second Lunar Sci. Conf., *Geochim. Cosmochim. Acta*, 1971, Suppl. 2, **1—3**.

[3] Proc. Third Lunar Sci. Conf., *Geochim. Cosmochim. Acta*, 1972, Suppl. 3, **1—3**.

[4] N. N. Greenwood and A. T. Howe, ref. 1, vol. 3, p. 2163.

[5] T. C. Gibb, R. Greatrex, N. N. Greenwood, and M. H. Battey, ref. 3, vol. 3, p. 2479.

[6] A. L. Turkevich, ref. 2, vol. 2, p. 1209.

[7] H. J. Rose, F. Cuttitta, C. S. Annell, M. K. Caron, R. P. Christian, E. J. Dwornik, L. P. Greenland, and D. T. Ligon, ref. 3, vol. 2, p. 1215.

[8] Apollo 15 Preliminary Examination Team, *Science*, 1972, **175**, 363.

[9] Apollo 16 Preliminary Examination Team, *Science*, 1973, **179**, 23.

[10] G. M. Brown, J. G. Holland, and A. Peckett, *Nature*, 1973, **242**, 515.

[11] A. P. Vinogradov, ref. 2, vol. 1, p. 1.

[12] J. Warner, A. M. Reid, W. I. Ridley, and R. W. Brown, *Earth Planetary Sci. Letters*, 1972, **17**, 7.

content, and the other two may be presumed to be similar.

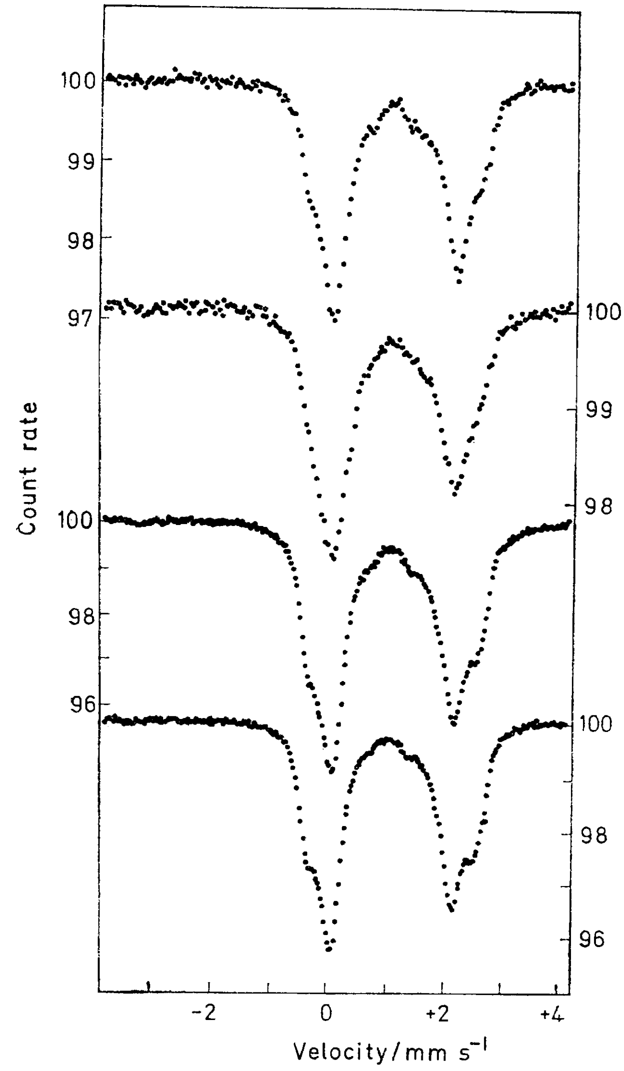

FIGURE 1 Mössbauer spectra of Apollo 14 and Apollo 15 soils at 295 K; from top to bottom, 14162, 14259, 15021, and 15601

Mössbauer spectra were recorded at 295 and 78 K for all four samples, and some typical examples are shown in Figures 1 and 2 with comparative data from Apollo 15 samples. The three soil fractions with a particle size <1 mm gave essentially identical spectra, and therefore only one is illustrated (14259). The marginally narrower lines and increased resolution of sample 14162 are probably indicative of a higher mineral and lower glass content in the larger fragments. This point will be clarified later.

Detailed interpretation requires a knowledge of the component minerals. Fortunately, such data are available for 14259 derived from electron-microprobe analysis of 856 individual grains.[13] About 45% of these were glasses from at least seven different mineral sources and with a wide range of composition and up to 20 wt % FeO: of the mineral fragments, 44% were plagioclases mainly in the range $An_{81}Al_{19}$—$An_{97}Al_3$ (the normative compositions are An ≡ anorthite, $CaAl_2Si_2O_8$; Al ≡ albite, $NaAlSi_3O_8$), and 3% were other feldspars; 16·7% were orthopyroxenes mainly in the range $En_{85}Fs_{15}$ to $En_{60}Fs_{40}$ with *ca.* 1—6% Wo (En ≡ enstatite, $Mg_2Si_2O_6$; Fs ≡ ferrosilite, $Fe_2Si_2O_6$; Wo ≡ wollastonite, $Ca_2Si_2O_6$); clinopyroxenes were 8·7% pigeonite and 15·8% augite ranging very widely in the enstatite–diopside–hedenbergite–ferrosilite quadrilateral with extremes in density of $En_{10}Wo_{25}Fs_{65}$ and $En_{65}Wo_{10}Fs_{25}$; 7·3% olivine, mainly close to $Fo_{67}Fa_{33}$ (Fo ≡ forsterite, Mg_2SiO_4; Fa ≡ fayalite, Fe_2SiO_4); *ca.* 3·1% ilmenite, $FeTiO_3$; 1·4% iron–nickel alloys, and less than 1% of troilite, FeS. At a crude estimate *ca.* 45% of the titanium is in glassy phases, and most of the rest may be presumed to occur as ilmenite.

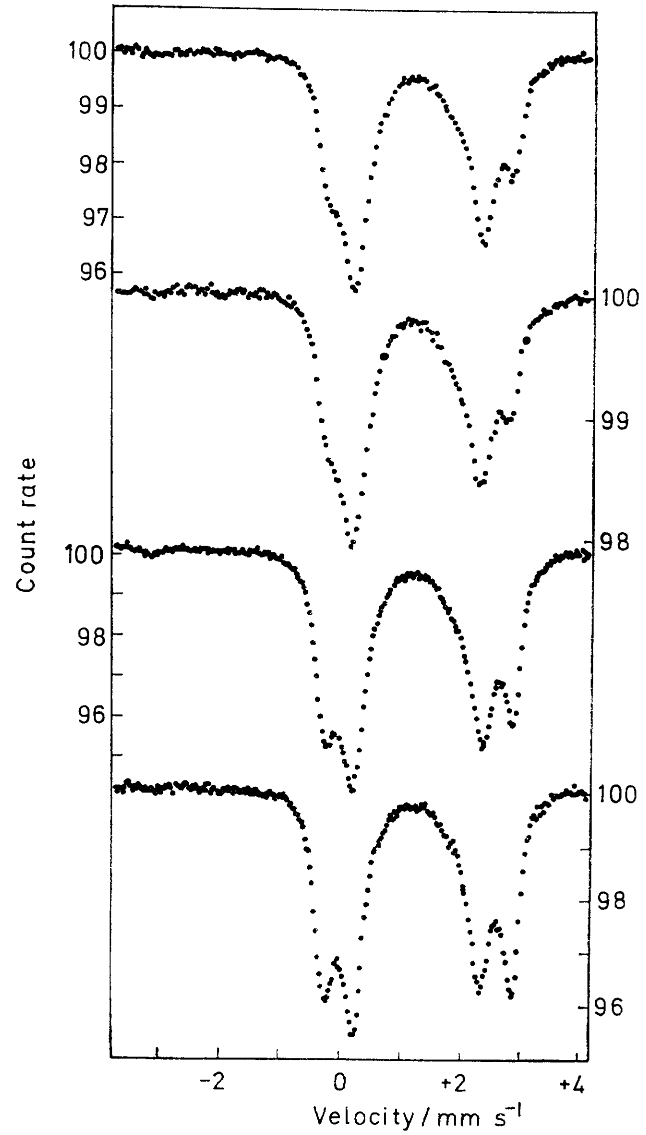

FIGURE 2 Mössbauer spectra of Apollo 14 and Apollo 15 soils at 78 K; from top to bottom, 14162, 14259, 15021, and 15601

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[13] Apollo Soil Survey, *Earth Planetary Sci. Letters*, 1972, **12**, 49.

A unique feature of this suite of minerals is that they are all in a highly reduced state. This is evident both from the chemical and microprobe analyses, and also by the failure to observe any major Fe^{3+} species in the ^{57}Fe Mössbauer spectra from Apollo 11 [4,14–17] and Apollo 12 samples.[18–21] Lunar ilmenite contains no Fe^{3+}, but does contain an excess of reduced Ti^{3+} ions.[22] Where an observation of an oxidised phase such as α-FeOOH has been made, the quantities found have been exceedingly small,[3] and there has usually been evidence of meteoritic impact.

The α-phase of the iron–nickel alloys produce a magnetic hyperfine splitting of *ca.* 333 kG at 295 K, *i.e.*, slightly larger than observed in pure iron. We were able to extract 7 mg of metal particles from soil 14259, and the detailed examination of these has been reported.[5] Electron microprobe analysis on 25 particles showed an average composition of 5·4 atom % Ni, 0·6 atom % Co with overall ranges of 2—13 and 0·3—1·0% respectively. A two-phase fragment of α- and γ-phase alloys was also found, and it was shown that this composition required a long period of equilibration at *ca.* 740 K. The possibility of an additional single-line resonance contribution to the spectrum from small inclusions of Fe–Ni alloy was also raised, and new evidence consistent with this is given later. The contribution of α-phase alloys to the resonance is of the order of 5 atom % in the soils but is difficult to establish accurately because of the broad non-Lorentzian line profile. By contrast, the Apollo 14 rock samples gave no evidence of metallic iron in the Mössbauer spectra (although it was found to be present in 14321 by microprobe analysis), and is below the 1% level. We were unable to detect troilite in any of our samples, and it is much less abundant than in the Apollo 11 soils.

The central absorption from the paramagnetic minerals comprises three quadrupole doublets. In order of decreasing splitting these have been universally attributed to olivine/M1 sites in pyroxenes, glass/M2 sites in pyroxenes, and ilmenite respectively. Although this is undoubtedly true at a crude level, it is soon evident that there are formidable problems attached to making quantitative measurements. As some of the pyroxenes have compositions not found naturally on Earth, reference data for the individual phases were not initially available. More recently, mineral separates have been obtained from the more crystalline rock samples, so that a more detailed discussion is now possible.

The spectra of the soils reported in the present work were curve fitted with six Lorentzian peaks with the line widths constrained in pairs. The resultant parameters for the silicate components are collected in Table 2 for the Apollo 14 soils and rocks (14300 series numbers) and Apollo 15 soils. They are fully consistent with other published data for bulk soils,[16] although it must be remarked that with composite spectra such as these, where the line-shapes only approximate to a Lorentzian, small systematic differences may occur depending on the choice of constraints in the curve fitting.

TABLE 2

Mössbauer parameters † for lunar soil and rocks

	295 K				78 K			
	M2/glass		M1/olivine		M2/glass		M1/olivine	
Sample	Δ	δ	Δ	δ	Δ	δ	Δ	δ
14003,20	2·08	1·13	2·84	1·16	2·15	1·23	3·06	1·27
14162,48	2·08	1·14	2·87	1·15	2·16	1·25	3·07	1·28
14163,50	2·09	1·13	2·86	1·15	2·15	1·23	3·05	1·27
14259,17	2·07	1·13	2·83	1·17	2·12	1·23	3·04	1·29
14301,45	2·09	1·15	2·87	1·16	2·15	1·27	3·09	1·29
14303,36	2·08	1·14	2·94	1·14	2·13	1·27	3·11	1·28
14310,66	2·07	1·14	—	—	2·12	1·27	3·03	1·29
14311,32	2·06	1·15	—	—	2·16	1·24	3·04	1·28
14318,35	2·24	1·19	3·00	1·20	2·14	1·27	3·11	1·29
14321,179	2·09	1·15	2·88	1·15	2·12	1·27	3·10	1·28
15021,143	2·06	1·13	2·83	1·15	2·12	1·25	3·07	1·29
15101,110	2·08	1·14	2·87	1·15	2·12	1·25	3·09	1·27
15211,37	2·08	1·13	2·88	1·15	2·14	1·24	3·08	1·28
15601,104	2·00	1·14	2·81	1·14	2·08	1·26	3·07	1·27
15602,35	2·03	1·13	2·79	1·16	2·12	1·22	3·10	1·25

† In mm s^{-1}, calibrated from iron metal at 295 K.

The ilmenite is close to stoicheiometric $FeTiO_3$, so that the Mössbauer parameters are essentially those of terrestrial samples, *i.e.*, a quadrupole splitting of $\Delta = 1{\cdot}06$ mm s^{-1} and chemical isomer shift of $\delta = 0{\cdot}70$ mm s^{-1} at 295 K relative to iron metal at the same temperature.

An olivine separate from Apollo 12 rock 12018 with average composition $Fo_{67\cdot3}Fa_{32\cdot7}$ has been reported [23] to show sharp Mössbauer resonance lines and partial resolution of the M1 and M2 site quadrupole splittings at high temperature. The parameters are given in Table 3. Other data for terrestrial olivines [23,24] suggest only a small dependence on composition. Although the two sites are not necessarily equally occupied, they both contain a high proportion of iron, and in the sample cited 42% was in the M1 site. Unfortunately, parameters were not given at lower temperatures. An olivine separate from Apollo 11 rock 10045 of composition $Fo_{72}Fa_{28}$ gave an unresolved doublet spectrum with a splitting of 2·86 mm s^{-1} at 295 K.[14] This is similar to but marginally greater than the splitting from M1 sites in pyroxenes.

Data are available for an orthopyroxene concentrate from rock 14310, and are shown in Table 3. The average composition of $En_{69\cdot7}Wo_{6\cdot6}Fs_{23\cdot7}$ is fairly typical of the orthopyroxenes in general. The majority of the iron (85%) was in the M2 sites so that the outer lines are comparatively weak in intensity.

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[14] P. Gay, G. M. Bancroft, and M. G. Brown, ref. 1, vol. 1, p. 481.

[15] S. S. Hafner and D. Virgo, ref. 1, vol. 3, p. 2183.

[16] C. L. Herzenberg and D. L. Riley, ref. 1, vol. 3, p. 2221.

[17] R. M. Housley, M. Blander, M. Abdel-Gawad, R. W. Grant, and A. H. Muir, ref. 1, vol. 3, p. 2251.

[18] P. Gay, M. G. Brown, I. D. Muir, G. M. Bancroft, and P. G. L. Williams, ref. 2, vol. 1, p. 377.

[19] S. S. Hafner, D. Virgo, and D. Warburton, ref. 2, vol. 1, p. 91.

[20] C. L. Herzenberg, R. B. Moler, and D. L. Riley, ref. 2, vol. 3, p. 2103.

[21] R. M. Housley, R. W. Grant, A. H. Muir, M. Blander, and M. Abdel-Gawad, ref. 2, vol. 3, p. 2125.

[22] G. Bayer, J. Felsche, H. Schulz, and P. Rüegsegger, *Earth Planetary Sci. Letters*, 1972, **16**, 273.

[23] D. Virgo and S. S. Hafner, *Earth Planetary Sci. Letters*, 1972, **14**, 305.

[24] W. R. Bush, S. S. Hafner, and D. Virgo, ***Nature*, 1970, 227**, 1338.

More extensive data have been obtained for the clinopyroxenes, and parameters for augites (space group *C2/c*) and pigeonites (space group $P2_1/c$) are given in Table 3. For pigeonite ($En_{58}Wo_{12}Fs_{30}$) *ca.* 78% of the iron is on M2 sites, and again the outer lines are much weaker.[25] At 295 K the lines are not resolved so that a nearly symmetrical doublet with a splitting of *ca.* 2·3 mm s^{-1} is seen. The augites usually have a much higher occupation of the M1 site by iron as a result of the strong preference of calcium for the M2 site, examples in the Table ranging from 28 to 50%. The exact site occupation is a function of the cooling history of the pyroxene and can be used to determine the thermal history of the rock,[25,26] but the effects are small and can be ignored in interpreting the bulk fines. Quite commonly pigeonite and augite co-exist as exsolution lamellae in very inhomogeneous crystals. In Table 3 we have classified the data for clinopyroxenes following the original description. However, most of the phases described as pigeonite or augite also featured some degree of exsolution, but with a smaller overall variation in composition than those left unclassified which were very heterogeneous. It is noteworthy that the quadrupole splittings at both the M1 and M2 sites are virtually independent of composition for all the ortho- and clino-pyroxenes. The only obvious trend is a slight decrease in quadrupole splitting with increasing calcium content.

TABLE 3

Mössbauer parameters for mineral separates (at 78 K*)

Mineral	Rock	Composition	M2		M1		Area ratio $\frac{M1}{M1 + M2}$	Ref.
			Δ	δ	Δ	δ		
Olivine	12018	$Fo_{67\cdot3}Fa_{32\cdot7}$ (at 546 K)	2·26	0·90	2·50	1·02	0·42	23
	10045	$Fo_{72}Fa_{28}$ (at 295 K)	—	—	2·86	1·15	—	14
Orthopyroxene	14310	$En_{70}Wo_{6}Fs_{23}$	2·15	1·27	3·01	1·29	0·15	25
Pigeonite	14053	$En_{58}Wo_{12}Fs_{30}$	2·12	1·27	3·03	1·29	0·22	25
	14053	$En_{60}Wo_{11}Fs_{29}$	2·12	1·25	3·00	1·28	0·24	26
	12053	$En_{60}Wo_{11}Fs_{29}$	2·10	1·27	2·98	1·29	0·20	26
	12038	$En_{54}Wo_{13}Fs_{33}$	2·10	1·26	2·96	1·28	0·24	26
	12021	$En_{59}Wo_{9}Fs_{32}$	2·13	1·27	3·02	1·28	0·18	19
	12053	$En_{57}Wo_{11}Fs_{32}$	2·11	1·27	3·01	1·29	0·18	19
Augite	14053	$En_{40}Wo_{32}Fs_{28}$	2·08	1·26	3·01	1·28	0·43	26
	12053	$En_{45}Wo_{29}Fs_{26}$	2·06	1·25	2·98	1·28	0·28	26
Pigeonite–Augite (heterogeneous with exsolution)	12018	$En_{50}Wo_{14}Fs_{35}$	2·12	1·27	3·03	1·29	0·25	19
	12018	$En_{46}Wo_{13}Fs_{41}$	2·10	1·27	3·04	1·29	0·33	19
	12021	$En_{31}Wo_{27}Fs_{42}$	2·06	1·26	2·98	1·29	0·40	19
	12021	$En_{17}Wo_{27}Fs_{56}$	2·02	1·25	2·98	1·29	0·50	19
	10044	$En_{44}Wo_{36}Fs_{20}$	2·06	1·26	2·92	1·29	0·38	15
	10044	$En_{36}Wo_{30}Fs_{34}$	2·03	1·26	2·96	1·29	0·40	15
	10003	$En_{44}Wo_{28}Fs_{27}$	2·07	1·27	2·97	1·29	0·34	15
	10003	$En_{43}Wo_{28}Fs_{29}$	2·09	1·27	3·01	1·30	0·29	15
	10003	$En_{30}Wo_{25}Fs_{45}$	2·08	1·27	3·03	1·31	0·38	15

* Δ = Quadrupole splitting/mm s^{-1}, δ = chemical isomer shift/mm s^{-1} relative to iron metal at room temperature.

Recently it has been pointed out that the fractional area of the outer doublet obtained by 4-peak fits to a *C2/c* clinopyroxene decreases with increase in temperature from 78 to 295 K.[27] This arises from a degree of variation in the M1 splitting and its temperature dependence which results in part of that component apparently merging with the M2 splitting at higher temperatures. The danger of overestimating the M2 site occupation in the lunar pyroxenes has been discussed.[28] The effect can be minimised by calculating the M1/M2 site occupancy from data at 78 K.

The major unknown component in the Mössbauer spectra of the lunar material is that originating from the glassy phases. In one instance a large glass bubble weighing 44 mg from rock chip 12057,10 has been examined in detail.[29] It gave a broad doublet spectrum with $\Delta = 2{\cdot}08$ mm s^{-1} and $\delta = 1{\cdot}05$ mm s^{-1} at room temperature. The composition from microprobe analysis was SiO_2, 44·2; TiO_2, 2·7; Al_2O_3, 11·6; FeO, 15·5; MgO, 8·0; and CaO 10·8% (w/w). Iron metal was not detected. It should be noted that this spectrum overlaps the resonance lines from M2 sites in pyroxenes, but need not be typical of all glasses. The only other data are for a partial glass separate, heavily contaminated with pyroxene, ilmenite, and magnetic iron, from soil 10084. This showed the basic pyroxene spectrum but with much broader lines and a larger M1 splitting.[30]

In the event, it appears that the olivine/M1 pyroxene content is best estimated from the area of the outside pair of peaks at 78 K, and the ilmenite content from the area of the inner pair of peaks at 295 K. The balance is then attributed to glass/M2 pyroxene. In the absence of any standardising data, or detailed knowledge of the recoilless fraction for each mineral, it is only possible to give an approximate estimate of the relative proportion of the iron in these phases by taking the concentration as linearly proportional to the spectrum area. Because of the uncertainty in the origins of the spectrum asymmetry, the figures in Table 4 were calculated from the three lines on the high-velocity side of the spectrum only. At least part of this asymmetry is due to iron–

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[25] K. Schürmann and S. S. Hafner, ref. 3, vol. 1, p. 493.

[26] S. Ghose, G. Ng, and L. S. Walter, ref. 3, vol. 1, p. 507.

[27] P. G. L. Williams, G. M. Bancroft, M. G. Brown, and A. C. Turnock, *Nature Phys. Sci.*, 1971, **230**, 149.

[28] E. Dowty, M. Ross, and F. Cuttitta, ref. 3, vol. 1, p. 481.

[29] S. Sullivan, A. N. Thorpe, C. C. Alexander, F. E. Senftle, and E. Dwornik, ref. 2, vol. 3, p. 2433.

[30] S. S. Hafner, B. Janik, and D. Virgo, 'Mössbauer Effect Methodology,' ed. I. J. Gruverman, vol. 6, Plenum Press, New York, 1971, p. 193.

TABLE 4

Distribution (%) of iron in mineral phases *

Sample	Ilmenite	M2/glass	M1/olivine
14003,20	8	73	19
14162,48	8	71	21
14163,50	11	71	18
14259,17	11	70	19
14301,45	6	70	24
14303,36	9	68	23
14310,66	4	78	18
14311,32	10	75	15
14318,35	7	70	23
14321,179	7	65	28
15021,143	3·0	69	28
15101,110	2·5	69	28
15211,37	2·3	70	28
15601,104	1·6	57	41
15602,35	1·3	63	36

* Calculated from the area of the high-velocity peaks only and excluding the metallic iron present as a separate phase.

nickel alloy inclusions, as we shall show in the next section.

An upper limit to the percentage of the iron as ilmenite is set by the Ti : Fe ratios in Table 1. Thus in the Apollo 14 soils, this limit is 15%. If *ca.* 45% of the titanium is in glass, as indicated by the microprobe analysis, then only 7% of the iron is in ilmenite. This figure is slightly lower than our result, but the extremely broad lines of the M2/glass contribution overlap the ilmenite lines slightly, and the area of the latter may be overestimated. Alternatively, the mean size of the glass particles may be smaller than that of the mineral fragments so that the figure of 7% is an underestimate. In any case, the fraction of iron as ilmenite in Apollo 14 soils is very similar to those from Apollo 12, but is very much less than the figure of ~20% found by Apollo 11.[18]

The Mössbauer analysis of all four fines is the same within experimental error. Table 1 shows that the Ti : Fe and Mg : Fe atomic ratios are also identical, so that the average composition of the olivines and pyroxenes must be very similar. This is perhaps not too surprising as all four samples came from a comparatively small featureless area of the lunar surface.

However, significant differences were seen in the rock samples. In particular the lower glass content resulted in much narrower lines and the lower intensity of the M1/olivine component and smaller quadrupole splittings recorded in **14310** and **14311** are consistent with these samples being richer in orthopyroxene and pigeonite and poorer in olivine and augite. These aspects have already been discussed.[5]

Mineral Separates from 14259,17.—The results obtained from the bulk Apollo 14 soils were comparatively disappointing, but because we had available 4·6 g of sample 14259,17, a major effort was made to obtain mineral separates from this sample. As already mentioned, this sample contained a high proportion of glass, and many otherwise crystalline particles were glass-coated thus preventing optical recognition of the core grains. The undertaking was therefore more difficult than the equivalent exercise for a rock sample.

The fines were initially graded by particle size by use of B.S.S. sieve sizes but without any significant mineral separation. 72·1% Of the particles had a diameter of <125 μm. This portion was washed with water to remove the finest material. Perhaps surprisingly these washings were found to contain well above the average amount of magnetic iron (*ca.* 7·6%).

A magnetic concentrate (7 mg) was obtained from the washed sample with a hand magnet, and proved to be *ca.* 80% magnetic iron–nickel alloy fragments. These were studied in detail and the results reported elsewhere.[5] A moderately magnetic separate proved to be only slightly enriched in magnetic iron.

The remaining material was then separated into seven approximately equal fractions with increasing densities by flotation in Clerici solutions. This procedure proved reasonably successful.

We have estimated the density ranges of the component mineral phases from the cell parameters of typical lunar samples, or from standard terrestrial data where they were not available. These are in Table 5, together

TABLE 5

Densities of lunar minerals

Mineral	10^{30} × Cell volume / m^3	Ref.	Density / g cm^{-3}	Lunar density range/g cm^{-3}
α-Iron–Nickel	23·6		7·87	7·9—8·0
Troilite FeS	361	31	4·84	4·84
Ilmenite $FeTiO_3$	315	32	4·80	4·80
Olivine				
(Fo)Mg_2SiO_4	294		3·16	
(Fa)Fe_2SiO_4	309		4·39	
$Fo_{67}Fa_{33}$				~3·6
Clinopyroxenes				
Pigeonite ($P2_1/c$)	432	26		
Augite ($C2/c$)				
(En)$Mg_2Si_2O_6$			3·08	
(Wo)$Ca_2Si_2O_6$			3·56	
(Fs)$Fe_2Si_2O_6$			4·06	
$En_{65}Wo_{10}Fs_{25}$–$En_{10}Wo_{25}Fs_{65}$				3·37—3·84
Orthopyroxenes	853			
(En)$Mg_2Si_2O_6$			3·11	
(Fs)$Fe_2Si_2O_6$			4·10	
$En_{85}Fs_{15}$–$En_{60}Fs_{40}$				3·25—3·50
Plagioclase	669	32		
(Al)$NaAlSi_3O_8$			2·60	
(An)$CaAl_2Si_2O_8$			2·76	
$An_{81}Al_{19}$–$An_{97}Al_3$				2·73—2·76

with the densities of the normative compositions (assumed to have the same cell dimensions).[31,32]

It can be seen that α-iron, troilite, and ilmenite should concentrate in the highest density fraction. That this did not occur is indicative of the way in which these phases intergrow along the phase boundaries of the silicates or occur as inclusions in glassy matrices. The density of the glasses is apparently very variable. A detailed study of 11 glass spherules from fines 14003 and 14049 has revealed densities in the range 1·6—3·9 g cm^{-3}, with voids, mineral inclusions, devitrified areas, and metallic inclusions being recorded.[33] It is particularly interesting that there is no suggestion of partial solution of injected iron particles into the glass. The iron inclusions are probably native to the matrix and produced by reduction of the iron in the glassy phase.

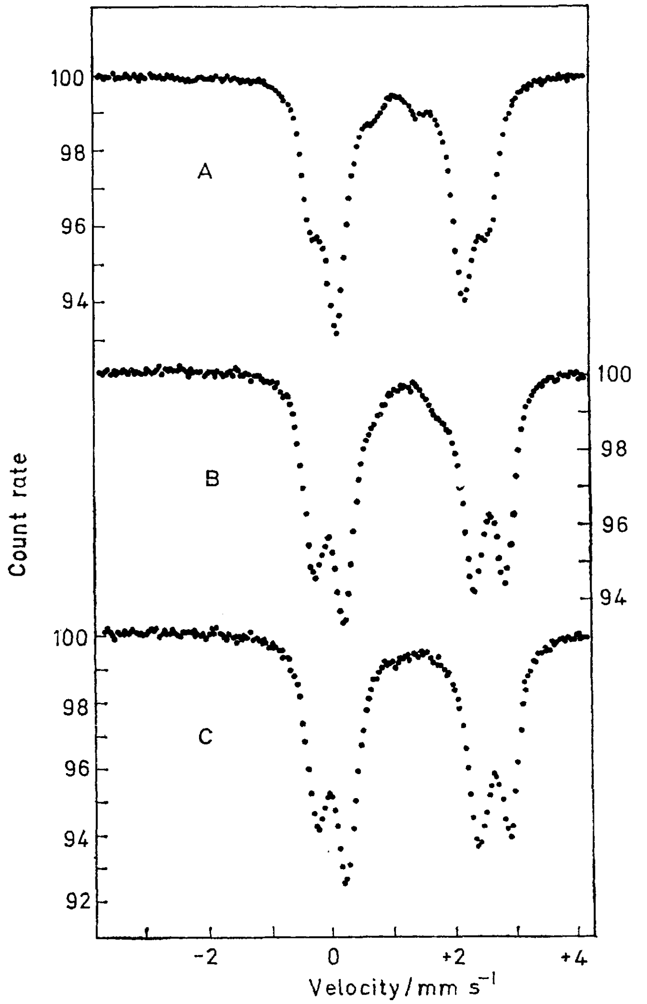

FIGURE 3 Mössbauer spectra at A, 295 K; B, 78 K; and C, 4·2 K of the heaviest density fraction, an olivine–augite concentrate, from soil 14259

The Mössbauer spectra at 295, 78, and 4·2 K of the heaviest density fraction are shown in Figure 3.

The general narrowing of the component lines indicates a substantial reduction in the glass content and this was confirmed by visual inspection. The magnetic iron content is substantially below that of the bulk soil, only *ca.* 4% of the iron is as ilmenite, and concentration of heavy opaque minerals has in general not occurred. The ilmenite doublet is poorly resolved at 78 K, and at 4·2 K has become a broad magnetic hyperfine pattern which is hidden under the silicate peaks.

From the density ranges for the component silicates, it can be seen that the heaviest fraction should contain mainly olivine and iron–calcium-rich augite with a high M1 : M2 occupation ratio. The large increase in the effective area of the outside doublet (see Table 6) confirms this. The increase in this area on cooling from 295 to 85 K is an example of the anomaly associated with the *C*2/*c* clinopyroxenes mentioned earlier. The relaxation phenomena reported for the pyroxenes in rock 12053 at low temperatures were not observed for this separate.[34]

TABLE 6

Parameters for the olivine–augite separate

		295 K	78 K	4·2 K
M1/olivine	Δ/mm s^{-1}	2·86	3·09	3·12
	δ/mm s^{-1}	1·14	1·27	1·29
	% Area	31	38	39
M2	Δ/mm s^{-1}	2·10	2·11	2·14
	δ/mm s^{-1}	1·14	1·26	1·28
	% Area	65	70	—
Ilmenite	Δ/mm s^{-1}	0·67	1·46	—
	δ/mm s^{-1}	1·08	0·99	—
	% Area	3·6	2·4	—

The second and third heaviest fractions (Figure 4) show a substantial reduction in the intensity of the outer doublet, and are clearly pigeonite–orthopyroxene concentrates. The relative areas of the outside component (high-velocity peaks only) are 23 and 22% respectively. The Mössbauer parameters at 77 K are essentially the same for all three separates, and the metallic iron content was substantially reduced.

The lighter fractions featured successively broader lines and may be presumed to contain a substantially higher proportion of glass. It is also noteworthy that the magnetic iron concentrated towards the lighter fractions. This confirms the connection with the glassy phases, a conclusion reached independently by several other groups.[21] In Figure 4 one of the iron lines can be seen distinctly on the baseline at the left-hand side of the spectrum for the lightest fraction.

The fourth and fifth heaviest fractions were further separated by use of a Frantz magnetic separator to concentrate paramagnetic minerals. In this way an almost white plagioclase concentrate was obtained which contained very little iron. However, as a means of separating iron-bearing minerals, the method proved disappointing. Nevertheless, interesting data were obtained with regard to the iron metal inclusions which we now discuss.

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[31] H. T. Evans, ref. 1, vol. 1, p. 399.

[32] D. B. Stewart, D. E. Appleman, J. S. Huebner, and J. R. Clark, ref. 1, vol. 1, p. 927.

[33] A. N. Thorpe, S. Sullivan, C. C. Alexander, F. E. Senftle, and E. Dwornik, ref. 3, vol. 3, p. 2465.

[34] F. C. Schwerer, G. P. Huffman, R. M. Fisher, and T. Nagata, ref. 3, vol. 3, p. 3173.

A major observation applying to all samples which was only mentioned briefly before is that the line component near zero velocity (with respect to iron metal), *i.e.* the low-velocity line of the M2 pyroxenes, is more intense that its twin. In early papers, this feature was either ignored or attributed to an unidentified component [20] or to a Goldanskii–Karyagin effect.[18] In principle the latter could exist at the more distorted M2 site. However, an alternative proposition has been put forward that the additional area is produced by superparamagnetic iron–nickel alloys.[21,35] We have already suggested the involvement of the γ-Fe–Ni phase in this context,[5] and the asymmetry is generally reported to be greater in the soils than in the rocks.

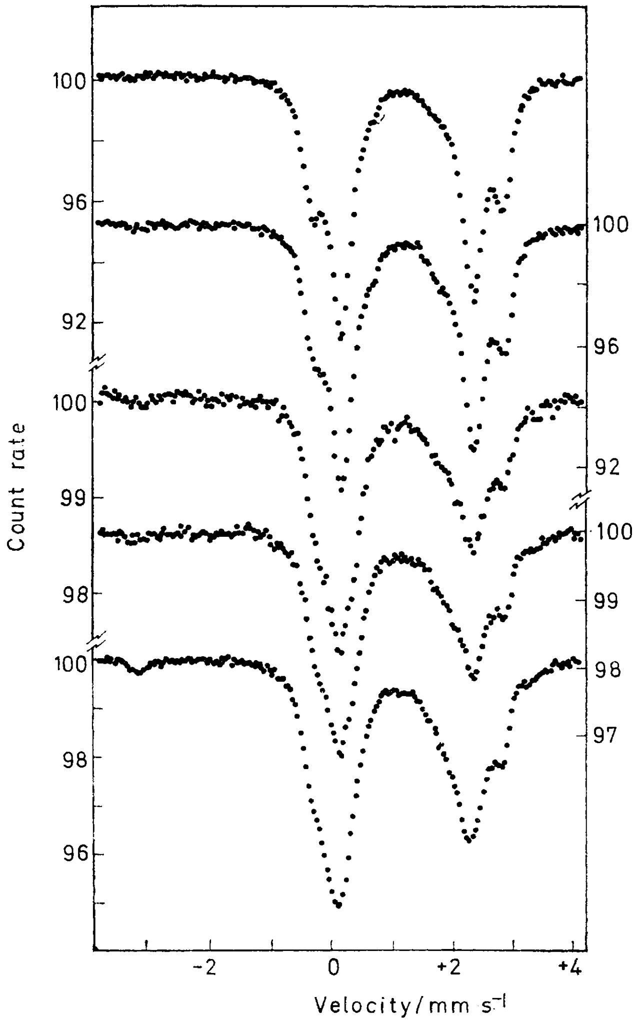

FIGURE 4 Mössbauer spectra of mineral separates from soil 14259. From top to bottom they are the 2nd, 3rd, 4th (separated at ½ amp), 6th, and 7th heaviest density fractions

Further evidence comes from our soil separates. In Table 7 are collected figures for the fractional excess of area in the low-velocity components of the central non-magnetic absorption, for the bulk soils, rocks, and mineral separates. The average value for the Apollo 14 soils of 7·0% is much greater than the figure of 4·9% for the Apollo 14 rocks and 4·2% for the Apollo 15 soils. However, the excess of area in the heaviest mineral concentrate from 14259 is only 2·1%, increasing as the glass content increases to a figure of *ca.* 10% for the lighter fractions.

TABLE 7

Fractional excess of area at 77 K (as %)

Bulk fines		Rocks		Mineral separates	
14003	7·1	14301	4·6	Fraction 1	2·1
14162	6·2	14303	3·3	Fraction 2	4·6
14163	7·0	14310	5·2	Fraction 3	4·0
14259	7·8	14311	6·3	Fraction 4 (½ amp)	19·5 *
		14318	5·1	Fraction 5 (1 amp)	12·2 *
15021	3·3	14321	5·0	Fraction 5 (5 amp)	10·0
15101	5·6			Fraction 6	13·8 *
15211	4·6			Fraction 7	8·9 *
15601	4·3			Washings	9·3 *
15602	2·1				

* Indicates a concentration of magnetic iron in the sample.

Particularly significant is the value of 19·5% for the magnetic separate at ½ amp from the fourth density fraction (see Figure 4). This corresponds to a strongly paramagnetic fraction, and this is confirmed by the increase in ilmenite content to 11% of the high-velocity area. This asymmetry is too large to attribute solely to a Goldanskii–Karyagin effect. Figures in Table 7 marked with an asterisk indicate samples where a significant enrichment in magnetic iron was also recorded. These figures are good evidence that a large proportion of the excess of area is indeed associated with ' paramagnetic ' iron–nickel alloy inclusions in the glassy phases.

Fines from Hadley Rille.—The five samples of fines from Hadley Rille which we received proved to be more interesting than those from the earlier mission. Sample 15021,143 was collected near the lunar module and should be representative of the <1 mm fines on the mare surface. Samples 15101,100 and 15211,37 were both <1 mm fines collected at Station 2 on the Appenine front below St. George Crater. Samples 15601,104 (<1 mm) and 15602,35 (1—2 mm) were collected at Station 9a on the edge of Hadley Rille. As can be seen from the analyses in Table 1, 15021 has a composition similar to the Apollo 12 mare, 15101 from the mountain front is closer to Apollo 14 soils, whereas 15601 from the Rille edge has an unusually low Ca and high Fe content and is closer in composition to a true mare basalt than the usual mare soils.

Mössbauer spectra were collected at 78 and 295 K as for the Apollo 14 samples. A wide-scan spectrum of 15021 at 295 K, together with a magnified view of the baseline region, is shown in Figure 5. Magnetic iron–nickel is present, but there is no evidence for a substantial proportion of troilite. The mean magnetic field proves to be 331 kG at 295 K, which would suggest a comparatively low nickel content. The area of the magnetic component is estimated to be 4·5% of the total area, and the other four soils appear to contain a similar amount.

Samples 15021, 15101, and 15211 as a group gave essentially identical spectra, as did 15601 and 15602,

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[35] R. M. Housley, R. W. Grant, and M. Abdel-Gawad, ref. 3, vol. 1, p. 1065.

and examples are illustrated in Figures 1 and 2. Area analysis was carried out as described for Apollo 14 fines, and the values are given in Tables 2, 4, and 7. The spectra are significantly different from those from Apollo 14 soils because of a substantial reduction in linewidth. This strongly indicates a reduction in the degree of glassification which is also confirmed by the smaller excesses of areas. The high plagioclase content of 15101 does not contribute to the spectrum, and the similarity of the spectrum to that for 15021 suggests that the iron-bearing minerals are largely mare-derived.

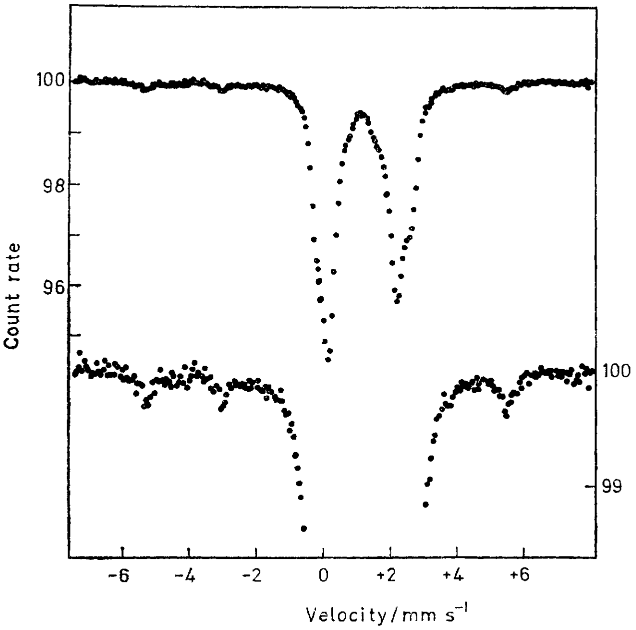

FIGURE 5 Mössbauer spectrum of Apollo 15 soil 15021 with a wider velocity scan. The lower curve is a magnified view of the baseline area showing the magnetic component

The samples from the Rille, 15601 and 15602, feature a much higher M1/olivine content and even lower ilmenite. As can be seen in Table 1, the Ti : Fe ratio is lower in 15601 than in 15021 and 15101, and the Mg : Fe ratio is also extremely low. The implication is that the pyroxenes at the Rille edge are rich in augite and low in pigeonite and orthopyroxene, whereas those at the Appenine front are the converse. This appears to be substantiated by recent microprobe analyses on some of the larger fragments in the regolith at these two sites.[36] More detailed interpretation of the Apollo 15 soils must await data from various other techniques from other laboratories.

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[3/1736 *Received*, 16*th August*, 1973]

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[36] K. L. Cameron, J. W. Delano, A. E. Bence, and J. J. Papike, *Earth Planetary Sci. Letters*, 1973, **19**, 9.