

variable FeO-MgO-CaO compositions. Olivines range from Fo<sub>72</sub> to Fo<sub>90</sub> and just overlap with olivine compositions reported (2) from types A, C, and D materials.

The present work confirms the conclusion of the Preliminary Analysis Team (2) that the lunar volcanic rocks crystallized under extremely low partial pressures of oxygen and water. However, the lack of Si in the metal phase or of Ti, Mn, and Mg in the sulfide phase, together with the high FeO contents in the silicate phases, would indicate less severely reducing conditions than prevailed during the evolution of the enstatite chondrites and achondrites. However the gross mineralogies observed immediately invite comparison with the eucritic meteorites. Recent microprobe studies of clinopyroxenes in eucrites have found extreme FeO-MgO-CaO zoning (5) similar to that which occurs in the lunar volcanic rocks. Eucrites have crystallized in extremely low partial pressures of O<sub>2</sub> and H<sub>2</sub>O and are also characterized by very low alkali abundances just like the lunar volcanic rocks (2). But there are also serious differences—for example, the relatively high TiO<sub>2</sub>, ZrO<sub>2</sub>, and Cr<sub>2</sub>O<sub>3</sub> contents of the lunar rocks. These differences are again emphasized by the high TiO<sub>2</sub> content of the clinopyroxenes and ZrO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> content of the ilmenites in the lunar rocks. Then the lack of Ni in the metal phase in the lunar volcanic rocks is very different from the relatively high Ni content reported in metal from eucrites and howardites (6).

If the eucrites are indeed of lunar origin (7), then the lunar surface must be chemically inhomogeneous, at least to a degree sufficient to explain the observed differences between the lunar rocks and eucrites. If the K-Ar age of  $3.0 \pm 0.7 \times 10^9$  years for the Apollo 11 rocks (2) is substantiated then the significantly older Rb-Sr ages ( $4.39 \pm 0.26 \times 10^9$  years) for the eucrites (8) would also imply different times of formation of various parts of the lunar surface. If, on the other hand, eucrites are not of lunar origin, then those significant similarities between eucrites and moon rocks would at least imply that both evolved in similar, but separate, environments.

N. G. WARE

Department of Geophysics and  
Geochemistry, Australia  
National University, Canberra

J. F. LOVERING

School of Geology,  
University of Melbourne,  
Victoria 3052, Australia

## References and Notes

- Analyses, using an A.R.L.-EMX microanalyzer, are based on a chemically well-known collection of natural and synthetic minerals. Raw comparative data have then been corrected for absorption [J. Philibert, *X-ray Optics and X-ray Microanalysis* (Academic Press, New York, 1963), p. 379; P. Duncumb and P. K. Shields, *The Electron Microprobe* (Wiley, New York, 1966), p. 284], fluorescence [S. J. B. Reed, *Brit. J. Appl. Phys.* **16**, 913 (1965)], and atomic number [P. Duncumb and S. J. B. Reed, *Natl. Bur. Std. U.S. Spec. Publ.* 298, 133 (1968)]. Experience indicates that the analyses are probably accurate to about 1 percent of the amount present for most major elements.
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## Semimicro Chemical and X-ray Fluorescence

### Analysis of Lunar Samples

**Abstract.** Major and selected minor elements were determined in seven whole rock fragments, five portions of pulverized lunar rock, and the lunar soil. Three different rock types were represented: vesicular, fine-grained basaltic rocks; medium-to coarse-grained, vuggy gabbroic rocks; and breccia. The ranges (in percent) for the major constituents of the lunar samples are: SiO<sub>2</sub>, 38 to 42; Al<sub>2</sub>O<sub>3</sub>, 8 to 14; total iron as FeO, 15 to 20; MgO, 6 to 8; CaO, 10 to 12; Na<sub>2</sub>O, 0.5 to 1; K<sub>2</sub>O, 0.05 to 0.4; TiO<sub>2</sub>, 8 to 13; MnO, 0.2 to 0.3; and Cr<sub>2</sub>O<sub>3</sub>, 0.2 to 0.4. The high reducing capacity of the samples strongly suggests the presence of Ti(III).

Thirteen samples weighing a total of 17 g were received for analysis. The samples consisted of lunar fines, seven whole rock fragments, and five portions

of rock previously pulverized at the Lunar Receiving Laboratory. Samples were prepared for x-ray spectroscopy (1) by fusing 60 mg of the sample with

Table 1. Chemical composition of lunar igneous rocks (in percent by weight).

Constituent	10003	10022		10024	10047
SiO <sub>2</sub>	37.8	40.1		39.0	41.3
Al <sub>2</sub> O <sub>3</sub>	11.0	8.60		9.50	9.80
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.00		0.00	0.00
FeO	19.8	18.9		18.5	19.0
MgO	7.20	7.74		8.11	6.10
CaO	11.0	10.7		10.0	12.2
Na <sub>2</sub> O	0.85	0.91		0.80	0.65
K <sub>2</sub> O	0.05	0.30		0.28	0.11
H <sub>2</sub> O-	0.00	0.00		0.00	0.00
Total Ti as TiO <sub>2</sub>	12.0	12.2		13.2	10.2
P <sub>2</sub> O <sub>5</sub>	< 0.2	< 0.2		< 0.2	< 0.2
MnO	0.29	0.25		0.24	0.29
Cr <sub>2</sub> O <sub>3</sub>	0.26	0.37		0.40	0.22
ZrO <sub>2</sub>	< 0.03	0.03		< 0.03	< 0.03
NiO	<0.001	< 0.001		< 0.001	< 0.001
Total	100.25	100.10		100.03	99.87
Total Fe as Fe <sub>2</sub> O <sub>3</sub>	22.0	21.0		20.5	21.1
R <sub>2</sub> O <sub>3</sub>	45.8	42.6		44.1	41.7

Constituent	10049	10050	10058*	10058†	10062
SiO <sub>2</sub>	41.0	40.9	41.4	41.7	38.8
Al <sub>2</sub> O <sub>3</sub>	9.50	8.90	10.7	11.8	12.1
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00	0.00
FeO	18.7	17.3	17.3	18.2	18.3
MgO	7.03	8.03	6.25	6.30	7.21
CaO	11.0	11.3	12.1	11.0	12.0
Na <sub>2</sub> O	0.71	0.66	0.79	0.68	0.69
K <sub>2</sub> O	0.36	0.05	0.07	0.09	0.07
H <sub>2</sub> O-	0.00	0.00	0.00	0.00	0.00
Total Ti as TiO <sub>2</sub>	11.3	12.6	11.1	9.55	10.3
P <sub>2</sub> O <sub>5</sub>	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
MnO	0.25	0.27	0.27	0.27	0.27
Cr <sub>2</sub> O <sub>3</sub>	0.32	0.35	0.21	0.24	0.25
ZrO <sub>2</sub>	0.03	< 0.03	< .03	< 0.03	< 0.03
NiO	< .001	< .001	< .001	< .001	< .001
Total	100.20	100.36	100.19	99.83	99.99
Total Fe as Fe <sub>2</sub> O <sub>3</sub>	20.8	19.2	19.2	20.2	20.3
R <sub>2</sub> O <sub>3</sub>	42.0	41.4	41.4	43.1	43.6

\* Whole rock. † Pulverized.

Table 2. Chemical composition of lunar breccia and soil fines (in percent by weight).

Constituent	10019	10048	10060	311079
SiO <sub>2</sub>	41.1	42.2	41.5	42.2
Al <sub>2</sub> O <sub>3</sub>	13.7	12.9	11.8	14.1
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00
FeO	15.7	15.7	17.0	15.3
MgO	7.86	7.54	7.52	7.94
CaO	11.9	11.4	11.6	12.1
Na <sub>2</sub> O	0.93	0.52	0.78	0.54
K <sub>2</sub> O	0.14	0.17	0.18	0.14
H <sub>2</sub> O <sup>-</sup>	0.00	0.00	0.00	0.00
Total Ti as TiO <sub>2</sub>	8.25	8.95	9.15	7.60
P <sub>2</sub> O <sub>5</sub>	< 0.2	< 0.2	< 0.2	< 0.2
MnO	0.22	0.22	0.23	0.21
Cr <sub>2</sub> O <sub>3</sub>	0.32	0.31	0.33	0.31
ZrO <sub>2</sub>	0.03	< 0.03	0.04	0.03
NiO	0.02	0.02	0.02	0.02
Total	100.15	99.91	100.13	100.47
Total Fe as Fe <sub>2</sub> O <sub>3</sub>	17.4	17.4	18.9	17.0
R <sub>2</sub> O <sub>3</sub>	40.3	40.0	40.5	39.3

940 mg of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. No heavy absorber was added to the mix. After cooling, the fused glass was brought to 1200 mg with powdered cellulose and then was ground. Three hundred milligrams of the fused mix was pressed into a 1/2-inch-diameter disc and Na, Mg, Al, and Si were determined with a soft x-ray spectrometer; P, K, Ca, Ti, Mn, Fe, Cr, and Ni analyses were made with an x-ray milliprobe. The rest of the fused mix was pressed into a 1-inch-diameter disc for determination of Si, Al, Fe, Ca, Ti, Mn, Zr, Cr, and Ni.

Chemical determinations were made on all samples for H<sub>2</sub>O<sup>-</sup>, SiO<sub>2</sub>, Na<sub>2</sub>O, MgO, R<sub>2</sub>O<sub>3</sub>, and total reducing capacity. FeO was determined, after catalytic oxidation, on the lunar fines (sample 311079).

The compositional data for the allocated samples are grouped according to rock type and numerical sequence in Tables 1 and 2. The samples listed in Table 1 are type B (gabbro) except for sample 10022, a basalt. Samples 10003, 10022, 10024, 10050, and 10062 were whole rock fragments. Samples 10047 and 10049 were pulverized at the Lunar Receiving Laboratory. Sample 10058 was received as a whole rock fragment and as a pulverized sample.

Chemical compositions of three samples of breccia and one of the lunar fines are given in Table 2. Of the breccias, 10019 was a whole rock fragment, and 10048 and 10060 were received as pulverized samples. These new data support the ranges of ferrous iron, titania, magnesia, and chrome previously reported (2). The overall similarity in major element composition for all the samples is apparent. Differences are noted in the minor element contents;

for example, the fines and the breccia are characterized by a relatively high NiO (200 ppm) when compared to the igneous rocks (< 10 ppm). In contrast to the previously reported high values for ZrO<sub>2</sub> (1, 2), the new data show that ZrO<sub>2</sub> abundances do not exceed 400 ppm in any of the samples but are more abundant in the breccias and lunar soil fines. As a minor constituent, chromium is relatively abundant (2100 to 4000 ppm Cr<sub>2</sub>O<sub>3</sub>).

Summations (Tables 1 and 2) for the samples tend to be high and, at first glance, appear to be attributable to metallic iron because it is analytically incorporated in the cited FeO values. Determinations of the total reducing capacity (3) of the samples (Table 3) were found to be as much as 4.6 percent higher (equivalent to 1.8 percent additional metallic iron) than can be accounted for by the total iron (as FeO) content obtained by x-ray fluorescence analysis. Optical examination, coupled with calculations based on the assumption that the NiO content is totally associated with meteoritic iron, indicate that the contribution from metallic iron and troilite is no greater than 0.5 percent. The excessive reducing capacity of the returned lunar materials suggests the presence of an element occurring as a major constituent and capable of existing in a lower valence state such as Ti(III). To eliminate the possibility of Ti(III) contributing to the total reducing capacity, a catalytic oxidation was made before a volumetric determination of total iron as FeO. Duplicate volumetric analyses on sample 311079 gave identical results for FeO as those obtained by x-ray spectroscopy.

The excessive reducing capacity and

Table 3. Comparison of total Fe (as FeO) determined by x-ray spectroscopy with total reducing capacity (as FeO) of the lunar materials (in percent by weight).

Sample	Rock type	Reducing capacity	FeO value	Difference (+) as FeO
10003	Gabbro	22.4	19.8	2.6
10019	Breccia	19.4	15.7	3.7
10022	Basalt	21.0	18.9	2.1
10024	Gabbro	22.3	18.5	3.8
10047	Gabbro	19.8	19.0	0.8
10048	Breccia	20.3	15.7	4.6
10049	Gabbro	21.8	18.7	3.1
10050	Gabbro	19.2	17.3	1.9
10058†	Gabbro	19.3	17.3	2.0
10058*	Gabbro	20.3	18.2	2.1
10060	Breccia	20.8	17.0	3.8
10062	Gabbro	20.5	18.3	2.2
311079	Fines	19.4	15.3‡	4.1

\* Whole rock. † Pulverized. ‡ The total iron content (as FeO) of sample 311079 was also determined chemically and found to be 15.2<sub>5</sub> and 15.3<sub>6</sub> percent.

high summations strongly suggest the presence of Ti(III) in the lunar samples. Investigations continue in this direction.

HARRY J. ROSE, JR., FRANK CUTTITTA

EDWARD J. DWORNIK, M. K. CARRON

R. P. CHRISTIAN, J. R. LINDSAY

D. T. LIGON, R. R. LARSON

U.S. Geological Survey,  
Washington, D.C. 20242

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3. The total reducing capacity was determined by dissolution of the samples with 5:3:3 HF:H<sub>2</sub>SO<sub>4</sub>:H<sub>3</sub>PO<sub>4</sub> in excess (NH<sub>4</sub>)<sub>2</sub>VO<sub>4</sub> (oxidant) and subsequent back titration of remaining vanadium (V). Two separate determinations of each sample gave identical results.
4. Publication authorized by the director, U.S. Geological Survey.

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## Emission Spectrographic Determination of Trace Elements in Lunar Samples

**Abstract.** *Eighteen minor or trace elements were detected and determined by emission spectroscopy. Direct d-c arc excitation of powdered samples was used with three variations in the procedure. Thirteen lunar samples consisting of four fine-grained igneous rocks, one medium-grained igneous rock, seven breccias, and one sample of fines were analyzed. The zinc and nickel concentrations in the breccias were approximately one order of magnitude greater than the concentrations of these elements in igneous rocks.*

Thirteen Apollo 11 lunar samples were processed and analyzed spectrographically for 44 elements. The samples we analyzed can be classified into four groups: (i) four samples of type A, fine-grained, vesicular igneous rocks; (ii) one sample of type B, medium-

grained vuggy igneous rock; (iii) seven samples of breccias; and (iv) one sample of fines less than 1 mm in grain size from the bulk sample. These sample groups have been described (1).

The 12 rock samples consisted of one or more chips and some accompanying