/1up

FINAL REPORT

TO

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Grant NGR-33-010-166

"Trace Geochemistry of Lunar Material"

Principal Investigator: Professor George H. Morrison
Department of Chemistry
Cornell University
Ithaca, New York 14850

Date: January 31, 1974

(NASA-CR-137386) TRACE GEOCHEMISTRY OF LUNAR MATERIAL Final Report (Cornell Univ.) 12 p HC $4.00 CSCL 03B

N74-20470

Unclas
G3/30 16606

CONTENTS

I. Lunar Samples

A. Samples Analyzed

Apollo 16		Apollo 17	
60501,35	soil	72161,13	soil
64501,17	soil	78501,27	soil
60315,53	igneous rock	72701,31	soil
60017,71	anorthositic gabbro	73141,15	soil
62255,19	" "	74220,38	orange soil
		71055,35	subfloor basalt
		72275,96	norite breccia

Up to 57 elements including majors, minors, rare earths (REE) and other trace elements have been determined in the above lunar samples. The analytical techniques used were spark source mass spectrometry (SSMS) and neutron activation analysis (NAA). The latter was done either instrumentally (INAA) or with group radiochemical separations (RNAA). The details of these methods have been published by this group elsewhere (1-3).

B. Apollo 16 Results

A number of striking differences in abundances of the elements in lunar soils at the various sites can be observed. With regard to the major elements only Si is about the same at all the sites. Apollo 16 has the lowest amounts of Fe, Ti, Mg, K, Mn, and Cr and the highest concentrations of Al and Ca. The high concentration of Al and Ca in the 60501 soil indicates that the lunar highlands are rich in these two elements. X-ray fluorescence experiments flown in lunar orbit during the Apollo 16 mission confirm these findings. Apollo 14 has the highest concentration of K and Na, and the lowest concentrations of Fe and Cr. Titanium is particularly high in the Apollo 11 soil. Zr, Ba and Rb (as well as Y and Nb) show a steady increase in going from Apollo 16, Luna 16, Apollos 15, 11, 12 and 14 sites. Lowest amounts of Cs, Cu, Ga, Mo, Sc, V, and Zn are found in 60501 soil. The depletion of Cs, Sc and V is particularly striking. Thus the material is depleted in siderophilic elements—Fe, (Co), Mo, Cu, Ga; chalcophilic elements—Zn, Ga, Mo, Fe; and lithophiles—(Na), K, (Rb), Cs, Mg, Sc, Ti, Zr, V, Cr, and Mn. However, as mentioned earlier the lithophiles—Ca and Al—are particularly enriched in the 60501 soil. The radiogenic elements Pb, Th and U as well as Hf and Rb are highest in Apollo 14 soil. Lowest amounts of these elements are found in Luna 16 soil with the exception of Hf which is lowest in Apollo 15 soil.

The rare earth elements are strikingly enriched in the Apollo 14 soil as compared with other sites. The soils from Apollo 11 and 12 resemble each other as do Apollo 15 and Luna 16. In general 60501 soil has lowest amounts of rare earth elements. This is again the same trend which was shown above in the depletion of lithophile elements. The negative Eu anomaly is greatest for Apollo 14, while it is very shallow for Apollo 15 and 16 soils. The lighter rare earths are fractionated somewhat from the heavier rare earths in Apollo 12, and to a much greater extent in Apollo 14.

The compositions of the soils of most of the lunar sites appear at each site to be approximated by the linear combination of three major indigenous rock types with the addition of a fourth "extra-lunar" component (4-6). One of the indigenous components appears to have a more or less universal moon-wide identification as a KREEP-enriched component and the proportion of the other two (mare basalt and anorthositic rock) depends on the sampling location. At some of the sites the soil can be approximated by a mixture of KREEP with either the mare basalt component or anorthositic component, and at other sites all three of the indigenous components must be considered.

A mixing model for the soil composition at the Apollo 16 site was made, where the country rock end members are represented by the two rock samples available to us for analysis; i.e. KREEP basalt, 60315 and a white fragment from 60017, an anorthositic gabbroic rock. In our study, soils 60501 and 64501 are viewed as the linear combination of these two rocks. Obviously these two rocks are not the ultimate end members but rather somewhere in between the linear combination. It should be noted that Bansal et al. (7) suggested that the Apollo 16 soils are mechanical mixtures of two end members, one of which must approach the composition of pure plagioclase and the other consisting of rocks rich in LIL elements (KREEP-like basaltic rocks).

A method of least-squares using normalized concentrations for each element was employed. The residuals in the material balance using the soil and the two end members were minimized using 40 of the elements analyzed and varying the proportions of the rock types. The following proportion of end members were obtained for each soil: soil 60501, 25% 60315 and 75% 60017; and soil 64501, 22% 60315 and 78% 60017. These results are not very different from the estimate made by the Apollo 16 LSPET (8) report of about 80% anorthositic component. The model was also tested using our KREEP-like basalt 60315 and an anorthositic rock, 67455, analyzed by Wänke (9) to constitute our soils. The results were: soil 60501, 29% 60315 and 71% 67455; and soil 64501, 26% 60315 and 74% 67455. Rock 67455 is a more anorthositic rock than our 60017, and therefore more KREEP basalt is required. Comparable proportions of end members were obtained using our model to constitute soils 68501 and 64421 analyzed by Bansal et al. (7).

Those elements that are in clear excess in the soils relative to the chosen lunar source rocks used in our mixing model are Cu and Zn. The Zn values in the soils analyzed here are in good agreement with those reported by Duncan et al. (10), Baedecker et al. (11) and Krahenbuhl et al. (12). Soil 64501 has incompatibly high Ga as well as the other elements mentioned. We believe that this suite of elements is an index of extra-lunar material of C-1 composition in Apollo 16 soils in addition to those used by Baedecker et al. (11), although Zn may have an indigenous origin as well. The excess Cu to Ni ratio establishes the C-1 source relative to a pure siderophile source of extra-lunar material.

Nickel presented a difficulty in this model because our sample of KREEP-like basalt contains a very high concentration (1380 ppm Ni compared to the LSPET (8) value of 191 ppm Ni). The anomalously high value of Ni in our sample is accompanied by a correspondingly high value of Co, and indicates that our sample probably contains a meteroritic component.

We subsequently received and analyzed another anorthositic gabbro 62255,19 whose composition corresponds to an almost pure plagioclase type rock. This was substituted in our mixing model instead of rock 60017. A 30:70 mix resulted for soil 64501 and 33:68 for soil 60501 for KREEP basalt and anorthositic gabbro, respectively.

C. Apollo 17 Results

The composition of basalt sample 71055 is generally similar to those analyzed by APET (13), except for a higher nickel content observed by us. The basalt has a very high titanium content (7.11%) similar to Apollo 11 basalts. It has a high iron content and correspondingly high Fe/Mg ratio similar to other mare basalts from Apollos 11, 12, 15 and Luna 16. It has a low sodium concentration, which along with high iron, magnesium, and titanium values distinguishes it from terrestrial basalts.

Sample 72275 is a noritic breccia which is fairly rich in KREEP component. It resembles KREEP-like rocks sampled by Apollo 16, e.g. 60315. KREEP associated elements Zr, Y, U, Th, Rb, Nb, Li, Hf, and Ba are also high in 72275. However, among the Apollo 17 noritic breccias, this sample which is petrographically classified as a foliated light gray breccia, is characterized by lower Sr and Na and higher P, Y, and Zr content than other breccias. It has a lower MgO/FeO ratio and higher FeO and CaO concentrations with about the same Al_2O_3 concentration. This implies that the foliated light gray breccias were derived from a different lithological unit than other noritic breccias.

The soils 72161 and 78501 are from the dark mantle, 72701 and 73141 from the light mantle, and 74220 is the orange soil. Soils 72701 and 73141 are very similar in composition, whereas 72161 and 78501 have noticeable differences in concentrations of some trace elements. In addition to dark mantle, soil 78501 probably contains subfloor material and debris mass wasted from the Sculptured Hills.

The Ni content of these soils is fairly constant (~200 ppm). Since basalts, which account for the bulk of these soils, are very low in Ni content (13 ppm in 71055), most of the Ni in the soils can be attributed to meteoritic contribution. This corresponds to ~ 1% of a chondritic component.

The Zn content of both basaltic and massif rocks is low (2-4 ppm), so that the higher concentrations observed in four soils reflects the orange glass content of these soils. Thus, the orange glass content of light mantle soils is lowest and of dark mantle soils is highest.

The chondrite normalized REE patterns for all four soils are similar with fairly shallow negative Eu anomaly. Rock 62255 is almost pure plagioclase and exhibits a pronounced positive Eu anomaly, as expected. Rock 72275, a KREEP-rich norite, has significantly higher REE abundances and a sharp negative Eu anomaly reflecting the KREEP-like components in this rock.

The orange soil sample 74220,38 is distinctly different from the other Apollo 17 soils. It is very low in Al, Ca, light rare earths, Ni, P, Rb, S, Th, U, and W, and enriched in Ti, Fe, Mg, Mn, Cr, Co, Cu, Ga, Pb, Sc, V, and Zn. Enrichment of the transition elements and Mg is especially striking. The orange color is attributed to the high Ti content and is similar to orange glass from other missions. The remarkably low Al content (3.22%) is even lower than in the basaltic lavas. Such basalts have extremely low Zn, Cu, and Ni contents. Orange soil is even richer in Zn and Cu than Apollo 11 soil 10085, which contains meteoritic debris as well as local basalt fragments. The exceptionally high Zn content (244 ppm) is not equaled by any lunar samples analyzed so far. The closest is Apollo 15 green glass (60-100 ppm). This high volatile element content of orange soil implies a source other than that of basalts.

A comparison of the overall composition of orange soil with glass samples from other missions reveals that it is definitely unlike highly aluminous glasses from Apollos 11, 12, 14 and Luna 16 soils, Apollo 15 green glasses, and Apollo 16 or Luna 20 glasses, or olivine phenocrysts from Apollo 12 basalts. Only the Apollo 11 red-brown to red-black glasses of Tranquillitatis B soil type are very close in chemical composition to the orange soil. Even the colorless, gray, yellow, and green glasses from Apollo 11 are different from the orange soil.

The unusual composition of orange soil is best explained as due to melting of mineral debris on the lunar surface by meteoritic impact giving splashes of liquid droplets. The impacting material must have been unusually high in Zn, Cu, and Ga and must have been dissolved in the liquid produced by the impact event finally crystallizing into "orange soil." Unexplained is the very high Zn content which cannot be attributed to any reasonable amount of meteoritic contamination during impact.

II. Allende Meteorite

While awaiting the receipt of the Apollo 16 samples, a detailed analysis was performed on a sample of the Allende meteorite. It has been suggested that this meteorite may serve as a "standard meteorite" powder similar to standard rocks provided by the USGS. In addition, the calcium-rich white inclusions of Allende are proposed as a component for the formation of the moon.

Using spark source mass spectrometry and neutron activation analysis, 57 elements were determined. The data have been published elsewhere (14).

III. Determination of Noble Metals

Because of the very low abundances of noble metals in most terrestrial and lunar materials, very little data exist on their concentrations in geological materials, even though considerable effort has been expended to develop adequate methods for their determination.

A method was therefore developed to determine ppb amounts of noble metals in terrestrial samples. The details of the method are published elsewhere (15). In essence, the method determines Au, Ru, Pd, Os, Ir and Pt in geological materials using thermal neutron irradiation, selective adsorption of the noble metal group on Srafion NMRR ion exchange resin, and high resolution gamma spectrometry.

The method was applied to the analysis of USGS standard rocks W-1, PCC-1, and DTS-1, as well as the Allende meteorite and lunar soil 72701. The agreement between literature values and the results obtained is excellent wherever data was available. The Pt value reported here for 72701 is the first value for this element reported for any lunar sample.

REFERENCES

1. G. H. Morrison, J. T. Gerard, A. Travesi, R. L. Currie, S. F. Peterson and N. M. Potter. Anal. Chem., **41**, 1633 (1969).
2. G. H. Morrison and A. T. Kashuba. Anal. Chem., **41**, 1842 (1969).
3. G. H. Morrison and A. M. Rothenberg. Anal. Chem., **44**, 515 (1972).

4. M. M. Lindstrom, A. R. Duncan, J. S. Fruchter, S. M. McKay, J. W. Stoeser, G. G. Goles and D. J. Lindstrom. Proc. Third Lunar Sci. Conf., Vol. 2, 1201 (1972), M.I.T. Press.

5. E. Schonfeld and C. Meyer, Jr. Proc. Third Lunar Sci. Conf., Vol. 2, 1397 (1972), M.I.T. Press

6. H. Wanke, H. Baddenhausen, F. Balacescu, F. Teschkle, S. Spetten, G. Dreibus, M. Palme, M. Quijano-Rico, H. Kruse, F. Wlotzka and F. Begermann. Proc. Third Lunar Sci. Conf., Vol. 2, 1251 (1972), M.I.T. Press.

7. B. M. Bansal, S. E. Church, P. W. Gast, N. J. Hubbard, J. R. Rhodes and H. Wiesmann. Earth Planet. Sci. Lett., **17**, 29 (1972).

8. LSPET. Science, **179**, 23 (1973).

9. H. Wanke, H. Baddenhausen, G. Dreibus, E. Jagoutz, H. Kruse, H. Palme, B. Spettel and F. Teschkle, Proc. Fourth Lunar Sci. Conf., Vol. 2, 1461 (1973).

10. A. R. Duncan, L. H. Ahrens, A. J. Erlank, J. P. Willis and J. J. Gurney. Lunar Science IV, 190 (1973), Lunar Science Institute, Houston.

11. P. A. Baedecker, C. L. Chou, L. L. Sundberg and J. T. Wasson. Earth Planet. Sci. Lett., **17**, 79 (1972).

12. U. Krahenbuhl, R. Ganapathy, J. W. Morgan and E. Anders. Science, **180**, 858 (1973).

13. APET. Science, **182**, 659 (1973).

14. G. H. Morrison, R. A. Nadkarni, N. M. Potter, A. M. Rothenberg, S.-F. Wong. Radiochem. Radioanal. Lett., **11**, 251-268 (1972); **12**, 77 (1972).

15. R. A. Nadkarni and G. H. Morrison, Anal. Chem., in press.

IV. Papers Published Under Grant NGR-33-010-166

G. H. Morrison, R. A. Nadkarni, N. M. Potter, A. M. Rothenberg, S.-F. Wong, "Multielement Analysis of Allende Meteorite by Neutron Activation Analysis and Spark Source Mass Spectrometry," Radiochem. Radioanal. Letters **11**, 251-268 (1972); **12**, 77 (1972).

G. H. Morrison, R. A. Nadkarni, J. Jaworski, R. I. Botto, J. R. Roth, "Elemental Abundances of Apollo 16 Samples," Proc. Fourth Lunar Science Conf., Houston, **2**, 1399 (1973).

G. H. Morrison, "Application of Activation Analysis to the Earth Sciences," Plenary Lecture, International Meetings on Activation Analysis, Paris, Oct. 2-6, 1972; J. Radioanal. Chem., in press.

G. H. Morrison and R. A. Nadkarni, "Elemental Abundances of Lunar Soils by Neutron Activation Analysis," International Meetings on Activation Analysis, Paris, Oct. 2-6, 1972; J. Radioanal. Chem., in press.

R. A. Nadkarni and G. H. Morrison, "Determination of the Noble Metals in Geological Materials by Activation Analysis," Anal. Chem., **46**, (Feb., 1974).

G. H. Morrison and R. A. Nadkarni, "Determination of the Noble Metals in Geological Materials by Multielement Neutron Activation Analysis," Abstracts of 36th Annual Meeting of the Meteoritical Society, Aug. 26-31, 1973, Davos.

G. H. Morrison, R. A. Nadkarni, J. Jaworski, R. I. Botto, J. R. Roth, "Elemental Abundances of Apollo 16 and 17 Samples." Abstract of Fifth Lunar Science Conf., 1974.