A QUEST FOR PORPHYRINS IN LUNAR SOIL: SAMPLES FROM APOLLO 11, 12 AND 14

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Abstract. Pigments exhibiting porphyrin-like behavior were detected in samples from Apollo 11 and 12. Those from Apollo 11 appeared to be directly related to the rocket exhaust of the descent engine; those from Apollo 12 from indigenous lunar material. Porphyrin-like pigments were not detected in a sample from Apollo 14.

1. Introduction

The purpose of the present communication is to review the results of porphyrin analyses on samples from the first two lunar missions (Hodgson *et al.*, 1970; 1971) and to report new results from the third lunar landing. The significance of the presence of porphyrins in lunar material appears to lie in their relevance to cosmogenic synthesis of organic matter. While terrestrial porphyrins are clearly biogenic, it can hardly be suggested that extraterrestrial porphyrins have a biogenic origin (Hodgson, 1971a). At most, they can perhaps be assigned only a prebiotic relevance. The search for lunar porphyrins pertains to the existence of extraterrestrial organic matter of considerable diversity and widespread occurrence (Ponnamperuma and Buhl, 1971). This interest is heightened by demonstrations of the ready condensation of porphyrins from relevant compounds (Hodgson, 1971b) and by the interpretation of interstellar diffuse absorption lines in terms of porphyrin spectra (Johnson, 1971).

2. Analytical Methods

Analyses for porphyrins in lunar samples were carried out by extracting the lunar soils as received by organic solvents followed by analytical demetallation using methanesulfonic acid, after which free-base porphyrins, if present, were recovered and demonstrably recomplexed with divalent cations. Exhaustive spectral monitoring, largely by fluorescence, was performed throughout the analytical procedures. Procedural blanks were run with the lunar samples; at the conclusion of the analyses, sensitivities were determined using authentic porphyrins.

Details of the methods used for the two lunar missions were published previously (Hodgson *et al.*, 1970; 1971); those for Apollo 14 were identical with those for Apollo 12.

3. Spectral Interpretation

Three spectral methods were used in the course of the three analyses. The principal observation was by fluorescence, but absorption and MCD (magnetic circular dichroism) were also used for the first two missions. The sensitivity of these two methods was substantially less than that for fluorescence, and few useful data were obtained.

Fluorescence data were obtained using a commercial internally-compensated spectrofluorometer, Turner model 210. Signals were recorded in both emission and excitation. Principal attention was paid to the excitation data since experience with many terrestrial geochemical samples containing porphyrins clearly showed that the excitation data were more informative and more reliable. Thus, direct emission spectra were commonly badly obscured by interfering substances, and it was difficult if not impossible on many occasions to detect porphyrins in emission while clearly visible in excitation. This led to the use of a cross plotting method for background-corrected excitation data for establishing emission curves showing emission maxima where they were obscured previously.

A criterion for the spectral indication of porphyrins by spectrofluorometry was adopted in the lunar work (as well as related terrestrial work): that the emission, whether inferred or direct, had to be directly coupled to a specific excitation peak in the neighborhood of the soret peak of porphyrins. Uncoupled peaks in either emission or excitation were summarily rejected as having no significance in the search for porphyrins.

Spectral artifacts, long known in spectrofluorometry, were observed and corrected for, using the foregoing criterion. The analyses of blank samples showed that the method involving the cross plotting approach was completely adequate.

4. Analytical Criteria

Continuous monitoring of the material extracted from the lunar samples afforded a number of opportunities for evaluating the extracts. At the outset it was possible to observe extraneous substances in some samples by doing a general check of fluorescence excitation throughout the visible range. Thus, rocket exhaust was readily detected in samples from Apollo 11 and the 'close-in' Apollo 12 sample, in the form of a strong broad excitation band centered on 460 nm for emission in the red. If a free porphyrin were present, it would exhibit an excitation peak in the soret region.

The second analytical criterion was that for active demetallation of a non-fluorescing porphyrin complex. This called for the emergence of a soret excitation peak in the course of a step-wise addition of the demetallating agent, MSA.

The presence of porphyrins should permit the recovery of free-base pigments at

the end of the demetallation step, and this formed the third analytical criterion: partition between aqueous acid solutions and organic solvents.

The fourth criterion depended on the fact that free porphyrins can readily be complexed with divalent cations, and that some such complexes are strongly fluorescent while others are largely non-fluorescent. To evaluate this criterion, it was customary to react the free-base pigments with nickel, zinc and/or copper in acetic acid, with continuous monitoring to observe the resulting changes in fluorescence. If the fluorescence of a pigment showing blue-red coupling died out with copper or nickel, and persisted with zinc, it satisfied this criterion for porphyrins.

5. Results

The results of the analyses previously reported are summarized below, along with those for an Apollo 14 sample reported here for the first time.

(a) *Apollo 11* – Five samples from the first lunar lander were examined. All were from a location very close to the lunar module (LM). All showed the presence of fluorescent substances attributed to exhaust from the descent engine. An excitation band at 390 nm for emission at 630 nm suggested free-base porphyrins, in addition. Analytical demetallation showed the emergence of a peak at 410 nm at about 3% MSA followed by a shift to 388 nm at 20% MSA. Free-base recovery showed clear-cut excitation at 390 nm peaking for emission at 625 nm. Metal complexing with copper suppressed the fluorescence. Abundance of the indicated porphyrins as recovered was estimated to be about 0.1 ng g^{-1} of lunar soil.

Samples of terrestrial dunite exposed to the exhaust gases of a lunar descent engine showed pigments very similar to those of the lunar sample. Thus, the broad excitation at 460 nm was again observed. Analytical demetallation gave similar results, with excitation at 430 nm followed by strongly increasing excitation at 387 nm after 29% MSA. In the procedure for free-base recovery, a pigment was obtained with major excitation at 388 nm. The abundance of the pigment in the artificially exposed dunite was about 50 times that for the lunar fines.

Pigments trapped directly from the exhaust of the same rocket engine showed the same features. In addition, a partition of the trapped material between aqueous hydrochloric acid and ether showed a strong excitation peak at 390 nm for emission in the porphyrin range. Again, the rocket combustion product clearly contained pigments exhibiting porphyrin-like behavior.

Similar treatment of rocket fuel (unsymmetrical dimethyl hydrazine) failed to show porphyrins, even after MSA demetallation.

Blank runs with samples of Allende meteorite and ignited sand gave negative results for porphyrins.

In summary, the Apollo 11 samples indicated the presence of pigments exhibiting porphyrin-like behavior, but the same pigments were also present in rocket engine exhaust. It was concluded, therefore, that indigenous porphyrins were not detected.

(b) *Apollo 12* – Two samples from the Apollo 12 mission were analyzed. One,

from near the lunar lander, showed rocket exhaust products. The other appeared completely free of such material. It was taken from a trench about 20 cm deep at a point about 500 m from the LM, and it showed the presence of pigments exhibiting porphyrin-like behavior.

The concentration of the pigments in the direct extract was too low for detection by MCD or by absorption spectrometry. Analytical demetallation, however, showed an excitation band emerging at 420–425 nm when the MSA content reached 50% by volume. The intensity of the band increased on the addition of further MSA. Free-base recovery procedures gave fluorescence excitation in 6N HCl at 390 nm for emission at 580 to 680 nm, with strongest signals at 620–630 nm. The next criterion of porphyrin identification was that of re-metallation. Copper and zinc salts were used, the former giving complete suppression of fluorescence and the latter retaining the fluorescence of the product. Thus, the remote Apollo 12 sample showed reactions consistent with well-known demetallation, solvent partition and demetallation steps, and in addition gave coupled spectra consistent with those of authentic porphyrins, but significantly different from those previously detected in rocket exhaust. The recovered abundance of the indicated pigments was about 0.05 ng g^{-1} of lunar soil, much lower than the exhaust porphyrins of the Apollo 11 mission.

Since the foregoing data suggested the presence of pigments exhibiting porphyrin-like behavior indigenous to the lunar soil, great care was taken to avoid misinter-pretation of the data. Thus, answers were established for relevant questions:

(1) Spectra – were the spectra due to true pigments or to instrumental artifacts?
(2) Identification – were the pigments true porphyrins?
(3) Source – did the pigments enter the sample from a contaminating source?

Analysts experienced in fluorescent analysis are aware of instrumental limitations, particularly of problems in the 600–700 nm range of emission, and of Raman features closely coupled to excitation light. These problems are associated primarily with emission spectra. Internally compensated instruments are particularly suited, however, for analysis by excitation. In the Apollo 12 analyses the running of procedural blanks showed that artifacts in emission did not interfere with excitation data; in fact, the excitation data were used to correct the emission data and to construct corrected inferred emission spectra. Further, from a procedural point of view the substances responsible for the fluorescence features were transferred, according to plan with fluorescent monitoring, from solution to solution, from fluorescence to non-fluorescence as required. Any suggestion that the instrumental data were optical artifacts cannot be accepted.

Identification of the pigments as porphyrins was strongly indicated but not proven. The ultimate proof would involve complete spectral data by several different methods, e.g. by absorption, MCD and fluorescence, sufficiently detailed to show non-soret features in addition to the major bands in absorption and emission. The several criteria – demetallation, partition and re-metallation, with continuous spectral monitoring – were necessary, but perhaps not sufficient, criteria for identification of the lunar pigments as porphyrins.

The source of indicated pigments was established negatively. Thus, they were shown not to arise in the lunar analytical laboratory nor in the lunar receiving laboratory (LRL) and they were therefore inferred to have been present in the sample as collected. Claims that massive contamination occurred in the LRL were found to be completely unfounded insofar as porphyrin analyses were concerned, as shown by completely negative data for an ignited sand sample co-exposed with the lunar soil in the transfer cabinets. No data are available for the possibility that porphyrins were introduced into the samples during the period between collection and delivery to the LRL. While the likelihood that such occurred is extremely small, it cannot be completely ruled out.

In summary, an Apollo 12 sample showed pigments resembling porphyrins. The identification as porphyrins was limited, however, and the source, while almost certainly lunar, was not positively established.

(c) *Apollo 14* – Data for the analysis of porphyrins in lunar soil from the Apollo 14 mission are reported here for the first time. Unlike corresponding data for Apollo 11 and 12, the Apollo 14 results were negative.

The sample was 14163 collected from the surface of the lunar soil at a point about 15 m from the LM. A portion of 4.45 g was extracted and analyzed in exactly the same way as the sample from Apollo 12. Again, no rocket exhaust was apparent. No porphyrins were detected by initial observation, by demetallation, nor by free-base recovery. There was no detectable difference between the lunar sample and the Allende blank. The abundance of porphyrins if present in the final preparation, was indicated to be less than 0.01 ng g^{-1} of lunar soil. The same solutions were subsequently analyzed by Rho and associates who showed the same results with even lower limits of detection.

6. Discussion

Analyses of lunar soils to data showed pigments resembling porphyrins in Apollo 11 due to synthesis in the lunar descent engine. Apollo 12 analyses indicated the presence of indigenous pigments exhibiting porphyrin-like behavior in a trench sample from Oceanus Procellarum. A surface sample from Fra Mauro revealed no such pigments.

The synthesis of porphyrins is surprisingly easy, as revealed by a number of exploratory reactions involving formaldehyde and simple nitrogen compounds including unsymmetrical dimethyl hydrazine (Hodgson, 1971a). In addition, high-temperature plasma reactions demonstrated the synthesis of porphyrins from reactants such as carbon dioxide and ammonia. Thus the appearance of porphyrins in rocket exhaust involving UDMH and an oxidant is not inexplicable. Of considerable importance is the role of an oxidant in the synthesis of porphyrins. The final step of aromatization follows condensation of the tetrapyrrole macrocycle, and it involves dehydrogenation at the mesoposition, a step readily accomplished by deliberate oxidation.

It is possible that the porphyrin-like compounds of Apollo 12 appeared in the analysis because oxidation of precursor compounds took place during the analysis. Thus, it is possible that precursors of porphyrins were present in the lunar soil, and

that exposure of these to laboratory air completed the synthesis of what appeared to be lunar porphyrins in the course of the analysis. If such were the case, analytical methods differing in respect to opportunities for oxidation would give sharply differing indications for the presence of lunar porphyrins.

The differing results for Oceanus Procellarum and Fra Mauro are undoubtedly due to real differences in the samples, either because they were trench and surface samples respectively, or because they were from two significantly different locations on the Moon. Current data are too limited to permit resolution of the question at this time.

Acknowledgements

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