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Sulphur isotopes in grain size fractions of lunar soils

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Abstract—Grain size separates of the mature soil 15271 and the grey soil 74241 show variations of sulphur concentrations and sulphur isotope ratios similar to those found previously for a mature soil and a sub-mature soil respectively. The orange soil 74220 shows an increase of sulphur concentration with decreasing particle size which is more marked than that found for other soils. In contrast with other soils the orange soil has a slight heavy isotope enrichment for large particles while the smallest particle sizes show essentially zero enrichment.

INTRODUCTION

WE HAVE PREVIOUSLY REPORTED the variations of sulphur concentrations and $\delta^{34}S$* values in grain size fractions of the two Apollo 17 soils, 72501 and 75081, (Rees and Thode, 1974a,b). These two soils are classified as mature and submature respectively (see for example, McKay *et al.*, 1974).

It was found that both the mature soil and the sub-mature soil had maximum sulphur concentrations and heavy isotope enrichments in the smallest particle size fractions. We suggested that the increase of sulphur concentration with decreasing particle size was brought about by the initial formation and comminution of the soil and that the heavy isotope enrichment was the result of subsequent sulphur loss from the soil. The variation of $\delta^{34}S$ values with particle size for the mature soil 72501 could be explained by each particle having a bulk enrichment of $\sim +5‰$ together with an outer shell of thickness $\sim 1.5\ \mu$ with an enrichment of $\sim +20‰$. Thus the heavy isotope enrichment in soils was considered to have both a bulk component and a surface correlated component.

It was considered desirable to make measurements on other soil samples to further investigate the relationships between sulphur concentrations, sulphur isotope ratios, grain size and soil maturity. We report here measurements made on grain size separates of the orange soil, 74220, the gray soil, 74241, and a mature Apollo 15 soil, 15271. In addition we report the results of bulk analyses of these soils and of the Apollo 16 soils, 63501 and 67601. The experimental techniques used have been described by Thode and Rees (1971) and Rees and Thode (1974b).

The McMaster isotope analyses of lunar rocks plotted in Fig. 1 are internally consistent, in that identical procedures were used in each case (HCl extraction, SF_6 analysis) and identical reference samples were used. All the $\sigma^{34}S$ values we

*$\delta^{34}S$, ‰ $= \{[(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard}] - 1\} \times 1000$, where the standard reference material is sulphur from the troilite of the Canyon Diablo meteorite.

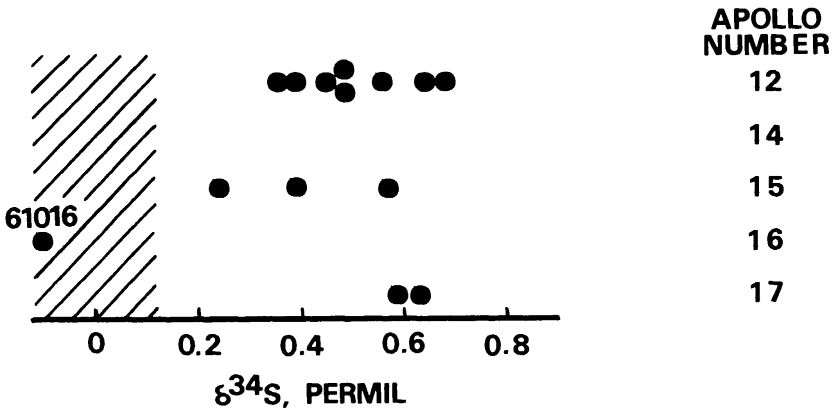

Fig. 1. McMaster isotope analyses of lunar rocks.

have obtained so far for basaltic rocks fall between +0.2‰ and +0.7‰, with a mean value of 0.51 ± 0.04‰ and with a standard deviation for an individual value of ±0.13‰. The only anorthosite rock analysed by us, 61016, clearly lies outside this range. The cross hatched area indicates the total spread for the analyses of reference samples. These have a standard deviation for an individual determination (fluorination of Ag_2S and mass spectrometer analysis) of ±0.07‰.

The lunar rocks therefore show small variations in their $\delta^{34}S$ values and are slightly enriched (~0.5‰) in ^{34}S relative to our standard, Canyon Diablo troilite. It is clear also that sample 61016 is different from all the others and within the limits of our reproducibility has a del value of zero. This rock sample, an anorthosite from the Highlands, is considered to be part of the original lunar crust and has an age of ~4.5 b.y. (Nyquist *et al.*, 1973).

The slight enrichment of lunar rocks in ^{34}S is probably due to either the loss of sulphur, a few percent, from a hot magma by a mechanism leading to isotope fractionation, or to the incorporation of small amounts of enriched soil into the hot magma as it pours out onto the lunar surface, or both. In regard to the first possibility, no correlation between sulphur content and $\delta^{34}S$ values has been established (Gibson *et al.*, 1975). Perhaps only the anorthosite, 61016, a sample unaltered since the lunar crust was formed, was free of soil contamination. The $\delta^{34}S = 0$ for this sample would therefore favour the second hypothesis.

RESULTS

Table 1 shows the results of analyses of bulk soil samples. Some previously reported data is also presented for purposes of comparison. The last column of the table shows the KREEP content, where available, as estimated by Schonfeld (1974) using mixing model calculations based on published chemical analyses. It is apparent that for Apollo 15 and 16 soils both sulphur concentrations and $\delta^{34}S$ values increase with increasing KREEP content. The positive correlation between sulphur concentration and $\delta^{34}S$ has already been noted for Apollo 15 soils (Thode and Rees, 1972a,b) and Apollo 16 soils (Kerridge *et al.*, 1975a,b) and contrasts with the negative correlation found in the case of Apollo 17 soils (Rees and Thode, 1974b).

Table 1. Sulphur contents and isotopic compositions of bulk soil samples.

Sample	Sulphur concentration, ppm	$\delta^{34}S$,‰	"KREEP",%*
15471†	570	7.45	11
15021†	689	10.36	20
	694	10.22	
15271	696	10.79	22
67601	294	7.45	6
63501	480	8.05	9
68501‡	581	8.6	15
60601‡	663	9.9	15
74220	420	0.69	—
74241	940	4.35	—

*From Schonfeld (1974).
†Previously reported in Thode and Rees (1972).
‡Previously reported in Rees and Thode (1974).

The bulk $\delta^{34}S$ values found for the Apollo 15 soil 15271 (10.79‰) and for the orange soil 74220 (0.69‰) are the highest and the lowest respectively that we have determined. Other workers report a wider range. For example, Kerridge *et al.* (1975b) find Apollo 16 soils with $\delta^{34}S$ values of up to 13.5‰, while Chang *et al.* (1974) have reported a value of −3.1‰ for a sample of orange soil. Nevertheless, 15271 and 74220 were selected for grain size fraction analysis on the basis of our own isotope analyses. The grey soil, 74241, with a bulk $\delta^{34}S$ value of 4.35‰, was selected as another example of a sub-mature or mixed soil and also because of its contiguity to the orange soil.

The results of the grain size fraction analyses are given in Tables 2, 3 and 4. In

Table 2. Grain size fraction data for soil sample 15271.

Fraction size range, μ	Percent mass in fraction	Sulphur content, ppm	$\delta^{34}S$,‰
500–1000	5.1	560	6.83
200–500	10.9	530	6.73
90–200	16.1	480	7.62
60–90	10.5	490	8.17
45–60	7.0	450	8.91
30–45	11.6	530	9.24
20–30	9.1	570	10.03
10–20	21.1	730	12.76
5–10	7.5	980	16.12
0–5	1.2	—*	20.20
Bulk (calculated)	—	600	10.6

*Too small for accurate weighing.

Table 3. Grain size fraction data for the grey soil 74241.

Fraction size range, μ	Percent mass in fraction	Sulphur content, ppm	$\delta^{34}S$,‰
500–1000	8.6	940	2.52
200–500	13.5	770	2.60
90–200	17.5	750	2.98
60–90	10.5	700	3.08
45–60	7.0	730	3.30
30–45	10.7	730	3.68
20–30	8.0	900	3.98
10–20	7.0	934	4.80
5–10	17.3 (5–10 and 0–5)	1200	6.69
0–5		1310	8.05
Bulk (calculated)		870	4.3

Table 4. Grain size fraction data for the orange soil 74220.

Fraction size range, μ	Percent mass in fraction	Sulphur content, ppm	$\delta^{34}S$,‰
500–1000	1.5	—*	—
200–500	7.1	190	1.85
90–200	16.3	280	1.06
60–90	11.3	200	0.43
45–60	8.4	~200†	1.22
30–45	13.5	250	1.40
20–30	10.3	350	0.03
10–20	20.3	440	−0.13
0–10	11.1	900	0.00
Bulk (calculated)	—	360	0.4

*Too small for analysis.
†Mechanical loss during sulphur extraction.

Figs. 2 and 3 the sulphur concentrations and $\delta^{34}S$ values are plotted against the outer layer function f. This function is the ratio of the volume of a shell of thickness 1.5 μ to the total volume of a spherical particle with radius equal to the mean particle radius for a given sieve fraction. The data for the previously analysed samples 72501 and 75081 (Rees and Thode, 1974a,b) are also shown for purposes of comparison.

In each case the smallest particles have the highest sulphur concentrations. The increase of sulphur concentration with decreasing particle size is less marked in the case of the mature soils, 72501 and 15271, than for the sub-mature soil 75081 or the grey soil 74241. The orange soil, 74220, shows the greatest increase. With the exception of the orange soil there is a minimum sulphur concentration for $f \sim 0.15$ corresponding to a particle radius of $\sim 25\ \mu$.

The $\delta^{34}S$ data for the mature soil 15271 are similar to that previously reported for 72501 and again show the dramatic increase of heavy isotope enrichment with decreasing particle size. In the same way the variations of $\delta^{34}S$ for the grey soil 74241 are analogous to those already reported for the sub-mature soil, 75081. The results for the orange soil are quite different. This soil shows a slight heavy isotope enrichment for the coarser particles while particles with radii of less than 15 μ, which make up $\sim$40% of the weight of the sample, have $\delta^{34}S$ values which are essentially zero. Microscopic examination of the grain size fractions of the orange soil indicate that the smaller size fractions are more uniformly orange than are the larger.

For each of the sieved samples values have been calculated, and are shown in the tables, of bulk sulphur concentration and bulk $\delta^{34}S$ values. The agreement between calculated and measured values is quite satisfactory. In each case the calculated sulphur content is less than the measured one, reflecting the greater sulphur losses resulting from handling the sieved samples in up to ten small fractions. The measured and calculated $\delta^{34}S$ values agree to within 0.3‰.

DISCUSSION

The outer layer function is useful for illustrating the variations of sulphur concentrations and $\delta^{34}S$ values with particle size. The curves obtained using f are similar to those that would be obtained using $1/r$ and show the presence of both bulk and surface correlated effects. As we have defined it, the use of f assumes that a particular soil has the same sulphur concentration for all particle sizes while Fig. 2 shows that this is definitely not the case. Thus the linear variation of $\delta^{34}S$ with f found for sample 72501 may not have special significance and may be an artifact of the data. Nevertheless we continue for the present, as a matter of convenience, to use this method of representing the data.

The grain size fraction data for the orange soil 74220 composed of fine glass spherules presented several surprises. First, the bulk sample gave a $\delta^{34}S$ value very close to zero, different from all other soils, indicating little ^{34}S enrichment and a most immature soil. Second, the $\delta^{34}S$ values decrease with decreasing grain size, just the reverse of other soils, and finally, the three smallest grain size fractions comprising over 40% of the mass of the bulk sample gave a del value essentially equal to zero. These results indicate a totally immature soil with possibly some second component in the larger grain size fractions giving rise to some slight ^{34}S enrichment.

Previously we postulated that a totally immature soil would have $\delta^{34}S$ values close to zero for all particle sizes (Rees and Thode, 1974b). We further postulated that the size distribution of this immature soil would favour coarse grains. The orange soil is therefore clearly immature on the first count, but contains a very high proportion of the fine grain size fractions, a property of a mature soil. It seems clear that the size distribution of the orange soil is unrelated to soil

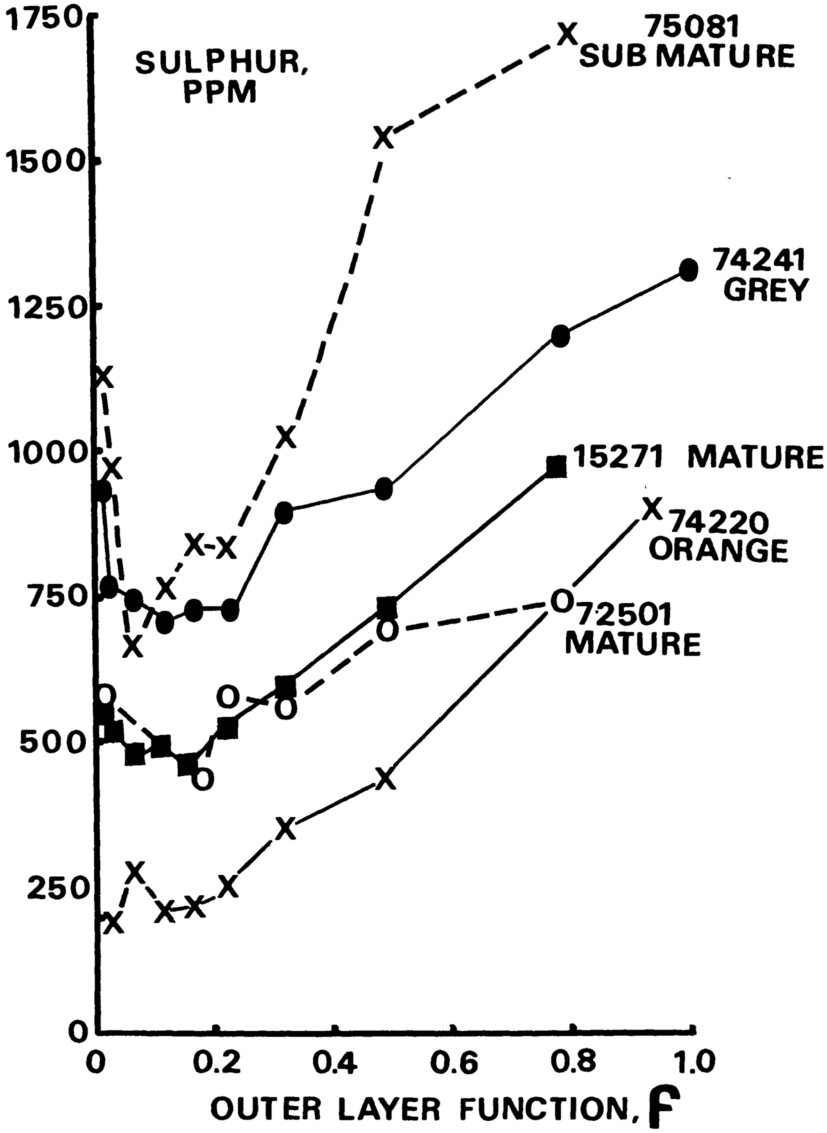

Fig. 2. Sulphur concentration versus outer layer function *f*.

maturation processes and that the glass spherules were formed by some process other than that involved in the formation of more normal soils.

These results are consistent with those of Taylor and Epstein (1973). Their partial fluorination experiments show the orange soil to be unusual, exhibiting no enrichment in ^{18}O and ^{30}Si in a thin surface layer of the soil particles. This result indicated little or no exposure time on the lunar surface for the orange soil since the enrichment of these isotopes in the surface layers is related to soil maturation. Taylor and Epstein (1973) also consider the very low solar wind components of hydrogen and carbon in the orange glass as additional evidence for very short exposure times.

Various origins of the orange glass have been proposed but the most plausible mechanism is that they are volcanic in origin and produced in lava fountains (Prinz *et al.*, 1973). Tera and Wasserburg (1976) conclude from their studies of the

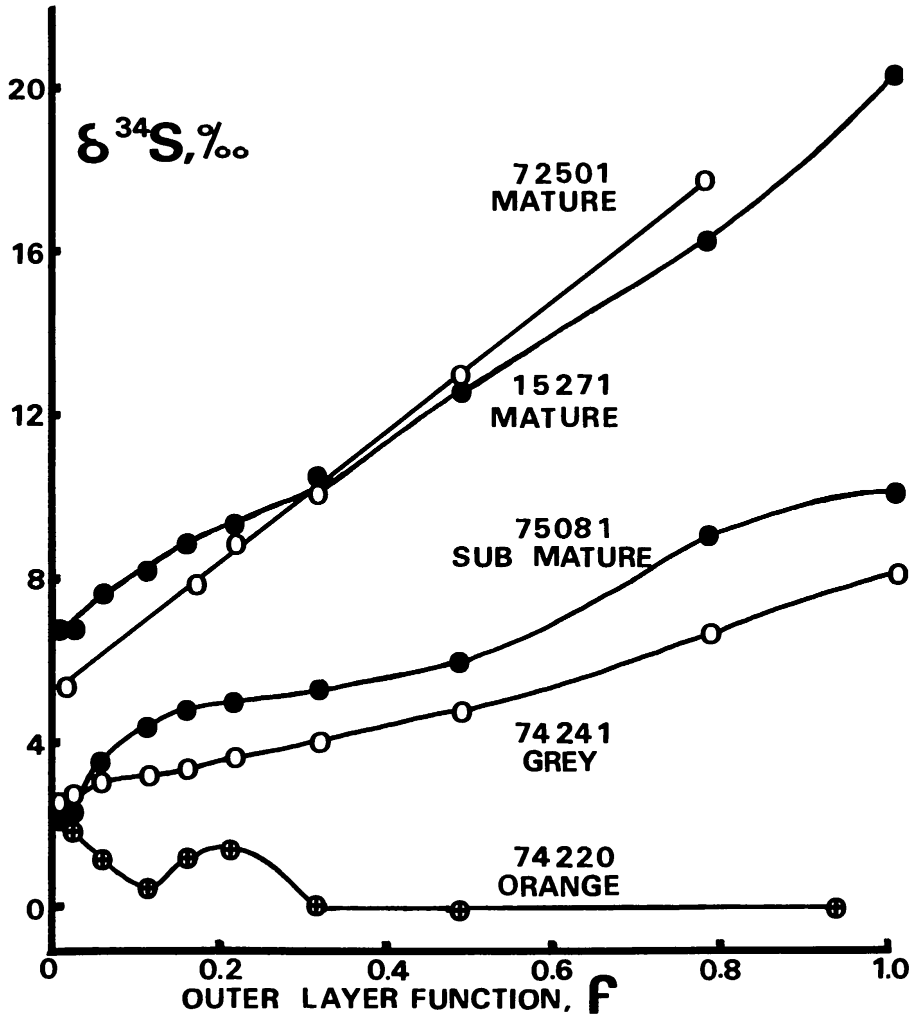

Fig. 3. $\delta^{34}S$ values versus outer layer function *f*. The chosen shell thickness of 1.5 μ is that which gives a linear variation in the case of 72501.

various types of Pb in and on the orange glass balls that the event took place ~3.48 b.y. ago. According to them the magma came from a reservoir deep in the interior of the moon with an age of 4.59 b.y. The initial magma is therefore considered to be primitive and undifferentiated. The $\delta^{34}S$ value near zero for the orange glass and for lunar rocks generally suggests that either little sulphur was lost from the moon in its early history, or its loss has been by a mechanism involving no isotope fractionation. However, sulphur loss and ^{34}S enrichment do occur in the soil on the surface of the moon due to impact processes. It seems clear that the orange glass remained buried during its lifetime and escaped these processes.

It is interesting to compare the sieve experiments for the two mature soils 72501 and 15271. As previously pointed out the ^{34}S enrichment process in the soil is both volume and surface correlated, and the total enrichment for a bulk sample appears to be a measure of the extent of soil maturation. So-called mature soils have $\delta^{34}S$ values grouped around +11‰ and sub-mature soils have intermediate values between those for basaltic rocks (near zero) and +11‰. From the bulk analyses, sample 15271 has the highest $\delta^{34}S$ value and on this basis is the most mature.

In the $\delta^{34}S$ vs. f plots, the selection of "a" = 1.5 μ yields a straight line for the data of sample 72501, but no value of "a" for the sieve data of 15271 gives a linear plot. Using "a" = 1.5 μ for both plots (see Fig. 3) we see that the slope for the 15271 curve is less than that for 72501, and that $\delta^{34}S$ values for the fine grain size fractions of 15271 are slightly less than those for 72501. These facts suggest a more complex history for this soil.

In actual fact 15271 from Station 6 on the Appenine front contains 7–11% green glass droplets (NASA Preliminary Science Report, Apollo 15, 1972). This green glass component is in many ways like the orange glass and is believed to have been formed in a similar manner. If the green glass droplets in the soil have not been subjected to impact processes to any extent, either before or after addition to the soil, and are completely immature with a $\delta^{34}S$ value close to zero as is the case for the orange glass, then the addition of this component to a mature soil would distort the $\delta^{34}S$ vs. f plot and suppress all $\delta^{34}S$ values. The amount of this suppression for the various grain size fractions will depend on how the grain size distribution of the green glass component compares with that of the 15271 soil.

A new $\delta^{34}S$ vs. f plot calculated by subtracting a 10% green glass component with $\delta = 0$ would have all its $\delta^{34}S$ values raised. A high proportion of small grain sizes in the green glass component similar to the orange glass would raise the δ values for the fine grain size fractions more than coarse grain size fractions. However, size data available for the green glass "clods" in soil 15401 (about 95% green glass) from DesMarais *et al.* (1973) suggest a grain size distribution not unlike that for the 15271 soil itself. Whether this is so for the green glass in 15271 and whether this green glass is immature and has $\delta^{34}S$ values near zero can be determined by direct analysis of green glass separates. In any case direct measurements on the green glass component should be of considerable interest in themselves.

Kerridge *et al.* (1975a) have pointed out that the input of meteoritic material has contributed significantly to the sulphur content of soils. The input of meteoritic sulphur combined with the loss of sulphur from the moon could under certain circumstances lead to a balance being established. In this case the sulphur content of a soil would not depend on the initial concentration but on the magnitude of the input and effectiveness of the mechanism responsible for the loss. If such a balance were to be established then the isotopic composition of the soil would depend on the isotopic composition of the input (presumably close to $\delta^{34}S = 0$) and the isotope effect involved in the loss process. McEwing (1976, in preparation) has measured the isotope effect involved in the thermal dissociation of FeS under vacuum at 1100°C. He finds a value of 13‰—that is, the elemental sulphur formed is 13‰ lighter than the FeS from which it derives. If a steady state were established in which the $\delta^{34}S$ of input and output were equal, then, with such an isotope effect, the $\delta^{34}S$ of the reservoir would rise to a maximum value of + 13‰.

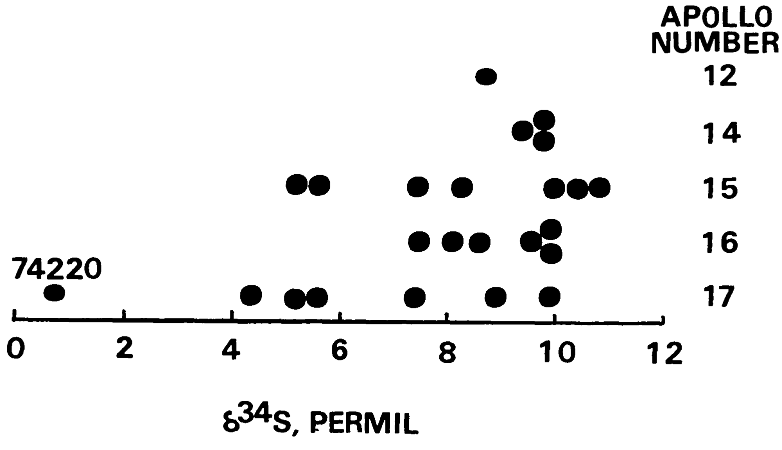

Fig. 4. McMaster isotope analyses of lunar soils. With the exception of the orange soil 74220, all analyses fall between 4 and 11‰.

It may be significant that the maximum $\delta^{34}S$ value for bulk soil measured by us is +11‰ (Fig. 4).

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References

Apollo 15 Prelim. Sci. Rep., NASA publication SP-289, p. 6–16.

Chang S., Lennon K., and Gibson E. K., Jr. (1974) Abundances of C, N, H, He, and S in Apollo 17 soils from Station 3 and 4: Implications for solar wind exposure ages and regolith evolution. *Proc. Lunar Sci. Conf. 5th*, p. 1785–1800.

DesMarais D. J., Hayes J. M., and Meinschein W. G. (1973) The distribution in lunar soil of carbon released by pyrolysis. *Proc. Lunar Sci. Conf. 4th*, p. 1543–1558.

Gibson E. K., Jr., Chang S., Lennon K., Moore G. W., and Pearce G. W. (1975) Sulphur abundances and distribution in mare basalts and their source magma. *Proc. Lunar Sci. Conf. 6th*, p. 1287–1301.

Kerridge J. F., Kaplan I. R., and Petrowski C. (1975a) Evidence for meteoritic sulfur in the lunar regolith. *Proc. Lunar Sci. Conf. 6th*, p. 2151–2162.

Kerridge J. F., Kaplan I. R., Petrowski C., and Chang S. (1975b) Light element geochemistry of the Apollo 16 site. *Geochim. Cosmochim. Acta* **39**, 137–162.

McKay D. S., Fruland R. M., and Heiken G. H. (1974) Grain size distribution as an indicator of the maturity of lunar soils (abstract). In *Lunar Science V*, p. 480–482. The Lunar Science Institute, Houston.

Nyquist L. E., Hubbard N. J., Gast P. W., Bansal B. M., Weismann H., and John B. (1973) Rb–Sr systematics for chemically defined Apollo 15 and 16 materials. *Proc. Lunar Sci. Conf. 4th*, p. 1823–1846.

Prinz M., Dowty E., and Keil K. (1973) A model for the origin of orange and green glasses and the filling of mare basins (abstract). *EOS* (*Trans. Amer. Geophys. Union*) **54**, 605–606.

Rees C. E. and Thode H. G. (1974a) Sulphur concentrations and isotope ratios in Apollo 16 and 17 samples (abstract). In *Lunar Science V*, p. 621–623. The Lunar Science Institute, Houston.

Rees C. E. and Thode H. G. (1974b) Sulphur concentrations and isotope ratios in Apollo 16 and 17 samples. *Proc. Lunar Sci. Conf. 5th*, p. 1963–1973.

Schonfeld E. (1974) The contamination of lunar highland rocks by KREEP: Interpretation by mixing models. *Proc. Lunar Sci. Conf. 5th*, p. 1269–1286.

Taylor H. P., Jr. and Epstein S. (1973) $^{18}O/^{16}O$ and $^{30}Si/^{28}Si$ studies of some Apollo 15, 16 and 17 samples. *Proc. Lunar Sci. Conf. 4th*, p. 1657–1679.

Tera F. and Wasserburg G. J. (1976) Lunar science ball games and other sports (abstract). In *Lunar Science VII*, p. 858–860. The Lunar Science Institute, Houston.

Thode H. G. and Rees C. E. (1971) Measurement of sulphur concentrations and the isotope ratios $^{33}S/^{32}S$, $^{34}S/^{32}S$, and $^{36}S/^{32}S$ in Apollo 12 samples. *Earth Planet. Sci. Lett.* **12**, 434–438.

Thode H. G. and Rees C. E. (1972a) Sulphur concentrations and isotope ratios in Apollo 14 and 15 samples (abstract). In *The Apollo 15 Lunar Samples* (J. W. Chamberlain and C. Watkins, eds.), p. 402–403. The Lunar Science Institute, Houston.

Thode H. G. and Rees C. E. (1972b) Sulphur concentrations and isotope ratios in lunar samples. *Proc. Lunar Sci. Conf. 3rd*, p. 1479–1485.