Sulphur isotopes in lunar and meteorite samples*

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Abstract—Measurements of ^{32}S, ^{33}S, ^{34}S and ^{36}S have been tested in small samples and contaminant levels assessed for the rare isotopes ^{33}S and ^{36}S. The linear mass dependence of the isotope abundance variations has been confirmed for the high heavy isotope enrichments found in the fine grain size fractions of the mature lunar soil 15021. The ^{34}S enrichment pattern in this soil closely resembles that found in other mature soils. A new leaching experiment on a ground bulk sample of the Allende meteorite did not yield a fraction containing excess ^{33}S. Possible reasons for this are discussed.

INTRODUCTION

We have previously reported measurements of ^{32}S, ^{33}S, ^{34}S and ^{36}S in lunar materials which showed that the sulphur isotope abundance variations are the result of linearly mass dependent fractionation processes (Thode and Rees, 1971, 1972; Rees and Thode, 1972). Measurement of ^{32}S, ^{33}S and ^{34}S in various Allende samples (Rees and Thode, 1977) showed similar mass fractionation effects in all cases except that of the last sulphur released in a chemical leaching experiment on a ground bulk sample. This sulphur showed a ^{33}S excess of approximately 1‰. At the time of these Allende measurements ^{36}S abundances were not measured because of a contaminant which interfered with $^{36}SF_5^+$ in the mass spectrometer.

Our previous determination of $\delta^{34}S^+$ values in grain size fractions of lunar soils (Rees and Thode, 1974; Thode and Rees, 1976) have been directed towards establishing the process or processes responsible for the heavy isotope enrichment of sulphur during the course of soil maturation. The enrichment in lunar soils of the heavy isotopes of oxygen, silicon, sulphur and potassium has been studied extensively (see for example Epstein and Taylor, 1971, 1972; Taylor and

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† $\delta^M S, ‰ = \left[\dfrac{(^M S /^{32}S) \text{ sample}}{(^M S /^{32}S) \text{ standard}} - 1 \right] \times 1000$

where M = 33, 34 or 36 and where the standard material is sulphur from the troilite of the Canyon Diablo meteorite.

Epstein, 1973; Kaplan *et al.,* 1970; Kaplan and Petrowski, 1971; Kerridge *et al.,* 1974; Rees and Thode, 1972, 1974; Thode and Rees, 1976; Barnes *et al.,* 1973; Kerridge *et al.,* 1975a, b). The role of sputtering in producing these enrichments has been discussed by Haff *et al.* (1977), Switkowsky *et al.* (1977), Kerridge and Kaplan (1978) and Housley and Grant (1979). It is not clear, in the case of sulphur, that sputtering is the dominant process and it seems probable that the isotope effects present in the thermal decomposition of troilite (McEwing *et al.,* in preparation) must also be taken into account.

We present here the results of an investigation of the effects of contaminants in the measurement of ^{33}S and ^{36}S in small samples. In addition we report the results of a further search for ^{33}S and ^{36}S anomalies in the Allende meteorite and of $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ measurements of grain size fractions of a mature lunar soil.

ANALYTICAL PROCEDURES

The procedures for the release from samples of sulphur, as hydrogen sulphide by acid hydrolysis, for the subsequent conversions of hydrogen sulphide to cadmium sulphide to silver sulphide to sulphur hexafluoride and the mass spectrometric analysis of sulphur hexafluoride have been described previously (Thode and Rees, 1971).

For certain of the results reported below, sulphur hexafluoride samples were passed through an additional stage of gas chromatographic purification. This was done in order to eliminate the source of contamination which prevented ^{36}S measurements in the original Allende experiments (Rees and Thode, 1977). The gas chromatograph used is similar to that on the main fluorination line (Thode and Rees, 1971) but has separate pumping systems for the sample injection and sample collection sides of the column, in order to prevent accidental contamination of the 'clean' side of the system by gases passing through a shared vacuum system.

RESULTS AND DISCUSSION

Small samples

A number of small silver sulphide samples were fluorinated to sulphur hexafluoride and analyzed for $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ in order to test for spurious ^{36}S and ^{33}S enrichments caused by the presence of contaminants.

Fig. 1 shows $\Delta^{36}S$ values* as a function of sample size for sulphur hexafluoride samples which have been put through the additional gas chromatographic clean-up procedure. There is no reason to expect non-linear effects in these samples so that $\Delta^{36}S$ values greater than zero are clear indicators of a contaminant at mass 131 ($^{36}SF_5^+$) in the mass spectrum of the sample. As may be seen the value of $\Delta^{36}S$ increases with decreasing sample size. This result is rather disappointing and indicates that the extra stage of clean-up is not totally effective. In order that the contaminant which is present in the system should not render ^{36}S measure-

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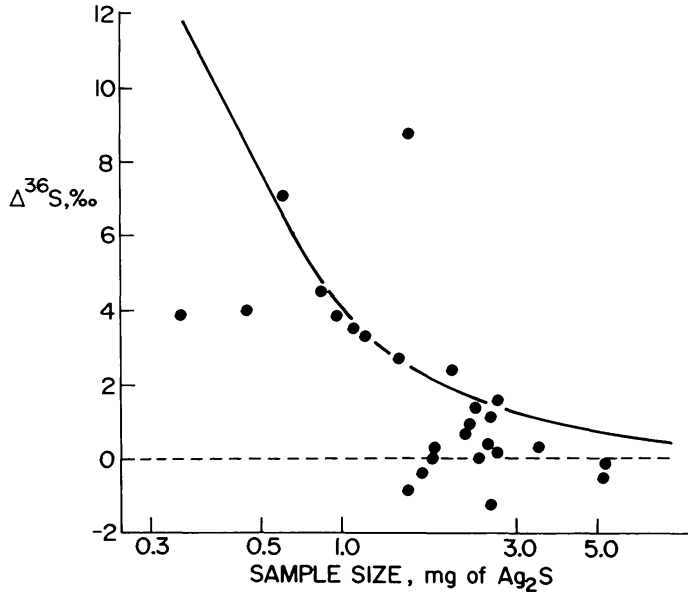*$\Delta^{36}S = \delta^{36}S - 2\delta^{34}S$; $\Delta^{33}S = \delta^{33}S - 0.5\delta^{34}S$

Fig. 1. $\Delta^{36}S$ values as a function of sample size. For these samples no non-linear effects are expected so positive $\Delta^{36}S$ values indicate the presence of a contaminant. The solid line represents a constant level of contamination which contributes a $\Delta^{36}S$ excess of 4‰ for a sample containing 1 mg of silver sulphide.

ments invalid it is necessary to use sample sizes in excess of 2 or 3 mg of silver sulphide.

Fig. 2 shows $\Delta^{33}S$ values as a function of sample size. The solid points are for samples for which no non-linear effects are to be expected while the X represents our previously reported determination of a ^{33}S excess in an Allende sample (Rees and Thode, 1977). This ^{33}S anomaly in Allende was found before the additional gas chromatographic clean-up procedures were introduced so the sample size tests were also performed without this additional clean-up. As may be seen, the
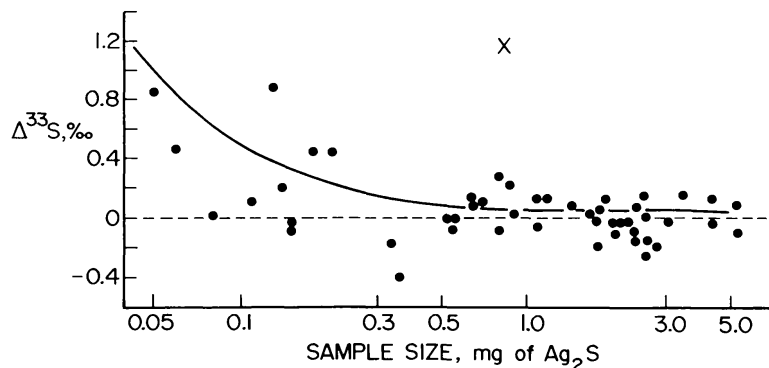
Fig. 2. $\Delta^{33}S$ values as a function of sample size. For the solid points no non-linear effects are expected so positive $\Delta^{33}S$ values indicate the presence of a contaminant. The solid line represents a constant level of contamination which contributes a $\Delta^{33}S$ excess of 0.05‰ for a sample containing 1 mg of silver sulphide. The cross (X) represents our previous determination of a ^{33}S excess in an Allende sample.

value of $\Delta^{33}S$ increases from zero as very small sample sizes are approached, indicating the presence of a contaminant at mass 128 ($^{33}SF_5^+$) in the mass spectrum of the sample. It is apparent, however, that samples must be considerably smaller than the 1 mg of silver sulphide in the anomalous Allende sample before the relative magnitude of the contaminant is such as to spuriously increase the $\Delta^{33}S$ values. These data confirm our confidence that the ^{33}S excess found in Allende is real and not an artifact of our experimental technique.

Lunar samples

Table 1 shows the results of sulphur isotope determinations on grain size separates of the mature soil 15021. For each size fraction for which sufficient material was available, sulphur was extracted in early (sometimes middle) and late fractions by acid hydrolysis.

Our previous examinations of the linearity of mass fractionation in lunar samples were limited to rocks and bulk soils. The present results extend to the fine grained fractions of a mature soil which have been exposed to the processes responsible for heavy isotope enrichment and so also, presumably, to the influx of sulphur associated with micro-meteorite bombardment. In those cases where the sample size available was adequate, as discussed in the previous section, the $\Delta^{33}S$ and $\Delta^{36}S$ values fall close to zero indicating that the linear mass fractionation trend extends to ^{36}S enrichments of up to ~32‰. There is therefore no evidence

Table 1. Sulphur isotope data for acid leaches from grain size fractions of lunar soil 15021.

Fraction	Size Range, μ	Acid Leach	$\delta^{33}S$,‰[1]	$\delta^{34}S$,‰[1]	$\delta^{36}S$,‰[1]	$\Delta^{33}S$,‰[2]	$\Delta^{36}S$,‰[2]	Sample Size, mg Ag$_2$S	$\delta^{34}S$,‰[3] Leach	$\delta^{34}S$,‰[3][4] Fraction
3	200–90	3–1	4.09	7.93	19.2	0.13	3.3	1.2	5.89	7.60
		3–2	5.29	10.64	23.7	−0.03	2.4	2.1	8.59	
4	90–60		4.95	10.12	21.5	−0.11	1.3	2.4	8.07	8.07
5	60–45	5–1	4.68	8.92	22.3	0.22	4.5	0.9	6.88	8.44
		5–2	6.35	12.46	32.0	0.12	7.1	0.7	10.41	
6	45–30	6–1	4.45	8.87	21.5	0.02	3.8	1.0	6.83	9.20
		6–2	5.46	11.06	26.1	−0.07	4.0	0.6	9.01	
		6–3	6.54	12.90	28.5	0.09	2.7	1.5	10.85	
7	30–20		5.65	11.60	23.9	−0.15	0.7	2.2	9.55	9.55
8	20–10	8–1	5.12	10.17	20.3	0.04	0.0	1.8	8.12	11.49
		8–2	6.05	12.07	23.7	0.02	−0.4	1.7	10.02	
		8–3	8.98	18.34	36.9	−0.19	0.2	1.8	15.28	
9	10–5		8.21	16.72	32.2	−0.15	−1.2	2.6	14.66	14.66
10	<5		9.43	19.61	43.1	−0.38	3.9	0.4	17.54	17.54

Footnotes:
(1) Values relative to mass spectrometer reference gas.
(2) $\Delta^{33}S = \delta^{33}S - 0.5\ \delta^{34}S$. $\Delta^{36}S = \delta^{36}S - 2\ \delta^{34}S$.
(3) Relative to Canyon Diablo Troilite.
(4) Calculated using isotopic mass balance.

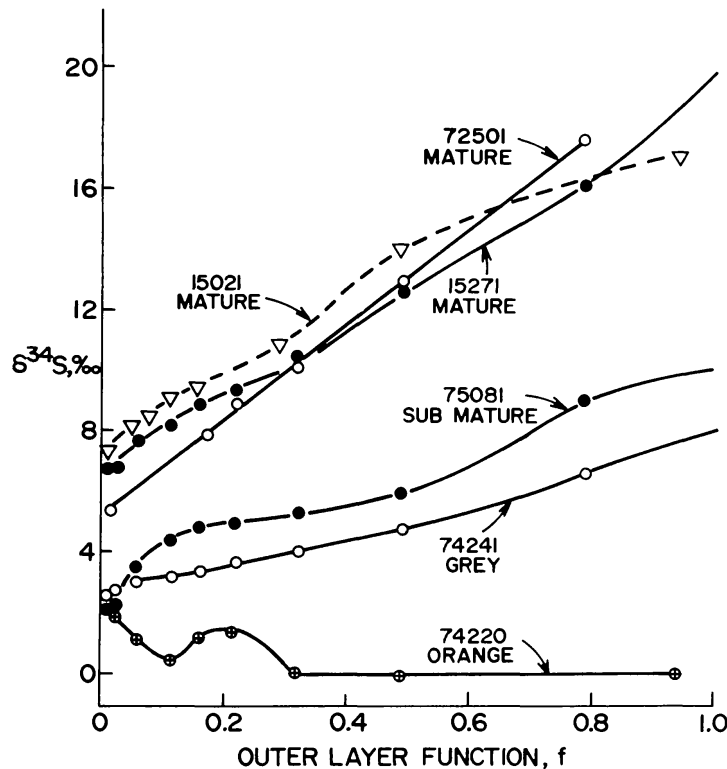**Fig. 3.** $\delta^{34}S$ values versus outer layer function f. The chosen shell thickness of 1.5 μ is that which gives a linear variation in the case of 72501. The new data is for 15021.

of a ^{33}S or a ^{36}S isotope anomaly in the lunar sulphur or in the sulphur associated with micro-meteorite bombardment. In this regard the relatively high sulphur content and high ^{34}S enrichment in the fine grained fractions of this mature soil indicate a considerable turnover of sulphur and the presence of a relatively high proportion of micro-meteorite sulphur (Kerridge *et al.*, 1975a).

Fig. 3 shows the $\delta^{34}S$ values for the individual grain size fractions plotted against the previously defined outer layer function, f (Rees and Thode, 1974). Results previously obtained on other soil samples are also shown. A straight line on this plot can be interpreted as showing the bulk or volume $\delta^{34}S$ value at the f = 0 intercept and the $\delta^{34}S$ value of a thin (but finite) 1.5 μ surface layer at the f = 1 intercept. The three mature soils we have studied show very similar patterns on this plot and lend support to our view that the heavy isotope enrichment of sulphur in lunar soils involves both a surface correlated component and a bulk component.

Allende meteorite

We have attempted, unsuccessfully, to perform a new leaching experiment which would confirm our determination of a ^{33}S excess in a sample of bulk Allende. Table 2 shows the results for the present experiment which was performed on a

Table 2. Sulphur isotope data for acid leach fractions from Allende bulk sample number 8.

Fraction	Acid	Time (hr)	Temp, °C	% Of Total S in Fraction		$\delta^{33}S$,‰[1]	$\delta^{34}S$,‰[1]	$\delta^{36}S$,‰[1]	$\Delta^{33}S$,‰[2]	$\Delta^{36}S$,‰[2]	Sample Size, mg Ag₂S
1	1NHCl	0.50	50	9.5	a)[3]	0.96	2.06	–	–0.07	–	
					b)	1.03	2.01	4.0	0.03	0.0	2.4
2	1NHCl	0.75	50	21.6		1.18	2.21	4.7	0.08	0.3	2.4
3	1NHCl	1.25	65	36.0		1.33	2.39	5.1	0.14	0.3	3.5
4	1NHCl	17.25	45	16.3		1.07	2.14	5.4	0.0	1.1	2.6
5	5NHCl	1.0	100	13.0		1.30	2.45	4.7	0.08	–0.2	5.3
6	5NHCl	1.0	100	3.2	a)	1.71	3.50	–	–0.04	–	5.3
					b)	1.65	3.51	6.4	–0.11	–0.6	
7	5NHCl	24.0	100	0.5	a)	1.69	2.59	–[4]	0.40	–	0.8
					b)	1.67	2.76	–	0.29	–	0.8
					c)	1.50	2.81	–	0.10	–	
					d)	1.63	2.86	–	0.20	–	
					e)	1.88	3.01	–	0.38	–	
					f)	2.03	3.12	–	0.47	–	

Footnotes:
(1) Values relative to mass spectrometer reference gas.
(2) $\Delta^{33}S = \delta^{33}S - 0.5\ \delta^{34}S$. $\Delta^{36}S = \delta^{36}S - 2\ \delta^{34}S$.
(3) 'a', 'b' etc. indicate repeat analyses of SF_6 gas samples.
(4) $\delta^{36}S$ data unreliable; see text.

split of a 5 g ground bulk specimen prepared for our original measurements. As may be seen the $\Delta^{33}S$ and $\Delta^{36}S$ values for the first six fractions are close to zero. The final fraction obtained was very small, ~0.1 mg of silver sulphide, and yielded a high apparent $\Delta^{36}S$ value which was rejected. The $\Delta^{33}S$ value for this sample, which was measured several times, falls in the same range as for the test samples of similar size which were discussed earlier. Thus this fraction showed no evidence of any real ^{33}S excess.

However, it must be pointed out that the present leaching procedure and that which produced a fraction with excess ^{33}S differed in several ways. In the original experiment (Rees and Thode, 1977) the ^{33}S excess was found in the last fraction, comprising ~3.5% of the total sulphur, after raising the hydrochloric acid concentration from 1.5N to 6N and increasing the temperature from 60°C to 100°C. This followed 22.5 h treatment with 1.5N acid at 60°C. In the present experiment the initial leaching was performed with lower acid concentration (1N) and subsequent leaching with strong acid (5N) released a much larger proportion of the total sulphur (fractions 5 + 6 + 7) than was the case in the original experiment. It seems possible that this difference in leaching procedure could lead to a small sulphide component, present in the last sulphur released in the original experiment, to be released in, for example, the 5th fraction of the present experiment, where its ^{33}S excess would be masked by the large proportion of normal sulphur also appearing in this fraction.

It had been our hope that the modified leaching procedure would be more,

rather than less, effective in isolating a fraction containing anomalous sulphur. A further effort will be made to concentrate and identify a possible isotopically anomalous sulphide component or to determine whether anomalous sulphur is heterogeneously distributed in the Allende meteorite.

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