

SULFUR ISOTOPIC ANALYSIS of the ORGUEIL METEORITE; Xia Gao and M. H. Thiemens*, Chemistry Dept., Univ. of California, San Diego, 0317, La Jolla, CA 92093-0317, *and also Institut für Physikalische Chemie der Universität Göttingen.

Among stony meteorites, CI chondrites have relatively high sulfur abundance. Previous studies have shown that many sulfur compounds, with valence states ranging from -2 to +6 exist in Orgueil (1, 2, 3, 4). Measurements of the $^{34}\text{S}/^{32}\text{S}$ ratio of the various forms of S have shown isotopic variation. It is, however, difficult to evaluate the possible causes of the variation with a single ratio measurement. The technique to accurately measure three isotopic ratios of S ($^{33}\text{S}/^{32}\text{S}$, $^{34}\text{S}/^{32}\text{S}$, $^{36}\text{S}/^{32}\text{S}$) has been developed in this laboratory (5). Different sulfur components have been segregated from the Orgueil meteorite to isotopically characterize the different classes of sulfur compounds. Multiple isotopic measurements of different S species have been utilized as it is important that a 4-isotope system, e. g. ^{32}S , ^{33}S , ^{34}S , ^{36}S , be used to identify and distinguish chemical/physical processes from that of nuclear.

The sequential chemical extractions of sulfur from Orgueil are as follows: First, powdered bulk sample is refluxed with CCl_4 for ~24hrs, followed by another 24hrs refluxing in a benzene and methanol (9:1) mixture. The solvents were evaporated to yield elemental S and organic S-containing compounds. The two extracts were subsequently oxidized with concentrated HNO_3 to sulfate and converted to Ag_2S for isotopic analysis (6). The chemical procedure of sulfide decomposition by 6N HCl and conversion of Ag_2S to SF_6 is described in (5). The meteoritic sulfate is obtained by evaporating the solution derived from the acid dissolution step and reducing to Ag_2S , as previously described. The residue of the acid dissolution was reacted with HF-HCl mixture for a few weeks to yield CF residue. This was further separated using CCl_4 ($\rho=1.5$) or CH_3I ($\rho=2.2$) to yield two density fractions. The lighter fraction with $\rho<1.5$ or 2.2 is combustible, indicative of organic matter. Mass spectrometric analysis shows that this compound may be a non-aromatic hydrocarbon, with a possible molecular weight of 279 amu.. It is, therefore, designated as an S containing polymer on the basis of its insolubility in acid and relatively high molecular weight. The polymer was oxidized by fuming HNO_3 and reduced to Ag_2S as described in (6). The S content, expressed as % S° , and isotopic composition of each phase are presented in Table 1. Bulk isotopic compositions were calculated from material balance.

Sulfur in the Orgueil meteorite (CI) exists in various chemical forms. The major S phases are sulfate, organic sulfur-containing compounds and elemental sulfur. S from sulfide and organic sulfur-containing polymer together account for 1 to 4% of total recovered sulfur. Apparently, both the bulk S content and isotopic composition vary in different specimens of the Orgueil meteorite, most likely as a result of variable amounts of elemental sulfur (S°). The S isotopic variation of bulk Orgueil may possibly indicate nebular heterogeneity with Orgueil acquiring S

from different regions and/or times, though there is no unique indice of sources. The isotopic compositions of the organic compounds and polymeric material were likely established during the formation processes, e. g. by Fisher-Tropsch and/or Miller-Urey reactions; however, the observation of isotopic variation of the same phase between the two fragments could also imply that it is derived from different S reservoirs, assuming the formation processes produced the same isotopic fractionation. Given that there is no available data on the sulfur fractionation in FTT or Miller-Urey reactions, the source of the variability is uncertain at present.

The internal isotopic range is 7.1‰ and 6.5‰ in $\delta^{34}\text{S}$ for Orgueil 1 and Orgueil 2 respectively, with sulfate possessing the lightest isotopic composition. This suggests that S in Orgueil has never reached isotopic exchange equilibrium (7). Apparently, Both sulfate and S^0 have been produced by secondary events: the sulfate is likely to be the product of aqueous alteration of pyrrhotite, while the S^0 , which often lines the walls of open cracks is suggestive of generation by metamorphic processes (8) and/or produced during sulfide oxidation processes (9). For the sulfide oxidation process, heavy isotope enrichment in sulfide and light in sulfate is expected, and agrees with our meteoritic measurements.

All the isotopic variations among the different S phases in Orgueil are due to chemical mass fractionation processes. No nuclear isotopic anomalies have been observed.

Sulfur Isotopic Composition of Orgueil (CI) Components (with respect to Canon Diablo Troilite)

Orgueil 1. (P500, Yale)					
chem. Phase	Conc. (%)	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	
Ben.-Meth.	0.37	1.46	2.89	5.5	
CCl ₄	0.04				
Sulfate	2.2	-0.52	-1.06	-2.0	
Sulfide	0.03	3.1	6.05		
CF, $\rho < 1.5$	0.06	1.07	2.10	4.3	
Bulk	2.70	-0.17	-0.36	-0.8	
Orgueil 2. (235, France)					
Ben.-Meth.	0.39	0.82	1.61	3.2	
CCl ₄	2.86	1.98	3.86	7.4	
Sulfate	1.78	-1.36	-2.70	-5.3	
Sulfide	None				
CF, $\rho < 2.2$	0.03				
Bulk	5.03	0.71	1.36	2.6	

Note: Ben.-Meth. represents the mixture of Benzene and Methanol.

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