CHAPTER 4
Lithospheric Sources of Sulphur

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4.1 SULPHUR IN THE COSMOS AND THE CRUST—MANTLE SYSTEM*

All the sulphur contributed to our environment by natural processes and human activity originates from reservoirs in the earth's crust. In many cases, the $\delta^{34}S$ can serve as a 'fingerprint' to identify sources of sulphur and trace its fate in the environment.

On a cosmic scale, sulphur belongs to the 10 most abundant elements. The rank order to atomic abundances in our solar system is: H, He, O, C, N, Ne, Mg, Si, S, Fe, Al, Ca, Ni, Na, Cr, etc. (Goles, 1969). It is widely believed that our planets and the planetary parent body(ies) of meteorites originate from a common reservoir of cosmic matter of homogeneous chemical and isotopic composition. Thus, the study of meteorites provides information about the mean sulphur concentration and $\delta^{34}S$ value of the earth as a whole. Typical S concentrations for iron and stone meteorites lie between 3 and 50 g kg^{-1} (Keil, 1969), and therefore an estimate of 10 g kg^{-1} for the mean sulphur content of the earth seems realistic. The mean $\delta^{34}S$ value seems easier to calculate. Troilite (FeS) of iron meteorites is isotopically uniform and samples from Cañon Diablo and Shikote Alin are used as the 'primary' standard defining the zero point of the $\delta^{34}S$ scale (see Chapter 1). Thus, we can postulate that the earth as a whole has a mean $\delta^{34}S$ value of 0‰.

With the differentiation of the earth into core, mantle, and crust, the bulk of the sulphur accumulated in the inner shells and the upper crust became systematically depleted in this element. This arose because sulphur was predominantly bound as iron sulphide droplets which had a higher density and proved to be immiscible in the silicate melt. A preliminary estimate of the S concentration in this depleted crust can be obtained from analyses of present-day igneous rocks which are also depleted in sulphur. This gives a range from about 300 mg kg^{-1} (mean value for granites) to 800 mg kg^{-1} (mean value for mafic rocks) (see Table 16−B−2a in Nielsen, 1978, and Schneider, 1978).

* H. Nielsen.

Because of the high temperature at which this differentiation took place, isotopic fractionation should have been very small and mantle and lower crust sulphur should have preserved the primaeval $\delta^{34}S$ value of zero. In reality, however, samples of mantle rocks (ultramafic inclusions in kimberlite pipes, materials from Ivrea structures, etc.) are slightly enriched in the heavy isotopes. This is believed to result from crustal contamination. The sulphur also brought up by present-day volcanic emissions is non-juvenile to a large extent. The $\delta^{34}S$ values close to zero have been found in uncontaminated ultramafic rocks from Czechoslovakia and, on average, the $\delta^{34}S$ value for continental basalts is $+1.4‰$ (SCOPE 19, 1983).
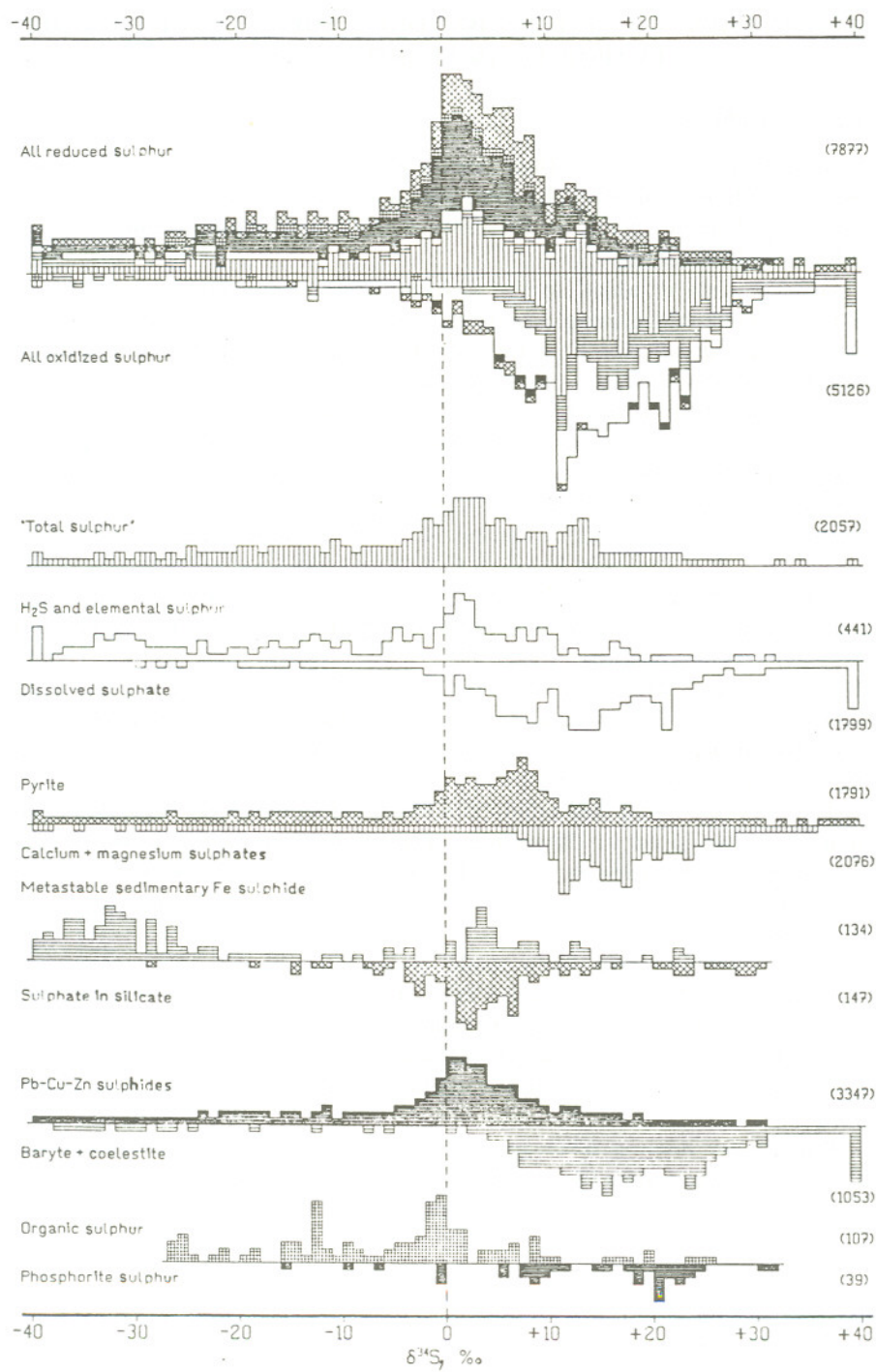
Immediately after the solidification of the primitive crust, volcanic eruptions and fumarolic activity began to convey immense quantities of H_2O, CO_2, S species, and other 'volatiles' to the surface. This in turn led to extensive weathering and inaugurated the 'sedimentary history' of our planet. Under the varying redox and pH conditions of the newly established 'exogeneous cycle', sulphur acquired different valence states, and formed gaseous compounds, sulphates, sulphides, and a manifold of S organic compounds. This led to an extremely inhomogeneous distribution in the sedimentary envelope. The sulphur concentrations vary from a few milligrams per kilogram in freshwater limestones to about 200 g kg^{-1} in anhydrite strata and to even more than 500 g kg^{-1} in local pyrite accumulations. From the isotopic viewpoint, the most exciting facet was the emergence of larger isotope fractionation during dissimilatory bacterial SO_4^{2-} reduction. As the biological sulphur cycle became established, large isotopic variations were promoted in sedimentary rocks.

This large variability renders it extremely difficult to determine the 'true' mean values for S content and $\delta^{34}S$ of crustal sulphur (Figure 4.1). All the hitherto published values are speculative and are a matter of controversial debate. As an example, Holser and Kaplan (1966) estimate the mean S content and $\delta^{34}S$ of the sediments as $+4.9 \pm 1.3$ g kg^{-1} and $+7.1 \pm 4.5‰$, respectively. Another compilation by Ronov, Wedepohl, and others cited in Nielsen (1978) suggests concentrations between 3.6 and 5.6 g kg^{-1} and $\delta^{34}S$ values between -9.0 and $+0.7‰$. The extreme values arise from different estimates of the total mass of evaporite sulphate.

The slightly positive $\delta^{34}S$ values in crustal sulphur are not only predicted by sophisticated budget evaluations (cf. SCOPE 19, 1983) but can easily be deduced by visual inspection of S isotope histograms based on representative and sufficiently numerous samples (Figure 4.1).

Figure 4.1 The $\delta^{34}S$ histograms of samples investigated at the Göttingen Stable Isotope Laboratory during the last two decades. Reduced sulphur species are drawn above and the oxidized species below the baseline. Numbers in brackets are the number of samples used in each histogram. Values lower than $-40‰$ or larger than $+40‰$ are shown at the ends of the scale

All reduced sulphur (7877)

All oxidized sulphur (5126)

'Total sulphur' (2057)

H_2S and elemental sulphur (441)

Dissolved sulphate (1799)

Pyrite (1791)

Calcium + magnesium sulphates (2076)

Metastable sedimentary Fe sulphide (134)

Sulphate in silicate (147)

Pb-Cu-Zn sulphides (3347)

Baryte + coelestite (1053)

Organic sulphur (107)

Phosphorite sulphur (39)

$\delta^{34}S$, ‰

4.2 SULPHUR AND OXYGEN ISOTOPE COMPOSITION OF MARINE EVAPORITE AND BARITE STRATA*

4.2.1 Introduction

Evaporites are relics of former oceans or non-marine water bodies which usually contain abundant anhydrite, gypsum, and a variety of other minerals such as polyhalite, glaserite, kieserite, kainite, langbeinite, leonite, halite, sylvite, and carnallite.

Gypsum dust is added to the environment during mining of evaporite deposits and manufacturing of building products. In addition, acidic pollutants can enhance dissolution of shallow natural evaporites. Sulphur and oxygen isotope data can serve to study these activities.

Evaporite strata tend to form in basins on the border of continents when prevailing conditions favour evaporation. Basins may also form during early stages of rifting where ocean water of a different provenance spills into a sub-sea-level graben (Burke, 1975). Whereas present-day oceanic sulphate has a $\delta^{34}S$ value near +21‰, marine evaporite sulphate varies between +10 and +35‰. It is generally believed that these reflect actual variations in the isotopic composition of SO_4^{2-} in the ancient oceans. Many scientists have studied the $\delta^{34}S$–age curve as constructed from evaporite data (Thode and Monster, 1964; Nielsen, 1965, 1972, 1973; Holser and Kaplan, 1966; Yeremenko and Pankina, 1971; Pilot *et al.*, 1972; Claypool *et al.*, 1980). In such studies, care must be taken to exclude samples influenced by isotopically selective processes such as sulphate reduction and contamination by SO_4^{2-} from continental waters.

The $\delta^{34}S$–age curve throughout the Phanerozoic has been studied so well that it can be used to differentiate gypsum-bearing units for subsurface mapping (van Everdingen *et al.*, 1982). In contrast, the secular isotopic variations are not so well charted in the Precambrian due to the scarcity of evaporite deposits.

Many attempts have been made to understand the mechanisms for changing the $\delta^{34}S$ values of marine SO_4^{2-} (Nielsen, 1965; Holser and Kaplan, 1966; Rees, 1970; Holland, 1973; Schidlowski *et al.*, 1977; Claypool *et al.*, 1980; Hoefs, 1981). Some models include the concept that the sulphur cycle is linked with the oxygen and/or carbon cycles (Schidlowski and Junge, 1981).

With fewer data, a $\delta^{18}O$–age curve has also been constructed for the Phanerozoic evaporites (Solomon *et al.*, 1971; Sakai, 1972; Pilot *et al.*, 1972; Claypool *et al.*, 1980; Viezer *et al.*, 1980).

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* J. Pilot.

4.2.2 Compilation of $\delta^{34}S$ and $\delta^{18}O$ data for marine evaporites

4.2.2.1 *General remarks on the data*

Tables 4.1 and 4.2 summarize marine evaporite $\delta^{34}S$ and $\delta^{18}O$ data from the following references: Nielsen and Ricke, 1964; Thode and Monster, 1965; Holser and Kaplan, 1966; Muller *et al.*, 1966; Rosler *et al.*, 1968; Yeremenko and Pankina, 1971; Perry *et al.*, 1971; Sakai, H., 1972; Pilot *et al.*, 1972; Klaus and Pak, 1974; Pak, 1974; Rambow and Nielsen, 1976, cited in Claypool *et al.*, 1980; Hinze and Nielsen, 1976, cited in Claypool *et al.*, 1980, p. 212; Claypool *et al.*, 1980; Cortecci *et al.*, 1981; Shakur, 1982.

Various criteria must be used to select the $\delta^{34}S$ and $\delta^{18}O$ values that best reflect the isotopic composition of contemporaneous oceanic SO_4^{2-}. Obviously the age and the horizon of the samples must be well documented. Isotope fractionation prior to and during precipitation must also be considered. Samples containing dispersed sulphides were probably influenced by bacterial reduction and the $\delta^{34}S$ value of unreacted SO_4^{2-} may have increased substantially prior to precipitation. Because of this phenomenon, Thode and Monster (1965) preferred to use minimum $\delta^{34}S$ values for a given age. However, there are also processes that deplete SO_4^{2-} in ^{34}S. Precipitated $CaSO_4$ is 1.65 ± 0.12 and $3.6 \pm 0.9‰$ enriched in ^{34}S and ^{18}O, respectively, compared to SO_4^{2-} (Thode and Monster, 1965; Lloyd, 1967; Holser *et al.*, 1979). In addition, secondary sulphate may form by oxidation of ^{34}S-depleted sulphides. Further, continental weathering and deep crustal sources may contribute. Hence, many authors prefer to use the mean value of a data set. The suitability of the selection criteria is confirmed if the $\delta^{34}S$ data from different basins and/or different regions of the same age (comparable stratigraphic horizons) coincide.

Table 4.1 presents data from samples for which horizons are well known. In most cases, the horizons have the authors' designation and not the international nomenclature. The time scale of Odin and Kennedy (1982) is used.

The $\delta^{18}O$ data are normalized to seawater SO_4^{2-} taken as $+8.6‰$, in accordance with Claypool *et al.* (1980). It is noted that many authors prefer a value closer to $+9.5‰$. For Table 4.2, the data measured at UCLA are corrected by $+0.5‰$, those from Cortecci *et al.* (1981) and Shakur (1982) by $-0.9‰$ and from Pilot *et al.* (1972) and Pilot and Harzer (1969) by $-0.5‰$.

Data are arbitrarily classified by region: North America, Middle America, Asia, Europe, Australia, and Africa. Samples from South America were only available from northern parts and are included in Middle America.

Table 4.1 A $\delta^{34}S$ data summary for marine evaporites: (number), minimum average, maximum

	North America	Middle America	Europe	Africa	Asia	Australia	Arctic	Total
Tertiary								
Pliocene	(1) 20.5			(2), 17.4 17.9, 18.3				(3), 17.4 18.8, 20.5
Miocene			(9), 20.9 21.8, 23.9					(9), 20.9 21.8, 23.9
Oligocene		(2), 17.1 21.3, 25.5						(2), 17.1 21.3, 25.5
Eocene	(21), 18.4 20.6, 24.3	(8), 10.9 16.9, 19.9		(1) 17.8				(30), 10.9 19.5, 24.3
Palaeocene	(10), 19.0 19.7, 20.3		(2), 19.0 19.3, 19.6		(2), 19.5 19.9, 20.4			(14), 19.0 19.7, 20.4
Total	(32), 18.4 20.3, 24.3	(10), 10.9 17.8, 25.5	(11), 19.0 21.3, 23.9	(3), 17.4 17.9, 18.3	(2), 19.5 19.9, 20.4			(58), 10.9 19.9, 25.5

Cretaceous

	Col 1	Col 2	Col 3	Total
Senonian			(1) 22.7	(1) 22.7
Turonian			(2), 16.8 17.7, 18.5	(2), 16.8 17.7, 18.5
Cenomonian				
Albian	(20), 12.8 14.7, 18.1		(7), 13.9 15.1, 18.6	(27), 12.8 14.8, 18.6
Aptian		(17), 13.4 16.0, 21.8		(17), 13.4 16.0, 21.8
Neocomian	(4), 15.8 16.1, 16.5			(4), 15.8 16.1, 16.5
Total	(24), 12.8 14.9, 18.1	(17), 13.4 16.0, 21.8	(10), 13.9 16.4, 18.6	(51), 12.8 15.6, 21.8

Table 4.1 *Continued*

	North America	Middle America	Europe	Africa	Asia	Australia	Arctic	Total
Jurassic								
Kimmeridgian				(1) 16.7				(1) 16.7
Oxfordian	(7), 15.4 16.6, 17.5							(7), 15.4 16.6, 17.5
Upper Jurassic	(1), 16.0		(34), 15.4 17.1, 21.0					(35), 15.4 17.1, 21.0
Undefined Jurassic	(11), 15.1 16.0, 17.0	(1) 15.6	(18), 12.9 15.1, 17.1	(1) 18.6	(5), 13.6 15.1, 16.7			(36), 12.9 15.5, 17.1
Lower Jurassic			(1) 8.1					(1) 8.1
Total	(19), 15.1 16.2, 17.5	(1) 15.6	(53), 8.1 16.3, 21.0	(2), 16.7 17.7, 18.6	(5), 13.6 15.1, 16.7			(80), 8.1 16.1, 21.0

Triassic

Upper (Keuper)	(9), 13.4 14.2, 15.7	(55), 10.9 15.3, 18.3	(9), 15.7 16.7, 17.8	(73), 13.4 15.3, 17.8
Middle (Muschelkalk)		(23), 17.6 19.6, 21.8		(23), 17.6 19.6, 21.8
Lower (Buntsandstein)				
Upper Buntsandstein (Rot)	(2), 28.2 28.3, 28.3	(17), 25.1 26.3, 28.7		(19), 25.1 26.5, 28.7
Upper Buntsandstein II		(15), 18.6 20.6, 23.4		(15), 18.6 20.6, 23.4
Middle Buntsandstein		(7), 10.7 12.8, 14.8		(7), 10.7 12.8, 14.8
Lower Buntsandstein		(4), 9.5 10.2, 11.7		(4), 9.5 10.2, 11.7
Total	(11), 13.4 16.8, 28.3	(121), 9.5 18.0, 28.7	(9), 15.7 16.7, 17.8	(141), 9.5 17.8, 28.7

Table 4.1 *Continued*

	North America	Middle America	Europe	Africa	Asia	Australia	Arctic	Total
Permian								
Upper Permian (Zechstein, Ochoan)	(18), 9.0 11.0, 13.8		(195), 7.9 10.7, 14.1					(213), 7.9 10.7, 14.1
Middle Permian (Guadalupian)	(27), 10.5 11.9, 13.4							(27), 10.5 11.9, 13.4
Lower Permian	(26), 12.2 13.7, 16.0		(45), 9.8 12.8, 16.2				(4), 12.9 13.3, 13.9	(75), 9.8 12.8, 16.2
Total	(71), 9.0 11.6, 13.8		(240), 7.9 11.1, 16.2				(4), 12.9 13.3, 13.9	(315), 7.9 11.2, 16.2
Carboniferous								
Pennsylvanian	(5), 13.3 16.3, 18.6						(16), 13.4 15.2, 20.8	(21), 13.3 15.5, 20.8
Mississippian	(188), 13.7 17.3, 20.6							(188), 13.7 17.3, 20.6
Total	(193), 13.3 17.3, 20.6						(16), 13.4 15.2, 20.8	(209), 13.3 17.1, 20.8

Devonian					
Upper Devonian	(79), 22.3 27.1, 34.0	(26), 19.7 24.0, 28.3	(1) 19.1	(2), 21.8 22.3, 22.7		(108), 19.1 26.2, 34.0
Souris River alone	(29), 24.0 28.4, 31.6					(29), 24.0 28.4, 31.6
Middle Devonian	(9), 18.5 19.4, 21.8			(12), 15.7 17.6, 19.3		(21), 15.7 18.4, 21.8
Lower Devonian	(23), 15.6 17.0, 17.9			(6), 18.6 20.3, 24.6		(29), 15.6 18.4, 24.6
Total	(111), 15.6 24.6, 34.6	(26), 19.7 24, 28.3	(1) 19.1	(20), 15.7 18.9, 24.6		(158), 15.6 23.7, 34.0
Silurian	(34), 23.5 26.5, 28.8					(34), 23.5 26.5, 28.8
Ordovician	(17), 15.1 27.6, 35.8	(2), 25.5 25.9, 26.3				(19), 15.1 27.4, 35.8
Cambrian						
Middle Cambrian	(3), 27.6 29.3, 31.1		(37), 25.2 28.8, 33.3	(4), 26.8 29.5, 32.0	(2), 22.0 29.5, 30.0	(46), 25.2 28.9, 33.3
Lower Cambrian			(25), 29.0 31.8, 35.5			(25), 29.0 31.8, 35.5
Total	(3), 27.6 29.3, 31.1		(62), 25.2 30.0, 35.5	(4), 26.8 29.5, 32.0	(2), 29.0 29.5, 30.0	(71), 25.2 29.9, 35.5

Table 4.1 *Continued*

	North America	Middle America	Europe	Africa	Asia	Australia	Arctic	Total
Proterozoic								
Lower Proterozoic	(3), 14.6 15.1, 15.9			(8), 15.8 18.6, 21.0	(4), 33.0 33.7, 35.0	(13), 14.6 18.0, 24.3		(28), 14.6 10.1, 35.7
Without Asian								(24), 14.6 17.8, 24.3

Table 4.2 $\delta^{18}O$ data summary for marine evaporites: $\dfrac{\text{(number), minimum}}{\text{average, maximum}}$

	North America	Middle America	Europe	Africa	Asia	Australia	Arctic	Total
Tertiary								
Pliocene				(2), 12.1 13.1, 14.1				(2), 12.1 13.1, 14.1
Miocene			(5), 10.8 12.4, 12.9					(5), 10.8 12.4, 12.9
Oligocene	11.9, 11.65 (2), 12.17							(2), 12.17 11.9, 11.65
Total	11.9, 11.7 (2), 12.2		(5), 10.8 12.4, 12.9	(2), 12.1 13.1, 14.1				(9), 10.8 12.4, 14.1
Cretaceous								
Turonian				(2), 15.4 15.4, 15.4				(2), 15.4 15.4, 15.4

Table 4.2 *Continued*

	North America	Middle America	Europe	Africa	Asia	Australia	Arctic	Total
Jurassic								
Oxfordian	(2), 12.8 13.5, 14.3							(2), 12.8 13.5, 14.3
Upper Jurassic			(12), 11.9 14.1, 16.6					(12), 11.9 14.1, 16.6
Undefined Jurassic	(1) 10.0							(1) 10.0
Lower Jurassic			(1) 15.9					(1) 15.9
Total	(3), 10.0 12.3, 14.3		(13), 11.9 14.2, 16.6					(16), 10.0 13.8, 16.6

Triassic

Upper Triassic (Keuper)	(2), 11.9 12.2, 12.5	(27), 10.6 14.6, 18.4	(5), 9.6 12.7, 13.8	(34), 9.6 14.2, 14.6
Middle Triassic (Muschelkalk)		(4), 14.4 14.8, 15.8		(4), 14.4 14.8, 15.8
Upper Buntsandstein (Rot)		(8), 12.9 15.3, 16.0		(8), 13.9 15.3, 16.0
Upper Buntsandstein II		(11), 13.1 15.2, 16.3		(11), 13.1 15.2, 16.3
Middle Buntsandstein		(8), 10.3 12.9, 16.0		(8), 10.3 12.9, 16.0
Lower Buntsandstein		(5), 10.8 13.7, 15.3		(5), 10.8 13.7, 15.3
Total	(2), 11.9 12.2, 12.5	(63), 10.3 14.5, 18.4	(5), 9.6 12.7, 13.7	(70), 9.6 14.4, 18.4

Permian

Upper Permian (Zechstein, Ochoan)		(32), 8.1 11.8, 15.2		(32), 8.1 11.8, 15.2
Middle Permian (Guadalupian)	(2), 9.3 9.6, 9.9			(2), 9.3 9.6, 9.9
Lower Permian	(24), 11.5 13.2, 14.7	(12), 10.6 12.6, 14.5		(36), 10.6 13.0, 14.7
Total	(26), 9.3 12.9, 14.7	(44), 8.1 12.0, 15.2		(70), 8.1 12.4, 15.2

Table 4.2 *Continued*

	North America	Middle America	Europe	Africa	Asia	Australia	Arctic	Total
Carboniferous								
Pennsylvanian	(37), 12.3 13.3, 15.4							(37), 12.3 13.3, 15.4
Mississippian								
Devonian								
Upper Devonian	(9), 12.9 15.1, 17.3		(4), 15.1 15.8, 16.3		(1) 13.7	(2), 17.1 17.5, 17.8		(16), 12.9 15.5, 17.8
Souris River alone	(6), 14.0 15.7, 17.3							(6), 14.0 15.7, 17.3
Middle Devonian	(4), 14.3 14.8, 15.5					(3), 12.5 13.4, 14.6		(7), 12.5 14.2, 15.5
Lower Devonian	(1) 15.0							(1) 15.0
Total	(20), 12.9 15.2, 17.3		(4), 15.1 15.8, 16.3		(1) 13.7	(5), 12.5 15.0, 17.8		(30), 12.5 15.2, 17.8

Silurian	(1) 10.6			(1) 10.6
Ordovician	(1) 15.9			(1) 15.9
Cambrian				
Middle Cambrian			(1) 13.1	(1) 13.1
Lower Cambrian		(10), 10.7 14.5, 17.1		(10), 10.7 14.5, 17.1
Total		(10), 10.7 14.5, 17.1	(1) 13.1	(11), 10.7 14.3, 17.1
Proterozoic				
Lower Proterozoic		(6), 14.2 16.7, 18.9	(1) 15.9	(7), 14.2 16.6, 18.9

4.2.2.2 *Description of the* $\delta^{34}S$– *and* $\delta^{18}O$–*age curves*

From the $\delta^{34}S$ data, it is possible to construct an age curve for the Phanerozoic and part of the Precambrian (Figure 4.2). Yeremenko and Pankina (1971) stated that the curve for samples of the Soviet Union coincide with the curve for other parts of the world. Claypool *et al.* (1980) stressed the reality of a universal age curve.

In the Precambrian, $\delta^{34}S$ values were +18‰ (the number of data is small and the age is not so precise as in the Younger Phanerozoic). There is an increase to more than +30‰ in the Cambrian. Through the Ordovician and Silurian ages, there is a small decrease to +26.5‰. In the Upper Silurian, the $\delta^{34}S$ values decrease sharply and reach a minimum at 18.4‰ in the Lower and Middle Devonian. This minimum is accentuated in the Lower Devonian in North America and the Middle Devonian in Australia.

In the Upper Devonian, there is a sharp rise to a mean value of +26.2‰ in North America and +27.1‰ in Europe. The mean $\delta^{34}S$ value for the Souris River formation, Canada, was found to be +28.4‰ and the highest value, +34‰. The few recorded values from Australia and Asia are lower.

Throughout the Carboniferous and Permian, there is a continuous decrease in $\delta^{34}S$. The minimum of all marine evaporites near +10.7‰ is found in the Upper Permian (Zechstein, Ochoan, Tatarian).

In the Lower and Middle Lower Triassic, there is a sharp increase in the mean $\delta^{34}S$ value in the Upper Lower Triassic (Rot) to +26.3‰ in Europe and +28.3‰ in North America (Monkeoppi formation). The highest reported value is +28.7‰. Then, $\delta^{34}S$ values decreased to +19.6‰ in European Middle Triassic and to +16‰ in Upper Triassic (North America, Europe), thereafter remaining relatively constant with a small increase in the Upper Jurassic. It is noted that the Rot data significantly affect the calculations for the Triassic in Table 4.1. Their omission decreased the average $\delta^{34}S$ by 2‰.

In the Cretaceous, there is a minimum in the Apt/Albian and thereafter a continual increase to +21.8‰ in the Miocene. Samples of European Oligocene from the Rhine Valley were not included in the data summary because of possible admixture of Upper Permian salt.

The $\delta^{18}O$ data are plotted in Figure 4.3, and are compared with the $\delta^{18}O$–age curve of Claypool *et al.* (1980).

The $\delta^{18}O$–age curve starts in the late Precambrian at +16.5‰, decreases in the Cambrian to +13.5‰, and remains there through the Ordovician and Silurian to Middle Devonian. There is a small increase in the Upper Devonian to +15.5‰, after which there is a steady decrease to a minimum in the Middle Permian. There is a sharp increase in the Upper Permian and Lower Triassic to +14.4‰. Thereafter, there appears to be a slow decrease through the Jurassic and Cretaceous with perhaps an increase through the Miocene to Pleistocene. However, data from Tertiary samples are sparse.

In summary, the variation in $\delta^{18}O$, ± 3.5‰, is much smaller than that found for $\delta^{34}S$ (more than ± 10‰). One contributing factor is the smaller
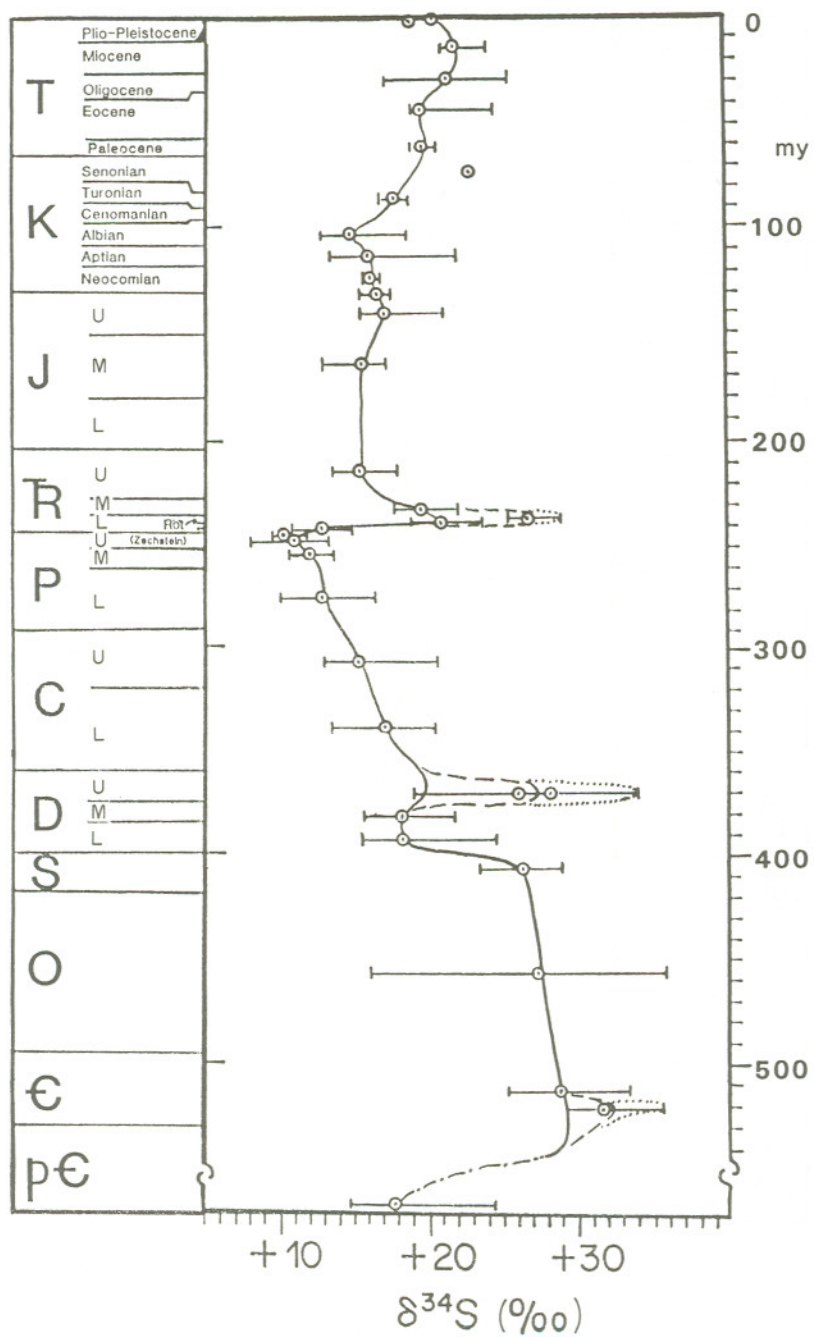
Figure 4.2 The $\delta^{34}S$–age curve for marine evaporites (data from Table 4.1; curve from Claypool *et al.*, 1980)
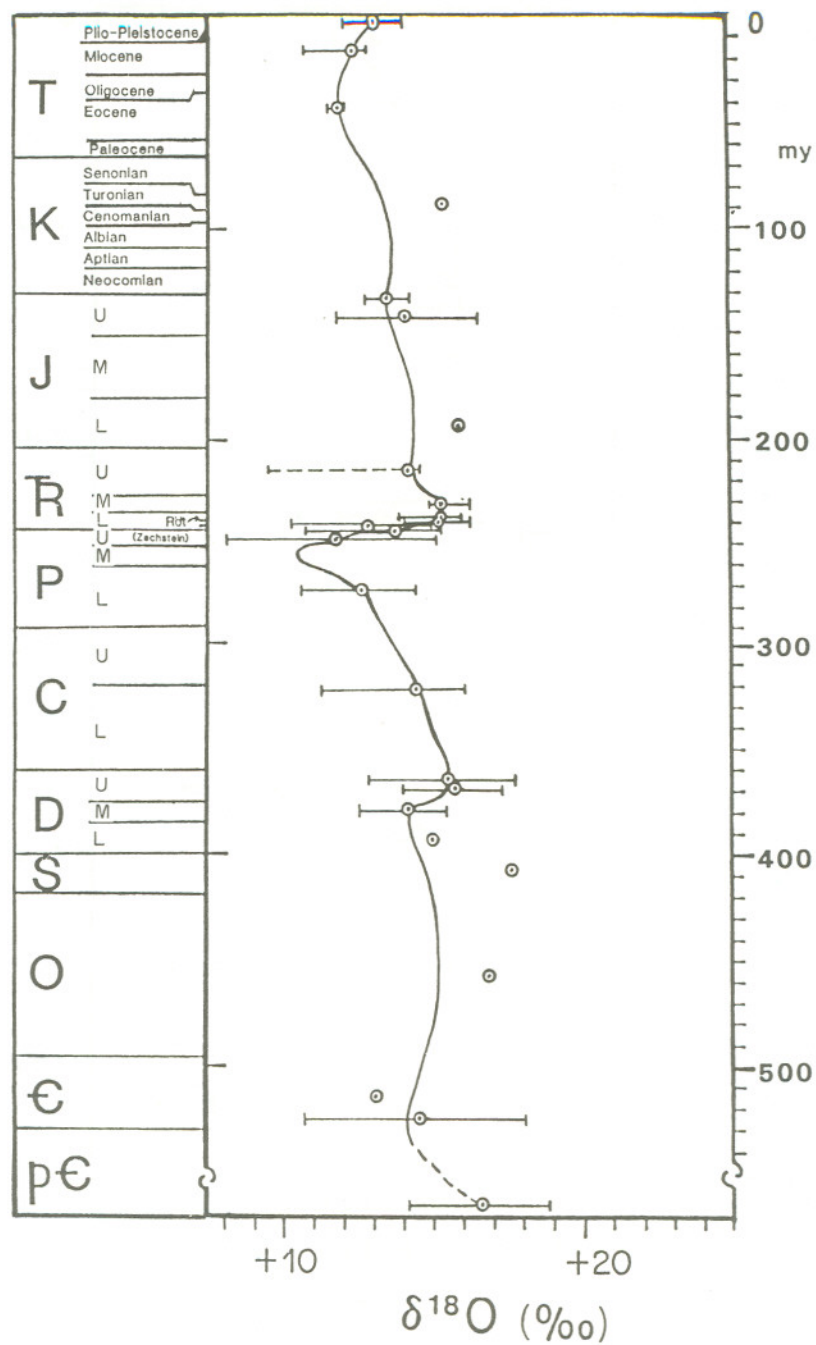
Figure 4.3 The $\delta^{18}O$–age curve for marine evaporites (data from Table 4.2; curve from Claypool *et al.*, 1980)

oxygen isotope fractionation during bacterial SO_4^{2-} reduction. More data are required for parts of the curves and $\delta^{18}O$ data are particularly lacking for deposits before the Devonian and after the Triassic.

4.2.2.3 *Minima and abrupt rises in the $\delta^{34}S$–age curve*

Considerable discussion has taken place in the literature on the rate of change of $\delta^{34}S$ in oceanic SO_4^{2-} with time (Nielsen, 1965; Holser and Kaplan, 1966; Holser, 1977). Rates lower than 0.3‰ per Ma have been proposed (Nielsen, 1974) and disputed (Holser, 1977). Differences among continents may be due to local events. However, Holser (1977) described five common features about the $\delta^{34}S$ variations among continents which may be summarized as follows:

(a) The mean $\delta^{34}S$–age curve established by worldwide sampling rises sharply at certain times (Figure 4.4).
(b) After a rise, the $\delta^{34}S$ value falls almost as rapidly so the event appears as a peak on the age curve.
(c) Each event seems to have taken place within one stratigraphic unit, sometimes in much less than 5 Ma.
(d) Each event is followed by a period when the mean oceanic $\delta^{34}S$ value is higher than the preevent level.
(e) The mean curve for $\delta^{18}O$ in marine sulfates at equivalent times appears either to display no discernible rise (Yudomski and Souris event) or a relatively small one (Rot event).
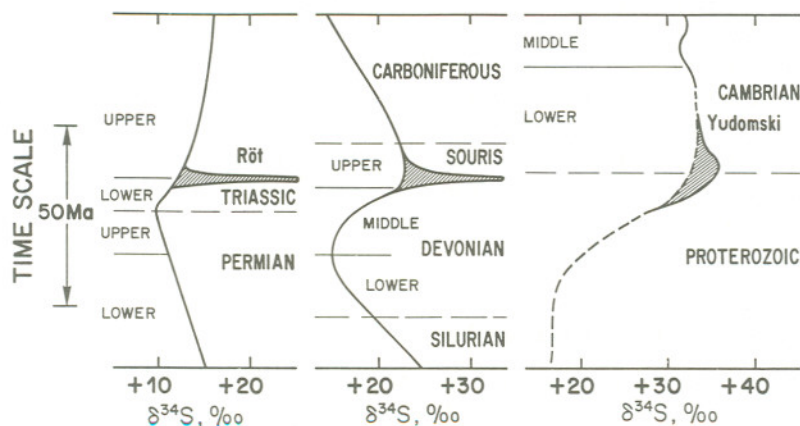
Figure 4.4 The $\delta^{34}S$ variations in marine sulphate during the Rot, Souris, and Yudomski

The concordance of these $\delta^{34}S$ peaks in different basins and continents reaffirms that most evaporite data are representative of oceanic SO_4^{2-} over time. Discordant $\delta^{34}S$ values from different basins and continents probably indicate mixing with continental waters and/or postdepositional alteration.

4.2.2.4 *Non-marine evaporites*

Non-marine evaporites are usually not older than Tertiary. An exception is the Lower Permian Rotleigend salt deposits where the $\delta^{34}S$ value is from +5 to +9‰ (Pilot *et al.*, 1972; Holser, 1979). The $\delta^{34}S$ values were found to range from +10 to +20‰ for Oligocene evaporites in the Rhine Valley. Lower values, e.g. +11‰ for the Buggingen deposits, are strong evidence for a contribution from leaching of Permian Zechstein evaporates by deep-seated circulating brines (Nielsen, 1967). Birnbaum and Coleman (1979) traced the source of sulphur for a non-marine evaporite in the Tertiary Ebro basin.

4.2.3 Data from marine barites

There are other natural sulphate minerals that might provide data from the oceanic isotope time curve but it is necessary to establish sample selection criteria. In particular, barite is interesting because it can precipitate under non-evaporitic conditions.

Cecile *et al.* (1983) studied the isotope composition of sulphur and oxygen in samples of various barite occurrences (nodules, thin strata, thick beds, massive, etc.) in sediments from the Middle Devonian to Middle Mississippian age. This investigation and earlier data (Sakai, 1971; Rye *et al.*, 1978; Morrow *et al.*, 1978; Schroll and Pak, 1980) show that $\delta^{34}S$ and $\delta^{18}O$ values for barites are either higher than, or correspond to, those of evaporites of the same age. Therefore, the lowest $\delta^{34}S$ and $\delta^{18}O$ values must correspond to unaltered SO_4^{2-} in basins where they were generated.

The best coincidence of isotopic data for barites and evaporites was observed for barites sampled from massive sediments as well as thin strata occurring in sediments with low carbon content. Barite concretions and thin strata occurring in organic-rich rocks are characterized by $\delta^{34}S$ and $\delta^{18}O$ values as high as +90 and +32‰ respectively, and must reflect sulphate reduction prior to sedimentation.

4.2.4 Reservoir of evaporite sulphur

Based on estimates of evaporite volumes of different ages, Migdisov *et al.* (1983) calculated the mass of sulphur they contain. Using the masses and average $\delta^{34}S$ values of different age evaporites, they determined an overall

average $\delta^{34}S$. The results are summarized in Table 4.3. The global mass of sulphate sulphur in evaporites is computed to be 10^8Tg S with a mean $\delta^{34}S$ of $+19.5‰$.

4.3   ISOTOPIC COMPOSITION OF SULPHUR IN SULPHIDE ORES*

Sulphide ores are a major source of anthropogenic sulphur. About one-third of the world's manufactured sulphuric acid is produced from sulphide ores. In 1980, this corresponded to about 16–18 million tonnes of sulphur based on the estimated total sulphur production of 50–55 million tonnes (Nriagu, 1978). Moreover, a substantial amount of sulphur is released to the atmosphere during smelting of sulphide ores. According to Ryaboshapko (1983), this process contributes 20–25% of the global emissions of sulphur oxides which reached 98 Tg S y^{-1} in the late 1980s. Therefore, the total production of sulphur from sulphide ores by that time was 20–25 Tg S,

Table 4.3 Volume, mass, and isotopic composition of sulphate sulphur in continental sediments (SCOPE 19, 1983)

Stratigraphic interval	Volume (10^6 km^3)		Mass of sulphate rock (10^8 Tg)	$\delta^{34}S$ of sulphate (‰)
	Gypsum and anhydrite	Total evaporite		
Neogene	0.129	0.410	2.97	+22.4
Paleogene	0.064	0.250	1.47	+18.1
Cretaceous	0.129	0.570	2.97	+16.6
Jurassic	0.168	0.750	3.86	+16.6
Triassic	0.142	0.550	3.27	+18.8
Permian	0.149	1.430	3.43	+10.8
Carboniferous	0.068	0.240	1.56	+16.7
Devonian	0.151	0.311	3.47	+20.1
Silurian	0.006	0.032	0.01	+26.2
Ordovician	0.020	0.045	0.46	+28.5
Cambrian	0.239	1.525	5.50	+29.3
Upper Proterozoic	0.060	0.360	1.38	+16.3
	1.325	6.473	30.35	+19.5
		Totals		Average

* L.N. Grinenko and V.A Grinenko.

which constituted an appreciable part of the total sulphur (169 Tg S y^{-1}) extracted from the lithosphere (Ivanov, 1983).

In order to use isotopic analyses of sulphur for monitoring anthropogenic sulphur fluxes to the atmosphere and hydrosphere, it is necessary to consider $\delta^{34}S$ variations in different sulphide ores. The main sulphide ores are pyrite, chalcopyrite, polymetallic (dominantly Pb–Zn), and copper–nickel deposits. The use of sulphur isotope data to establish the systematics of sulphide ore formation (sulphur source, temperature, and physicochemical parameters) has been reported in several hundred publications (cf. Barnes, 1979). These data were used to construct histograms of the distribution of sulphur isotopes in various deposits in order to find their average $\delta^{34}S$ (Grinenko and Grinenko, 1974).

There are sulphur isotope data for more than 70 pyrite–chalcopyrite deposits in various regions of the Soviet Union, Japan, Canada, Australia, Africa, and Central Europe. These are summarized in Figure 4.5 along with data from pyrite–polymetallic deposits. Many deposits have $\delta^{34}S$ values ranging from −2 to +5‰. Exceptions are highly metamorphic Precambrian deposits in Finland, Sweden, Karelia, the United States, Canada, and India where the ^{34}S depletion is greater. In deposits of the Urals, Altai, Caucasus, and Japan, the average $\delta^{34}S$ values range from +0.5 to +4‰. The average $\delta^{34}S$ value for sulphides of such deposits is +3.5‰, quite close to the meteorite value.

Several pyrite–polymetallic deposits such as Meggen, Rammelsberg (Central Europe), Shimokava (Japan), Casteliano, and Santa Lucia (Cuba) exhibit wide variations of $\delta^{34}S$ values within individual ore bodies and average values far removed from the meteorite composition. Deposits such as Meggen, Rammelsberg, and Shimokova have $\delta^{34}S$ values up to +18‰ whereas deposits in Cuba are depleted in ^{34}S (down to −23‰). High depletions in ^{34}S (average, −18‰) are observed also in stratiform deposits of Nairne, Australia.
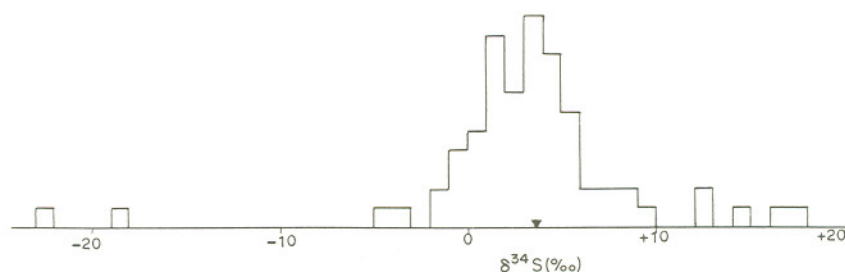
Figure 4.5 Distribution of $\delta^{34}S$ values in pyrite–chalcopyrite and pyrite–polymetallic deposits. One average value is entered for each deposit

Ores of almost 50 copper–molybdenum deposits of the United States, Peru, Mongolia, Kazakhstan, East Transbaikal, and Canada (Figure 4.6) are characterized by a relatively small range (5‰) in sulphur isotopic variation within an individual deposit. The average $\delta^{34}S$ values in ores of some deposits are close to that of meteorite sulphur, whereas for all deposits, the mean value ranges from −5 to +3‰ (average +0.3‰).

Of the world's significant copper–nickel ore deposits, many in the Soviet Union have been extensively studied with sulphur isotopes. The $\delta^{34}S$ values of most of these deposits are close to zero (Figure 4.7). Deposits in the north-west part of the Siberian platform are an exception with $\delta^{34}S$ values for sulphides in the range from +8 to +10‰. Within an individual deposit, the isotopic composition of sulphides varies by less than 10‰. The average $\delta^{34}S$ values for many deposits, regardless of continent, age, morphology, structure, ore content, etc., fall between 0 and +3‰. The mean $\delta^{34}S$ value of sulphide sulphur in copper–nickel deposits is +3.5‰ (Figure 4.7).

Of particular interest are stratal–copper deposits in sandstone found in the United States and the Soviet Union. As seen in Figure 4.8, the isotopic composition of sulphur in such deposits varies over a wide range, from −18 to +18‰. An individual deposit is also characterized by a large variation of $\delta^{34}S$ values in sulphides. The average $\delta^{34}S$ value is +1.5‰ for this type (Figure 4.8).

The literature contains about 90 publications on the isotopic composition of sulphur in lead–zinc deposits, most of which belong to the stratiform type
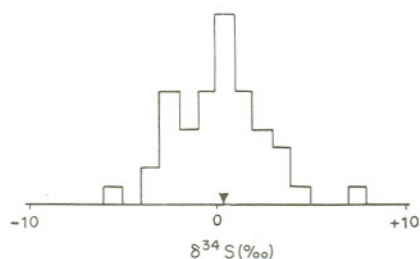
Figure 4.6 Distribution of $\delta^{34}S$ values in copper–molybdenum deposits
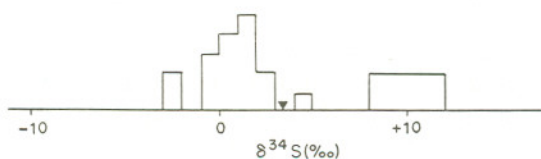
Figure 4.7 Distribution of $\delta^{34}S$ values in copper–nickel deposits
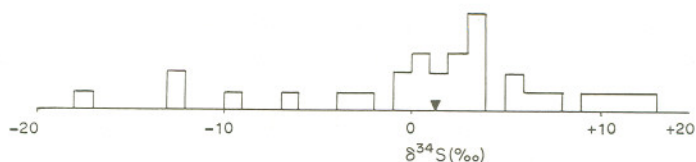
Figure 4.8 Distribution of δ³⁴S values in stratal–copper sandstones
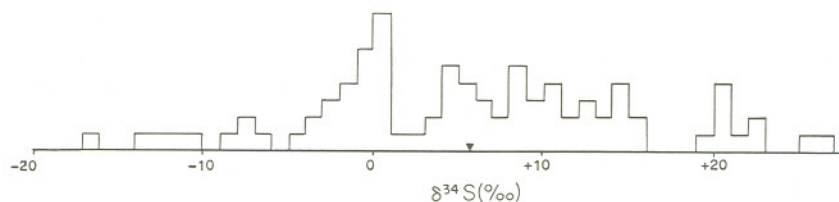
Figure 4.9 Distribution of δ³⁴S values in lead–zinc deposits

(Figure 4.9). Some large deposits such as Broken Hill (Australia), Cartagena (Spain), Greenhow and Skyreholme (England) are isotopically uniform with mean $\delta^{34}S$ values close to the meteorite value. However, most lead–zinc deposits are characterized by large sulphur isotope variations with $\delta^{34}S$ values varying from -14 to $+22‰$, the average being $+5.6‰$ (Figure 4.9).

In summary, the mean $\delta^{34}S$ value of sulphur emissions produced by processing copper–molybdenum ores should be close to the meteorite value. The same is true for most pyrite and copper–nickel sulphide ores, although some exceptions are enriched in ^{34}S or more rarely ^{32}S. Sulphur from many copper and lead–zinc ores differs greatly in isotopic composition from that of meteorites.

The isotopic signatures of different ores can be applied to regional monitoring of industrial sulphur acquisition by the environment during ore processing. The largest 'isotopic leverage' (difference between natural background $\delta^{34}S$ values and those of anthropogenic sulphur) is observed during processing of lead–zinc and copper ores from stratiform deposits. In many mixed-type deposits, i.e. pyrite–polymetallic, the isotopic leverage can also be large.

Data for all types of deposits summarized in Figure 4.10 provide an estimate of the average isotope composition of sulphur compounds released during sulphide ore processing. Most of the deposits are slightly enriched in ^{34}S, and the average $\delta^{34}S$ value may be taken as $+3.4‰$.
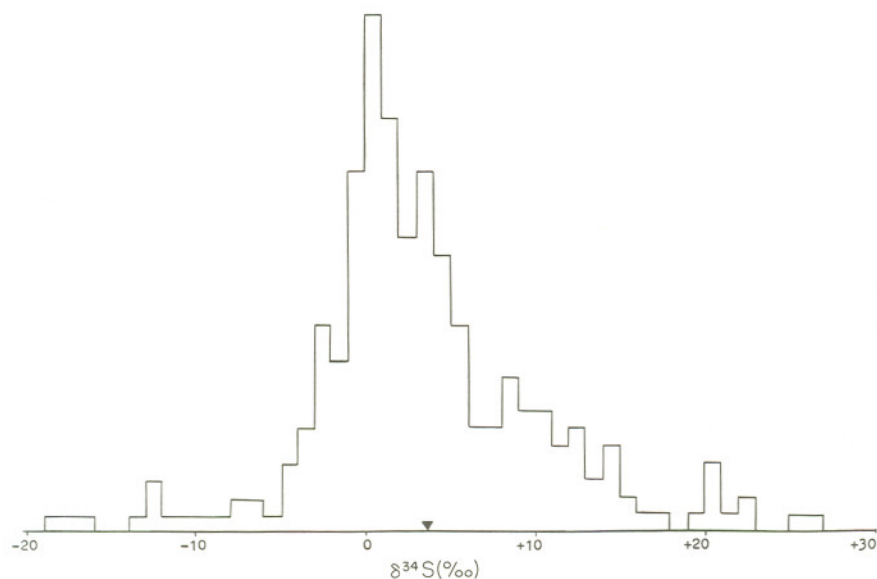
Figure 4.10 Distribution of $\delta^{34}S$ values in main types of sulphide deposits

4.4   NATIVE ELEMENTAL SULPHUR DEPOSITS*

The world annual production of native sulphur is about 17 million tonnes or nearly one-third of the total sulphur consumed by the chemical industry (Nriagu, 1978) and 10% of the sulphur produced annually from the lithosphere in the late 1970s (Ivanov, 1983).

The main uses of native sulphur are for sulphuric acid production, chemical manufacture, and fertilizers. Therefore the bulk of produced native sulphur enters the soil as SO_4^{2-} and is transported into continental basins.

Major production of native sulphur occurs in the United States, Poland, the Soviet Union, Mexico, Iraq, China, Italy, and South America (Table 4.4). Most industrial sulphur deposits occur in sedimentary rocks. These so-called exogenic deposits constitute 90% of the world reservoir of native sulphur. Endogenous or volcanic sulphur makes up the remaining 10% (Vlasov, 1971).

Sulphur isotope data for major and some minor elemental sulphur deposits are summarized in Table 4.5. Negative $\delta^{34}S$ values are found in small native sulphur deposits such as Novodimitrovskaya, USSR, Boraitotto, Italy, and Moss Bluff, USA. In some industrial sulphur deposits, the native sulphur

* A. Yu. Lien.

Table 4.4 Annual world production of native sulphur and its isotope composition (data from Ruckmick *et al.*, 1979)

| | Sedimentary | | | | | | |
| | Syngenetic | | Epigenetic | | Volcanic | | Total |
Country	Tg S	$\delta^{34}S$ (‰)	Tg S	$\delta^{34}S$ (‰)	Tg S	$\delta^{34}S$ (‰)	Tg S
USA	1.90	6.7	4.30	7.7	0.01	1.0	6.21
Poland	5.00	12.9	—	—	—	—	5.00
USSR	2.57	13.6	—	—	0.03	1.0	2.60
Mexico	—	—	1.70	7.7	—	—	1.70
Iraq	0.75	15.9	—	—	—	—	0.75
China	0.20	—	—	—	0.05	—	0.25
South America	—	—	—	—	0.09	1.0	0.09
Italy	0.04	9.9	—	—	0.02	1.0	0.06
Turkey	0.01	—	—	—	—	—	0.01
Others	0.01	—	—	—	0.01	?	0.02
Total	10.48	11.9	6.00	7.7	0.21	1.0	16.69
Percent	62.79		35.95		1.26		100.0

is isotopically similar to associated evaporite sulphate. This is attributed to intensive bacterial sulphate reduction with small isotopic selectivity.

An estimate of the average isotopic composition of produced native sulphur can be based on large occurrences. These include deposits in cap rocks of salt domes in the Gulf of Mexico, the Delaware field in west Texas, USA (Ault and Kulp, 1959), deposits in the Polish and Soviet Sub-Carpathians, the Mishrak deposit in Iraq, and stratal sulphur deposits in Sicily.

The average $\delta^{34}S$ values of native sulphur in two large deposits, Spindleton and Boling, Gulf of Mexico, USA, are +3.1 and +5.7‰ respectively, whereas in Challenger Knoll it is +14.2‰.

The average $\delta^{34}S$ value for stratal and stratiform deposits of the Delaware basin is +6.7‰. It is estimated that sulphur production in this region will substantially increase in the near future (Bodenlos and Nelson, 1979; Ruckmick *et al.*, 1979).

Tarnobzheg, the largest deposit in Poland, contains 20% elemental sulphur with an average $\delta^{34}S$ value of +12.9‰. In the Soviet Sub-Carpathians, the average $\delta^{34}S$ value for industrial sulphur is +13.6‰.

Table 4.5 Comparison of average $\delta^{34}S$ values of native sulphur and sedimentary sulphates in exogenic deposits

Deposit	$\delta^{34}S$ (‰)		References
	Sulphate	Sulphur	
Large industrial deposits			
USSR			
Shor-Su, deposit 'L–K'	18.4	+17.4	Vinogradov et al. (1964)
deposit 'K'	18.1	+8.8	Vinogradov et al. (1964)
Gaurdak	14.0	+4.5	[a]
Middle Volga	13.6	+12.6	[a]
Sub-Carpathian	19.8	+13.2	[a]
Iraq, Mishrak	19.4	+15.9	[a]
Sicily	+20.7	+10	(Figure 4.11)
USA, Gulf of Mexico,			
Spindleton	17.0	+5.7	Feely and Kulp (1957)
Boling	16.2	+3.1	Feely and Kulp (1957)
Challenger Knoll	14.8	+14.2	Davis and Kirkland (1979)
Delaware basin (USA)	10.7	+6.7	Davis and Kirkland (1970)[a]
Small deposits			
USSR			
Novodmitrovskoe	11.0	−4.3	[a]
Romnenskoe	22.6	−6.5	[a]
Krasnovodskoe	12.3	−19.0	[a]
Italy, Borraitotto, Sicily	21.5	−0.9	Dessau *et al.* (1962)
USA, Moss Bluff, Gulf Coast	17.3	−6.4	Feely and Kulp (1957)

[a] Data of author.

The world's largest sulphur deposit, Mishrak in Iraq, has the heaviest isotopic composition of sulphur, with an average $\delta^{34}S$ of +15.9‰.

The $\delta^{34}S$ values of sulphur ores in four rather large deposits of Sicily (Baccarato, Cozzodisi, Trabia, Ciavolotta) vary from +4 to +14‰, with an average of +10‰ (Figure 4.11).

Native sulphur in volcanogenic deposits corresponding to about 1% of the world production have $\delta^{34}S$ values within a narrow range near +1‰ (Lein, 1968; Vinogradov, 1970).
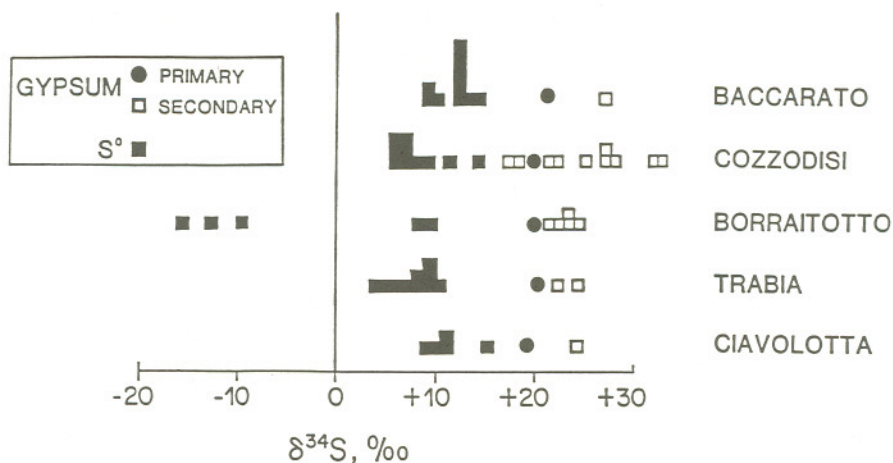
Figure 4.11 Histogram of $\delta^{34}S$ values for sulphate and native sulphur deposits of Sicily (Dessau *et al.*, 1962)

Three peaks in the distribution of exogenic native sulphur deposits are evident in the stratigraphic scale corresponding to arid continental periods and evaporite formation (Figure 4.12). The first peak occurred in the Upper Permian, and includes stratiform deposits of native sulphur in west Texas, USA, and middle Volga, USSR. The second peak in the Jurassic includes the large sulphur deposits in cap rocks of salt domes in and around the Gulf of Mexico and the Gaurdak deposit in the Turkmenian SSR. The third peak
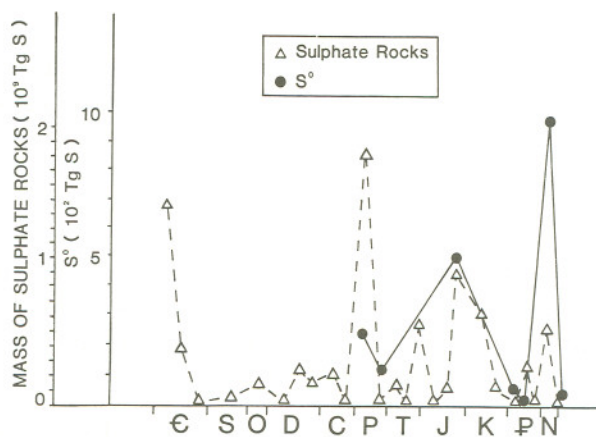
Figure 4.12 Stratigraphic distribution of the world's reservoirs of sulphate rocks and native sulphur

in the Miocene includes stratiform sulphur deposits in Sicily, Soviet and Polish Sub-Carpathians, Crimea, and Iraq. These peaks correspond to more than 90% of the total exogenic sulphur.

Three main factors determine the isotopic composition of native sulphur from exogenic deposits:

(a) Age and isotopic composition of initial evaporites
(b) Isotope fractionation during sulphate reduction
(c) Extent of secondary changes depending primarily on the depth of occurrence

The average isotopic composition of native sulphur produced globally, estimated from production data for different countries and the average $\delta^{34}S$ value of their largest deposits (Tables 4.4 and 4.5), is +10‰.

4.5 SULPHUR ISOTOPE COMPOSITION OF FOSSIL FUELS

4.5.1 Peat and lignite*

Peat represents the first stage of maturation of dead plant material. Therefore, its sulphur must be considered in the sequence of the transformations from living plants to lignite and coal.

Sulphur is an essential constituent of the living cell. Plants can take up SO_4^{2-} or SO_2 directly from the environment. The S organic compounds resulting from assimilatory SO_4^{2-} reduction are depleted in ^{34}S by 1 to 5‰. Thus the 'primary' organically bonded sulphur in peat will have slightly lower $\delta^{34}S$ values than the source sulphate.

Peat-producing bog areas beneath rain slopes of mountain chains have practically no contact with groundwater sulphate so that the mosses and other plants must obtain sulphur from the atmosphere. Assuming a $\delta^{34}S$ value of +3 to +6‰ for this atmospheric sulphur (Chapter 5), the expected range for peat is about 0 to +4‰. Later, some of the buried sulphur is remobilized to volatile sulphur organics (dimethyl sulphide, etc.) with a slight isotope fractionation, and the range of $\delta^{34}S$ values in the remaining peat becomes broader. Peat samples from rain slopes in the Harz Mountains, FRG, vary in $\delta^{34}S$ value from −3 to +10‰. The S/C ratio in all samples is lower than 1:100, which is similar to that of land plants.

Dissolved sulphate in groundwater will penetrate bogs in local depressions. This is a favourable habitat for SO_4^{2-} reducing organisms, particularly at deeper burial levels. The reduced sulphur reacts with the decaying organic matter and iron to form S organic compounds and iron sulphide concretions.

* H. Nielsen.

During mining, these concretions are readily weathered under the more aerobic conditions to form sulphuric acid.

The range of $\delta^{34}S$ values for sulphide in the concretions depends on the conditions of SO_4^{2-} reduction. Low concentrations of SO_4^{2-} will be reduced more or less quantitatively and the $\delta^{34}S$ value of the sulphide will be nearly the same as the SO_4^{2-}. At higher concentrations, the remaining SO_4^{2-} will follow the Rayleigh equation if the system is effectively closed (Chapter 1). In that case, the cores of the concretions are more depleted in ^{34}S than the rims. The range of $\delta^{34}S$ values in a given concretion depends upon its formation time with respect to the extent of SO_4^{2-} reduction. If SO_4^{2-} reduction approaches 100%, the average $\delta^{34}S$ values of the concretions should be the same as the initial SO_4^{2-}. An example is the lignite deposit in the impact crater of the Norlinger Ries in southern FRG where the $\delta^{34}S$ values for sulphide range from -27 to $+25‰$. Evaporite strata are lacking around the Ries structure and therefore the SO_4^{2-} content of the ground water must have been low. The mean value of $\delta^{34}S = -3.5 \pm 15‰$ suggests that this groundwater SO_4^{2-} originated from the leaching of sedimentary rocks.

In northern Central Europe, the ground waters are usually much richer in SO_4^{2-} due to the wide distribution of Zechstein salt domes. Such ground waters form an almost 'infinite' sulphate reservoir so that reduction proceeds under quasi-open system conditions. Therefore, the sulphide is uniformly light and the S content is high. The sulphide $\delta^{34}S$ values in lignite seams from the mining district south of Helmstedt, eastern FRG, range from -24 to $-10‰$. The mean $\delta^{34}S = -15.2 \pm 6.2‰$ agrees with the assumed provenance of these sulphides from reduction of Zechstein solutions with $\delta^{34}S = +11‰$.

In some cases, elemental sulphur may be formed in abundance in the upper 0.5 m of peat deposits. Sulphur isotope data revealed that one such occurrence arose by sulphide oxidation (Krouse, 1980; see Section 7.1.3).

4.5.2 Coal*

The extent of sulphur contribution to the environment from the mining and utilization of coal is well known. For example, in 1969 the combustion of coal was responsible for 58.2% of atmospheric pollutant SO_2 in the United States (US Department of Health, Education and Welfare, 1969). Although SO_2 is the main form in which sulphur is released into the atmosphere by coal utilization, sulphur may also be introduced into the environment as sulphate during the mining of coal or from the weathering of coal stockpiles

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* J. W. Smith.
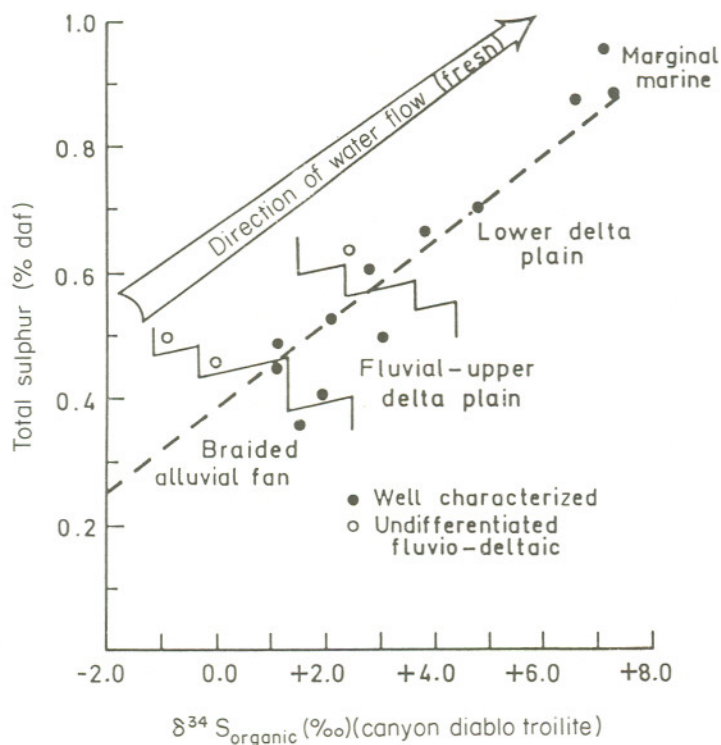
Figure 4.13 Effect of deposition environment on the content and isotopic composition of sulphur in coal

and waste dumps. Subsequent bacterial action may then convert this sulphate to S-containing gases.

Earlier workers were most interested in the source(s) of sulphur in coal and concentrated their studies on atypical coals with unusually high organic or total sulphur contents (Kavcic, 1958; Rafter, 1962; Vinogradov and Kizilshtein, 1969). Coals of the former type are comparatively rare, and coals in the latter category are now unlikely to be utilized without beneficiation to reduce the content of sulphur-containing minerals. In addition, within-seam variations in the isotopic composition of coal seam components are now firmly established.

These within-seam variations in the distribution and isotopic composition of organically combined sulphur and of finely disseminated and massive

Table 4.6 Relationship between isotopic composition and concentration of sulphur in coal and environments of deposition and maturation (from data of Smith and Batts, 1974; Price and Shieh 1979; and Smith *et al.*, 1982)

Environment of deposition and maturation	Sulphur content	Forms of sulphur	$\delta^{34}S$ (‰)
Freshwater conditions during deposition and maturation	< 1%	Mainly organic with minor disseminated pyrite	Organic + 4 ± 3
High sulphate concentrations, normally marine, during plant growth and early deposition	Commonly ≥ 2%	Organic and pyrite sulphur contents of same order	Organic and pyrite sulphur with similar values, e.g. −16% reflecting single sulphate source
Freshwater environment during plant growth followed by marine invasion in early deposition	In unaffected portions of seam < 1%. High pyrite sulphur contents along seam margins	Mainly organic with minor disseminated pyrite in unaltered coal. Massive pyrite along seam margins	Organic + 4 ± 3 Pyrite along margins +20 reflecting rapid complete reduction of available marine sulphate
Freshwater environment during plant growth followed by later marine invasion during maturation	In unaffected portions of seam < 1%. High pyrite sulphur contents along seam margins	Mainly organic with minor disseminated pyrite in unaltered coal. Massive pyrite along seam margins	Organic + 4 ± 3 Pyrite along margins increasing from +5 to +28 with increasing depth of penetration of sulphate reflecting kinetically controlled sulphate reduction
Postlithification invasion of seam by sulphate in solution	Usually ≥ 1%	Main feature high additional sulphate filling veins	Organic and pyritic sulphur still reflect environments of deposition and maturation; sulphate usually +13 to +30

pyrite (Smith and Batts, 1974; Price and Shieh, 1979) have provided fundamental information that allows five environments for coal deposition and maturation to be recognized (Table 4.6). It is clear from the above that isotopic data for total sulphur cannot be used to assess the isotopic composition of emissions to the atmosphere. Further, the few data from a given deposit may not be representative of the coal actually recovered. However, Table 4.6 serves as a guide to the isotopic composition of coals after projected beneficiation. For example, in the Australian and Illinois coals, which have been described in detail, only massive pyrite is likely to be separated by commercial beneficiation processes, and it is possible to calculate the effect of the removal of this pyrite on the isotopic composition and sulphur content of the washed coal.

In low sulphur coals containing 1% total sulphur and 0.2% pyritic sulphur from Australian fluvio-deltaic sequences, variations in organic and total sulphur contents reflect directly associated variations in brackishness (available SO_4^{2-}) (J.W. Hunt and J.W. Smith, unpublished data, 1984). Figure 4.13 demonstrates that even in coals of undoubted freshwater origin and low pyrite content, significant variations in sulphur isotope composition exist.
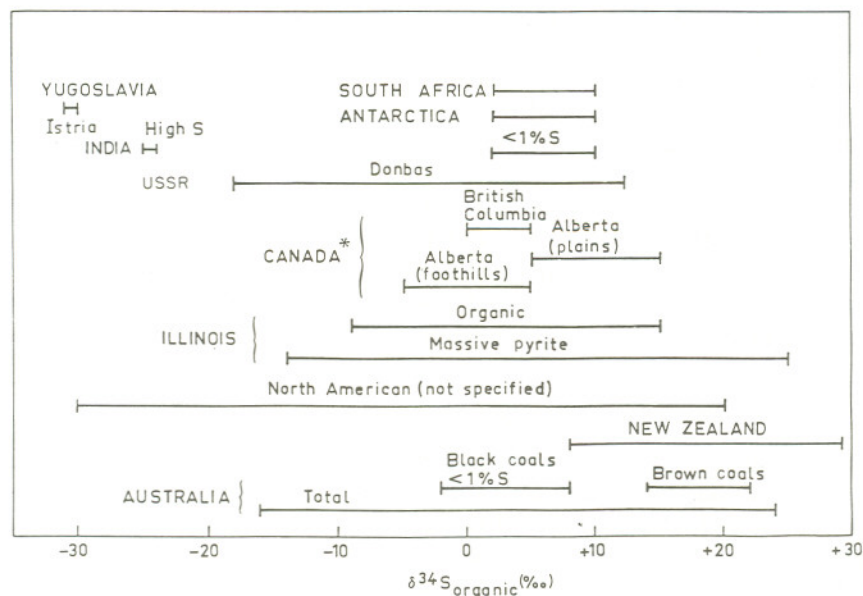
Figure 4.14 The isotopic composition of sulphur in coal (data from references cited; *data from H.R. Krouse, personal communication)

The published isotopic data on sulphur in coal are displayed in Figure 4.14. No attempt has been made to weight this information with regard to number of samples examined, size of deposit, etc. The only objective of the figure is to demonstrate the variability in measured $\delta^{34}S$ values.

In conclusion, with the exception of some studies described in Chapter 8, data on the isotopic composition of sulphur in coal were not collected for the purpose of evaluating sulphur emissions to the atmosphere, and on examination are clearly unsuited to that purpose. Acceptable data will require an extensive global assessment of the isotopic composition of coals as utilized.

4.5.3 Oil*

4.5.3.1 *Introduction*

Oxidized sulphur compounds formed during combustion and refining of oil may enter the atmosphere, continental water basins, and the world ocean systems. Oil and oil products *per se* may introduce sulphur into sediments of oceans and continental reservoirs as the result of tanker spills and offshore drilling practices.

Data on the isotopic composition of sulphur in oil were first reported by Thode *et al.* (1958) for reservoirs of different ages in Canada and the United States. Later, Thode and Monster (1970) studied oils in the Middle East (Arabia, Kuwait, Northern and Southern Iraq, Iran). These studies revealed that in large reservoirs and oil provinces of the same age the sulphur isotopic composition of oil is markedly uniform, even where the concentration of sulphur varies widely. In contrast, the $\delta^{34}S$ values vary considerably among oilfields (from -5.2 to $+28.2‰$).

Similar investigations in the Soviet Union initiated by Eremenko (1960), Pankina (1978) and Eremenko and Pankina (1962, 1963) dealt with oils occurring over a wide stratigraphic range. These studies, which included entire columns from many oil- and gas-bearing provinces, revealed a much greater spread in $\delta^{34}S$ values (about 50‰).

4.5.3.2 *Summary of $\delta^{34}S$ data for oil*

Sulphur isotope data for oils can be summarized according to the age of the reservoir strata. Oil is difficult to date and in many locations such as the Middle East (Thode and Rees, 1970) and Timano-Pechora, USSR, rocks of different ages may contain the same oil pool.

The most ancient oil-bearing deposits are found in Proterozoic Riphean and Vendian complexes. There are different productive zones in the East Siberian platform. Minor showings are observed also in the central (Moscow syncline) and eastern (Upper Kama depression) parts of the Russian

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* R. G. Pankina.

platform. Oil of the Vendian and Riphean periods was found to have an average S content and $\delta^{34}S$ value of 1% and +15‰ respectively (Table 4.7). Oils in Cambrian deposits of the East Siberian platform (Irkutsk amphitheatre) and Sub-Baltic syneclise are the most enriched in ^{34}S of the entire stratigraphic column (+19 to +25‰, Table 4.8). The $\delta^{34}S$ values of these two regions differ by only 4‰ even though the locations are thousands of kilometres apart and the depositional environments are substantially different.

Ordovician deposits in the Gusev (Baltic syncline) and Kibarty (Timano-Pechora Province) areas have average $\delta^{34}S$ values of +6.8 and 7.3‰ respectively and low sulphur contents (0.28–0.31%). Similar data were

Table 4.7 Sulphur isotopic composition of oils from Proterozoic reservoir rocks

| | | | Sulphur | |
| | | | Content (%) | $\delta^{34}S$ (‰) |
Age	Area	Field, well		
Vendian	Upper Kama depression	Vereshchaginskoe, 60	1.3	+13.8
Vendian	Upper Kama depression	Sokolovskoe, 52	0.68	+14.0
Vendian	Irkutsk amphitheatre	Markovskoe, 28–R	0.7	+15.2
Vendian	Irkutsk amphitheatre	Krivolukskoe, 3–Sp	0.6	+15.2
Vendian	East Siberian platform	Diyavolskoe	0.98	+17.8
Riphean	East Siberian platform	Kuyumbinskoe, 9	0.88	+14.2

Table 4.8 Sulphur isotopic composition of oils from Cambrian reservoir rocks

| | | | Sulphur | |
| | | | Content (%) | $\delta^{34}S$ (‰) |
Area	Field, well	Reservoir strata		
Irkutsk amphitheatre	Markovskoe, 1	Osinsky horizon	1.01	+22.3
Irkutsk amphitheatre	Markovskoe, 61	Osinsky horizon	0.7	+22.5
Irkutsk amphitheatre	Osinskoe, 1	Osinsky horizon	0.4	+25.3
Baltic syneclise	Plunge	Tiskretskaya suite	0.58	+19.3

obtained for deposits in Ontario, Canada, and west Texas, North Dakota, and Montana, USA (Thode *et al.*, 1958; Thode, 1981).

Minor oil occurrences in Silurian deposits of the Kuldig area, Sub-Baltic (syneclise), were found to have an average $\delta^{34}S$ value of $+3.4\permil$. In Ontario, west Texas, North Dakota, and Montana, the mean $\delta^{34}S$ values were closer to $+9\permil$. The discrepancy may relate to the fact that in the Timano-Pechora gas- and oil-bearing province, Silurian and Devonian reservoir rocks contain the same oil pools.

Economically viable reservoirs of oil occur in Devonian deposits of the Soviet Union, United States and Canada. The average $\delta^{34}S$ values among different fields span a wide range (0 to $+16\permil$, Table 4.9). In western Canada and the United States most of the data fall between $+10$ and $+15\permil$. It is interesting to note that the excursion in the evaporite $\delta^{34}S$ time curve during this time (Figure 4.2) is about the same as the range found for the oil.

Oils produced from Upper Carboniferous strata from many regions of the Soviet Union are characterized by a rather homogeneous $\delta^{34}S$ value near $+5\permil$ in spite of the significant range in sulphur content (0.4–3.2%) (Table 4.10). In contrast, many data in the Pennsylvanian of Wyoming, USA, are near $-5\permil$ (Vredenburgh and Cheney, 1971) and a range from -6 to $+9\permil$ has been found in the Mississippian in Wyoming and western Canada (Thode *et al.*, 1958; Vredenburgh and Cheney, 1971; Orr, 1974).

Oil in Permian deposits of the Soviet Union tends to have average $\delta^{34}S$ values near $-2.5\permil$ whereas the mean for Wind River Basin, Wyoming, is about $1\permil$ lighter (Vredenburgh and Cheney, 1971). Orr (1974) found the mean $\delta^{34}S$ value for the Big Horn Basin, Wyoming, to be near $+1\permil$ (Table 4.11).

Triassic commercial oil pools in the East Sub-Caucasus have low sulphur contents (0.14%). The average $\delta^{34}S$ value for the Urozhainenskoe deposit is $+6.2\permil$. Oil in the Karagandinskoe deposit in the Sub-Caspian has a $\delta^{34}S$ value of $+5.2\permil$. Triassic oils in the Miziiskaya platform (Bulgaria) are also enriched in ^{34}S ($+3.1\permil$). Triassic deposits in northern Iraq have a mean $\delta^{34}S$ value around $2\permil$ whereas negative values around $-5\permil$ were found for the Wind River Basin in Wyoming (Table 4.12).

Commercial oil pools in Jurassic reservoirs of large areas of the Soviet Union and the Wind River Basin (Table 4.13) are variably depleted in ^{34}S.

Cretaceous oils vary in S content from less than 0.1% in the Wind River Basin to greater than 5% in the Athabasca oil sands of Alberta, Canada. The $\delta^{34}S$ values vary from -7 to $+12\permil$. For some areas, the $\delta^{34}S$ values are markedly uniform throughout the Cretaceous at locations up to 200 km apart (e.g. $-5.5 \pm 2\permil$ in northern Iran). In contrast, in the Lower Cretaceous of Alberta, Canada, heavy oils with greater than 2% S and light

Table 4.9 Sulphur isotopic composition of oils from Devonian reservoir rocks

Area	Field	Age	Sulphur Content (%)	$\delta^{34}S$ (‰)
USSR				
Pripyat trough	Rechitskoe	D_2	0.3	+7.4
Zhigulevsko-Pugharevsky	Sol Ravine	D_3	0.72	+6.4
Zhigulevsko-Pugharevsky	Mukhanovskoe	D_3	0.72	+7.6
Zhigulevsko-Pugharevsky	Mikhailovsko-Kokhanovskoe	D_3	0.66	+10.2
Zhigulevsko-Pugharevsky	Pokrovskoe	D_3	1.08	+8.5
Sernovodsko-Abdulinsky	Radaevskoe	D_3	2.8	+4.4
Tatarsky roof	Romashkinskoe	D_3	1.6	+2.4
Tatarsky roof	Shkapovskoe	D_3	1.81	+0.1
Tatarsky roof	Leonidovskoe	D_3	1.55	+2.7
Permsko-Bashkir sky roof	Kushkulskoe	D_3	1.6	+5.8
Pripyat trough	Rechitskoe	D_3	0.58	+12.5
Pripyat trough	Ostashkovichskoe	D_3	1.02	+14.0
Pripyat trough	Tishkovskoe	D_3	0.7	+15.9
Canada (Thode *et al.*, 1958)				
Alberta	Leduc	D_2	0.3	+12.0
Alberta	Excelsior	D_2	0.66	+15.3
Alberta	Stettler	D_3	1.45	+13.1
Alberta	Stettler	D_3	1.78	+10.9
Alberta	Leduc	D_3	0.26	+12.5
Alberta	Golden Spike	D_3	0.19	+15.0
USA (Thode, 1981)				
Montana	18T 30NR 48E	D	—	+10.1

oils with less than 1% S have $\delta^{34}S$ values near +6 and +11‰ respectively (Thode *et al.*, 1958).

The S content and $\delta^{34}S$ value in the Gazli deposit of Middle Asia are 0.1% and +3.2‰ respectively. In the Armavir deposit, West Caucasus, the average $\delta^{34}S$ value is +8.2‰ whereas the S content is 0.16%. In West Siberia, the $\delta^{34}S$ value and S content vary from +0.5 to +6.6‰ (+3.2 on average) and from 0.7 to 1.93% respectively. As seen in Table 4.14, there is no apparent relationship between the S content and $\delta^{34}S$ values.

Table 4.10 Sulphur isotopic composition of oils from Carboniferous reservoir
rocks

Area	Field	Age (formation)	Sulphur Content (%)	δ³⁴S (‰)
USSR		Pennsylvanian		
	Peschano-Umetskoe	(Bobrikovsky)	0.4	+3.8
Zhigulevsko-chevsky roof	Karpovo-Syboskoe	(Bobrikovsky)	2.6	+4.7
Zhigulevsko-chevsky roof	Sol ravine	(Bobrikovsky)	1.38	+5.5
Zhigulevsko-chevsky roof	Krasnoyarskoe	(Bobrikovsky)	1.59	+3.8
Zhigulevsko-chevsky roof	Mukhanovskoe	(Bobrikovsky)	1.25	+5.6
Zhigulevsko-chevsky roof	Tarkhanskoe	(Bobrikovsky)	2.2	+4.9
Sernovodsko-Abdullinskaya depression	Radaevskoe	(Bobrikovsky)	3.2	+3.2
Bashkirsky roof	Arlanskoe	(Bobrikovsky)	3.02	+5.8
USA				
Oklahoma[a]	—	(Springer)	0.17	−0.1
Oklahoma[a]	—	(Misener)	0.06	−5.6
Kansas[a]	—	(Cherokee)	0.24	−3.9
Wyoming	—	(Tensleep)	2.39	−5.1
Wyoming	Circle Ridge[b]	(Tensleep)	2.6	−5.1
Wyoming	Black Mountain[c]	(Tensleep)	3.0	−3.8
Wyoming	Fourbear[c]	(Tensleep)	3.1	+5.0
Wyoming	Manderson[c]	(Phosphoria)	1.8	+5.6
Wyoming	Forget	(Phosphoria)	1.8	+5.0
Wyoming	—	Mississippian (Madison[a])	1.9	−3.9
Wyoming	Black Mountain[c]	(Madison[a])	3.2	−3.0
Canada[a]				
Saskatchewan	—	(Charles)	0.54	+1.8
Saskatchewan	—	(Mission Canyon)	1.8	+5.0
Saskatchewan	Coleville-Smiley	(Banff Sand)	2.6	+4.9
Alberta	Turner Valley	(Madison)	0.35	+8.8

[a] Thode *et al.*, 1958.
[b] Vredenburgh and Cheney, 1971.
[c] Orr, 1974.

Table 4.11 Sulphur isotopic composition of oils from Permian reservoir rocks

Field or area	Sulphur	
	Content (%)	$\delta^{34}S$ (‰)
USSR		
Mukhanovskoe	1.82	−2.3
Vostochno-Chernovskoe	1.82	−2.9
Novo-Klyuchevskoe	1.82	−1.6
Kohkanovskoe	2.5	−2.0
USA		
Wind River Basin, Wyoming[a]	2	−3.3
Big Horn Basin, Wyoming[b]	2.5	+1.1
West Texas[c]	—	+1.0

[a] Vredenburgh and Cheney, 1971.
[b] Orr, 1974.
[c] Thode and Monster, 1965.

Table 4.12 Isotopic composition of sulphur oils from Triassic deposits

Field or area	Sulphur	
	Content (%)	$\delta^{34}S$ (‰)
USSR		
Urozhoinenskoe, East Sub-Caucasus	0.14	+6.2
Karagandinskoe, Sub-Caspian depression	—	+5.2
Bulgaria		
Miziiskaya platform	—	+3.1
Iraq (Thode and Monster, 1970)		
Butmah Field	—	+1.9
Alan Field	—	+2.8
USA (Vredenburgh and Cheney, 1971)		
Crow Mountain, Wind River Basin, Wyoming	1.9	−6.0
Nugget, Wind River Basin, Wyoming	2.2	−4.0

Cenozoic oils have a 40‰ spread in $\delta^{34}S$ values, greater than for any other age (Table 4.15). The most positive $\delta^{34}S$ value (+28‰) is found along with low S content ni the Uinta Basin, Utah, USA. The most negative $\delta^{34}S$ values (average, −11‰) are found in oils in the Tadzhik depression, USSR.

Table 4.13 LIsotopic composition of sulphur in oils from Jurassic reservoir rocks

| | Sulphur | |
Field or area	Content (%)	δ^{34}S (‰)
USSR		
Shurchi, Amydarjinskaya syneclise	0.87	−7.5
Akdzhar, Kaganskoe upwelling	0.90	−7.9
Dzharkak, Kaganskoe upwelling	0.74	−6.4
Karaul-Bazar, Kaganskoe upwelling	0.47	−7.1
Shurtepe, Kaganskoe upwelling	0.96	−7.7
Yulduzkak, Kaganskoe upwelling	0.76	−6.8
Urtobulok, Chardzhousky step	—	−8.8
Zamnokulskoe, Sub-Caucasus	—	−5.6
Kraxhanbas, Sub-Caucasus	—	+3.7
Martyshi, Sub-Caucasus	—	+26.3
Mulymjnskoe, West Siberia	—	−2.5
Mortymjinskoe, West Siberia	—	−2.2
USA (Vredenburgh and Cheney, 1971)		
Wind River Basin, Wyoming	2.2	−4.6

Table 4.14 Sulphur isotopic composition of Lower Cretaceous oils in Western Siberia

| | Sulphur | |
Field, well	Content (%)	δ^{34}S (‰)
Fyodorovskoe, 79	1.17	+2.0
Fyodorovskoe, 79	1.93	+4.4
Fyodorovskoe, 79	0.93	+5.9
Chipalskoe, 54	1.02	+4.7
Chipalskoe, 58	1.22	+5.0
Chipalskoe, 58	1.0	+6.6
Pokachevskoe, 35	0.7	+1.9
Pokachevskoe, 23	0.8	+4.1
Malobalykskoe, 7	1.37	+5.5
Malobalykskoe, 7	1.06	+6.5
Aganskoe, 12	0.90	+0.5
Aganskoe, 3	0.86	+2.0
Ust-Balykskoe, 63	1.35	+2.8
Average		+3.2

Table 4.15 Sulphur isotopic composition of Cenozoic oils

Area	Age (formation)	Sulphur Content (%)	$\delta^{34}S$ (‰)
USSR			
Tadzhik depression	(Alay)	0.60	−11.0
Fergana depression	(Bukhara)	0.50	−4.5
Sub-Caucasus	(Kyma)	0.80	−1.2
Sub-Carpathians	Eocene	0.42	+3.8
Iraq (Thode and Monster, 1970)			
Kirkuk	Tertiary	—	−5.5
Bai Masson Field	Tertiary	—	−7.1
Jambur Field	Tertiary	—	6.5
USA (Thode *et al.*, 1958)			
Green River, Utah	Eocene	0.11	+28.2

Variations in the $\delta^{34}S$ values of sulphur in oil are shown according to the age of the reservoir rocks in Figure 4.15. The evaporite $\delta^{34}S$–time curve is also drawn. Two observations are noteworthy. In Precambrian and Cambrian host rocks, the $\delta^{34}S$ values of the oil are homogeneous and close to the evaporite value. The spread in $\delta^{34}S$ values seem to be greater in younger reservoirs. Perhaps this reflects variations in shallower deposition environments and migration. Older oil may migrate upwards into younger rocks. Although migration of younger oil into older rocks has been observed, it is less likely to occur.

4.5.3.3 *Estimate of the mean $\delta^{34}S$ value of oil*

The sulphur content and isotopic composition of oils along with their distribution in Phanerozoic geological systems permit a rough estimate of the mean $\delta^{34}S$ value of oil sulphur that can potentially enter the environment.

In spite of significant variations, $\delta^{34}S$ values for the bulk of samples examined fall within the range −5 to +10‰ (Figure 4.15). Oils from Cretaceous, Devonian, Carboniferous, and Jurassic reservoirs constitute most of the world resources. The sulphur content of these oils is usually about 1%.

The sulphur isotopic composition of oils characterized by a high S content (2.5%) greatly differs from the bulk of oils. Such oil pools are usually small in a given stratum. Since their sulphur isotopic compositions are divergent,
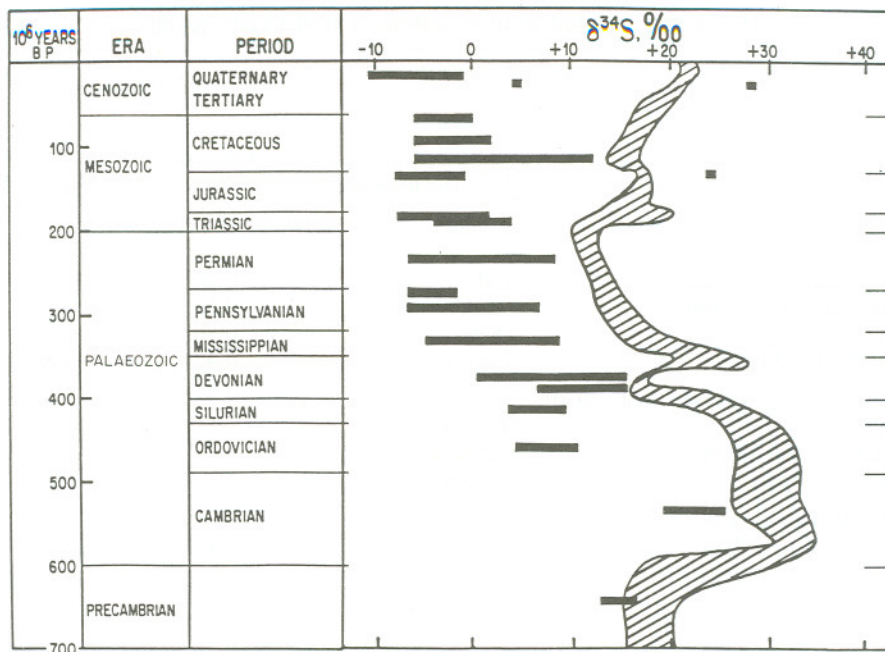
Figure 4.15 Variation of δ³⁴S values of oil with age of reservoir rocks

one can consider the possibility that their deviations mutually balance, resulting in an average sulphur isotopic composition near zero.

   Therefore, it would appear that the isotopic composition of oil sulphur that can potentially contaminate the environment varies from −5 to +10‰. Data for oil utilization in Australia are given in Section 8.8.2.

4.5.3.4 *Use of sulphur isotope analyses to determine petroleum contamination in sediments*

Venkatesan *et al.* (1982) examined hydrocarbon distributions in pristine and polluted marine environments. In both reducing and oxidizing pristine sediments, the δ³⁴S values for extractable organic sulphur were lower than −15‰ as the consequence of bacterial SO_4^{2-} reduction. In contrast, petroleum-derived S in compounds resistant to weathering was found to be more enriched in ³⁴S: 0‰ for Prudhoe Bay, Alaska; −5 to +5‰ for Gulf Coast oils; and +8 to +15‰ for natural seeps in southern California. At a number of locations, positive δ³⁴S values were found in sediments for which organic geochemical analyses indicated crude oil contamination.

4.5.4 H₂S in hydrocarbon deposits*

Hydrocarbon deposits contain different concentrations of H_2S as a free gas or dissolved in formation waters. During recovery and refining, H_2S and products of its oxidation may contaminate the environment, especially the atmosphere (see Section 8.2).

Thode *et al.* (1958) were the first to study the isotopic composition of H_2S in gas deposits. They analysed H_2S associated with oil in Devonian reservoir rocks in Alberta, Canada. Although the H_2S content varied significantly, $\delta^{34}S$ values were markedly uniform and approximated those of oils from the same wells (Table 4.16). The authors concluded that the H_2S was formed during maturation of the oil with negligible isotope fractionation.

The isotopic composition of H_2S from gas- and oilfields was studied in many areas of the Soviet Union including the Volga–Ural region and the Tadzhik, Fergana, and Amu-Dariya depressions (Eremenko and Pankina, 1962, 1963; Pankina and Mekhtiyeva, 1964; Pankina, 1978). In these deposits, production zones are found at depths of less than 1000 m and temperatures less than 60 °C. The H_2S content is low and the $\delta^{34}S$ values have a total spread of 40‰. Diversity of $\delta^{34}S$ values was found in individual strata: -14 to $+8$‰ in Lower Carboniferous, -22 to $+10$‰ in Middle Carboniferous, -3 to -1‰ in Lower Permian, -12 to $+11$‰ in Upper Permian, -16 to -1‰ in Jurassic, and $+11$ to $+17$‰ in Palaeocene deposits.

In contrast to the data of Table 4.16, the isotopic composition of H_2S in these shallow occurrences often differed from that of the associated oil. H_2S of younger deposits was relatively enriched in ^{34}S whereas in older gases H_2S was either depleted in ^{34}S with respect to the oil or occasionally had the same isotope composition. Isotopic data and microbiological examination revealed that H_2S at these low temperatures was formed by the biological

Table 4.16 Isotopic composition of H_2S and associated oil in Devonian reservoir rocks, Alberta, Canada (Thode *et al.*, 1958)

Formation	Location	H₂S (%)	δ³⁴S (‰) H₂S	δ³⁴S (‰) Oil
D–2	Leduc	0.016	+15.5	+11.9
	Leduc	1.6	+12.6	+12.6
	Leduc	3.1	+13.7	+11.0
D–3	Stettler		+13.7	+10.8
	Stettler		+12.6	+11.0
	Big Valley		+13.1	+11.7
	Bashaw		+13.9	+13.2

* R. G. Pankina.
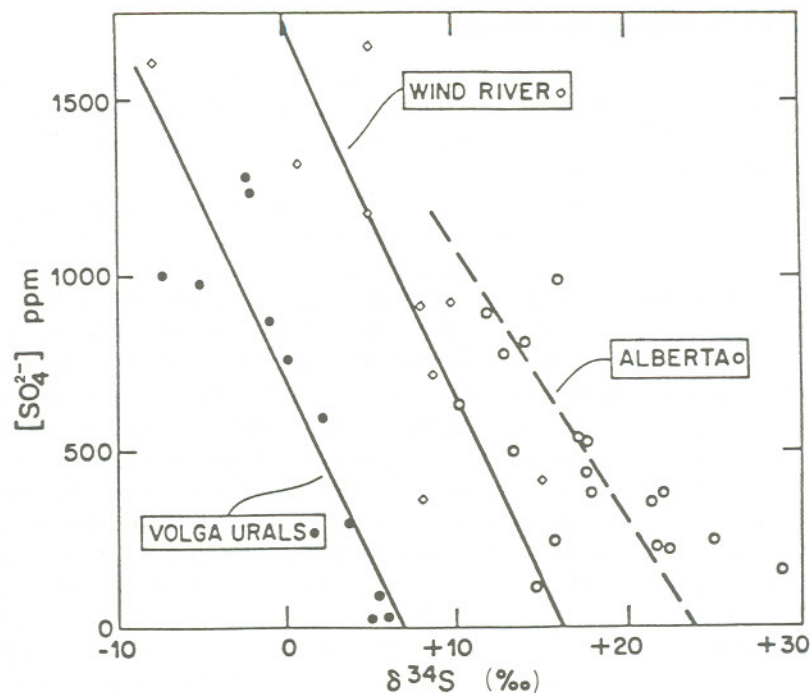
Figure 4.16 Sulphate concentration versus $\delta^{34}S$ values of H_2S in formation waters of the Bobrikov horizon, Volga-Urals (Pankina and Mekhtiyeva, 1964), Wind River Basin, Wyoming (Vredenburgh and Cheney, 1971), and Devonian strata of Alberta, Canada (after Krouse, 1977). The lines are drawn to show the trends. Theoretically the data should fit a logarithm function if the kinetic isotope effects were constant throughout the deposit

reduction of SO_4^{2-} in the formation waters. Significant variations in the isotopic composition of H_2S arise from the diversity of concentrations and isotopic composition of SO_4^{2-} as well as the isotopic selectivity and the extent of reduction (Pankina, 1978). As reduction proceeds, the H_2S becomes more enriched in ^{34}S (Figure 1.2) and the SO_4^{2-} concentration decreases. If the system remained closed, the accumulated H_2S at 100% reduction would have the same $\delta^{34}S$ value as the initial SO_4^{2-}. Trends consistent with this concept were found not only in the Volga-Urals (Pankina and Mekhtiyeva, 1964) but also in the Wind River Basin of Wyoming (Vredenburg and Cheney, 1971) and the Devonian of Alberta (Figure 4.16).

The large gas deposit at Lacq, France, is found at 150 °C in Lower Cretaceous–Jurassic strata at a depth of 3300–4300 m. The H_2S content is 15.3% and the $\delta^{34}S$ value of refined sulphur is +14.5‰ (Grinenko and

Vdovykin, 1966). These authors concluded that the H_2S formed by complete reduction of Jurassic sulphates.

The Orenburg gas–condensate deposit has been extensively studied (Gavrilov *et al.*, 1973; Pankina, 1978). It is situated on the northern side of the Caspian depression and is associated with Lower Permian–Upper Carboniferous systems. The gas bed is 520 m thick in the central part and the thickness of oil seams is 20 m. The stratal temperature is rather low, from $+27$ to $+32$ °C. The H_2S content changes from 1.3‰ in the upper dome and western part to $+4.5\%$ in the east pericline. The $\delta^{34}S$ values increase from $+2.0$ to $+5.8$‰ in the same direction. The H_2S in this deposit was either formed by SO_4^{2-} reduction in formation waters of more ancient Carboniferous systems (Pankina, 1978) or in the same strata downdip (Gavrilov *et al.*, 1973).

Vredenburgh and Cheney (1971) studied H_2S in gases associated with oils down to a depth of 4000 m in the Phosphoria (Permian), Tensleep (Pennsylvanian), and Madison (Mississippian) formations of the Wind River Basin, Wyoming, USA. The $\delta^{34}S$ values of H_2S varied from $+0.2$ to $+13.2$‰. Above 2700 m, the differences between the isotopic compositions of H_2S and SO_4^{2-} were rather significant. The authors concluded that this H_2S was generated by bacterial SO_4^{2-} reduction. Below this depth, the isotopic composition of H_2S and SO_4^{2-} were similar. This deeper H_2S was attributed to thermochemical processes.

Bely and Vinogradov (1972) studied H_2S in some deposits of the Amu-Daria syncline associated with Upper Jurassic systems. They attributed the isotopically heavy H_2S ($\delta^{34}S$ values from $+13.4$ to $+18.2$‰) to SO_4^{2-} reduction by organic matter.

Orr (1974) considered H_2S to have several sources:

(a) Microbial reduction of SO_4^{2-}. This is the main source at temperatures below 60 °C.
(b) Thermal decomposition of organic sulphur compounds in oils, bitumens, and kerogen. The rate of this process increases with temperature and H_2S generation may be accompanied by a small isotope selectivity. The quantity and isotopic composition of H_2S thus formed depend on the reduced sulphur which enters the organic matter during deposition and diagenesis.
(c) Non-microbial SO_4^{2-} reduction at temperatures above 80 °C. This may be accompanied by a slight isotopic fractionation.

Two other less likely sources are reaction of pre-existing elemental sulphur with organic matter and volcanic emanation (Orr, 1977).

Maximov *et al.* (1975) differentiated two groups of gases in deposits of the Jurassic system of the Amu-Dariya syncline: (a) gases with low

concentrations of H_2S (0.01–1%) depleted in ^{34}S (−16.0 to −0.7‰) and (b) gases with high concentrations of H_2S (1.0–6.5%) enriched in ^{34}S (+12.5 to +25.0‰, typical of evaporites). Deposits with high concentrations of H_2S are situated at depths from 2500 to 3200 m and temperatures from 95 to 110 °C. This H_2S was attributed to chemical reduction of sulphates. Data for subsequently discovered H_2S deposits in the Amu-Dariya syncline (Belenitskaya *et al.*, 1981) were consistent with the trends reported by Maximov *et al.* (1975).

In the south of the Caspian depression, the Astrakhan gas–condensate deposit is productive in the Middle carboniferous at a depth interval of 4035–4837 m and temperatures above 100 °C. The H_2S content is as high as 25% and the $\delta^{34}S$ values vary from +11 to +13‰. H_2S with similar isotopic composition occurs in the Tengiz (+12.3‰) and Zhanazhol (+11.7‰) deposits situated in the south-east Astrakhan region and on the eastern margin of the Caspian depression respectively (Pankina *et al.*, 1983). In all of these deposits, H_2S is evidently formed by chemical reduction of sulphates.

Krouse (1977) summarized data for H_2S in Devonian strata of Alberta, Canada. The $\delta^{34}S$ values for shallow depths and temperatures below 80 °C varied from +10 to +20.0‰, whereas in deeper horizons and higher temperatures it ranged from +20 to +25‰ (Figure 4.17). He concluded that H_2S in the shallower environments was biogenic, whereas above 80 °C it formed by thermochemical reduction of sulphate. In deep 'sour gas' (H_2S-rich) occurrences in Alberta, the H_2S content may exceed 90% (Figure 8.2). On the basis of carbon isotope data, Krouse *et al.* (1988) concluded that in
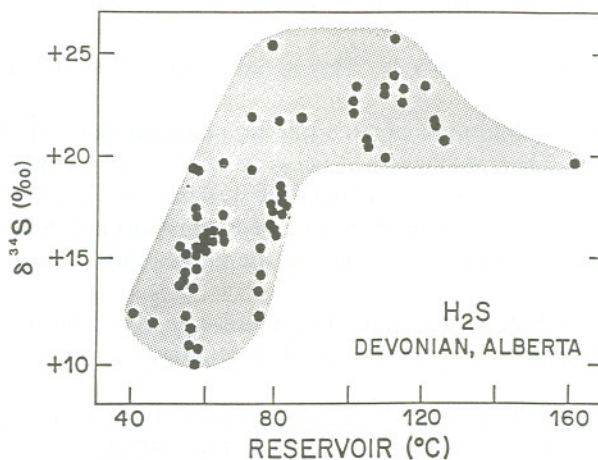
Figure 4.17 Variation of $\delta^{34}S$ values of H_2S with reservoir temperature in Devonian strata of Alberta, Canada (after Krouse, 1977)

some reservoirs in western Canada, H_2S was generated through reduction of sulphate by light hydrocarbon gases.

The $\delta^{34}S$ values of H_2S dissolved in oil and formation water are similar in a given stratum (Figure 4.18).

Free H_2S and H_2S dissolved in underlying formation water usually have similar isotopic compositions. For instance, $\delta^{34}S$ values of H_2S and water were respectively: +4.0 and +4.7‰ in the Orenburg deposit, +12.1 and +12.6‰ in the Astrakhan deposit, and +14.6 and +14.1‰ in the Urtabulak-Dengizkul deposit. Occasionally, wide variations are found for the dissolved species (Table 4.17).

Figure 4.19 shows that the isotopic composition of H_2S in strata of the same age in the same area is highly dependent upon H_2S concentration. Negative and positive $\delta^{34}S$ values were found to be associated with low and
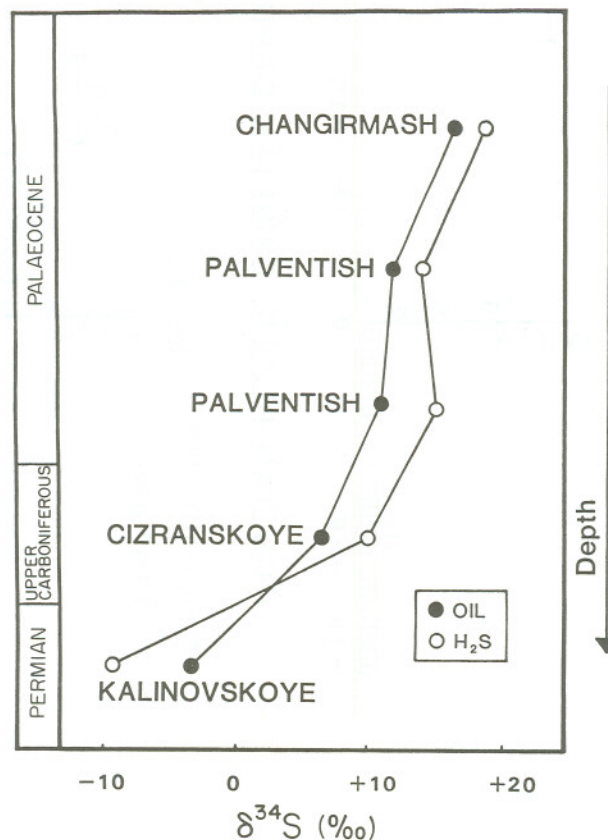
Figure 4.18 Relationship between $\delta^{34}S$ values of H_2S dissolved in oil and water in different regions of the Soviet Union

AMU-DARYA SYNECLISE (J)

Fields of
Bulchara terrace

Fields of
Chardzhou terrace

H_2S(%)

SO_4^{2-}

H_2S

6

4

2

H_2S

−15 −10 −5 0 +5 +10 +15 +20 $\delta^{34}S$,(‰)
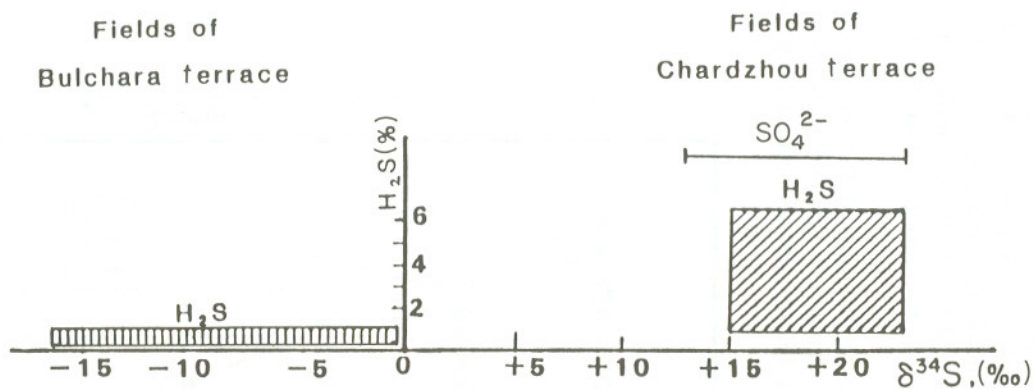
RUSSIAN PLATE, CASPIAN DEPRESSION

Fields of middle
Volga area

$C_2 - P_1$

Orenburg
field

H_2S(%)

SO_4^{2-}

6

H_2S

4

H_2S

2

−15 −10 −5 0 +5 +10 +15 +20 $\delta^{34}S$,(‰)
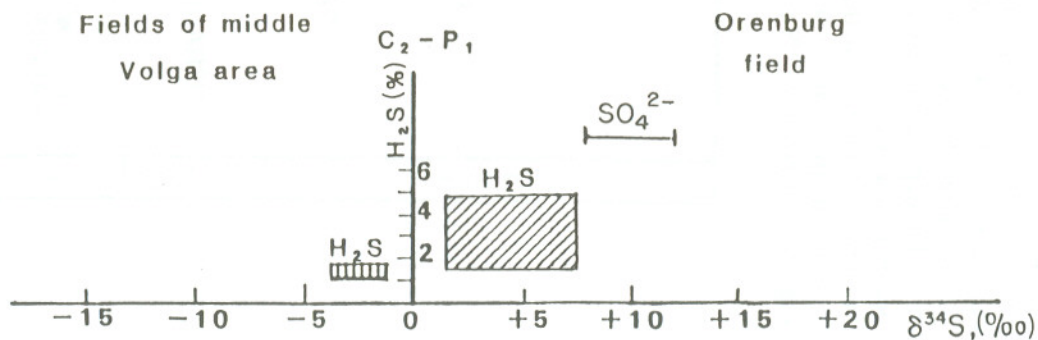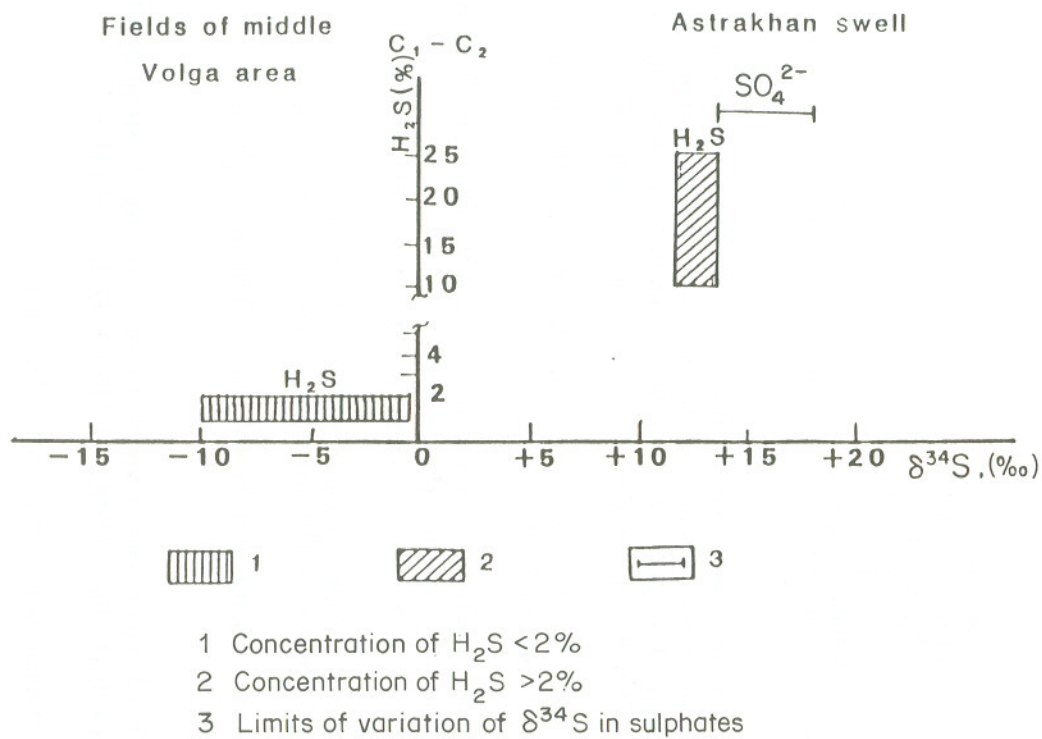
Figure 4.19 Relation of the isotopic composition of H_2S to concentrations in gas accumulations in the Amu-Darya syneclise and the Russian Plate (Pankina and Mekhtiyeva, 1981)

Fields of middle Volga area

$C_1 - C_2$

$H_2S(\%)$

Astrakhan swell

SO_4^{2-}

H_2S

25, 20, 15, 10

4, 2

H_2S

-15 -10 -5 0 $+5$ $+10$ $+15$ $+20$ $\delta^{34}S, (\permil)$

1
2
3

1 Concentration of $H_2S < 2\%$
2 Concentration of $H_2S > 2\%$
3 Limits of variation of $\delta^{34}S$ in sulphates

Table 4.17 Isotopic composition of H_2S dissolved in water (Pankina, 1978)

Age of deposit	Region	Number of determinations	Variations of $\delta^{34}S$ values (‰)	Average $\delta^{34}S$ value (‰)
Paleogene	Middle Asia	11	−11.3 to +18.2	+1.8
Jurassic	Middle Asia and Volga-Urals	12	−17.0 to +4.7	−1.4
Permian	Middle Asia and Volga-Urals	2	−9.8 to −1.9	−5.5
Carboniferous	Middle Asia and Volga-Urals	15	−8.9 to +11.8	+3.0

high concentrations respectively. In the case of the latter, mean values of +13, +5, and +18‰ can be assigned to Carboniferous, Permian, and Jurassic strata. This arises because H_2S generated by thermochemical reduction of evaporites is consistent with the oceanic $\delta^{34}S$–time curve (Figure 4.2).

Estimation of the worldwide average $\delta^{34}S$ value for H_2S in oil- and gasfields must consider the following:

(a) Higher concentrations of H_2S tend to have $\delta^{34}S$ values slightly higher than associated evaporites (Figure 4.19).
(b) The average $\delta^{34}S$ value for evaporites has been estimated at +19‰ (Section 4.2).
(c) H_2S is not uniformly associated with evaporites of all ages.
(d) Minor occurrences of H_2S usually have negative $\delta^{34}S$ values.

It is difficult to quantitatively incorporate all of these factors. A qualitative estimate for the mean value is +15‰.

4.6   FLUX OF VOLCANOGENIC SULPHUR TO THE ATMOSPHERE AND ISOTOPIC COMPOSITION OF TOTAL SULPHUR*

4.6.1 Volcanogenic sulphur flux to the atmosphere

The sulphur flux to the atmosphere from the lithosphere during surface volcanism was estimated at 28 Tg S yr^{-1} (Lein, 1983). This value is higher by one order of magnitude than those published previously (Kellogg *et al.*, 1972; Friend, 1973; Cadle, 1975; Granat *et al.*, 1976). The estimate of Lein

* A. Yu. Lien.

(1983) considered not only eruptions but also gas emissions during fumarolic and solfataric stages. This approach, described by Ivanov (1981), was made possible by direct determinations of sulphur concentrations in fumarole and solfatara gases and their fluxes to atmosphere (Stoiber and Jepsen, 1973; Okita and Shimozuru, 1975; Berlyand, 1975).

As the result of improved instrumentation, many direct determinations of SO_2, H_2S, COS, and SO_3 fluxes to the atmosphere from volcanoes have been recently reported. A review of these data (Tables 4.18 and 4.19) leads to two basic conclusions:

(a) Volcanic activity during the past two decades has appreciably increased. Since 1961, many large and disastrous eruptions were recorded. Up to 13.4×10^5 tonnes of SO_2 were transported to the stratosphere during the eruption of El-Chichon in Mexico (Evans and Kerr, 1983).
(b) Direct determinations of the sulphur flux from more than 40 volcanoes with fumarole-solfatara activity (compared to 11 reported previously) confirmed the previous estimate of the average SO_2 emission from fumaroles of an individual volcano, i.e. 245 tonnes SO_2 day^{-1} (Lein, 1983).

The daily average emission per volcano was estimated at 275 tonnes by Berresheim and Jaeschke (1983). These investigators concluded, as did Lein (1983), that the sulphur flux from unstable gas jets of volcanoes is at least

Table 4.18 Volcanogenic sulphur flux during eruptions

Volcano	SO_2 (tonnes d^{-1})	References
Etna	3740	Haulet *et al.* (1977)
Etna	1000–5000	Malinconico (1979)
Etna	1600	Jaeschke *et al.* (1982)
Cerro Negro	2000	Taylor and Stoiber (1973)
Fuego	10 000	Rose *et al.* (1973)
Fuego	55 000	Crafford (1975); Rose *et al.* (1982)
Santiaguito	1500	Stoiber and Jepsen (1973)
Kilauea	1280	Naughton *et al.* (1975)
St Augustine	86 400	Stith *et al.* (1978)
St Augustine	86 400	Stith *et al.* (1978)
St Helens	60 000	Evans and Kerr (1983); Casadevall *et al.* (1981); Hobbs *et al.* (1981)
Pacaya	1500	Cadle *et al.* (1979)
El-Chichon	1 340 000	Evans and Kerr (1983)
Tolbachik	5888	Abramovsky *et al.* (1977)
Ardukoba	10 000	Allard (1980)

Table 4.19 Sulphur flux to the atmosphere from fumaroles

Volcano	SO$_2$ (tonnes d^{-1})	References
Japan		
Mihara	345	Berresheim and Jaeschke (1983)
Osima	345	Okita and Shimozuru (1975)
Asama	142	Okita and Shimozuru (1975)
Asama	787	Okita and Shimozura (1975)
Guatemala		
Santiaguito	420	Stoiber and Jepsen (1973)
Fuego	40	Stoiber and Jepsen (1973)
Fuego	423	Crafford (1975)
Fuego	393	Rose *et al.* (1982)
Pacaya	260	Stoiber and Jepsen (1973)
Pacaya	300	Stoiber and Bratton (1978)
Nicaragua		
Telika	20	Stoiber and Jepsen (1973)
Momotombo	50	Stoiber and Jepsen (1973)
San-Kristobal	360	Stoiber and Jepsen (1973)
Masaya	180	
USA		
Kilauea	280	Naughton *et al.* (1975)
Kilauea	200	Harding and Miller (1982)
Mauna-Ulu	30	Stoiber and Malone (1975)
Sulphur Banks	7	Stoiber and Malone (1975)
St Augustine	432	Stith *et al.* (1978)
St Augustine	86	Stith *et al.* (1978)
Martin Mountain	3	Casadevall *et al.* (1981)
State Washington	600–3600	Hobbs *et al.* (1981)
Mt St Helens	10–50	Casadevall *et al.* (1981)
Mt St Helens	1000–1900	Hobbs *et al.* (1981)
Mt St Helens	900	Hobbs *et al.* (1981)
Italy		
Etna	3325	Zettwoog and Haulet (1978)
Etna	1130	Zettwoog and Haulet (1978)
Etna	1000	Malinconico (1979)
Etna	142	Jaeschke *et al.* (1982)
Etna	955–1600	Jaeschke *et al.* (1982)
Karymsky	173	Berlyand (1975)

one order of magnitude higher at the fumarolic stage than during eruptions. Proceeding from this conclusion, these authors obtained a total annual flux to the atmosphere of 11.8 Tg S including 7.6 Tg S as SO$_2$ (15.2 Tg SO$_2$ yr^{-1}). Of this amount, 14.2 Tg SO$_2$ are released annually from fumaroles and only 1 Tg SO$_2$ during eruptions.

The value obtained by Berresheim and Jaeschke (1983) is almost three times lower than the current estimate. This can be explained by the different numbers of active volcanoes assumed in the calculations. We considered 578 active volcanoes (Vlodavets, 1966) with average daily emissions of 245 tonnes SO_2 (or 0.092 million tonnes annually) from the fumarolic area of each volcano. Berresheim and Jaeschke considered 520 volcanoes but used only 100, with an average emission of 275 tonnes d^{-1} per volcano. This number seems low since they classified 365 volcanoes as very active. If, from a total of 578 volcanoes, one subtracts 55 that erupt annually and 100 with low daily fumarolic emissions (10–50 tonnes SO_2), 423 remain with individual average emissions of 275 tonnes SO_2 d^{-1}. Their global emission would be 42.8 Tg SO_2 or 21.4 Tg S yr^{-1}, which is close to our estimation.

Therefore, from recent estimates, the flux of volcanic sulphur to the atmosphere varies from 11.8 to 28 Tg S yr^{-1}.

It should be emphasized that:

(a) Not all sulphur compounds such as H_2S, COS, and SO_3 are included since their measurement is difficult (Hobbs *et al.*, 1981).
(b) The sulphur flux during large eruptions may be underestimated by an order of magnitude.
(c) Most data refer to flux to the stratosphere rather than to lower layers of the atmosphere. Therefore, the higher estimate of 28 Tg S yr^{-1} is favoured.

4.6.2 Isotopic composition of volcanogenic sulphur

Sulphur occurs in different valence states in volcanogenic emissions: H_2S and its derivatives, S^O, SO_2, and H_2SO_4 (acid and its salts). Sulphur enters the atmosphere usually in the form of gaseous compounds (SO_2 and to a lesser extent H_2S, SO_3, COS) as well as solid particles which may contain sulphur minerals and absorbed sulphur compounds. The isotopic composition of individual sulphur compounds depends on the stage of volcanogenic activity, type of eruption, temperature, kinetic istope effects and exchange during redox reactions, valence, and contamination of the magmatic source by crustal sulphur. In summary:

(a) At high temperatures and pressure, isotopic equilibrium between some sulphur compounds is established rather quickly. The SO_2 and H_2S are enriched and depleted in ^{34}S respectively, compared to total sulphur.
(b) The differences in isotopic compositions of the various molecules ($\Delta\delta^{34}S$ values) decrease as the temperature increases.
(c) The greater solubility of SO_2 compared to H_2S favours the enrichment of ^{32}S in the gas phase and ^{34}S in the water phase.

4.6.2.1 *Isotopic composition of gases emitted to the atmosphere during eruption*

The chemical and isotopic compositions of evolved gases were measured during a rift eruption (7–14 November 1978) of basalt magma near Ardukoba volcano, Azal rift, Ethiopia (Allard, 1980). Four samples taken immediately above the magma in the eruptive rift at 1070 °C were found to have consistent $\delta^{34}S$ values near $-3‰$. Two samples from lava flows near 800 °C had $\delta^{34}S$ values near $0‰$ whereas a third sample from the same environment was $-4.8‰$.

The $\delta^{34}S$ value of the total sulphur in gases (mainly SO_2), evolved from basalt lavas in two eruptions of the Kiluaea volcano (1971 and 1974), varied from $+0.3$ to $+5.4‰$, averaging $+0.9‰$. These values approximate those of total sulphur entrapped in the basalt (Sakai *et al.*, 1982).

Degassing is peculiar to subaereal basalt eruptions (Moore and Fabbi, 1971; Sakai *et al.* 1982). Assuming that the primary basalt magma contained 1100 ppm sulphur, then a sulphur concentration of 150 ppm after degassing means that nearly 90% of the total sulphur was removed from the magma as SO_2.

The sulphur flux to the atmosphere from the eruption of Ardukova is calculated from the portion of sulphur released (950 ppm) and the amount of basalt discharge (43×10^6 tonnes). This corresponds to 1.1×10^4 tonnes SO_2 d^{-1}. This is higher than the average value of SO_2 flux to the atmosphere from Mount Etna (cf. Haulet *et al.*, 1977; Malinconico, 1979).

Therefore, at rift discharges of basalt magmas, nearly 6×10^3 tonnes of sulphur may enter the atmosphere per day, the $\delta^{34}S$ value being close to that of meteoritic sulphur.

4.6.2.2 *Isotopic composition of ash emitted to the atmosphere during eruptions*

Volcanic eruptions are accompanied as a rule by the discharge of ash to the atmosphere. The volume and the height of the rise of this material depend on the type and scale of the eruption (Table 4.20).

The sulphur isotopic compositions of mineral particles in ash emitted with gases and thermal waters during the eruption of Ontake (Japan) on 8 October 1979 were studied by Kusakabe *et al.* (1982). Ontake is a Quaternary andesite stratovolcano in the central parot of Honshu Island, similar to andesite volcanoes of Kamchatka and Kuril Islands. It was a weak eruption ($t = 110–185$ °C) lasting less than a day. The volcanic dust sampled soon after the eruption contained pyrite, anhydrite, and elemental sulphur. The $\delta^{34}S$ values of pyrite and native sulphur varied from -1.8 to $-6.4‰$, the average value for 18 samples being $-4.8‰$. The $\delta^{34}S$ values of anhydrite

Table 4.20 Classification of volcanic activity (Berresheim and Jaeschke, 1983)

Type	Explosive index[a]	Composition[b]	Rise (km)	SO$_2$ (tonnes d^{-1})	Frequency of activity per year[c]
A−1 Iceland	0–5	a, ab	1	10^3	
A−2 Hawaiian	0–5	a	1	10^3	10.46
A−3 Strambolian	5–20	ab	Max. 2	300–10^3	760.00
A−4 Vulcanian	20–40	ab, b	2–7	10^4	9.40
A−5 Vexuvian	40–60	ab, b	5–10	7 × 10^4	4.13
A−6 Plinian	60–80	b, bc	10–20	1–2 × 10^5	0.53
A−7 Pelean	80–99	b, bc	20–40	1–2 × 10^5	0.12
A−8 Krakatao	99–100	b, bc	40		

[a] Explosive index = mass of solid material/total mass of solid and liquid material (Rittmann, 1981).
[b] Composition of products: a—dominance of lava; b—prevalence of fresh solid material; c—dominance of ancient volcanic rocks.
[c] Average number of erupting volcanoes 55 per year; data for the period from 1961 to 1979.

fell within the range +8.3 to +14‰, the average being +10.8‰ (seven samples).

Soluble sulphate on the surface and total S extracted with Kiba reagent from ash emitted by the explosion of Mt St Helens, Washington, USA, on 18 May 1980 were found to have δ^{34}S values near +9‰ (H.R. Krouse, unpublished data). This suggests that the surface sulphate resulted from high-temperature oxidation of sulphur-containing minerals in the ash.

The above data, based on fresh samples, suggest that the δ^{34}S values of the total sulphur in volcanic ash discharges tends to be positive. Positive δ^{34}S values could arise if the sulphur is magmatic (near 0‰) and the heavier isotopes are favoured in the condensed phases. However, the sulphur may have other than a magmatic origin. In the case of Mt St Helens, the northern flank was blown away to the extent of 4 km^3 and a decrease in elevation of 600 m. Therefore during an explosive eruption, a variety of geological strata with different δ^{34}S values might be pulverized.

4.6.2.3 *The sulphur isotope composition of gaseous emissions from fumaroles and solfataras*

It is well known that the concentration and isotopic composition of sulphur in fumaroles (t = 200–1000 °C) and solfataras (t = 100–200 °C) are rather variable and depend primarily on the state of the volcanic system in which they are found.

Table 4.21 contains the phenomenological classification of non-eruptive volcano activities and their duration. Evidently, an important contribution of sulphur to the atmospheric budget might be expected only from the last two categories including fumarolic and solfatara activity over the time scales of months to centuries.

The isotopic composition of high-temperature fumarolic gases approximates the meteorite value (Nakai and Jensen, 1967; Grinenko and Grinenko, 1974). Recently, data were reported for long-term observations of the chemical and isotopic compositions of high-temperature gases emitted from the hottest fumarole, A–1,in Showashinzan volcano on Hokkaido (Mizutani and Sugiura, 1982). The $\delta^{34}S_{tot}$ was +2‰ whereas the isotopic composition of SO_2 varied within the range +0.3 to +5.6‰ (Table 4.22). The above authors suggested that temporal changes were caused by increased infiltration of surface waters and atmospheric gases, as well as shifts in chemical reactions with decreased temperature and pressure.

In a complex geochemical study of fumarolic gases from volcanoes of the Satsuma Iwo-Jima group (Matsubaya *et al.*, 1975), $\delta^{34}S$ values for H_2S were found to vary within the range +8.9 to +11.2‰ (Table 4.22). This was explained by fractionation of isotopes during chemical reactions in gas jets.

The above data show that $\delta^{34}S$ values for all sulphur compounds studied in high-temperature gases (600–850 °C) fall within the range −13 to +12‰ with an average of +5.6‰.

It is generally accepted that sulphur compounds in moderate- and low-temperature fumarole and solfataras gases have a more diverse isotopic

Table 4.21 Classification of volcanic activity between eruptions (Berresheim and Jaeschke, 1983)

Stage	Duration	Type	SO_2 (tonnes d^{-1})	Number of volcanoes
B−1 Preeruptive	Days–weeks	Rhythmical gas evolutions before eruption	600–10^3	55
B−2 Intraeruptive	Hours–days	Gas evolutions between paroxysmal eruptions	500–10^3	
B−3 Posteruptive	Weeks–years	Fumarole activity	50–500	365
B−4 Extraeruptive	Years–centuries	Fumarole activity and solfatar	10–50	100

Table 4.22 Isotopic composition of sulphur compounds in gases of high-temperature fumaroles

Volcano	Date of sampling (Reference[a])	Temperature of gas (°C)	$\delta^{34}S$ (‰)		
			H$_2$S	SO$_2$	Sulphur
Showashinzan, A−1	(1)	800		−4.8	—
	(2)	661		−1.8	—
		559		+0.4	—
		483	−8.0	−1.3	—
	8.1960 (3)	722	—	+4.4	+4.4
	8.1961 (3)	703	—	+0.3	+0.3
	8.1962 (3)	635	−1.7	+1.8	+1.4
	10.1973 (3)	600	—	+5.2	—
	9.1974 (3)	588	—	+5.0	—
	8.1977 (3)	642	−11.0	+5.6	+1.9
	11.1977 (3)	617	—	+4.8	—
	10.1978 (3)	554	—	+3.9	—
Showashinzan, B−5	(3)	446	+4.4	+9.3	+4.6
Showashinzan, C−2	(3)	605	+5.1	+7.1	+6.8
Showashinzan, A−6	(3)	695	—	+5.5	+5.5
Nasudake, M−1	(3)	489	−0.7	+4.4	+1.9
Satsuma, Iwo-Jima	8.1974 (4)	835	+9.9	+11.6	+12.1
	8.1974 (4)	751	+11.2	+11.7	+12.1
	9.1974 (4)	732	+8.9	+12.2	+12.2
	9.1974 (4)	751	+9.3	+11.8	+11.5
Bezymyanny	1967 (5)	700	+1.4	+12.2	—
Avachinsky	(5)	—	−0.9	+8.3	—
Mutnovsky	(5)	480	−12.7	+3.7	—
Kuyu	Ku−5 (3)	500	+7.3	+10.6	+6.9

[a] (1) Sakai (1957). (2) Sakai and Nagasawa (1958). Mizutani and Sugiura (1982). (4) Matsubaya *et al.* (1975). (5) Vinogradov (1980).

composition than in high-temperature cases (compare Figure 4.20 and Table 4.22). Enrichments in ^{34}S, up to +20‰, are observed for sulphate sulphur from some solfataras and volcanic thermal springs. The reasons for such enrichments are unclear but might be explained by chemical reactions (Sakai, 1957; Rafter *et al.*, 1958; Grinenko and Lein, 1967; Taylor and Stoiber, 1973; Grinenko and Grinenko, 1974) and in certain cases (Mendeleev volcano, Kunashir Island; Cape Reykjanís, Iceland) by the involvement of isotopically heavy seawater sulphates (Vinogradov, 1964, 1966, 1970; Hubberten *et al.*, 1975; Sakai and Matsubaya, 1977).
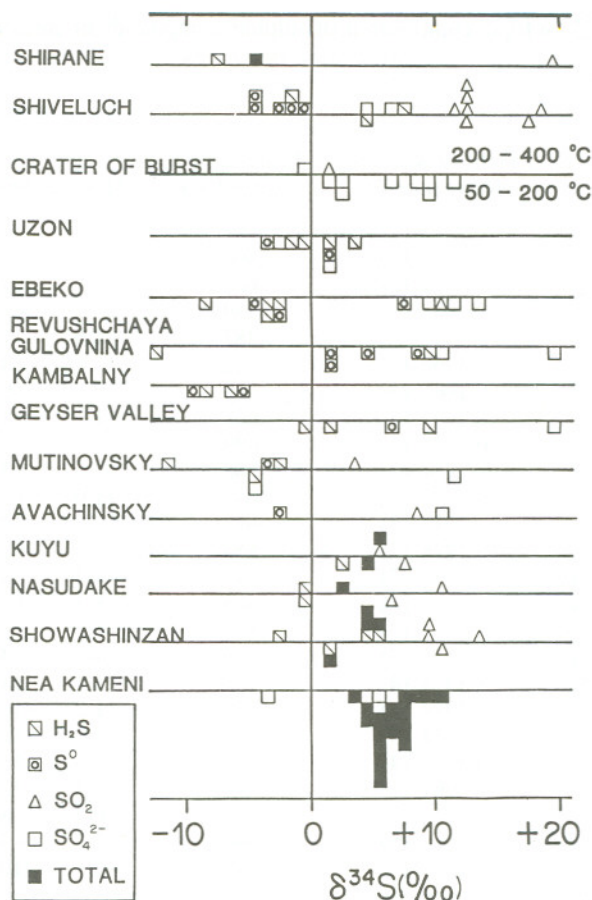
Figure 4.20 Sulphur isotope composition of different compounds in medium (200–400 °C; data above line) and low (50–200 °C; data below line) temperature fumaroles and solfataras

4.6.3 The isotopic composition of total volcanic sulphur entering the atmosphere

Numerous attempts were made to calculate average $\delta^{34}S$ values for volcanic sulphur. Using data from six fumaroles in the White Island volcano, Rafter *et al.* (1958) obtained an average of +2.5‰. A similar value, +2.2‰, was obtained by Borisov (1970) who applied statistical mathematics to 267 isotopic analyses of various sulphur compounds. When these data are combined with those for gases emitted from basaltic magma (Allard, 1980; Sakai *et al.*, 1982), it would appear the total volcanic sulphur to the atmosphere during eruptions has a $\delta^{34}S$ value near zero.

Table 4.23 Sulphur isotope balance for volcanic emissions

Activity	Total S (10^6 tonnes yr^{-1})	$\delta^{34}S$ (‰)
Eruptions	1.45	0
Fumarole activity	26.6	+5
Ash	?	+10
Total	28	+5

The quantity of sulphur entering the atmosphere annually during eruptions is 1.45 Tg S (Lein, 1983). To this should be added 26.6 Tg S yr^{-1} emitted from fumaroles and solfataras with an isotopic composition equal to +5‰ (Table 4.23).

The quantity of ash sulphur reaching the troposphere is difficult to estimate. During more intensive eruptions (e.g. Plinian, Pelean, Krakatoa), huge incandescent clouds of ash were discharged. One can affirm only that the basic forms were oxidized sulphur compounds. The amount of ash released from El-Chichon, Mexico, in March–April 1982 was comparable to the Krakatoa eruption in 1884. On the basis of few measurements, surface secondary sulphate minerals were found to have a $\delta^{34}S$ of about +10‰.

In summary, the total volcanic sulphur entering the atmosphere is enriched in ^{34}S compared to the meteorite value, with an average of $\delta^{34}S$ value of about +5‰.

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