Isotopic composition of the major contributors to atmospheric sulfur

By H. NIELSEN, *Geochemisches Institut, Isotopenlabor, Göttingen*

ABSTRACT

Only a few S isotope data from atmospheric precipitates are available. These results demonstrate the possibility to discriminate between sulfur burdens from different natural and/or anthropogenic sources. The δ^{34}S patterns of the major suppliers of atmospheric sulfur are discussed. Their δ ranges overlap so completely that we cannot use S isotope data of atmospheric samples to calculate the net contribution rates from the individual sources at a global scale. For selected areas, however, such conclusions can frequently be drawn. The most reliable results are to be expected from areas with only two (at maximum three) major sulfur suppliers with well known S isotopic composition and large δ difference between the individual sources. Limitations are given mainly by the complex origin of atmospheric sulfur from a variety of different sources (especially in highly industrial regions) and by the broad δ ranges even in relatively "uniform" suppliers. Furthermore the fate of the sulfur compounds after emission to atmosphere may be quite complex. Additional fractionation processes efface the "fingerprint" character of the S isotope composition. In some cases these difficulties may be overcome, when the S isotope values are correlated with other geochemical data.

Preface

The various papers of this issue dealing with atmospheric sulfur compounds give an idea of the complexity of the atmospheric sulfur cycle. Methods are warranted that enable a clear discrimination between sulfur burdens coming from the different natural and anthropogenous sources, and some preliminary sulfur isotopic investigations are claimed to play this role. The present paper gives a critical review of the possibilities and limitations of this method.

Tracing back atmospheric sulfur to its terrestrial or marine sources is possible only from a detailed knowledge of the S isotopic composition of the source materials in question. A large amount of data already exists for this purpose, but the information is so widely dispersed in literature that a main purpose of the present article must be to summarize our knowledge of the S isotopic distribution patterns of typical source materials and of the isotope fractionation effects encountered in the mechanisms of sulfur transfer to atmosphere.

Fundamentals of S isotope fractionation

Sulfur has 4 stable isotopes with mass numbers 32, 33, 34, and 36. In stable S isotope work the abundance ratio between the two main isotopes ^{34}S and ^{32}S is determined, and published values generally are given in the "delta notation"

$$\delta^{34}\text{S}(\%_0) = \frac{R_{\text{spl}} - R_m}{R_m} \times 1\,000 \qquad (1)$$

where R means the abundance ratio ^{34}S/^{32}S. Spl stands for unknown sample and m for the troilite sulfur of iron meteorites, the isotope ratio of which is thought to be similar to that of mean terrestrial sulfur.

Isotope fractionation comes from small differences in the behaviour of the isotopic species due to their mass difference. Physical fractionation processes (diffusion, evaporation) are of no account in sulfur isotope geochemistry, and most of the extended natural variation in S isotopic composition comes from differences in chemical reaction rates. These differences
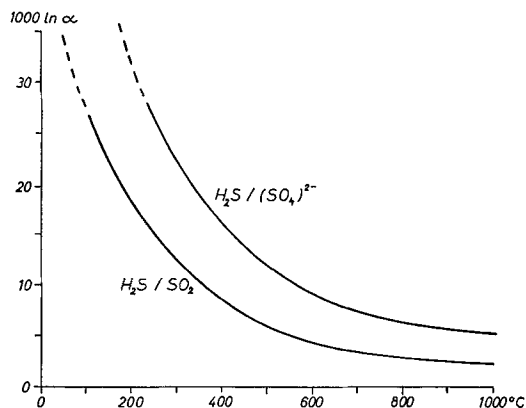
Fig. 1. Sulfur isotope fractionation in the equilibrium isotope exchange systems H_2S–SO_2 and H_2S–$(SO_4)^{2-}$ after Sakai (1957).

Fig. 2. $\delta^{34}S$ histogram of volcanic sulfur from different parts of the world (204 samples; dotted area = samples from Santorini volcano) after Puchelt et al. (1971) compared with the $\delta^{34}S$ variation in other terrestrial sulfur compounds (dashed line ≈ 10 000 data from the Göttingen lab.).

result from different levels of vibrational energy (zero point energy), and large isotope effects are especially involved in bond breaking reactions. In the case of "wet" chemical sulfate reduction

$$^{32}SO_4{}^{2-} \xrightarrow{\ k_1\ } {}^{32}S^{2-}$$
$$^{34}SO_4{}^{2-} \xrightarrow{\ k_2\ } {}^{34}S^{2-} \tag{2}$$
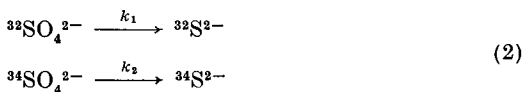
the ratio of the over-all reaction constants k_1/k_2 is about 1.025 at earth surface temperatures.

In the low temperature range, sulfate can only be reduced either by very strong reducers, which are not available in natural environments, or by enzymatic reactions in the cells of microorganisms. This bacterial sulfate reduction shall be discussed later.

Inorganic reduction of oxidized sulfur species under natural conditions, therefore, works only at elevated temperatures, and in general this means at deeper levels of the earth's crust. There the reactions mostly do not go to completeness, and lead to chemical and isotopic equilibria.

In the case of co-existing H_2S and SO_2 in a volcanic vent, for instance, this equilibrium can be described by the bulk reaction equation:

$$^{32}SO_2 + {}^{34}H_2S \rightleftharpoons {}^{34}SO_2 + {}^{32}H_2S \tag{3}$$
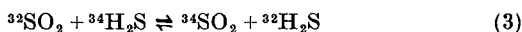
The thick arrow indicates that "heavy" sulfur favourably enters the SO_2 (or generally spoken the stronger bonded molecule). The fractionation in the above equilibrium system can be
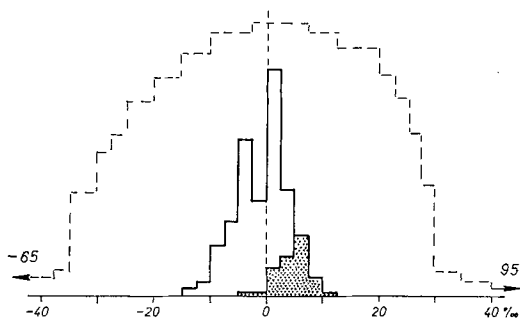
given by the fractionation factor α

$$\alpha = \frac{R_{SO_2}}{R_{H_2S}} \tag{4}$$

For natural processes α differs from unity only in the permil or percent range, and therefore it is more convenient to give one of the following values, which in the above case are almost identical with each other:

$$1\,000(\alpha - 1) \approx 1\,000 \ln \alpha \approx \delta_{SO_2} - \delta_{H_2S} \tag{5}$$

As is shown in Fig. 1 the fractionation effect is strongly temperature dependent and can thus be used to establish an "isotope thermometer". Theoretically at normal surface temperatures the δ difference between H_2S and SO_2 due to this mechanism should exceed 40‰, but below 100°C the reaction rates are too low to achieve equilibrium conditions. The fractionation in volcanic vents therefore does not exceed 25‰, corresponding to an exit temperature of 100°C (Sakai & Nagasawa, 1958). Normally the δ differences to be expected from natural inorganic fractionation processes are within this 25‰ range.

Importance of bacterial sulfate reduction

Fig. 2 compares the typical $\delta^{34}S$ range resulting from inorganic processes with the δ spread observed in natural samples. The total range covers about 160 ‰, but the majority of all samples lies within a δ range of about 50‰.

This is still twice as large as the range to be expected from inorganic processes only. We have strong evidence, that this large variation in S isotopic composition is due mainly to the activity of a distinct group of micro-organisms, mainly strains of **Desulfovibrio desulfuricans** (see paper by Schlegel, page 11 of this issue). Their common feature is to live in anaerobic environments and to feed their oxygen supply by enzymatic reduction of dissolved sulfate.

In principle, the reduction mechanism follows eq. (2), but special conditions, which are not completely understood, may lead to a partial isotope exchange between not-yet-reduced sulfate-enzyme complex and not-yet-escaped H_2S within the cell. Therefore the over-all depletion in ^{34}S (or decrease in $\delta^{34}S$) of the bacterially produced H_2S with respect to the co-existing sulfate varies from about 20 to 55‰.

Furthermore the mode of sulfate supply has a strong influence on the local S isotope budget, and with respect to these conditions we have to distinguish between different model environments:

(a) The simplest model case is achieved in a body of stagnant deep water, which has become anoxic due to insufficient vertical mixing (thermal or salinity stratification). At the first moment sulfate reducer communities grow rapidly, but H_2S can be produced only until the environment becomes poisoned. Typical examples are the Black Sea and local oceanic depths. In all these cases the H_2S is extremely depleted in ^{34}S (in the Black Sea for instance by $\approx 55\%$), while the sulfate consumption and its change in $\delta^{34}S$ remains negligible.

(b) When the H_2S is continually extracted from the system—for instance by bubbling out or by precipitation of iron and other metal sulfides—the bacteria continue to reduce sulfate until no more food or sulfate remains available. In this case the extraction of preferably the light sulfur isotope from the sulfate reservoir changes drastically the observed δ patterns: the $\delta^{34}S$ of the residual sulfate increases with decreasing sulfate concentration, and consequently the H_2S produced at a later stage of bacterial activity also exhibits higher δ values.

As far as the ratio k_1/k_2 of the reduction in eq. (2) roughly remains constant—this fits for a broad range of sulfate concentrations—the change in $\delta^{34}S$ of residual sulfate and of actu-
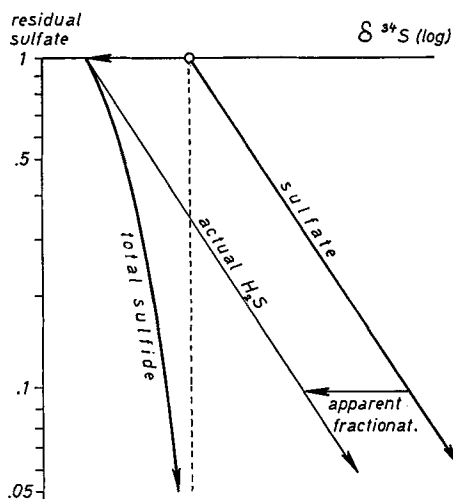

Fig. 3. $\delta^{34}S$ variation in sulfate and sulfide due to sulfate reduction in "closed system" with respect to sulfate supply.

ally produced H_2S with decreasing sulfate concentration follows the curves in Fig. 3. These curves can be calculated from the Rayleigh distillation equation and have been proved directly by laboratory experiments and by measurements on natural samples.

The curves indicate that we can expect extremely heavy residual sulfate in the final stage of bacterial activity in a "closed system" environment. Furthermore, sulfides immediately precipitated from the produced H_2S must exhibit a large δ spread, even from one mineral grain to the next.

On the other hand, lacking supply of metal ions enables the H_2S to migrate to geological "traps" where it is accumulated together with gas or petroleum. Crude gas in some deposits contains 10 or more volume % of H_2S. The H_2S may also weakly be oxidized to native sulfur, and the world's largest sulfur deposits with up to some million tons of elemental sulfur each have been formed in this manner (Sicily, Gulf Coast area etc.). Furthermore freshly produced elemental sulfur and thio-compounds are able to react with petroleum constituents and may thus increase the sulfur contents of the oils by orders of magnitude above the "primary" level. In contrast to immediately precipitated sulfides, this reduced sulfur has become homogenized during migration, and with sulfate consumption in the source region
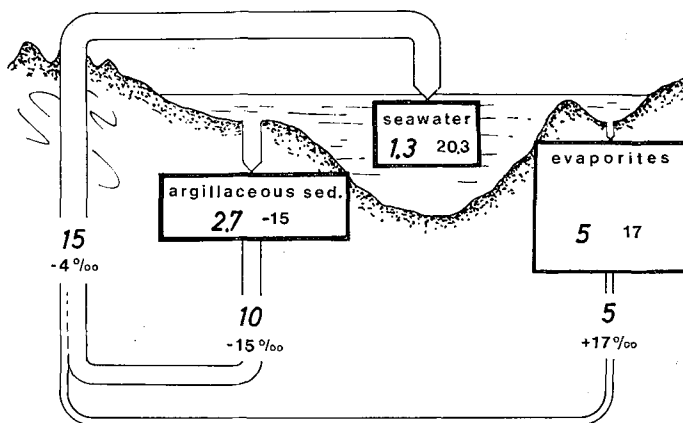
Fig. 4. The exogenous sulfur cycle. Values in italics = sulfur amount of the reservoirs in 10^{15} metric tons or transfer rates in 10^{12} metric tons/yr other values = $\delta^{34}S$ (from Nielsen, 1972).

its $\delta^{34}S$ value follows the curve of "total H_2S" in Fig. 3. When the supply of organic matter exceeds that of sulfate, the reduction will go to completeness, and the sulfide δ then approaches the starting δ value of the sulfate. This is, however, an exception and typical δ values within reservoirs of H_2S, elemental sulfur or petroleums are expected to range about 15‰ below the value of the sulfate source.

(c) The most effective environment for bacterial sulfate reduction is freshly precipitating ooze. It is characterized by an initial period of largely free supply of dissolved sulfate from the overlying water and by a sufficient amount of iron to precipitate the H_2S immediately. During an early period of sediment formation therefore high amounts of biogenic sulfide can be accumulated. If compared with other marine sediments the S concentration may be higher by an order of magnitude while the $\delta^{34}S$ values may be up to 55‰ lower.

The mechanism which accumulates isotopically light sulfides in argillaceous sediments is active since the beginning of life and has thus divided up the sulfur of the "exogenous cycle" into a "light" fraction of sedimental sulfides and a "heavy" sulfate fraction, the latter being partly dissolved in the present oceans and partly precipitated as gypsum and anhydrite in evaporite beds. A simplified model of this sulfur cycle is shown in Fig. 4. The figures written in italics give the total S contents of each reservoir in 10^{15} metric tons and the an-

nual transfer rates in 10^6 tons while the other figures give the δ or mean δ values.

The exogenous sulfur cycle has never been in steady state conditions and therefore the S contents and δ values within the individual reservoirs have varied significantly during the geological past. Modern sea water sulfate has a $\delta^{34}S \approx +20‰$, and for the last 400 million years the record of evaporite sulfates of marine origin indicates a total variation of marine $\delta^{34}S$ between a minimum of about $+10$ and a maximum of about $+30‰$ (for detailed references see Nielsen, 1972). If we consider marine and evaporite sulfates to be the only important sulfate sources for bacterial H_2S production and if we take into account a mean ^{34}S depletion of 15‰ the δ of the reduced species should range from -5 to $+15‰$ with a most probable value close to $+5‰$.

$\delta^{34}S$ distribution of natural contributors to atmospheric sulfur

Under the following captions (a) through (e) the S isotopic composition of sulfur brought to atmosphere from the major natural sources is briefly discussed. The δ patterns are shown in the upper part of Fig. 8. The net contribution rates of the individual suppliers are only poorly known. For example some of the values given by Friend are only half as large as those published by Eriksson, 1963. At a rough rank order the importance of the individual contrib-

utors to the global atmospheric sulfur budget increases from (a) to (e), but locally conditions may be completely different.

(a) *Volcanic exhalations.* Most of the sulfur now present on earth surface originates in the outgassing of deep crustal or mantle regions, but the actual contribution of volcanic sources to the atmospheric sulfur content is as low as 2 per cent. Fig. 2 gives the typical δ range of sulfur from gentle exhalations. Direct information about the S isotopic distribution in catastrophic eruptions is not available, but it appears reasonable to expect values in the same range. The investigations of Castleman et al. (p. 222 of this issue) demonstrate the complex fate of the sulfur brought to stratospheric levels by such events.

(b) *H_2S from anoxic depths in the ocean.* As has been pointed out above, this H_2S is extremely "light". Its transfer to atmosphere is possible only under special conditions, for instance when deeper water masses are stirred by heavy storms. Large amounts of H_2S, for instance, are delivered off the coast of South West Africa when the normal upwelling of the Benguela Stream is restored after a period of suppressed circulation.

(c) *H_2S from sea marshes and intertidal flats.* Generally the H_2S produced in recent sediments is isotopically "light". The contribution from these sources, however, must not be overestimated because coverage by one meter of aerated sea water is sufficient to oxidize ascending H_2S quantitatively (Östlund, 1962). Therefore H_2S can be brought to atmosphere only from intertidal flats by the squeezing effect of the ascending flood or when the uppermost sediment layers are stirred by heavy storms.

(d) *Sea spray.* In maritime regions sulfate from sea spray is a major constituent of atmospheric aerosols. No major isotope fractionation is involved in the bubble spray mechanism (Luecke & Nielsen, 1972) and therefore sea spray sulfate has a rather uniform $\delta^{34}S$ of $\approx +20‰$.

Little is known about sulfur-containing organic substances in the oceanic surface film and in the spray droplets. As far as these substances originate directly in decomposed biological material, their $\delta^{34}S$ should not differ too much from the sea water value of $+20‰$, but "secondary" compounds from the H_2S production zone might have low δ values. Per-

haps sulfur-organic molecules are a vehicle to bring up reduced sulfur to atmosphere through the oxidizing barrier of the aerated sea water.

(e) *Biogenic volatile S compounds in continental areas.* Continental rocks generally are poor in sulfur, and therefore the uptake of sulfur into the biological cycle is much more economized than in the ocean. On the other hand gaseous sulfur compounds, once formed, will easily escape to atmosphere.

The primary sulfur source for continental organisms is dissolved sulfate, and if we exclude the addition of fertilizers, this sulfate comes either from rain water or from ground water, that means from oxidized sedimental or igneous sulfides or from leached evaporites. The $\delta^{34}S$ values of these source materials vary over the whole δ scale, but we can expect that the dissolved sulfate is well homogenized and that its δ ranges close to zero. This must also be assumed for the sulfur compounds delivered to atmosphere, because no major isotope fractionation is involved in the uptake of sulfur to plant material. Furthermore the sulfate supply for bacterial H_2S production is generally so low that the bacteria work under "closed system" conditions.

$\delta^{34}S$ distribution of anthropogenic sulfur in the atmosphere

Sulfur and its compounds, for instance sulfuric acid, belong to the most important raw materials and reagents in chemical industry and other technical branches. The yearly production of sulfur and sulfur compounds has exceeded 10 million tons of elemental sulfur, and a substantial fraction of this sulfur is released to atmosphere in the course of production and utilization. Nevertheless this contribution to atmospheric pollution is much smaller than the amount coming from combustion of fossil fuels in spite of the fact that sulfur is present in oils and coals only as an impurity in the permil or percent concentration range. The δ distribution patterns of the different source materials of anthropogenic sulfur pollution are discussed under the captions (f) through (i), and a summarizing graph for all sulfur contributors is given in Fig. 8.

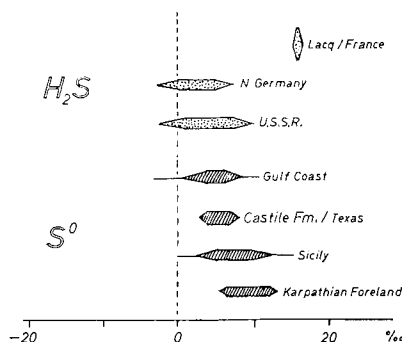(f) *Native sulfur and H_2S.* Native sulfur has been mined in Sicily for more than 2 000 years.

Fig. 5. $\delta^{34}S$ distribution in typical natural H_2S reservoirs and in deposits of native sulfur.

During the last century much larger resources have been discovered in the Gulf Coast area and in other parts of the world. Annual production capacities range up to a million tons for individual mining districts.

In recent years the H_2S contents of some crude gas deposits have become powerful competitors to the "classical" sulfur producers. Production rates up to a million tons of elemental sulfur per year, for instance, are reported for the gas deposit of Lacq in southern France.

H_2S reservoirs and deposits of native sulfur have very similar genetical histories, and therefore the $\delta^{34}S$ patterns are comparable with each other, as is shown in Fig. 5.

(g) "Kies" and other sulfide ore deposits. Most of the sulfuric acid production comes from sulfide roasting in smelters; that means the sulfides are oxidized at controlled access of air and the SO_2 evolved from this procedure is
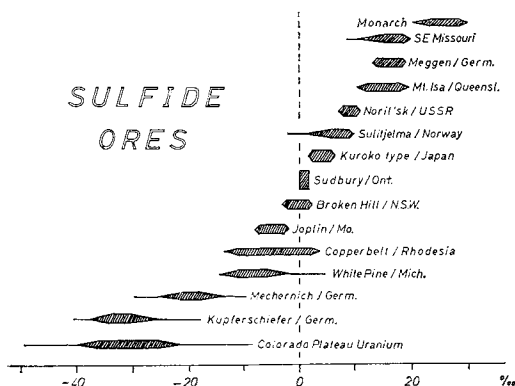

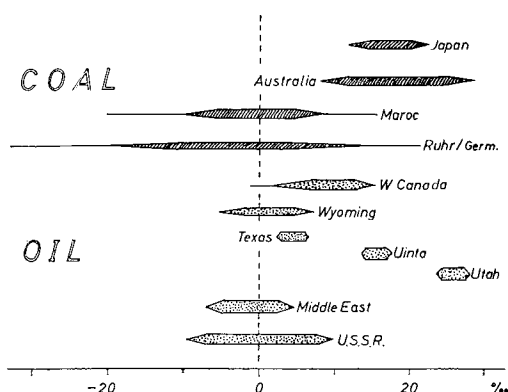Fig. 6. $\delta^{34}S$ distribution in typical sulfide ores.

Fig. 7. $\delta^{34}S$ distribution in coals and crude oils.

catalytically oxidized to SO_3. A lot of SO_2 leaves the smelter chimneys and helps to bring up the local atmospheric sulfur level.

Sulfide ore deposits have been formed in quite different ways and thus differ greatly in their S isotope distribution patterns, as is shown in Fig. 6.

The Kupferschiefer ores, for instance, are deposited from an anoxic environment by bacterial activity. Their δ range therefore is comparable to that of normal marine sediments. Deposits associated with large basic intrusions, such as the Sudbury Ni ores have δ values close to zero. The largest sulfide deposits are those belonging to the so-called "stratiform" and "Kies" type—for instance Mt. Isa and Broken Hill in Australia, Sulitjelma in Norway, Meggen and Rammelsberg in Germany, the Kuroko ores of Japan and many others. The sulfur of these deposits is thought to come from reduction of marine sulfate at depth with (partial) isotope exchange equilibration. Due to this mechanism the sulfide δ's lie in the range about 15‰ below the contemporaneous sea water—that means in the range from ≈ -5 to $+15$‰ with a most probable value close to $+5$‰.

Smelter exhausts or products manufactured with sulfuric acid may thus vary in $\delta^{34}S$ much more than all the other contributors to atmospheric pollution, but in general the sulfur from a single mining area is rather homogenous in its S isotope composition.

(h) Fossil coals. Coals originate in plants of continental or swamp areas. Most of the sulfur contents comes from pyrite inclusions, and the
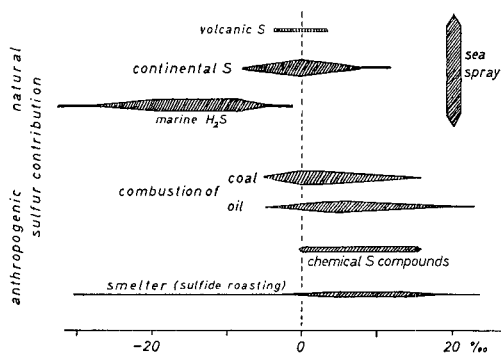
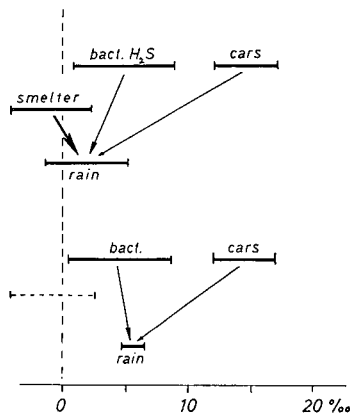Fig. 8. Synopsis of $\delta^{34}S$ distribution in the major source materials of atmospheric sulfur.

Fig. 9. S isotopic composition in rain water in the Salt Lake area with and without contribution from copper smelter after Grey & Jensen (1972).

δ ranges in coals of different ages and origins vary greatly, as is demonstrated in the upper section of Fig. 7. Nakai & Jensen (1967) have shown that during coal combustion at normal combustion temperatures the pyrite is oxidized partly to isotopically heavy sulfate, which remains in the ash, and partly to "light" sulfur dioxide. The SO_2 escaping to atmosphere therefore is depleted in ^{34}S with respect to the source material by $\approx 5\%_0$.

(*f*) *Petroleum and gasoline.* It has already been mentioned that oils frequently exhibit $\delta^{34}S$ values about 15‰ below the correlated sulfate values. In many cases oils from a given source rock are so uniform in $\delta^{34}S$ that in case of doubt the value can serve as a "fingerprint" to check the origin. The lower section of Fig. 7 gives the δ ranges for some typical crude oils, and as far as gasoline comes from uniform source materials it will have the same δ value.

Practical applications

Fig. 8 summarizes the $\delta^{34}S$ ranges for the major contributors to atmospheric sulfur. This synopsis is helpful to make up model calculations for the S isotopic composition of precipitates, due to varying rates of sulfur supply from the different contributors. Furthermore such calculations give a realistic insight into the possibility of discrimination between individual sulfur suppliers.

If only natural sources are considered, we should expect characteristic δ distribution patterns for continental, maritime and transitional areas. The $\delta^{34}S$ values of precipitates in

continental areas should show a clear grouping around zero with only minor variations due to wind direction and seasonal influence. Sulfate in oceanic areas far from the continental margins, on the other hand, should exhibit the unaffected sea spray value of $+20\%_0$. Precipitates in coastal areas should be highly variable in their $\delta^{34}S$ values, due to varying contribution from different sources.

The sulfur brought to atmosphere by human activities generally covers the same δ range. In contrast to natural suppliers the "source area" is often rather narrow and well defined—for instance an urban area or an industrial plant—and in some cases it is possible to determine the $\delta^{34}S$ of the major sulfur output directly. Under such favourable conditions highly reliable conclusions on the net contribution of the individual suppliers can be drawn.

This is demonstrated in a pretty example from the Salt Lake region, published by Grey & Jensen (1972). In the area of investigation atmospheric sulfur was expected to come from automobile exhaust in the urban area of Salt Lake City, from biological H_2S production at the margins of Salt Lake and from the plume of a large copper smelter. During the investigation an extended strike brought the smelter to a standstill and thus enabled to determine the atmospheric sulfur concentrations and δ values with and without the smelter exhaust. The results are graphically shown in Fig. 9.
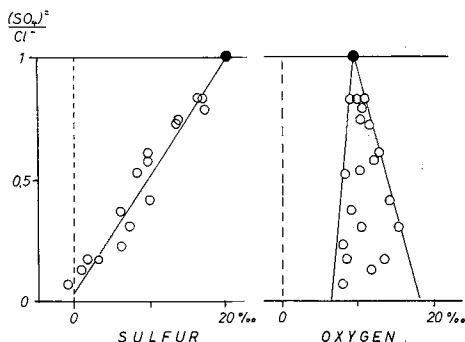
In most other areas the premises are much

Fig. 10. Variation of $\delta^{34}S$ and $\delta^{18}O$ of sulfate with sulfate/chloride ratio in rain water at Gracefield, Wellington, New Zealand after Mizutani & Rafter (1969).

less favourable and then also the evaluation is less simple and needs additional information from other investigations. The complexity of the problem is best demonstrated in the example of precipitates in coastal areas. The first investigations on this topic date from Östlund (1959) and from Jensen & Nakai (1961).

The published $\delta^{34}S$ values, especially those of the 1961 paper, show a dominating influence of anthropogenic sulfur in precipitates from industrial areas of Japan (δ from $\approx +3$ to $+7\permil$) while in non-industrial areas the δ values were found distinctly higher ($+13$ to $+16\permil$). The authors explained these latter values with an admixture of biogenic sulfide sulfur from intertidal flats etc. to sea spray sulfate as the main sulfur constituent, but they could not prove this assumption.

A first attempt to solve this question was undertaken by Mizutani & Rafter (1969) by a combined $\delta^{34}S$ and $\delta^{18}O$ investigation on rain water sulfate from Wellington, New Zealand. Since sea water sulfate has a very uniform $\delta^{18}O$ value differing strongly from that of atmospheric oxygen, the combined $\delta^{34}S/\delta^{18}O$ data enable to discriminate between oceanic sulfate (sea spray) and sulfate from atmospheric oxidation of other sulfur species. The results shown in Fig. 10 give a clear indication for the admixture of sea spray to all samples with intermediate $\delta^{34}S$ values.

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ИЗОТОПНЫЙ СОСТАВ ОСНОВНЫХ ВЕЩЕСТВ, ПОСТАВЛЯЮЩИХ СЕРУ В АТМОСФЕРУ

Имеется лишь немного данных об изотопном составе серы в атмосферных осадках. Тем не менее они указывают на возможность различать серные загрязнения из различных естественных и/или антропогенных источников. Обсуждаются δ-образцы ^{34}S основных источников атмосферной серы. Их δ-интервалы настолько перекрываются, что мы не можем использовать данные об изотопах серы для вычислений скоростей ввода серы от индивидуальных источников в глобальном масштабе. Однако для отдельных областей такие выводы можно часто получить. Наиболее надёжные результаты следует ожидать для областей только с двумя (максимум с тремя) основными источниками серы с хорошо

известным изотопным составом S и большими разностями в величинах δ между индивидуальными источниками. Ограничения возникают в основном благодаря комплексному происхождения атмосферной серы из многообразия различных источников (особенно, в сильно индустриализованных областях) и широте δ-интервалов даже для относительно «однородных» источников. Далее, судьба веществ, содержащих серу, может быть очень сложной после ввода их в атмосферу. Процессы дополнительного фракционирования замывают черты первоначального изотопного состава. В некоторых случаях эти трудности можно преодолеть, когда величины изотопных составляющих коррелируются с другими геохимическими данными.