INVESTIGATION OF S^{34} IN NATURE AND IN THE LABORATORY

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ABSTRACT

The results of a survey on the relative abundance of sulfur isotopes are presented, together with a review of previous work on the same subject. The possible causes of the variations found, and the biological and geological significance of these variations is discussed. In addition, the equilibrium constant for the isotopic exchange between hydrogen sulfide and hydrosulfide solution is determined experimentally and the results related to theoretical calculations based on partition functions.

Investigation of S^{34} in Nature and in the Laboratory

INTRODUCTION

Historical:

Isotopes were first discovered in connection with the radioactive disintegration of uranium and thorium by Soddy in 1911 (1). Some of the elements of the series, as well as the end product, lead, were found to exist in two or more forms with the same chemical and physical properties, but with different atomic weights and radioactive properties. Thus lead in the same mineral with thorium was found by Richards (2) to have a higher atomic weight than lead associated with uranium. Elements formed by nuclear processes were found, as expected, to vary in isotopic content. However, investigations carried out by Aston (3) and Dempster (4,5) by means of their mass spectrographs on stable isotopes of lighter elements, revealed that the isotopic content of these elements was remarkably constant in nature.

After the discovery of deuterium by Urey (6) in 1931, careful density measurements by a number of workers showed that the proportion of heavy hydrogen in natural water varied slightly. Urey and Rittenberg (7), using the well known methods of statistical mechanics, were the first to show that differences in the chemical properties between light and heavy hydrogen could be expected. These theoretical predictions were soon confirmed by experiment. It was shown further that similar differences should exist for the isotopes of other light elements up to oxygen (8); subsequent investigation did reveal slight differences in the isotopic content of these elements in nature. Recently, Thode and Smith (9) in a survey of oxygen found variations of up to 4% in the isotope ratio. Similary, Nier and coworkers (10) reported a 5% variation in carbon isotopes and still more recently boron isotopes have been investigated by Thode and coworkers (11) who found that the isotope ratio varied by 3.5%. In spite of this evidence for variation in isotope ratios, it is still generally assumed that the isotopic abundance of elements in nature is constant.

In the past two years, sulfur isotopes have been extensively investigated in this laboratory (12). Notwithstanding the fact that sulphur is well up in the periodic table, a total variation of 5% was found in the ratio of S^{32} to S^{34}. Sulphates were found to be enriched and hydrogen sulphide from well water depleted in the heavier isotopes, free sulphur, mineral sulphides and meteoritic sulphur (13) occupying intermediate positions. (Recently, Trafimov (14) has investigated terrestrial and meteoritic sulphur. Though his results were not very accurate, they do nevertheless show a higher proportion of S^{34} in sea water sulphate than in other forms of sulphur. These investigations of the sulphur isotopes have been extended to include orgnic sulphur, sulphate from sea water, and igneous sulphur. The results are reported in this thesis.

Theoretical:

An extensive study of partition function ratios of isotopic species has been made by Urey (15). It has been shown that under equilibrium conditions one isotope of a particular element is more strongly favoured in some compounds than in others. For example, if perchlorate ion is made to equilibrate with any other species containing chlorine, Cl^{37} will tend to concentrate in the perchlorate ion. Similarly, evaluation of partition functions in this laboratory by A. Tudge (16) show that there is a tendency for the heavy isotope of sulphur to concentrate in the higher valence state of sulphur. The ratios of some partition functions are given below in Table I where $Q\ (S^{34})$ is the heavier isotope, and $Q\ (S^{32})$ that for the lighter isotope.

Thus the tendency for the heavier sulphur isotope to concentrate in sulfate ion would seem to account for the high percentage of S^{34} in sea water and the low percentage in hydrogen sulfide from well water, especially in view of the fact that sulphate found in the same wells had a higher S^{34} content than the hydrogen sulfide associated with it (12).

From the partition function ratios in the table, the equilibrium constant for the reaction

$$S^{34=} + H_2S^{32} \rightleftharpoons S^{32=} + H_2S^{34}$$

is found to be 1.013 at 25'C. and 1.015 at 0'C. (Previous calculation in this laboratory by H. Bowlden using a method

Table I

Partition Function Ratios of some Sulphur-containing species

Molecule or ion	$Q(S^{34})/Q(S^{32})$	
	25'C.	0'C.
$S^{=}$	1.000	1.000
H_2S	1.013	1.015
$(S_2)^{\frac{1}{2}}$	1.013	1.015
$(S_8)^{\frac{1}{8}}$	1.016	1.018
SO_2	1.045	1.053
SO_3	1.084	1.096
$SO_4^{=}$	1.088	1.101

which takes into account moments of inertia as well as vibration frequencies gave a slightly lower value, viz. 1.01 at 25°C, and 1.012 at 0°C).

In practice the above equilibrium cannot be set up owing to the formation of hydrosulphide ion. Unfortunately, vibration frequencies for the hydrosulphide ion are not available in the literature: however, the system

$$HS^{34-} + H_2S^{32} \rightleftharpoons HS^{32-} + H_2S^{34}$$

has been studied. The procedure and results are outlined below.

Mass Spectrometry:

Determination of all the sulphur dioxide samples were made with a 180° direction-focussing Nier-type mass spectrometer with automatic recording device and manual shunt selector. The instrument and the principles governing its use have been previously described in detail (17, 18). The isotopes ratios were determined by measuring the peak heights at masses 64 and 66. Contributing to these peaks are the ions $S^{32}O^{16}O^{16}$ (64), $S^{34}O^{16}O^{16}$ (66) and $S^{32}O^{16}O^{18}$ (66). (The extremely rare combination $S^{33}O^{16}O^{17}$ (66) was neglected. Since O^{18} contributes to the 66 peak, the isotopic content of the oxygen in the sulphur dioxide must be taken into account. To convert from the 64/66 ratio to the S^{32}/S^{34} ratio, the following relationship, which is applicable for low O^{18} content, is used:

$$\frac{S^{32}}{S^{34}} = \frac{1}{\frac{(66)}{(64)} - 2.\frac{O^{18}}{O^{16}}} (12).$$

In the combustion of the samples, the same oxygen was used throughout (tank oxygen) having an O^{13}/O^{16} ratio of 0.00208.

To make a comparison of the samples, the same procedure was followed as in previous work of this type. Thus, as in former experiments (12), each sample was compared with a standard (pyrite from Park City, Utah, U.S.A.) which was analyzed immediately before and after each unknown. In this way, any slight variations in the S^{32}/S^{34} ratios due to fluctuations in the instrument were offset. By this method, relative abundances can be determined with a precision of 0.1% or better.

ISOTOPIC EXCHANGE REACTION

Experimental:

2.80 g. (0.050 mole) of anhydrous sodium hydrosulphide prepared by the method of A. Rule (19) (with slight modification) from sodium ethoxide and hydrogen sulphide was dissolved in 7.00 ml. of water in a flask which was then immersed in a dry ice-methanol bath and evacuated. After warming up to 0°C, the amount of hydrogen sulphide formed by hydrolysis was found by measuring the pressure of gas above the solution. It was found that 0.0011 mole of hydrogen sulphide was formed, representing 2.2 per cent of the total sulphur. The flask was then kept in an ice bath for 8.00 days to ensure complete equilibrium between gas and solution. (The reaction was carried out at 0°C rather than at room temperature in order to obtain the greatest possible fractionation.

After equilibration, the hydrogen sulphide was passed through lead acetate solution, precipitating lead sulphide. Similarly a sample of the original sodium hydrosulphide was added to lead acetate solution. The samples of lead sulphide were washed, dried, and burned in a stream of oxygen, which had been passed through active charcoal at -80°C and then sulphuric acid to remove water and hydrocarbon impurities. The Sulphur Dioxide formed was first passed through phosphorous pentoxide to remove any water occluded by the lead sulphide, and then through a trap immersed in liquid air. After the combustion was complete the excess oxygen was removed under vaccuum and the trap allowed to warm up to -85°C, (dry ice and acetone) and any carbon dioxide was then removed by pumping for a few seconds. The sulphur dioxide was then redistilled into a sample tube. Thus, sulphur from both the hydrogen sulphide and the sodium hydrosulphide was converted to sulphur dioxide, which is the most convenient form for the mass spectrometric analysis of sulphur.

The isotope ratio of the two samples was compared by analyzing the sample from the hydrosulphide immediately before and after that from the hydrogen sulphide.

Results:

The results obtained for the $S^{32}O_2/S^{34}O_2$ ratios and the corresponding S^{32}/S^{34} ratios are shown in Table II. The equilibrium constant for the reaction studied is given by

$$K = \frac{(H_2S^{34})\ (HS^{32-})}{(H_2S^{32})\ (HS^{34-})} = \frac{(S^{32})\ (\text{Sol'n})}{(S^{34})\ (\text{Sol'n})} \times \frac{(S^{34})(\text{gas})}{(S^{32})(\text{gas})} = 1.007.$$

(See Table II). Or in other words, there is a concentration of the heavier isotope in the gaseous phase to the extent of 0.7%.

Summary and Discussion:

The isotopic exchange equilibrium constant for the system hydrogen sulphide gas - hydrosulphide solution has been determined by equilibrating the components for eight days and was found to be a 1.007 ± 0.001 at ~~25~~°C. This means that there is an enrich-

0°C

Table II

Isotope Ratios in the Equilibration of
Hydrogen Sulphide and Hydrosulphide solution.

	$S^{32}O_2/S^{34}O_2$ ratio	S^{32}/S^{34} ratio
Hydrogen Sulphide	20.25 ± 0.01	22.11
Hydrosulphide Sol'n	20.36 ± 0.015	22.24
	20.39 ± 0.01	22.28
	Avge.	22.26

$$\frac{S^{32}/S^{34}(\text{sol'n})}{S^{32}/S^{34}(\text{gas})} = \frac{22.26}{22.11} = 1.007 \pm 0.001.$$ at 0°C

1.006 ± 0.001 at 25°C

ment of 0.7% of S^{34} in the gaseous phase. The result appears to be in harmony with calculations based on partition function ratios; for it would be expected that approximately one-half the effect would be found for the reaction.

$$H_2S^{32} + HS^{34-} \longrightarrow H_2S^{34} + HS^{32-} \qquad \text{(K=1.007, found)}$$

as for the reaction

0°C

$$H_2S^{32} + S^{34=} \longrightarrow H_2S^{34} + \cancel{H}S^{32=} \qquad \text{(K=1.015, calculated)}$$

1013 at 25°C

as is the case. It might be predicted further that an equilibrium constant of approximately 1.008 would be found for the reaction

$$HS^{32-} + S^{34=} \longrightarrow HS^{32-} + S^{32=}.$$

Since in previous work (12) it was found that hydrogen sulphide from natural water contained a relatively low concentration of S^{34}, it might have been expected that in the above experiment the hydrogen sulphide would be depleted in the heavier isotope. However, in hydrogen sulphide waters, the above experimental conditions are not met: For the pH is sufficiently low that virtually no hydrosulphide ion is formed. Furthermore, the formation of hydrogen sulphide in nature may well be a unidirectional, not an equilibrium process.

DISTRIBUTION OF S^{34} IN NATURE

Experimental:

Samples of sulfur dioxide were prepared from sea water sulfate, cystine, egg albumen, and what is considered to be igneous sulfur and the isotopic content of the sulfur measured by means of a mass spectrometer.

To make a comparison of sulfur from cystine, samples of hair were obtained from a number of individuals. Each sample was hydrolyzed by boiling with 20 percent hydrochloric acid (20). This process breaks down the keratin into the various amino acids which are then filtered (as the hydrochlorides) from any residue, partially neutralized with sodium acetate, and boiled with lead acetate solution. The lead sulfide which formed was filtered off, washed, dried and burned in a stream of oxygen as in the above experiment.

To obtain sulfur dioxide from sea water, strontium nitrate was added to precipitate strontium sulfate. This was then mixed with excess of iron powder and heated in a porcelain crucible over a Fisher burner for 1½ to 2 hours (21). (The reduction with iron was found to proceed more easily and completely than by the previous method using carbon (12). The slag which formed was then decomposed with concentrated hydrochloric acid and the evolved hydrogen sulfide bubbled through lead acetate solution. The lead sulfide was then burned to sulfur dioxide as before.

Of the seven samples of igneous sulfur investigated, six were sulphide or disulphide. Conversion to sulphur dioxide was effected by grinding the samples to a fine powder and burning in a stream of oxygen as with lead sulphide. The remaining sample, anhydrite ($CaSO_4$), was finely powdered, heated with iron dust, and worked up in the same way as the strontium sulphate.

Two samples of sulphur from egg albumen were obtained by allowing the eggs to decompose over a period of several weeks in a bottle equipped with an outlet leading to a solution of lead acetate. The lead sulphide was burned as before.

Results:

The ratio of sulphur isotopes obtained for seven different samples of cystine are given in Table III. Each sample of hair was from a different individual, with the exception of No. 1, which was cystine purchased from Eastman Kodak Co. Each sample examined was compared with a sample of Park City pyrite, which was used as a standard through all the determinations and which had an S^{32}/S^{34} ratio equal to 22.120. As can be seen from the table, the values found are surprisingly constant, in view of the large variations found previously for other samples of sulphur. (See Fig. 1). The total variation is approximately 0.8%. It might be mentioned that no correlation could be found between the isotope ratio and the age, race, colour of hair or sex of the individual with the number of samples analyzed to date.

The isotope ratio of sulfur from sea water sulphate was likewise found to be relatively constant. The results show an overall variation of one percent (Table IV). The S^{32}/S^{34} ratio

Table III

Isotopic Constitution of Sulphur from Cystine

Sample No.	Source	S^{32}/S^{34} ratio
1	Commercial cystine, Eastman Kodak	22.32 ± 0.01
2	Human hair[1]	22.35 ± 0.01
3	"	22.27 ± 0.01
4	"	22.18 ± 0.02
5	"	22.21 ± 0.01
6	"	22.20 ± 0.01
7	"	22.23 ± 0.01
	Average	22.25 ± 0.02

[1] Each sample taken from a different individual.

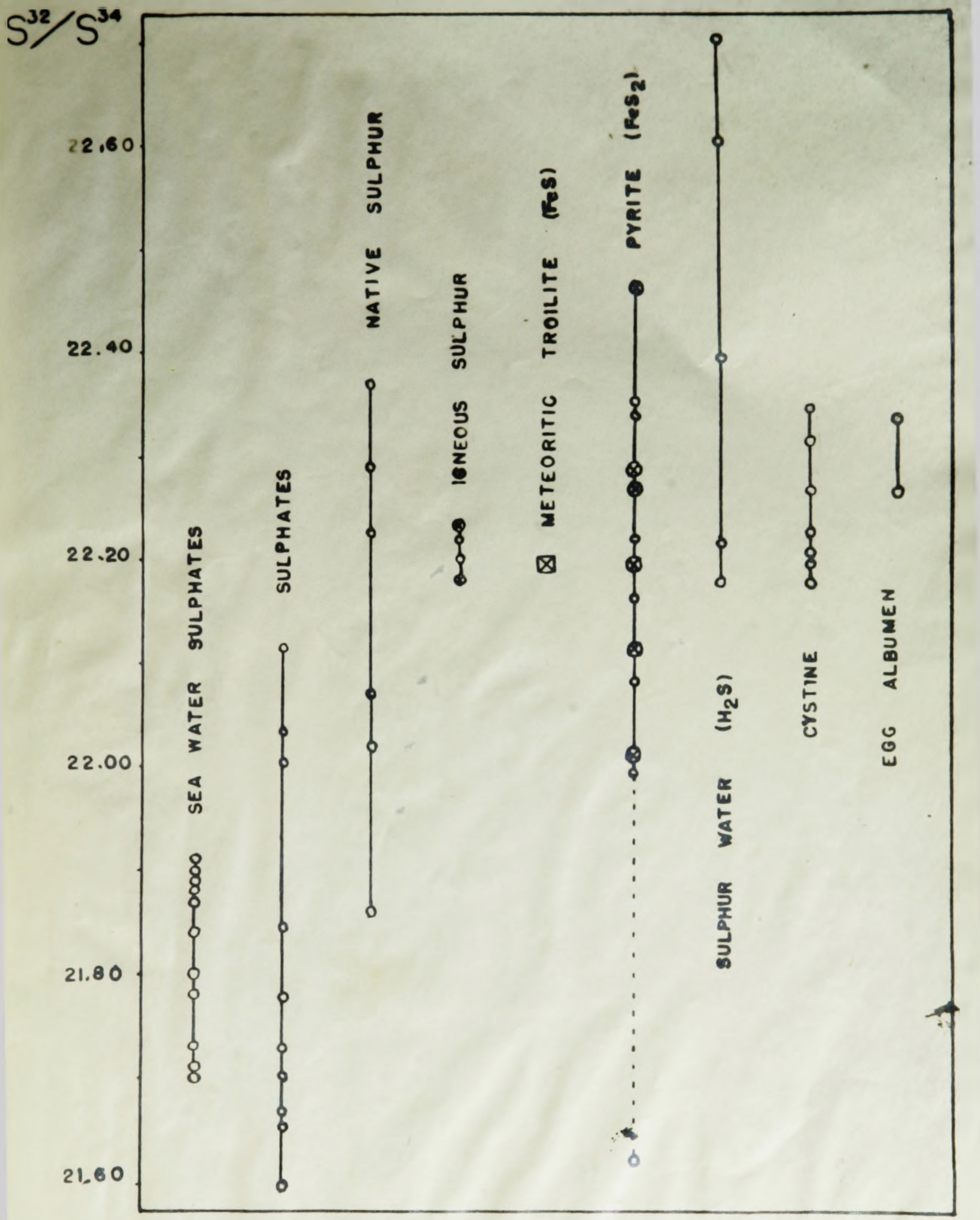

Fig. 1. Distribution of S^{34} in Nature.

Table IV

Isotopic Constitution of Sulphur from Sea Water Sulphate

Ocean	Location	S^{32}/S^{34} ratio
Arctic	Resolute Bay, Cornwallis Is.	21.73 ± 0.02
"	Resolute Bay, Cornwallis Is.	21.71 ± 0.01
Atlantic	Halifax Harbour, N.S.	21.70 ± 0.02
Pacific	Straits of Juan de Fuca, Victoria, B.C.	21.78 ± 0.02
"	Pacific Naval Lab. #27 Depth 200yd.	21.80 ± 0.01
"	39°23'N 129°55'W surface	21.84 ± 0.01
"	" 2500M	21.88 ± 0.01
"	31°49.5'N 125°58'W surface	21.87 ± 0.015
"	" 2500M	21.91 ± 0.02
"	25°31'N 119°46'W surface	21.90 ± 0.015
"	" 2500M	21.89 ± 0.01

is significantly higher for the Pacific Ocean than for either the Atlantic or the Arctic Ocean. Furthermore, in a series of samples from the Pacific Ocean, a small difference was found in the isotopic abundance between samples taken from the surface and from 2500 metres down. The preparation and analysis of these samples was repeated several times to prove beyond doubt that this difference does exist. However, the difference does disappear in the sample taken from the southernmost point. The cause of this variation would form an interesting subject for further investigation. Another significant point is that there is an increase in the S^{32}/S^{34} ratio (average between surface and 2500M down) with decreasing latitude (Fig. 2). It might be of interest to investigate sea water from still further south to see if this tendency continues.

The isotopic composition of igneous sulfur was found to be almost identical for every sample except one. From the results shown in Table V and Fig. 1, it is seen that the one sample of sulfate falls far below the rest and into the range of other sulfates. The value for the remaining six samples is very nearly the same as that found for meteoritic sulfur by MacNamara and Thode (13). These results are not surprising; for it would be expected that substances which were formed at high temperatures from the primary source of terrestrial sulfur and which had not undergone any subsequent changes (sedimentation or metamorphosis) would show a constant value for the isotope ratio. Thus it is highly probable that in these samples as well

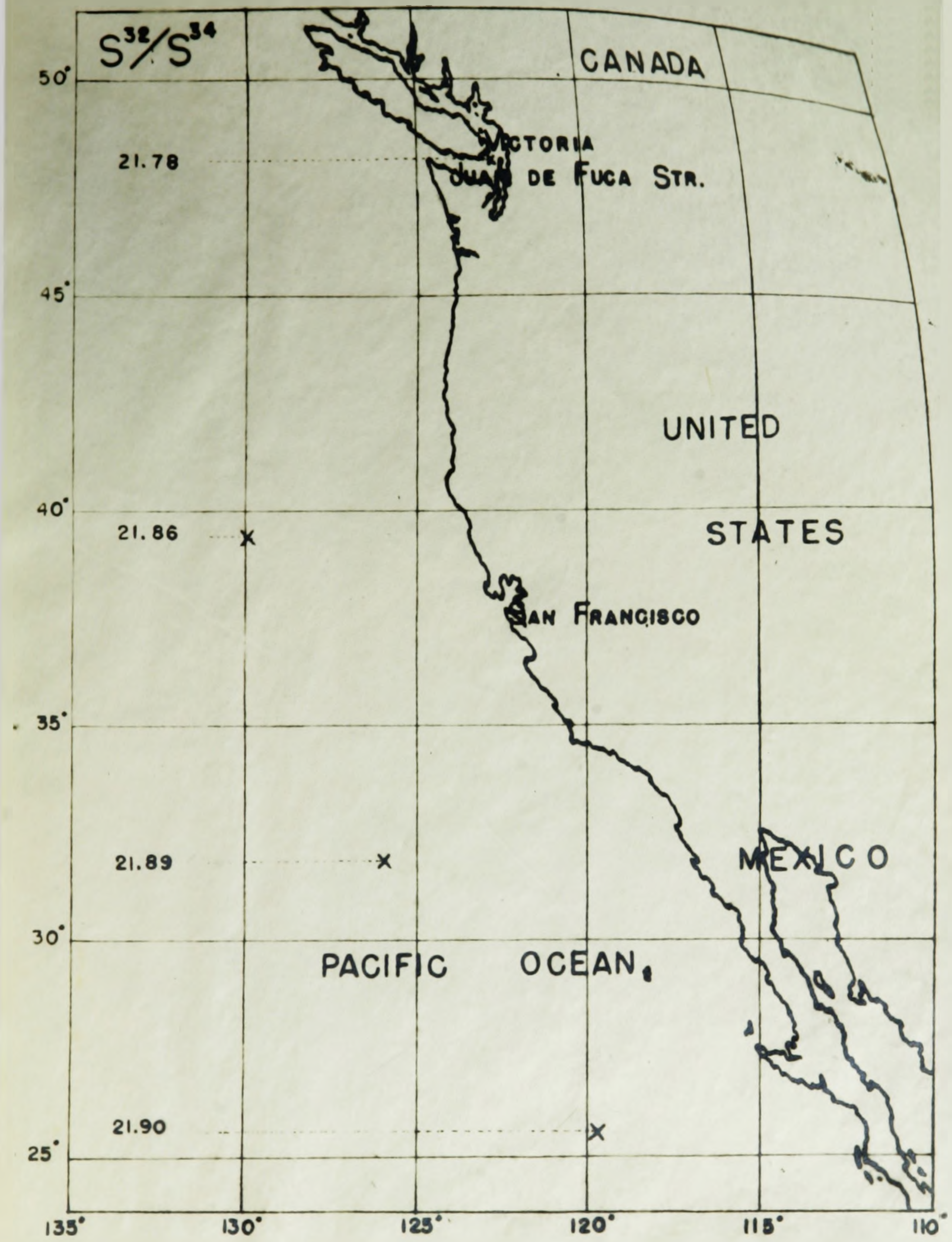

Fig. 2. Distribution of S^{34} in Sea Water Sulphate at Various Latitudes.

Table V

Isotopic Constitution of Igneous Sulphur

Sample No.	Type of Mineral	Location	S^{32}/S^{34} ratio
1	Pyrite	Lamaque, Que.	22.18 ± 0.01
2	Pyrite	Macdonald Quarry Bancroft, Ont.	22.20 ± 0.01
3	Pyrite from Massive Sulphide	Sudbury, Ont.	22.18 ± 0.02
4	Anhydrite	Lamaque, Que.	21.98 ± 0.01[1]
5	Massive Sulphide	Falconbridge, Ont.	22.23 ± 0.02
6	Pyrite and Pyrrhotite	Sudbuey, Ont.	22.23 ± 0.01
7	Pyrite	Lamaque, Que.	22.22 ± 0.01
8	Pyrrhotite[2]	~~unknown[2]~~ 40 miles N.E. of Yellowknife.	22.18 ± 0.01

[1] Probably not igneous.

[2] Obtained from Donald Hurd, McMaster U.

as in meteorites we have the isotopic composition of the sulfur as it was when the earth and the other planets were formed. Furthermore it is quite likely that the sample of anhydrite (Table V) is not really igneous.

Two samples of sulfur from egg albumen were analyzed and the values of the isotope ratio were found to lie in the same range as that for cystine (Table VI and Fig. 1). Since both substances are proteinoid in nature and are formed by similar chemical processes, the above result is not surprising. However, since only two samples were analyzed, it is possible that further investigation would reveal a greater variation.

Summary and Discussion:

The isotopic content of sulphur from a number of natural sources has been determined. From each source the isotope ratio has been found to be relatively constant, as compared with the large variations found in previous work. The values for cystine and for egg albumen are all higher than the values for sulphates in spite of the fact that most organic sulphur originates from sulphate in the soil. Now, since animals obtain nearly all their amino acids ultimately from plants, it would appear that some fractionation of the isotopes of sulphur occurs in the synthesis of amino acids from mineral sulphate by plants.

More important, however, is the fact that the above results impose some limitations on the isotopic tracer

Table VI

Isotopic Constitution of Sulphur from Egg Albumen

Sample No.		S^{32}/S^{34} ratio
1		22.27 ± 0.02
2		22.34 ± 0.01
	Average	22.31 ± 0.02
Average from Cystine		22.25 ± 0.02

techniques employed in biological and medical research: for it is assumed in tracing the progress of a certain element through a living organism, that the chemical properties of the isotopes of the element are identical with respect to the biochemical processes taking place. Apparently such is not the case. Although further investigations of specific biological processes are required before definite conclusions can be drawn, it would nevertheless be wise in carrying out biological research of this type not to overlook the possibility of isotope fractionation by the organism under study.

The small though significant variation in the isotope ratio in sea water suggest that here, too, various processes, probably biochemical in nature, give rise to isotope fractionation. In these biochemical processes an important part would be played by the various sulphur bacteria, some of which reduce sulphate to hydrogen sulphide, others oxidize sulphur to sulphate and so on. The fact that certain sulphate deposits in Ontario laid down from an inland sea several hundred million years ago have the Same S^{34} content as sea water sulphate, (12) suggests that the isotopic content of the sulphur in the sea has remained the same over a long period of time.

Because of the remarkably constant isotope ratio for meteoritic sulphur, it would seem advisable to use this material as a standard for reckoning relative abundances and for absolute abundance work. On this basis, the constant S^{32}/S^{34} ratio for igneous sulphur and its close agreement with meteoritic sulphur may well furnish a means of determing whether or not a sample is igneous. However, more samples must be analyzed before we accept this hypothesis.

This close correspondence of meteoritic with terrestrial igneous sulphur gives further strong support to the view that meteorites were formed within the solar system from the same material as the other planets.

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