Isotopic Composition of Sulfur in Precipitation and Sea-Water

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Introduction

As an attempt to approach the question of the origin of airborne sulfur, it was intended to make measurements of natural S^{35} and determine the S^{32}/S^{34}-ratio of sulfur in rain-water. For different reasons the S^{35} counting had to be omitted, but the S^{32}/S^{34}-ratio, and the sulfur contents of a number of samples of precipitation and sea-water were made.

Experimental

The rain, snow, and lake water samples were percolated through a cotton-wool filter and then through a chloride saturated anion exchange column with a volume of 175 ml, at a rate of 100 ml/min. The sulfate was eluted with sodium chloride solution and the column washed several times with distilled water. Barium sulfate was precipitated in the usual manner from the eluate, and the sulfur content was calculated from its weight and the original volume of water. In one case (Sample S 4) the efficiency of the sorption step was tested by using two columns in series. No trace of sulfate could be detected in eluate from the second column. The figures for sulfur content in Table 1 are thus reproducible within ± 2 % of their values. From the sea-water samples, barium sulfate was precipitated directly.

In collecting rain-water from roofs, each sample was taken after the rain had washed the roof thoroughly. Between 50 and 300 liters were taken, corresponding to at least 50 mg of sulfate sulfur.

For mass-spectrometric analysis the barium sulfate samples were converted to cadmium sulfide, which was mixed with vanadium-V-oxide. By heating this mixture gave sulfur dioxide for the mass-spectrometer. This procedure is described by GAVELIN et al. (1959).

Description of locations

Stockholm: A copper roof at the Royal Institute of Technology in the NE part of central Stockholm. Snow taken from ground. Lat. 59° 21′ N, Long. 18° 05′ E.

Huddinge: A tile roof in Huddinge, a scattered residential area 13.5 km SSW of the above locality. Lat. 59° 14′ N, Long. 17° 59′ E.

Köping: A felt roof in the E part of the city of Köping on Lake Mälaren, 120 km W of Stockholm. Lat. 59° 31′ N, Long. 16° 01′ E.

Flahult: A tile roof at a farm in Flahult, Småland, 7.5 km S of Jönköping. Lat. 57° 42′ N, Long. 14° 08′ E.

Texas: Rain-water taken with a plastic funnel at the Institute of Marine Research, Port Aransas, Texas, on the coast of the Gulf of Mexico. Lat. 27° 50′ N, Long. 97° 04′ W.

Table 1. Assay and isotopic composition of sulfatic sulfur in various waters

Sample No.	Date y/m/d	Sample of	Location	Sulfur content mg/l	Isotope ratio	
					$\delta S^{34}/S^{32}$	S^{32}/S^{34}
S 1	57/02/11—16	Snow	Stockholm	0.49	+ 0.7	22.21
S 2	57/02/16—17	"	"	1.34	+ 1.8	22.18
S 3	57/06/23—24	Rain	Köping	1.08	+ 3.4	22.15
S 4	57/09/00—02*	"	Stockholm	2.63	— 1.7	22.26
S 5	57/09/12	"	"	6.27	+ 0.3	22.22
S 6	57/09/13	"	"	2.40	— 0.1	22.23
S 7	57/09/19	"	"	1.70	— 0.9	22.25
S 8	57/09/24	"	"	2.04	+ 2.2	22.18
S 9	57/10/17	"	"	3.18	+ 1.8	22.18
S 10	57/10/17	"	Huddinge	1.75	+ 1.8	22.18
S 11	57/10/18	"	"	0.93	+ 1.4	22.19
S 12	57/10/18—20	"	Flahult	2.54	+ 2.6	22.17
S 17	58/01/11 } 58/02/10 }	"	Texas	—	+ 1.4	22.19
S 18	58/01/— —**	"	Washington	—	+ 0.6	22.21
S 13	57/04/xx***	Sea water	Arctic Sea	914	+ 15.1	21.89
S 14	57/09/30	"	North Sea	722	+ 14.7	21.90
S 15	57/10/10	"	Bothnia	150	+ 15.6	21.88
S 16	57/10/24	Lake water	Mälaren	15.5	— 2.2	22.27

* Aug. 31 to Sept. 2
** Actual day unknown
*** Various days during April

Washington: Rain-water taken with a plastic funnel in Nahcotta, Washington, on the Pacific Coast. Lat. 46° 31′ N, Long. 124° 02′ W.

Arctic Sea: Various small quantities of surface water taken during a cruise from the Shetland Islands to North of Iceland. April 1957.

North Sea: Surface water taken at the lightship of Fladen, 55 km SSW of Göteborg in Cattegat. Lat. 57° 12′ N, Long. 11° 48′ E.

Bothnia: Surface water at the lightship of Finngrundet in the Gulf of Bothnia, 190 km NNE of Stockholm. Lat. 61° 15′ N, Long. 18° 39′ E.

Mälaren: Untreated water for Stockholm municipal water system. The intake is at a depth of 18 m in Lake Mälaren, 25 km W of Stockholm. Lat. 59° 20′ N, Long. 17° 48′ E.

Results

In Table 1 are given the results obtained. The exact locations are given above. The isotope ratios refer to the average-meteorite standard, used by the University of Hamilton group, accepted to have a S^{32}/S^{34}-ratio of 22.225 (GAVELIN 1959). If R_s is the S^{34}/S^{32}-ratio for the standard (1/22.225) and R_x the corresponding ratio for the unknown sample, δ is defined according to

$$\delta = \frac{R_x - R_s}{R_s} \cdot 1000$$

The reproducibility of the values are ± 2 % of the value in sulfur assay, ± 0.9 in δ, and ± 0.02 in S^{32}/S^{34}-ratio.

Discussion

The most striking result to be recognized by looking at Table 1, is the marked constancy of the isotopic ratio of the sulfur in precipitation, regardless of location and time of year, and despite large differences in sulfur concentration. Even the coast rains at the Gulf of Mexico and the Pacific give the same ratio as the east wind snow over Scandinavia. The mean of all isotopic ratios in precipitation is 22.20 and the extremes are 22.26 and 22.15. The average isotopic ratio obtained for sea-water sulfate, 21.91, differs slightly from the average of 21.80, compiled by RANKAMA (1954), and measurements by FEELY and KULP (1957). Our values are much closer to the higher ratios given by Thode et al. for the Pacific

(also partly referred by Rankama).* The unexpected high S^{32}/S^{34} value for Lake Mälaren is probably due to local conditions in the soil and ground of the Mälar basin.

There is a large difference in isotopic ratio between sea-water and precipitation, but very little probability of chemical or other fractionation processes on the path of the sulfur from the sea-water drops to the rain. It can therefore be considered quite true, that the sulfate sulfur in precipitation is *not* likely to originate principally from sea-water spray. Natural materials having isotope ratios closer to those of precipitation, and which are possible sources of airborne sulfur, are among others volcanic gases, sulfur in coal and petroleum used industrially, and biogenic hydrogen sulfide e.g. from marshes and swamps. More comprehensive estimates of the sulfur isotope balance of the atmosphere, surface waters, and the earth's crust might perhaps throw some light on which source could be the most important.

* In a recent paper (Geochim. et Cosmochim. Acta **16**, p. 213 (1959)) Ault and Kulp have obtained a very small spread around an avergage of 21.76. Our primary standard was a Sudbury nickel sulfide ore submitted 1956 by Jan Monster at the University of Hamilton (Sample No. 10708), stated to have the value 21.203. In Table 6 in Ault's paper Sudbury sulfides are measured to 22.11. It is thus extremely likely that the difference between our and Ault's values of sea-water is a question of standards.

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