Oxygen Isotopic composition of dissolved Sulfate in Mediterranean Sea Water samples

by

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Some measurements of the oxygen isotopic composition of sulfate ions dissolved in oceanic water were carried out by Longinelli and Craig [1967], Lloyd [1967] and Rafter and Mizutani [1967]. Only the samples measured by Rafter and Mizutani represented a complete set from a single hydrocast in the Pacific Ocean. This means that detailed isotopic work has not yet been made on limited oceanic areas to check the behaviour of dissolved sulfate in single water bodies or at the contact between different water masses.

In particular, the Mediterranean has not yet been studied from the point of view of the isotopic composition of its dissolved sulfate. Some results are given here of a series of isotopic measurements carried out on Mediterranean sea water samples. The main purpose of this research was to check whether or not there are any relationships between temperature, δO^{18} (H_2O) and $\delta O^{18}(SO_4^{2-})$. Such relationships have not been found in open ocean samples; however an almost closed basin like the Mediterranean could behave differently because of the limited exchange between Mediterranean and Atlantic waters and the relatively high mixing rates between different water bodies.

The technique used for the purification of the samples, their reduction with graphite at about 1000°C and the conversion to CO_2 of the CO formed is the same as described in previous papers [Longinelli & Craig, 1967; Longinelli, 1968]. The standard deviation (σ) of the sulfate measurements is ± 0.15 per mil. The samples studied and the results obtained are listed in tables 1, 2, 3 and 4. The isotopic data are given here in the δ terminology where δ is defined by :

Table 1

Isotopic results, temperature and depth of samples collected on September 18, 1967 at 43°32.1′ N and 07°30.1′ E (off Villefranche-sur-Mer, France)

Depth (m.)	t°C	$\delta O^{18}(H_2O)$	$\delta O^{18}(SO_4^{2-})$
0	20.74	+ 1.27	+ 9.1
50	14.15	+ 1.19	+ 9.2
100	13.19	+ 1.12	+ 9.2
150	13.11	+ 1.21	+ 9.2
400	13.29	+ 1.29	+ 9.3
700	13.14	+ 1.32	+ 9.1
900	13.06	+ 1.28	+ 9.2
1100	13.00	+ 1.25	+ 9.1
1400	12.96	+ 1.31	+ 9.2
1700	12.84	+ 1.30	+ 9.2
1900	12.96	+ 1.34	+ 9.3

Table 2

Isotopic results, temperature and depth of samples collected on April 29, 1968 at 35°39.2'N and 4°19.0'W (east of Gibraltar).

Depth (m.)	t°C	$\delta O^{18}(H_2O)$	$\delta O^{18}(SO_4^{2-})$
0	19.65	+ 0.75	+ 9.0
100		+ 0.78	+ 9.1
200		+ 0.92	+ 9.0
300		+ 1.17	+ 9.1
400		+ 1.37	+ 9.2
500		+ 1.35	+ 9.1
600		+ 1.38	+ 9.2
700		+ 1.35	+ 9.2
800		+ 1.28	+ 9.1
900		+ 1.39	+ 9.1
1000	13.29	+ 1.46	+ 9.2

Table 3

Isotopic results, temperature and depth of samples collected on June 15, 1967 at 42°33.9'N and 15°40.9'E (Adriatic Sea).

Depth (m.)	t°C	$\delta O^{18}(H_2O)$	$\delta O^{18}(SO_4^{2-})$
0	19.25	+ 1.03	+ 9.1
20	15.13	+ 1.09	+ 8.5
30	14.31	+ 0.95	+ 8.8
50	13.77	+ 0.97	+ 9.2
75	12.94	+ 1.03	+ 9.3
100	12.58	+ 1.12	+ 9.1
110	12.37	+ 1.08	+ 9.2

Table 4

Isotopic results, temperature and distance from the coast of samples collected on May 2, 1967 off the mouth of Arno river.

Distance(m)	t°C	$\delta O^{18}(H_2O)$	$\delta O^{18}(SO_4^{2-})$
0	17.2	— 2.5	+ 9.2
50	17.6	— 0.8	+ 9.3
100	17.6	— 0.2	+ 9.1
500	17.9	+ 0.4	+ 9.2
1000	18.1	+ 0.8	+ 9.1

$$\delta = \frac{O^{18}/O^{16}\,\text{stand.} - O^{18}/O^{16}\,\text{sample}}{O^{18}/O^{16}\,\text{stand.}} \times 1000$$

The results are given versus SMOW (Standard Mean Ocean Water) standard as defined by CRAIG (1961). From the results obtained, it is apparent that $\delta O^{18}(SO_4^{2-})$ is constant at all depths and thus does not depend on temperature, $\delta O^{18}(H_2O)$ or depth and location of the samples. It must be pointed out that, in the case of samples collected east of Gibraltar, a separation between Atlantic and Mediterranean water can be clearly traced from the $\delta O^{18}(H_2O)$ data. No difference exists in the case of $\delta O^{18}(SO_4^{2-})$. A few samples from the Adriatic seem to differ somewhat from the average values; however the difference is relatively small and the determination should be repeated to confirm it. No definite interpretation has been given up to now of the constancy of $\delta O^{18}(SO_4^{2-})$ in ocean water throughout the world; LONGINELLI & CRAIG (1967) suggested that this fact may be the result of long term isotopic equilibrium between sulfate and ocean water; LLOYD (1967) suggested the hypothesis that kinetic isotopic effects in a sulfur cycle could account for the uniform isotopic composition of oceanic sulfate. A better knowledge of isotopic behaviour during the complex oxydation-reduction processes in natural environments is needed to interpret the experimental values.

While in the case of marine sulfate, some data existed previously, the value of the O^{18}/O^{16} ratio in phosphate dissolved in oceanic water has been until now completely unknown. The main difficulties in measuring the isotopic composition of the dissolved ions were in separating the phosphate from an extremely diluted solution and purifying the (PO_4^{3-}) ions from organic matter and other contaminants without introducing oxygen-isotope fractionations. The technique used here is similar to that described by LAL et al. (1964); natural sponges were treated first with 5 M HCl for about 30 minutes, and successively with HF and HCl for several hours. The sponges are then impregnated with iron hydroxide and held in sea water at the desired depth for about 6-8 hours. The phosphate, adsorbed by iron hydroxide is then acid leached, carefully purified following well known procedures (LONGINELLI, 1965) and precipitated as BiPO$_4$. This is dried in a vacuum furnace at 130°C for about 3 hours and then reacted with BrF$_3$ or BrF$_5$ in a metal line made of nickel (or stainless steel) and fluorothene. The oxygen is removed quantitatively, converted to CO$_2$ and measured mass-spectrometrically. The procedure was tested repeatedly using solutions of sodium phosphate whose oxygen isotopic composition had been carefully measured. After the complete treatment, no isotopic fractionation was detected in the phosphate leached from the sponges. In the case of sea water samples purification from the large amounts of organic matter and iron is time consuming and the reproducibility of the measurements is generally poor ($\sigma = \pm 0.3\%$). In spite of this, a few samples were collected in the Mediterranean and processed. The samples measured up to now and the results obtained are the following : n. 1 (September 18, 1967) position 43°32.1'N, 07°30.1'E; depth 400 meters, water temperature 12.9°C, $\delta O^{18}H_2O = + 1.2$ (vs. SMOW), $\delta O^{18}(PO_4^{3-}) = + 17.1$ (vs. SMOW); n. 2 (April 28, 1968), position 35°39.2'N, 04°19.0'W; depth 1000 meters, water temperature 12.8°C, δO^{18} (H$_2$O) $= + 1.4$ (vs. SMOW), $\delta O^{18}(PO_4^{3-}) = + 17.0$ (vs. SMOW). The two data obtained are more negative by about 2 ‰, compared with the equilibrium values at 13°C as calculated from the phosphate equation (LONGINELLI, 1966) in the case of an oxygen isotopic composition of the water equal to SMOW. Unfortunately, the oxygen isotopic composition of the dissolved phosphate can be measured, in the Mediterranean, only at depths greater than 300-400 meters because of the depletion in phosphate in surface waters. Consequently the possible temperature dependence of the phosphate-water fractionation cannot be determined hare due to the quasi constancy of the temperature in these deeper waters.

More measurements are now being done to confirm the results obtained but only a group of data from open ocean samples at different temperatures will allow us to know the range of the isotopic composition of the dissolved phosphate and its behaviour under various conditions of temperature and δO^{18} (H$_2$O).

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