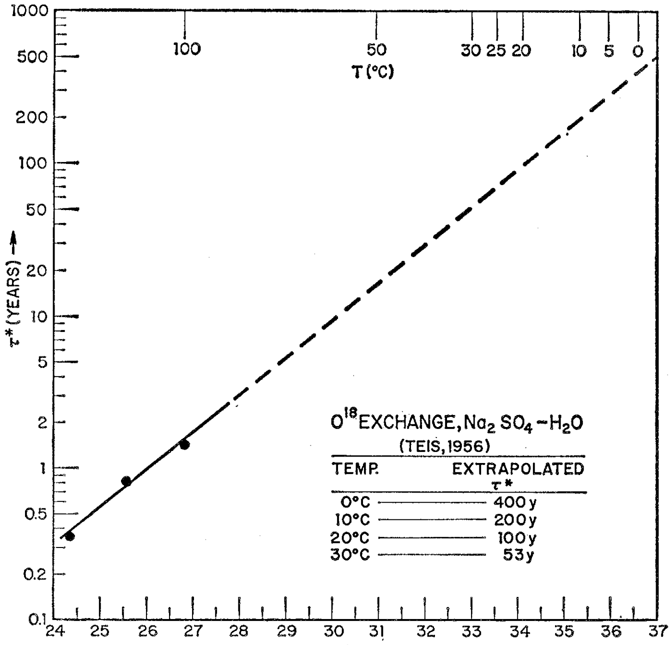
Reports

Oxygen-18 Variations in Sulfate Ions in Sea Water and Saline Lakes

Abstract. *A new method measures the oxygen-isotopic composition of dissolved sulfate ions and barium sulfate. Sulfate ions in the oceans are enriched in oxygen-18 by 9.5 per mille relative to mean ocean water and show only minor variations, probably because the exchange rate with water is slow enough to prevent local equilibrium with surface waters. Sulfate ions in saline lakes and brines have oxygen-18 enrichment of from 7 to 23 per mille relative to mean ocean water; the value of the highest enrichment observed is about the same as that of atmospheric oxygen.*

The development of oxygen-isotope temperature scales for marine organisms, based on the oxygen-18 content of carbonate (*1*) and phosphate (*2*), leaves sulfate as the major remaining anion for paleotemperature research. Because each isotopic temperature equation has two variables—temperature and isotopic composition of the water—at least two such equations are necessary; in fact as many as possible are required because of uncertainties introduced by postdepositional exchange and other effects. However, before other isotopic temperature scales can be applied to paleotemperature studies, one must establish that ions such as phosphate, sulfate, and nitrate, which exchange oxygen with water much more slowly than does carbonate ion, in fact reach isotopic equilibrium with the water in which they reside. Carbonate ion in sea water is probably always in local isotopic equilibrium with the surrounding water, but other ions may retain the memory of their original oxygen long after they reach the sea and come slowly to a "regional" equilibrium relative to the average water and temperature they encounter during their time of residence in the ocean. Sulfate ion, which is abundant in sea water (2700 ppm) and some lakes and subsurface waters, may exchange so slowly that it can be used for studies of mixing rates in natural waters.

Most studies of oxygen exchange between sulfate ion and water (*3*) have produced quantitative data only in highly acid solutions, in which the exchange is rapid. Hoering (*3*) showed that in such solutions the rate-determining step is the decomposition of H_2SO_4 to H_2O and SO_3. The characteristic time constant τ^*, defined by $\ln (1 - F) = -t/\tau^*$ where F is the fraction of total exchange in time t, increases at 25°C from 5 minutes to 14 years (a factor of 10^6) as the H_2SO_4 concentration decreases from 15 to 3 mole/liter, according to Hoering's data. In neutral solutions of Na_2SO_4 Teis (*4*) could measure values for τ^* of 0.36, 0.82, and 1.43 years at temperatures of 138°, 118°, and 100°C, respectively; in alkaline solutions (0.04 to 0.08*N*) at 138°C, no exchange was observed during several days. A crude extrapolation of these data to low temperatures (Fig. 1) indicates that time constants of the order of 100 years in neutral solutions,



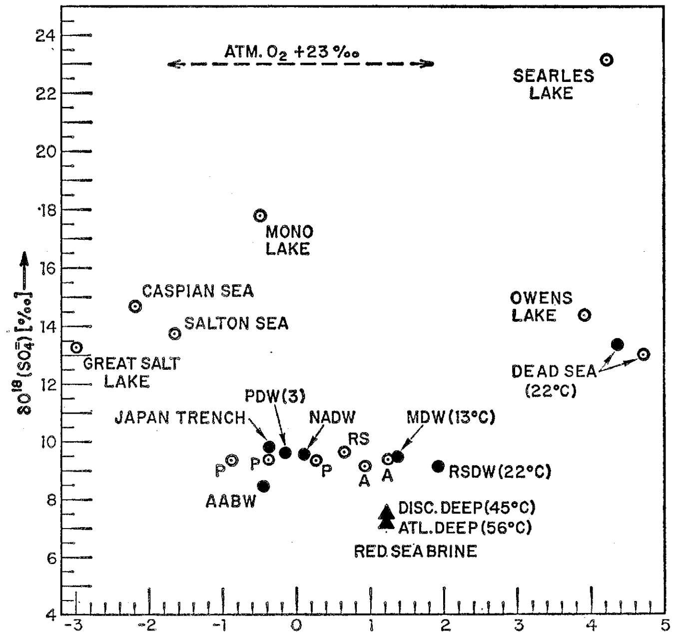


Fig. 1 (left). Extrapolated mean lifetimes for sulfate ion–water oxygen-isotope exchange, from high-temperature data of Teis (*4*). Fig. 2 (right). Oxygen-18 content of sulfate ions in sea water and in saline lakes versus the oxygen-18 content of the water. Solid circles, deep water; open circles, surface waters or mixed waters of shallow lakes. Abbreviations: *NADW*, North Atlantic Deep Water; *PDW*, Pacific Deep Water (three samples); *MDW* and *RSDW*, Mediterranean and Red Sea Deep waters; *AABW*, Antarctic Bottom Water. *P*, *A*, and *RS* denote Pacific, Atlantic, and Red Sea surface waters, respectively; triangles are Red Sea geothermal brine samples from the two known locations.

and much longer in alkaline solutions, may be expected.

As a first step in understanding the oxygen-isotopic composition of natural sulfates we have developed a rapid and precise analytical method for the oxygen in dissolved sulfate ions and in $BaSO_4$, and have studied the sulfate dissolved in the major water masses of the oceans and in some saline lakes and brines. The sulfate is precipitated in $BaSO_4$ according to standard gravimetric procedure. A 10-ml sample of sea water is diluted to 100 ml, acidified with 1 ml of 1*N* HCl, and heated to boiling; 10 ml of 0.25-molal solution of $BaCl_2$ is added, and the precipitate is digested about 15 minutes, filtered, washed until free of chloride, and dried in a partial-vacuum oven at 120°C. The standard procedure is designed to obtain a coarse precipitate by minimizing supersaturation; we found that precipitation at 25° and 100°C gave the same isotopic values as did drying at 70° instead of 120°C (Table 1).

The $BaSO_4$ is reduced with carbon by induction heating in a graphite crucible covered with a graphite lid so that gas escapes from the four small holes used for platinum-wire suspension. The sample of about 11 mg is ground in a mortar with 10 to 15 times the stoichiometric amount of carbon (for CO); spectrographic graphite is used for this carbon and for the crucible. The sample is degassed at a few hundred degrees (below red heat) for some 15 minutes and then heated for 40 to 45 minutes at 1000° to 1100°C; almost all evolution of gas occurs within the first 15 minutes at high temperature. Carbon reduction of $BaSO_4$ in platinum crucibles, studied by Halperin and Taube *(5)* and by Rafter *(6)*, is complete at 1000°C; they obtained CO–CO_2 mixtures with 75 and 16 percent CO_2, respectively. With the graphite crucible, our mixture varied from about 98 percent CO_2, with a new crucible, down to about 80 percent CO_2 after about ten reactions. The heating chamber is connected to a liquid–nitrogen cooled trap so that CO_2 is continually condensed.

The residual CO is converted to CO_2 by continual sparking of the gas with a Tesla coil above the cold trap by use of two platinum sheets, each about 1 by 2 cm, suspended by platinum wire from tungsten electrodes leading through the glass, and by maintaining a glow discharge until the final pressure is 20 to 30 μ-Hg; the method and the kinetics are detailed elsewhere *(7)*. The reaction is complete within about 20 minutes in our system, leaving a residuum of about 0.01 cm^3 of CO and about 10^{-4} cm^3 of N_2, with no detectable H_2 (less than 5×10^{-5} cm^3 at standard temperature and pressure, as measured by gas chromatography), showing that any water absorbed or contained in the $BaSO_4$ does not contribute oxygen to the CO_2.

The method was checked by heating CO_2 of known isotopic composition over the graphite crucible until about half of it was reduced to CO, and then sparking the CO back to CO_2. Within the precision of the volume readings (1 percent) all the CO_2 was recovered and the isotopic composition of the oxygen was unchanged (± 0.1 per mille).

Gas-chromatographic analysis showed the final product of the sulfate reduction to be pure CO_2 when pure $BaSO_4$ was used. However, attempts to reduce natural barite crystals from deep sea cores, which had been treated with acids until the barite contained only about 0.5 percent of rutile and zircon, resulted in the presence of a small amount of SO_2 in the CO_2; this SO_2 must be removed before accurate mass-spectrometer analyses can be made on the CO_2.

Results on samples of ocean water are listed in Table 1, together with the isotopic composition and other

Table 1. Isotopic composition of oxygen in sulfate ion and in water in sea-water samples, relative to the SMOW isotopic standard. Last column: numbers of determinations (each of sulfate reduction and analysis) appear in parentheses; samples with more than two determinations generally represent duplicate precipitations; no significant differences between precipitations were observed.

Sample				Composition (per mille)			
Source; date	Depth (m)	Salinity (‰)	*T* (°C)	δ $[H_2O]$	δ $[SO_4^=]$	δ$[SO_4]$, mean deviation	
		Pacific Ocean					
Scripps Pier, 32°52′N, 117°15′W; 19 July 66	0	33.60	17.9	—0.38	9.39 9.44* 9.40	±0.15 ± .12	(7) (2)
7°09′N, 145°35′W; 4 Apr. 61	10	34.83	26.5	+ .26	9.35	± .02	(2)
Gulf of Alaska, 57°08′N, 150°0′W; 23 Aug. 61	0	32.76	13.1	— .88	9.37	± .13	(2)
29°11′N, 120°59′W; 16 Apr. 61	4065	34.68	1.5	— .17	9.54	± .04	(3)
Marianas Trench, 11°17′N, 142°10′E; 14 Apr. 62	8287	34.71	2.0	— .15	9.59	± .10	(2)
31°33′N, 129°58′W, 10 m from bottom; 5 Aug. 66	4614	34.68	1.5	— .17	9.71	± .08	(2)
Japan Trench, 33°37′N, 141°58′E, top of gravity core; 31 May 66	9247			— .40	9.83	± .06	(2)
		Atlantic Ocean					
33°38′N, 9°45′W; 29 July 62	0	36.52	22.1	+ .92	9.06 9.18† 9.12	± .06	(2)
21°05′N, 46°34′W; 15 July 62	0	37.40	26.0	+1.24	9.40	± .06	(2)
North Atlantic Deep Water 21°05′N, 46°34′W; 15 July 62	3000	34.94	2.7	+0.10	9.55	± .09	(3)
		Antarctic Ocean					
Antarctic Bottom Water, Weddell Sea, 64°55′S, 52°10′W, *Eltanin* cruise 12, sta. 3; 17 Mar. 64	2926	34.66	— 1.2	— .45	8.44	± .10	(3)
		Mediterranean Sea					
Tyrrhenian Basin; 13 Aug. 62	2828	38.41	13.2	+1.33	9.47	± .19	(4)
		Red Sea					
Surf. inflow from Gulf of Aden, 12°04′N, 44°23′E; 18 Sep. 62	10	36.21	29.0	+0.65	9.63	± .23	(2)
Red Sea Deep Water, 15°18′N, 41°54′E, 17 Sep. 62	834	40.59	21.7	+1.92	9.29 8.98† 9.14	± .15	(2)
Brine, *Discovery* Deep *(13)*	~2000	255	44.8	+1.21	7.51	± .12	(3)
Brine, *Atlantis II* Deep *(13)*	~2000	255	55.9	+1.21	7.21	± .05	(2)

*Precipitated at room temperature; all other precipitations were at 100°C. †Precipitate dried at 70°C; all others dried at 120°C.

Table 2. Isotopic composition of oxygen in sulfate ion and in water in saline lakes, relative to SMOW. Except for the values for Owens Lake and Searles Lake (supplied by local companies), the sulfate concentrations are from the literature. Chloride measurements on samples from Mono Lake and the Caspian Sea agreed with those in the literature.

Sample		Composition (per mille)			
Source; date	Depth (m); T (°C)	($SO_4^=$) (ppm)	δ [H_2O]	δ [$SO_4^=$]	SO_4, mean deviation
Dead Sea, 31°13′N, 35°21′E; 21 Jan. 60	0; 21.6	900	+4.72	12.97	±0.11 (2)
Dead Sea, 31°20.3′N, 35°26′E; 21 Jan. 60	120; 21.9	540	+4.36	13.34	± .00 (2)
Great Salt Lake, 13 km SW Antelope Is.; 13 Oct. 54	Bot.; 17.2	16,400	−3.01	13.27	± .22 (2)
Salton Sea, NW end; 10 Apr. 64	5; ~22	7000	−1.66	13.73	± .18 (2)
Owens Lake, brine; 14 Sep. 54	*	23,400	+3.92	14.41	± .17 (2)
Caspian Sea; 19 Apr. 66	?; 18.3	3000	−2.22	14.68	± .00 (2)
Mono Lake; 2 July 64	1; 12	7900	−0.46	17.82	± .09 (2)
Searles Lake brine; 11 Sep. 55	†	48,700	+4.22	23.16	± .13 (2)

* Reservoir sample from wells as deep as 3 m. † From 18-m level of well GS-12.

characteristics of the water. The isotopic data for both sulfate and water are given as delta values (*8*) relative to the SMOW (mean ocean water) isotopic standard, which has approximately the $O^{18} : O^{16}$ ratio of mean ocean water. The mean average deviation of the sulfate data is about ± 0.10 per mille, and, excluding the Antarctic bottom water and the Red Sea brines, the total oceanic range is only 0.7 per mille, with a mean value of 9.50 (*9*).

The deep-ocean samples were chosen, on the basis of temperature, salinity, and water isotopic composition (*10*), to be as representative as possible of the core waters of the respective water masses. Comparison of the Pacific samples shows no tendency for samples stored for up to 6 years to change significantly in isotopic composition. There is a slight tendency in both Pacific and Atlantic samples for deep-water sulfate to be 0.2 to 0.3 per mille heavier than in surface samples. Two Pacific samples were collected essentially on the bottom: one (August 1966) was taken above a temperature probe, with a special bottle; the other, from the Japan Trench, is from the top of a gravity core. These bottom samples are about 0.2 per mille heavier than normal deep water; the difference may represent a slight effect of interaction with sediment.

In Fig. 2 the sulfate data are plotted versus the isotopic composition of the water. The data clearly show no correlation of sulfate composition with water composition; the sulfate values are quite independent of water composition and of temperature in both surface and deep samples, nor does the difference in isotopic composition between sulfate ion and water correlate with temperature. These data thus indicate a relatively long exchange time and lack of local equilibrium in the normal ocean samples.

We now show that these data probably represent a "regional" equilibrium with mean oceanic temperatures and water composition. Because of the uniformity of surface and deep-water data, we assume as a first approximation that the ocean is a uniformly mixed reservoir in which input of sulfate from the continents and removal by precipitation and sulfate reduction are balanced at a steady-state sulfate concentration and isotopic composition. Then the steady-state isotopic composition of the sulfate, δ, can be written:

$$\delta = [\delta^* + (\tau^*/\tau)(\delta_i - \epsilon)]/[1 + (\alpha\tau^*/\tau)]$$

where δ^* is the equilibrium δ value, τ^* is the isotopic-exchange time constant, α is the effective fractionation factor in sulfate removal from the ocean, $\epsilon = (\alpha - 1)$, δ_i is the isotopic composition of the sulfate input into the sea, and τ is the effective mean lifetime of a sulfate ion in the sea. The isotopic composition of the water is taken as 0.0 for convenience. The value of τ is crudely given by the ratio of the amount of sulfate in the sea (3.72×10^{15} tons) to the annual input, some 3.63×10^8 tons as calculated from river data (*11*); that is, about 10^7 (years).

Thus if τ^* were even as long as 10^4 years (see Fig. 1), the sulfate composition would not differ significantly from an average equilibrium value. Since a sulfate ion spends most of its time in the deep sea, the values tend to become uniform. If one uses a two-layer model of the sea, in which the deep water is exposed to the atmosphere at high latitudes, the observed mean depletion in radiocarbon of about 15 percent in deep water, relative to surface water, corresponds to residence times for water molecules, relative to mixing, of about 4000 and 80 years in deep and surface waters, respectively (*12*). The calculation is crude, but, if the exchange rates shown in Fig. 1 are at all realistic, the sulfate should exchange almost to equilibrium in the deep water but change only slightly during its time in the surface water.

The Red Sea Deep Water and the high-temperature brines may in fact represent an approach to a new equilibrium at higher temperatures. Even a relatively modest time of residence in Red Sea Deep Water (perhaps 50 years) may produce a slight reequilibration. Craig has shown, on the basis of isotopic data, that the Red Sea brine originates from Red Sea water flowing through an evaporite sequence (*13*), and the higher temperature of this water may have produced further reequilibration at high temperature. In general, one expects higher temperatures to produce a smaller fractionation and thus drive the sulfate composition closer to that of the water, as observed in the Red Sea. None of these effects can account for the composition of the Antarctic bottom water from the Weddell Sea, the data on which represent two individual precipitations, so that the deviation appears to be real, although we can offer no explanation of the result.

Table 2 lists the data on sulfate ions in saline lakes and brines. As the O^{18} enrichment in these ions extends up to the value of the isotopic composition of atmospheric oxygen (23 per mille) (Fig. 2), we may speculate that sulfate ions derived from oxidation of igneous sulfides have initially an isotopic composition near that of atmospheric oxygen, and that this composition is modified by exchange and bacterial reduction in the direction of equilibrium with water. However, in none of these lakes is equilibrium likely to be achieved. Bentor (*14*) has shown that all sulfate in the Dead Sea comes from the Jordan River, and that the present turnover time for sulfate in the Dead Sea is only about 370 years. The Salton Sea is known to become anoxic at certain times in the summer, during which times sulfate is reduced (*15*). It is evident that detailed studies of sulfate input and annual variation are required in order to explain the scatter of these lake and brine data (*16*).

We have analyzed one sample of reagent $BaSO_4$ (*17*), which has a delta value of 6.87 ± 0.10 per mille; we cite this sample because its composition provides a useful standard for intercomparison of analytical results on sulfates. The further extension of this work clearly depends on laboratory measurements of exchange-rate constants and equilibrium fractionation factors; because of the many data now available on sulfur-isotope ratios, addition of data on another isotope in sulfates should provide important geochemical information on sulfates, as well as contributing to the possible development of another isotopic temperature scale.

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8. The delta units are defined by $R/R_{SMOW} = (1 + \delta)$, where R is the ratio $O^{18} : O^{16}$ and SMOW is the defined standard mean ocean-water isotopic standard [H. Craig, *Science* **133**, 1833 (1961)], which is very close to the true oceanic mean. The delta values are expressed in per millage. Water samples are analyzed by equilibrating CO_2 with the water and by analyzing the CO_2; the analytical precision (2 σ) is within 0.04 per mille. Carbon dioxide from sulfate is measured relative to CO_2 in equilibrium with SMOW at 25°C; in converting the sulfate data to delta values versus SMOW itself, as given in the tables, the fractionation factor (25°C) between CO_2 and H_2O was taken as 1.0407 [J. O'Neil and S. Epstein, *J. Geophys. Res.* **71**, 4955 (1966)].
9. Distilled water, used for dilution and washing, analyzed —9.0 per mille; in one instance (from the Marianas Trench sample) a duplicate portion was diluted and the precipitate washed with enriched water of $\delta = +45$ per mille. The resultant sulfate analyzed + 9.84, or 0.25 per mille heavier, indicating that not more than 0.5 percent of the water oxygen can appear in the final CO_2, and that the error from such oxygen is less than 0.1 per mille. In another experiment we precipitated only 10 percent of the sulfate in a sample and found the precipitate to be 1 per mille lower in oxygen-18 than the total sulfate.
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12. H. Craig, in *Earth Science and Meteoritics (F. G. Houtermans Volume)*, J. Geiss and E. Goldberg, Eds. (North-Holland, Amsterdam, 1963), pp. 103–114. The water residence times relative to mixing are much longer than the carbon residence times in such a model because carbon exchanges rapidly with the atmosphere.
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16. H. C. Urey [*J. Chem. Soc.* **1947**, 562 (1947)] has calculated theoretical sulfate isotopic enrichments relative to liquid water of 19.4, 14.7, and 5.0 per mille at 0°, 25°, and 127°C, respectively. Although many of the lake and brine samples show enrichments in this range, we consider it much more likely that ocean-water sulfate ions are close to equilibrium with water, and that the calculated values are too high because of the many uncertainties in calculation of partition-function ratios for dissolved ions by treating them as perfect gases.
17. Baker and Adamson "Reagent $BaSO_4$"; 99-percent minimum purity. Our yields range from 92 to 100 percent, the low figures reflecting absorption of moisture during weighing.
18. Supported by NSF grants NSFgp-3347 and NSFga-351, and by ONR grant NONR-2216(23). A.L. was on leave from Laboratorio Geologia Nucleare, Pisa, while the work was done. We thank P. Kroopnick, S. Drais, and B. Hom for aid with the analyses. M. Lloyd has obtained similar data on ocean-water sulfates; we thank him for discussion.

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Rapid Methods of Determining Cooling Rates of Iron and Stony Iron Meteorites

Abstract. *Two rapid and simple methods have been developed for determining the approximate cooling rates of iron and stony-iron meteorites in which kamacite formed by diffusion-controlled growth along planar fronts. The first method requires only measurements of the mean kamacite bandwidth and the bulk nickel content. The second method requires the determination of the nickel composition near the taenite-kamacite interface with an electron microprobe.*

Recently we have developed (*1*) a method for determining the cooling rate of meteorites with Widmanstätten structure (octahedrites and pallasites). This structure formed within the temperature range of 700° to 300°C as the meteorite cooled within a parent body. The method is more precise (±10 to 40 percent) than previous calculations of cooling rates (*2*), but is complicated to apply because it involves the comparison of a complex computer calculation with nickel diffusion gradients in carefully selected and oriented kamacite and taenite bands. We have therefore developed two simplified methods for determining the cooling rates (at 500°C) of meteorites exhibiting Widmanstätten structure.

Kamacite (α) and taenite (γ) in iron meteorites are essentially Fe-Ni solid solutions containing, respectively, 5 to 7.5 percent and 15 to 50 percent Ni by weight. As the meteorite cooled through the temperature range 700° to 300°C, α phase nucleated in γ phase and grew by solid-state diffusion. The α plates form the unique pattern called the Widmanstätten structure. At lower temperatures decreasing diffusion rates caused compositional zoning next to the borders of taenite and kamacite. These can be easily measured with an electron microprobe (*1–3*).

The complex method (called hereafter the precise method) which we have developed (*1*) for determining the cooling rate of the Widmanstätten structures uses the known phase equilibria and diffusion coefficients in the Fe-Ni system. It also takes into account all the following factors which influence the formation of the Widmanstätten structure: (i) the bulk nickel content of the meteorite; (ii) undercooling below the equilibrium α-precipitation temperature; (iii) impingement of neighboring kamacite plates; (iv) the cooling rate of the meteorite; (v) pressure. Goldstein and Ogilvie (*2*) have shown that the pressure at the positions of the iron meteorites within the parent bodies was apparently not sufficient (< 10 kb) to influence the growth of kamacite. The other factors (i to iv) determine the ultimate kamacite bandwidth and the shape of the retained diffusion gradients in both taenite and kamacite. This method, as well as the two described below, also assumes that minor elements in the meteorite have not significantly affected either the diffusion coefficients of nickel or the Fe-Ni phase equilibria dur-