rocks along the San Andreas fault. The field boundary in Fig. 3 appears to be close to the geothermal gradient. This proximity suggests that in the natural situation the lower limit of earthquakes might be quite irregular in depth. Local cold spots along the fault might result in local pockets of high seismic activity along the fault. Such features have been described in California (*2*); it would be of great interest to test this suggestion by detailed temperature measurements in the areas in question. Finally, our observations do not support the view (*3*) that earthquakes disappear because of a reduction of strength with depth; the stress difference to cause sliding actually increased, if points are compared along the geothermal gradient. For example, the stress difference to cause sliding on the fault in gabbro at 4 kb and 400°C was about 11 kb, nearly 3 times that at 1 kb and 25°C. At still higher temperatures, a drop in strength seems likely; the level at which this strength drop occurs may bear little relation to the lower limit of earthquakes.

W. F. BRACE
Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge 02139
J. D. BYERLEE
Office of Earthquake Research and Crustal Studies, U.S. Geological Survey, Menlo Park, California 94025

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12. The rock sample was a precisely ground cylinder 16 mm in diameter and 35 mm long. The sawcut, if present, was located midway between the ends and made an angle of 30° to the cylinder axis. The graphite sleeve was 1.3 mm thick; the annealed seamless copper foil, 0.32 mm thick. An extensive series of experiments was conducted at room temperature to determine any possible stabilizing effect of the graphite-copper jacket. The results revealed that a stabilizing effect on sliding existed only below a pressure of 2 kb. It took the form of lowering the amplitude of stick-slip to nearly zero. The shearing stress to cause frictional sliding increased about 10 percent as compared with an experiment at the same pressure, in which a polyurethane jacket 3 mm thick was used. Because of these effects, most experiments here were conducted at or about 2-kb pressure; at this pressure results of room-temperature experiments in which the copper-graphite jacket was used were nearly identical with results from experiments using polyurethane. In any event, stabilizing effects present at room temperature would probably not be important at high temperature because of the increased ductility of the copper.
13. Our apparatus resembled in a general way the one described by Griggs *et al.* (*9*, p. 46). It was internally heated, with low friction O-ring seals. Stiffness of the loading system was about 10^5 kg/cm. Pressure was known to 1 percent; temperature to about 10°. Strain rate was calculated from the rate of advance of the screw-driven piston.
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Carbon-13 in Black Sea Waters and Implications for the Origin of Hydrogen Sulfide

Abstract. *A combination of measurements of carbon-13 and the hydrogen sulfide content in Black Sea waters with available data on the total carbon dioxide in these waters indicates that the contribution of organic sulfur to the hydrogen sulfide lies between 3 and 5 percent and increases with depth. Likely causes for the increase are increasing productivity or upward movement of the anoxic zone during the last 2000 years.*

The amount of dissolved oxygen in the Black Sea decreases rapidly with depth and reaches zero between 125 and 250 m; the depth at which the amount reaches zero depends mainly on the distance from shore (*1*). There is a thin transition zone in which small amounts of oxygen and hydrogen sulfide coexist, and at greater depth the concentration of hydrogen sulfide increases, rapidly at first, but begins to level off at 1000 m. Comparison of variations in the C^{13}/C^{12} ratio and in the concentrations of dissolved oxygen and hydrogen sulfide, respectively, reveals strong resemblances. In combination with data on the concentrations of inorganic carbon and hydrogen sulfide, the carbon-13 data allow one to calculate the relative contributions of reduced seawater sulfate and liberated organic sulfur to the hydrogen sulfide content at any depth in the Black Sea.

During the Black Sea cruise of R.V. *Atlantis II* in the spring of 1969 the water column at eight stations (Fig. 1) was sampled with Teflon-lined Nansen bottles for the determination of C^{13}/C^{12} ratios in the dissolved inorganic carbon (ΣCO_2). The samples were preserved, extracted, and analyzed according to the procedures described by Deuser and Hunt (*2*), except that oxygen was used for stripping CO_2 from the water samples. By this process hydrogen sulfide was oxidized to sulfur, and the process proved very effective in producing clean CO_2 samples for mass analysis. The C^{13}/C^{12} ratios are reported in the δ-notation where

$$\delta C^{13}(\text{‰}) = [\frac{(C^{13}/C^{12})\text{ samp.}}{(C^{13}/C^{12})\text{ stand.}} - 1] \times 1000$$

The reference standard is the Pee Dee belemnite (PDB) carbonate (*3*). Reproducibility of the entire procedure is better than ± 0.1 per mil.

The results of δC^{13} measurements made on 81 samples from the eight stations are plotted against water depth in Fig. 2a. Individual profiles were

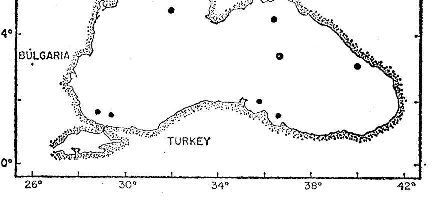

Fig. 1. Hydrographic stations in the Black Sea for which δC^{13} profiles were determined.

Table 1. Data used in calculating the contribution of organic sulfur to the H_2S content of the Black Sea.

Depth (m)	δC^{13} (‰)	ΣCO_2 (*12*) (μmole/liter)	H_2S (*4*) (μmole/liter)	S_{bio} (μg-atom/liter)	S_{bio} (% of S in H_2S)
500	–4	3790	180	6.6	3.7
1000	–5.5	4050	280	11	4.0
1500	–6.5	4240	310	15	4.8

similar enough to justify their superposition in a single graph for the purposes of this report. About 100 O_2 and H_2S determinations on samples from the same stations are shown in Fig. 2b (*4*). The precision of the H_2S determinations is better than ± 1 percent of the concentrations, except for concentrations of less than 5 μmole/liter. The depths of the points in Fig. 2, a and b, differ because samples for C^{13} and dissolved-gas determinations had to be collected on separate casts in most instances. Analytical coverage of the deeper waters is relatively scarce because most of the stations were near the shelf and sampling was concentrated particularly on the O_2–H_2S transition zone. Much of the scatter of the points above 300 m is due to the differences in the depth of that zone among stations.

Comparison of the two plots of Fig. 2 shows a striking resemblance in the changes of the variables with depth. The correlation in the upper waters between O_2 content and δC^{13} corresponds to that found in the ocean and is due to the synthesis of organic matter near the surface and to its oxidation at depth (*2, 5*). In the open ocean the oxygen concentration very rarely reaches zero. Both O_2 content and δC^{13} increase with depth below an oxygen minimum and reach a more or less steady value in the deep water. The continued correlation in the Black Sea between δC^{13} and O_2 content down to the depth where dissolved oxygen disappears and the almost smooth transition into an inverse correlation with H_2S in the anoxic zone strongly suggest that these phenomena, too, are related to decomposition of organic matter. Danilchenko and Chigirin (*6*) studied in detail the mechanism of H_2S formation in the Black Sea. They concluded that H_2S formed through bacterial reduction of sulfates, a process which involved the simultaneous oxidation of organic matter to CO_2. They stated that this process was responsible for 99.4 to 99.6 percent of all the H_2S. Redfield *et al.* (*7*) also concluded that sulfate reduction accounts almost fully for the formation of H_2S. On the basis of the same data, however, Kriss (*8*) argued that the extent of sulfate reduction in the water column was insufficient to cause the characteristic increase of H_2S with depth and that a considerable fraction, perhaps half of the H_2S, originated from the putrefaction of organic matter, especially the breakdown of proteins. Light hydrocarbons (particularly methane and ethane) in the deep water amount to less than 10 μg-atom of carbon per liter (*9*), an implication that in this process, if it is quantitatively important, the organic carbon is predominantly oxidized to CO_2. Kriss also reported that sulfate-reducing bacteria are most common in the top layers of the sediment and concluded that H_2S is predominantly formed at the bottom of the Black Sea and from there rises into the water column. Although on the basis of the carbon-13 data alone one cannot settle the argument about the place of H_2S formation (sediment or water column), these data do provide a means to calculate the fraction which has arisen from the decomposition of organic matter as opposed to that which is due to the reduction of sulfate.

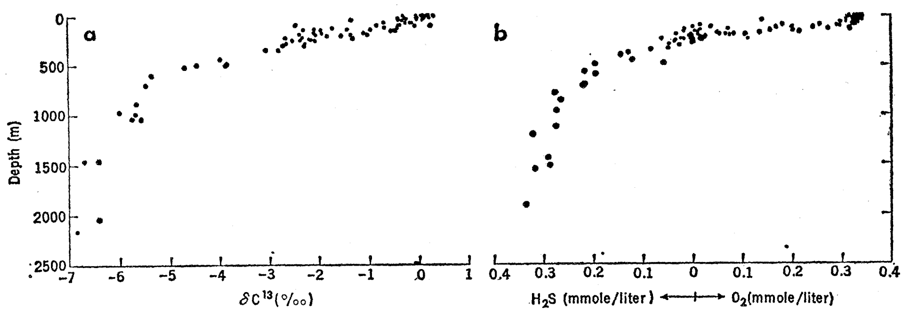

Fig. 2. Superposed profiles of (a) δC^{13} and (b) dissolved O_2 and H_2S (*4*) at the eight stations shown in Fig. 1.

Carbon-13 data from the Atlantic and the Pacific (*2, 5*) indicate that, typically, the δC^{13} of the deep sea, that is, below the depth at which significant input of biogenic carbon into the total CO_2 occurs, changes very little with depth and is about 1.5 to 2.5 per mil below the value near the surface. By analogy, we may conclude that in the absence of the now prevailing anoxic conditions the δC^{13} in the deep parts of the Black Sea would lie near -1.5 per mil (δ_{DW}). Analyses of plankton indicate that the average δC^{13} of living organisms in the Black Sea (δ_{OM}) is -23 per mil (*10*). Using this information, we can calculate the contribution of biogenic carbon in microgram-atoms per liter (C_{bio}) to the total CO_2 at any depth in the Black Sea from the measured δC^{13} (δ_m) and the quantity of the total CO_2 in micromoles per liter ($\Sigma\, CO_2$) at that depth:

$$C_{bio} = \frac{\delta_{DW} - \delta_m}{\delta_{DW} - \delta_{OM}} \times \Sigma CO_2$$

The atomic ratio of sulfur to carbon in marine organic matter varies between 0.007 and 0.025 (*11*). Using 0.015 as a likely mean value, we obtain the amount of biogenic sulfur in the water (S_{bio}) as

$$S_{bio} = 0.015\, C_{bio}$$

and this value, expressed in microgram-atoms per liter, can be directly compared to the measured amount of H_2S at that depth.

Results calculated from values for $\Sigma\, CO_2$ (*12*) and the mean values for δC^{13} and H_2S content of Fig. 2 for 500, 1000, and 1500 m are shown in Table 1. These data indicate that organic matter contributes between 3 and 5 percent to the H_2S at all depths in the Black Sea. The figures also suggest that the organic contribution to the H_2S increases with depth. The trend is independent of the assumed ratio of sulfur to carbon in organic matter and of the estimate of δ_{DW} but is due to the apparent fact that the increase in the concentration of H_2S levels off faster below 500 m than the decrease of δC^{13} does (Fig. 2).

It may thus be concluded that organic matter contributes a small, but significant, fraction of the hydrogen sulfide in the Black Sea. This fraction is much higher than the 0.5 percent conceded by Danilchenko and Chigirin (*6*) and about twice as high as the value inferred by Redfield *et al.* (*7*) on the basis of ratios of sulfate to chloride, but putrefaction most certainly does not have the importance attributed to it by Kriss (*8*). The increase of the organic sulfur contribution with depth can have any of the following causes.

1) If the conclusion of Kriss (*8*) is correct that most of the H_2S is formed in the sediment and from there rises into the water column, the H_2S near the bottom should have formed later than that at shallower depths. A greater percentage of biogenic sulfide at depth can then signify either an increase in the productivity of the Black Sea in the very recent geological past (*13*) or an upward growth of the anoxic zone with a concomitantly increased influx of dead organisms to the sediment.

2) If the H_2S is formed predominantly in the water column, the release of organic sulfur must increase more rapidly than sulfate reduction with depth. This could be due either to differences in the depth habitats of the bacteria involved in the two processes or to differences in resistance to decomposition between the proteins (which contain most of the organically bound sulfur) and the organic matter involved in sulfur reduction.

3) If there are significant differences in the response of the organic constituents to bacterial degradation, the observed effect might be due solely or in part to differences in the C^{13} content of these constituents. This seems unlikely, however, because δC^{13} values of the organic matter in the top layers of the sediment are indistinguishable from those of the living plankton.

Since there is at present no evidence to support the hypotheses presented in paragraphs 2 and 3 above, it appears that either of the two explanations proposed in paragraph 1 best fits the facts at hand.

W. G. DEUSER
Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543

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Production of Carbon Monoxide and Gaseous Hydrocarbons in Seawater: Relation to Dissolved Organic Carbon

Abstract. *Carbon monoxide, ethylene, and propylene were produced in illuminated, cell-free distilled water or natural seawater systems to which dissolved organic matter produced by phytoplankton had been added. Methane and the higher saturated gaseous hydrocarbons were not produced. In the dark, little or no carbon monoxide and no hydrocarbons were produced in the distilled water systems; only carbon monoxide was produced in natural seawater, but less was produced than in the light.*

Vertical distributions of carbon monoxide and the gaseous hydrocarbons have been reported for some oceanic areas (*1*). The profiles show distinct maxima at various depths within the photosynthetic zone, which suggests a relation to biological activity. To explore such a relation in the laboratory, we first analyzed a bacteria-free culture of the ultradiatom *Chaetoceros galvestonensis* for these gases at various times during a period of growth and senescence. The concentrations of carbon monoxide (CO) and the two- to four-carbon hydrocarbons, except isobutane, increased markedly with time in illuminated cultures. Methane was not formed. Unexpectedly, however, the unsaturated hydrocarbons (*2*) and especially CO also increased in sterile controls (without cells) that were incubated in the light, although the gas concentrations attained at any given time were much lower (Table 1). This suggested that these gases might somehow be produced from the dissolved organic carbon fraction (DOC) in the (natural) seawater from which the culture medium was prepared.

To examine this possibility, a series of experiments was conducted with distilled water or natural seawater, each enriched with DOC produced by cultured phytoplankton. Distilled water in Pyrex carboys was sterilized in an autoclave. The natural seawater was sterilized by exposing it in carboys to gamma radiation (about 54,000 rad; ^{60}Co source). This seawater was pooled from several sources and had previously been foamed (*3*) in other experiments to remove surface-active material (normally amounting to about 10 percent of the natural DOC). The carboys were then placed on magnetic stirrers and purged overnight with CO- and hydrocarbon-free air, prepared by passing compressed air (breathing quality) through palladium-coated alumina pellets at 400°C. All siphons and purging tubes were autoclaved, and cotton plugs were used in the gas lines as further precaution against microbial contamination (*4*). Sterile technique was employed at all times until the samples were drawn and stoppered.

"Blank" samples (designated set A) were drawn by completely filling (through a tube extending to the bottom) autoclaved, 500-ml, standard-taper, glass-stoppered Pyrex bottles. A sample for analysis of DOC was also taken (*5*). Sterile, cell-free culture filtrate, obtained by pooling and membrane-filtering (with 0.2-μm filters) several bacteria-free phytoplankton cultures (*6*), was then added as a means of introducing "realistic" DOC. After the system was purged and stirred for 1 to 2 hours a second set of 500-ml samples (set B) was drawn, together with a sample for DOC analysis. More filtrate was then added to increase DOC and, after another period of stirring and