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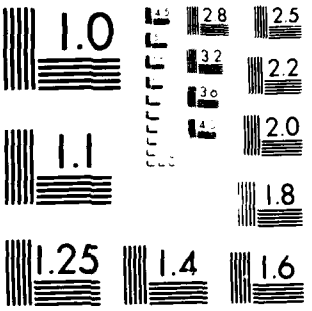
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Stable Carbon Isotopes in Sea Water

Werner G. Deuser
191-32-8738
(617) 548-1400 ext. 339

John M. Hunt
284-C1-0480
(617) 548-1400 ext. 329

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617-548-1400 X551

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(1) Long-Range Objectives and Summary

The program aims at an understanding of the relationships that exist between the many varied phases of carbon in the ocean, their relation to other phases in the oceanic environment, and the source, fate and regeneration of carbon phases. Stable isotopes provide an excellent means for detecting many of these relationships because they represent characteristic natural labels which allow us to trace the path of carbon in its natural cycle from one phase to another. Our results have a direct bearing on the identification of water masses and the extent and rate of vertical and horizontal mixing in the ocean.

Thus far our efforts have been concentrated on the distribution of the carbon isotopes in the dissolved inorganic and organic carbon phases. We have found a pronounced correlation between the concentration of dissolved oxygen and the C^{13}/C^{12} ratio of the dissolved inorganic carbon (Deuser and Hunt, 1969). This correlation is due to the photosynthetic carbon fixation in the near-surface waters and its remineralization at depth. The two processes affect the C^{13}/C^{12} ratio because photosynthesis is accompanied by a strong isotopic fractionation leading to a C^{12} enrichment of organic matter with respect to the source carbon. The shift in the isotope ratio produced by the addition of oxidized organic carbon to the inorganic carbon in the ocean can be

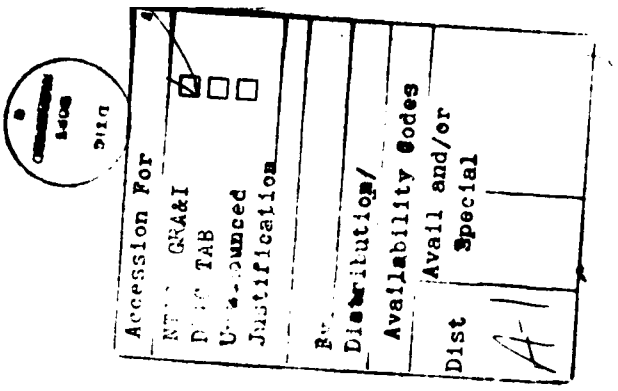
used to calculate the input of organic carbon at any depth. This input may be as high as 10% of the carbon present.

Our data from the Atlantic showed an excess of biogenic carbon at the depth of the oxygen minimum. This suggests horizontal advection of waters low in oxygen and high in biogenic carbon and supports the theory that the oxygen minimum layer is not merely a locally originating phenomenon but rather forms in the eastern tropical regions of high productivity and spreads horizontally from there.

(2) Progress over the Past Year

Much of our effort during the past year was centered on a thorough investigation of the carbon cycle in the Black Sea. The Black Sea has two features which make it particularly interesting: (a) it is a basin which is nearly isolated from the Mediterranean and thereby the world's oceans, (b) below an aerated top layer of 125 to 250 m thickness the water is anoxic, i.e. it contains no dissolved oxygen but rather hydrogen sulfide whose amounts increase with depth. Both features have a profound effect on the carbon balance in the basin. The determination of flux rates in a small basin like the Black Sea can aid greatly in unravelling the more complex situation in the ocean.

The results of two phases of our investigations in the Black Sea have been published and the remainder is in preparation for publication. All are



summarized below.

Analyses of the C^{13}/C^{12} ratios in plankton from various parts of the Black Sea (Deuser, 1970a) showed that this ratio is extremely uniform throughout the basin, an expression of the good horizontal circulation and mixing of the surface water. We also encountered the first reported instance of a beginning carbon shortage at the height of a spring bloom of diatoms. The accelerating carbon fixation of the rapidly multiplying population had resulted in a situation where the amount of organic carbon in the cells began to surpass that of the carbon available for fixation. This was particularly surprising in view of the high inorganic-carbon content of the Black Sea which is about double that of normal sea water.

Determinations of the C^{13}/C^{12} ratio in the dissolved inorganic carbon yielded results strongly deviating from those in the open ocean (Deuser, 1970b). δC^{13} and the concentration of H_2S showed a strong negative correlation throughout the water column. Near the bottom we obtained δC^{13} values of -6.5‰. The observed correlation made it possible to make inferences on the origin of hydrogen sulfide in the Black Sea and on changes in the circulation and mixing patterns. We determined that between 95 and 97% of the H_2S has its origin in the bacterial reduction of sulfate and that the remainder stemmed from the putrefaction of organic matter. This latter fraction increases with depth. The most likely causes for the increase are increasing productivity

and a thinning of the aerated top waters over the past 2000 years, the estimated residence time of Black Sea deep water.

We also analyzed the dissolved organic carbon in a Black Sea profile for both concentration and C^{13}/C^{12} ratio; the latter is still in progress. Our results on the concentrations, in contrast to the few available Russian data, show a profile very similar in shape to the profiles of H_2S and δC^{13} of the inorganic carbon. This leads us to suspect the Russian data which show small erratic variations throughout the water column. In our profile the DOC increases smoothly from 2 mg C/l at the O_2-H_2S transition zone to 6 mg C/l at the bottom. Surface values lie near 2.5 mg/l. δC^{13} of the DOC decreases with depth below the transition zone, indicating that the chemical composition of the organic matter changes from the top to the bottom. The results of this work are presently in preparation for publication.

Additional information on the carbon cycle in the Black Sea has been gained from our studies of the organic and inorganic fraction of the sediment. These studies are supported by NSF but complement our ONR-supported ones. Results of this work were reported at the symposium on the Black Sea which took place at WHOI at the beginning of August. They are now being prepared for publication.

A bibliography of scientific literature on the Black Sea and its costs was compiled by P.N. Laking to assist participants in the Black Sea Program.

Related to our isotope program was a round of interlaboratory calibrations preparatory to the GEOSECS program. Three laboratories analyzed, each in its own way, the C^{13}/C^{12} ratio of identical sets of 24 sea water samples from a depth profile collected at a test station west of San Diego. Our results and those of one of the other two laboratories showed equally high internal precision as well as accuracy but ours was the only complete set of 24 good measurements. This test, better than anything else, demonstrated the reliability and quality of our sample preservation, extraction and analytical procedures. The results of this intercalibration round were presented at the Annual Meeting of the American Geophysical Union in Washington, D.C. (Deuser, 1970) and are presently in press Kroopnick,Deuser and Craig, 1970).

During the past year we also constructed a constant-volume manometer for measuring routinely the extraction yield of our samples. This instrument allows us to determine the total inorganic carbon content (ΣCO_2) of our samples with an accuracy of better than $\pm$ 0.1%, a level not easily achieved by far more sophisticated alternate methods commonly in use.

(3) Proposed Research Program for 1971

As we anticipated at the end of last year's proposal we are now getting ready to begin the next phase of our program which is a detailed look at the interaction between the bottom and the water column. Analyses

of the near-bottom samples of the GEOSECS profile, referred to above, bore out our expectation that the ocean floor actively participates in the oceanic carbon cycle-- not only as a sink but also as a source of carbon for the overlying waters. This participation finds its expression in an increase of ΣCO_2 and a change in the C^{13}/C^{12} ratio in the water. The nature and extent of the carbon flux from the sediment into the water column are not known. Because of the greatly different C^{13}/C^{12} ratio of organic and carbonate carbon, stable isotope studies in connection with measurements of ΣCO_2 are best suited to yielding information on the two important questions (1) what is the source of the carbon entering the water-- organic matter or carbonate? and (2) how much carbon enters the bottom water from this source or these sources? The answers to these questions have great significance for the eventual determination of the oceanic carbon balance and cycle and, perhaps more important, for a more realistic evaluation of the radiocarbon data on deep waters which cannot be taken at face value for the purposes of residence time calculations for deep waters (Craig, 1969). As the uptake of carbon from the bottom ought to be cumulative along the path of a parcel of water through the deep sea its relative importance will grow with the "age" of the parcel, i.e. the time elapsed since it last was in exchange with the atmosphere.

There is as yet no knowledge at all on the effects which the type of sediment, temperature, oxygen content, and water depth have on the

carbon input to the bottom water. We, therefore, propose to initiate our studies of the near-bottom waters by analyzing a series of water profiles to be collected in environments greatly different with respect to these variables. Fortunately there exists a wide spectrum of such environments in the Caribbean which are in relative proximity to one another and to Woods Hole. We propose to take water profiles, with closely spaced samples near the bottom, along two transects in the Caribbean. One transect is to run from between the islands of Tortuga and Margarita into the center of the Cariaco Basin and the other from the banks between eastern Honduras and Jamaica into the center of the Cayman Trench.

The Cariaco Basin is anoxic from a depth of about 375 m to the bottom at about 1400 m. Its temperature is constant at 17°C throughout the anoxic waters (Richards and Vaccaro, 1956). In some respects the conditions are similar to those in the Black Sea but there are important differences. One is the much freer exchange with the open ocean and another important difference for our studies is the nearness to other basins (Bonaire and Venezuelan Basins) which have very similar carbon input from above but are aerated. A study of this area, therefore, provides a unique opportunity to gain an insight into the effects of both oxygen and temperature. For comparison, one station each is planned in the Bonaire Basin and in the southern part of the Venezuelan Basin, just north of the Cariaco Basin.

The Cayman Trough contains the greatest depth in the Caribbean and is located very close to shallow banks. A transect of stations

across this bathymetric contrast includes a transition from waters greatly supersaturated in calcium carbonate to strongly undersaturated ones at the bottom of the trench. The trench thus provides an excellent opportunity to assess the relative importance of inorganic versus organic carbon input along the sea floor over a great depth range.

Detailed study of the carbon fluxes in these two environments which incorporate extremes of the parameters most likely to influence the carbon exchange between the sediment and the water column should aid greatly in the subsequent efforts to determine quantitatively the influence of this exchange on our present models of large-scale circulation and residence times of water masses in the major oceans.

The cruise plans are presently being finalized. Our program is scheduled for the last leg of the South Atlantic cruise of R/V Knorr in 1971. Our sampling will require about five days on station.

(4) References

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(5) Publications Resulting from the Contract

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Laking, P.N., 1970, Bibliography of Scientific Literature on the Black Sea. W.H.O.I. Ref. 70-32. Unpublished Manuscript. 280 p.

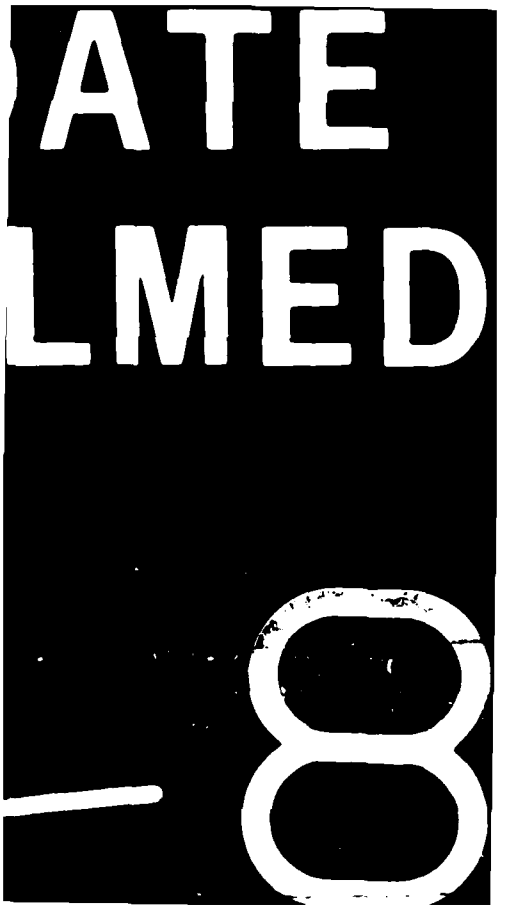
(6) Consultation and Testimony for Members of Congress by John M. Hunt

1. A statement on waste disposal in the ocean was presented to the U.S. House of Representatives Subcommittee on Fisheries and Wildlife Conservation on Tuesday, July 28, 1970. This Committee is chaired by Representative Dingell of Michigan. The testimony referred to the hazards of dumping mercury and other heavy metals into the ocean. I subsequently provided more detailed information by letter concerning the overall problem of oil pollution for Congressman Dingell and Congressman Hastings Keith of Massachusetts.

2. Testimony was presented to the Antitrust and Monopoly Subcommittee of the U.S. Senate on August 12, 1970. This Subcommittee is chaired by Senator Hart of Michigan. My statement referred to the dangers of increasing oil pollution to the ecology of the marine environment.

(7) Budget

The budget has been kept very close to last year's figures. There is one item of new equipment which is a small pinger needed for close depth control during the sampling of the near-bottom waters. Travel includes two tickets to join the ship at Barbados and travel and per diem for the attendance of one scientific meeting.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