

tion 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

References and Notes

1. G. Neumann, *Ann. Hydrogr. Marit. Meteorol.* **71**, 1 (1943).
2. W. G. Deuser and J. M. Hunt, *Deep-Sea Res.* **16**, 221 (1969).
3. H. Craig, *Geochim. Cosmochim. Acta* **12**, 133 (1957).
4. I thank K. Grasshoff for making available his determinations of the O_2 and H_2S concentrations.
5. H. Craig, *J. Geophys. Res.* **75**, 691 (1970); and W. G. Deuser, in preparation.

6. P. T. Danilchenko and N. I. Chigirin, *Tr. Sevastopol'skoi Biol. St. Akad. Nauk SSSR Ser. 2* **1926**, No. 10, 141 (1926).
7. A. C. Redfield, B. H. Ketchum, F. A. Richards, in *The Sea*, M. N. Hill, Ed. (Interscience, New York, 1963), vol. 2, p. 26.
8. A. E. Kriss, *Marine Microbiology* (Oliver & Boyd, London, 1963), chap. 4, p. 242.
9. J. W. Swinnerton and V. J. Linnenbom, in *Hot Brines and Recent Heavy Metal Deposits in the Red Sea*, E. T. Degens and D. A. Ross, Eds. (Springer-Verlag, New York, 1969), p. 252.
10. W. G. Deuser, *Nature* **225**, 1069 (1970).
11. A. P. Vinogradov, *The Elementary Chemical Composition of Marine Organisms* (Sears Foundation for Marine Research, Yale University, New Haven, 1953), Memoir 2, p. 138; K. Mita, *Bull. Jap. Soc. Sci. Fish.* **27**, 239 (1961); T. Matsumoto, M. Satake, Y.

- Hirata, *J. Oceanogr. Soc. Jap.* **20**, 110 (1964).
12. B. A. Skopintsev, F. A. Gubin, R. V. Vorobeva, O. A. Verzhinina, *Tr. Morskogo Gidrofiz. Inst. Akad. Nauk SSSR* **13**, 89 (1958); O. A. Alekin and N. P. Moricheva, *Dokl. Akad. Nauk SSSR* **167**, 423 (1966).
13. Complete renewal of the water below 30 m in the Black Sea requires about 2500 years, according to H. U. Sverdrup, M. W. Johnson, R. H. Fleming, *The Oceans* (Prentice-Hall, Englewood Cliffs, N.J., 1942), p. 651.
14. I thank P. G. Brewer for collecting samples for me at station 1472 and E. Ross for assistance in the laboratory. Supported by the Office of Naval Research under contract N00014-66-C0241 and by NSF grant GA-1659. Contribution No. 2450 from the Woods Hole Oceanographic Institution.

4 February 1970

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_2 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

Table 1. Gas production in sterile systems after 14 days of incubation. Initial gas concentrations were zero. Sets A, B, and C are explained in the text. L, illuminated samples; D, dark samples; T, trace.

Set	Sample	Initial DOC (mg/liter)	CO (10 ⁻⁵ ml/liter)	CH ₄ (10 ⁻⁵ ml/liter)	C ₂ (10 ⁻⁶ ml/liter)	C ₃ H ₆ (10 ⁻⁶ ml/liter)	C ₃ H ₈ (10 ⁻⁶ ml/liter)	n-C ₄ H ₁₀ (10 ⁻⁷ ml/liter)	i-C ₄ H ₁₀ (10 ⁻⁷ ml/liter)	
	L	Chaetoceros galvestonensis culture								
		460	0	28	53	17	11	0	0	
	L	Culture medium control								
		110	0	2.5	2	0	0	0	0	
	L	Distilled water plus DOC								
A	L	0.4	9	0	4.5	4	0	0	0	
B	L	1.5	13	2	4.5	4.7	0	0	0	
C	L	2.3	21	2	4.5	5.7	0	T	0	
	L	Distilled water plus DOC								
A	L	0.2	7	0	5	4.5	0	0	0	
B	L	1.5	15	0	8	7.5	0	0	0	
C	L	7.4	70	0	20	15.5	T	T	T	
A	D	0.2	1.8	0	T	0	0	0	0	
B	D	1.5	1.3	0	T	0	0	0	0	
C	D	7.4	4.1	0	T	0	0	0	0	
	L	Natural seawater plus DOC								
A	L	0.8	58	0	6	3	T	T	T	
B	L	2.3	71	0	10	8.5	T	T	T	
C	L	7.4	83	0	16	14	T	T	T	
A	D	0.8	24	0	0	0	0	0	0	
B	D	2.3	16	0	0	0	0	0	0	
C	D	7.4	10	0	0	0	0	0	0	

purging, sample set C and its corresponding DOC sample were drawn. To avoid introducing room air into the headspace of the carboy and thus into water not yet withdrawn, purging was continued while samples were being drawn.

Duplicate samples from all three sets at time zero were immediately analyzed for CO and the one- to four-carbon hydrocarbons (7). In all but the earliest experiments, the remaining bottles were divided into two groups, "light" and "dark," and the bottles in the latter group were kept in total darkness until analyzed. The early experiments dealt only with illuminated samples. The "light" group of bottles was placed in constant illumination under 40-watt, cool-white fluorescent tubes. Pairs within each set were arranged on the table so that one member of each pair would receive central illumination (about 3000 lux) whereas the other would receive peripheral illumination (roughly 2000 lux).

At appropriate times, pairs of light and dark bottles from each set were analyzed. Sterile connections were used to deliver each sample into the stripping chamber, and maximum precautions against contamination were taken whenever the bottles were open. The residue (about 50 ml) that remained in each bottle was filtered onto a corresponding membrane filter and incubated on nutrient agar as a check on the sterility of the samples at the time of analysis. Data obtained from those experiments in which the samples were shown to be uncontaminated are given in Table 1.

In all sterile, illuminated samples, CO and the unsaturated hydrocarbons increased in concentration with time (Fig. 1), whereas no saturated hydrocarbons were formed. In sterile, dark samples, there was little or no production of either CO or hydrocarbons in the experiments with distilled water. In the experiment with natural seawater, some CO (but no hydrocarbons) was produced in the dark. Production of only CO in the dark was also observed in an earlier experiment with natural seawater, in which extra DOC was not added. In this case, the seawater had been sterilized by filtration, but some of the individual samples were contaminated, and the experiment is not considered here. In the illuminated samples, agreement between members of each pair was close, but the sample which was exposed to greater illumina-

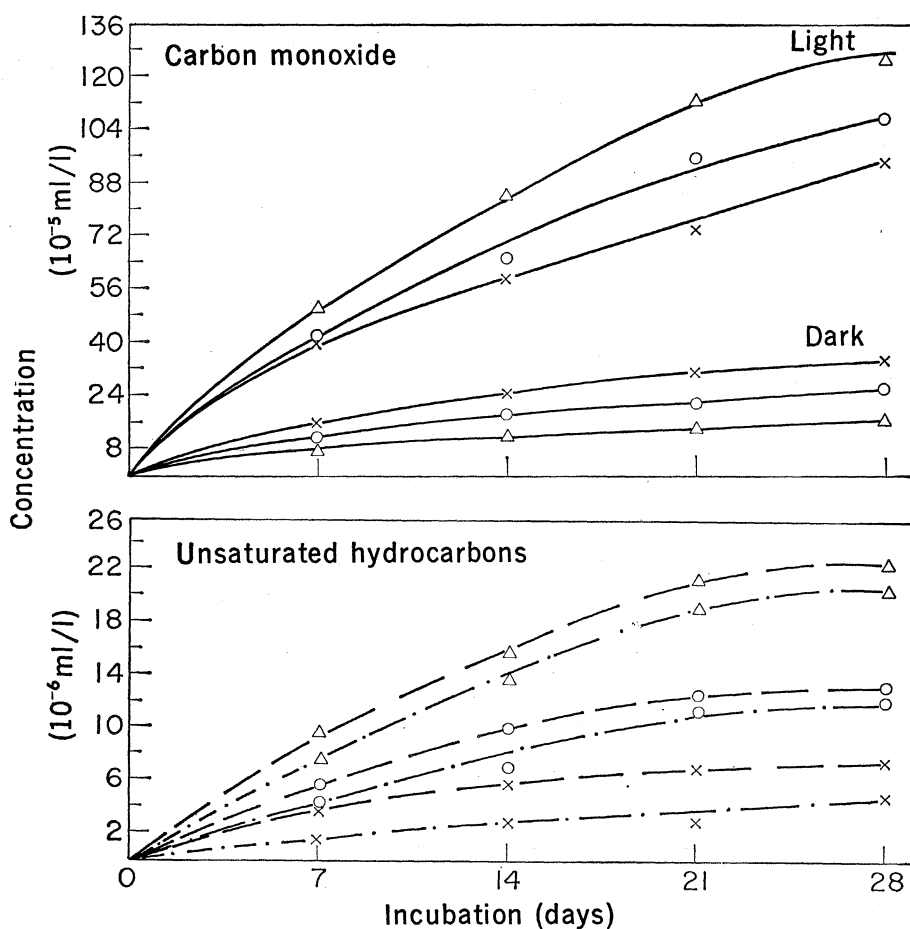


Fig. 1. Time course of carbon monoxide and unsaturated hydrocarbon production in illuminated and dark samples of sterile natural seawater, with initial DOC concentration as a parameter. Solid lines, CO; dashed lines, C₂; dash-dot lines, C₃H₆. No hydrocarbons were formed in the dark. Initial DOC concentrations: set A (crosses), 0.76 mg of carbon per liter; set B (open circles), 2.31 mg of carbon per liter; set C (triangles), 7.41 mg of carbon per liter.

tion always showed a higher concentration of CO and the unsaturated hydrocarbons than its partner. In all illuminated samples, where there was an increase in concentration of a component, the increase was greatest in set C (highest DOC concentration), intermediate in set B (intermediate DOC concentration), and lowest in set A (no added DOC). In the one experiment where DOC was added to natural seawater, however, the greatest increase of CO in the dark was in set A, and the least was in set C (Fig. 1).

The world ocean may be a source of CO (8). The situation with respect to the unsaturated gaseous hydrocarbons has yet to be clarified. Dissolved organic matter appears to constitute the major reservoir of organic material in the oceans (9), and our work suggests that it is one source from which CO and the unsaturated gaseous hydrocarbons might be produced in the illuminated zone. Additional, and perhaps greater, production by organisms is also possible. The nature of net production of CO and hydrocarbons in the ecosystem is not known.

D. F. WILSON

J. W. SWINNERTON

R. A. LAMONTAGNE

Ocean Sciences Division,
Naval Research Laboratory,
Washington, D.C. 20390

References and Notes

1. V. J. Linnenbom and J. W. Swinnerton, *Proceedings of the Symposium on Organic Matter in Natural Waters*, Univ. of Alaska, 1968 (in press); *Proceedings of the International Conference on the Caribbean*, Curaçao, 1968 (in press); J. W. Swinnerton and V. J. Linnenbom, *Science* **156**, 1119 (1967).
2. The gas chromatographic column used in most of the experiments did not separate ethane from ethylene (see 7); consequently only the combined concentration of these gases is shown. However, these gases were separated in some later experiments, and only ethylene was produced in the cell-free systems. Moreover, other analyses show that the ethane-ethylene system usually follows the same pattern of production as propane and propylene.
3. G. T. Wallace, Jr. and D. F. Wilson, *Naval Res. Lab. Rep. No. 6958* (1969).
4. Bacterial contamination may have no apparent effect or it may cause serious changes in the concentrations of one or more gases. For example, one strain caused the concentration of CO to decrease rapidly to zero with a concomitant production of CH₄.
5. The DOC was determined by a modification of the procedure of D. W. Menzel and R. F. Vaccaro [*Limnol. Oceanogr.* **9**, 138 (1964)]. In our hands, the method shows "DOC" concentrations of 0.20 to 0.25 mg of carbon per liter in distilled water blanks.
6. We used discarded stock cultures of various diatoms and flagellates. The cultures were of various ages and had been grown in artificial seawater enriched with nitrate, phosphate, silicate, trace metals, and vitamins and buffered with tris-(hydroxymethyl)aminomethane-HCl. Each culture was checked for sterility before being used.
7. J. W. Swinnerton and V. J. Linnenbom, *J. Gas Chromatogr.* **5**, 570 (1967); ———, C. H. Cheek, *Limnol. Oceanogr.* **13**, 193 (1968).
8. J. W. Swinnerton, V. J. Linnenbom, R. A. Lamontagne, *Science* **167**, 984 (1970).
9. For example, see J. D. H. Strickland, in *Chemical Oceanography*, J. P. Riley and G. Skirrow, Eds. (Academic Press, London, 1965), vol. 1, p. 592.
10. We thank R. C. Beckett for the analyses of DOC and J. Gawthrop for technical assistance.

12 March 1970; revised 11 May 1970

In spite of the appearance of the returned lunar samples, the lunar seismic signal continued to ring for a remarkably long time—a characteristic of very high Q material. The lunar rocks, when studied in the laboratory, exhibited a low Q (2). Perhaps most startling of all, however, was the very low sound velocity indicated for the outer lunar layer deduced from the LEM impact signal. The data obtained on the lunar rocks and fines agree well with the results of the Apollo 12 seismic experiment (2, 3). These rock velocities are startlingly low. The measured velocities on a vesicular medium grained, igneous rock (10017) having a bulk density of 3.2 g/cm³ were $v_p = 1.84$, and $v_s = 1.05$ km/sec. The results for a microbreccia (10046) with a bulk density of 2.2 g/cm³ were $v_p = 1.25$ and $v_s = 0.74$ km/sec for the compressional (v_p) and shear (v_s) velocities.

It was of some interest to consider the behavior of these lunar rocks in terms of the expected behavior based on measurements of earth materials. Birch (4) first proposed a simple linear relation between compressional velocity and density for rocks. This relation was examined further by Anderson (5) who showed that this was a first approximation to a more general relation, derivable from a dependence of the elastic moduli with the density through a power function. Comparison of the results obtained from the returned lunar rocks with the predictions of these relationships expresses graphically the manner they deviate from the behavior of rocks found on earth. The velocities are remarkably lower than what would be predicted from either the Birch or Anderson relationships.

To account for this very low velocity, we decided to consider materials other than those listed initially by Birch (4) or more detailed compilation of Anderson and Liebermann (6). The search was aided by considerations of much earlier speculations concerning the na-

Properties and Composition of Lunar Materials: Earth Analogies

Abstract. *The sound velocity data for the lunar rocks were compared to numerous terrestrial rock types and were found to deviate widely from them. A group of terrestrial materials were found which have velocities comparable to those of the lunar rocks, but they do obey velocity-density relations proposed for earth rocks.*

Certain data from Apollo 11 and Apollo 12 missions present some difficulties in that they require explanations for the signals received by the lunar seismograph as a result of the impact

of the lunar module (LEM) on the lunar surface (1). In particular, the observed signal does not resemble one due to an impulsive source, but exhibits a generally slow build-up of energy with time.

Table 1. Comparison of compressional velocities of lunar rocks and various earth materials.

Lunar rocks and cheeses	v_p (km/sec)	Sedimentary rocks	v_p (km/sec)	Metamorphic rocks	v_p (km/sec)	Igneous rocks	v_p (km/sec)	Minerals	v_p (km/sec)
Sapsego (Swiss)	2.12	Dolomite	5.6	Schist	5.1	Granite	5.9	Corundum	10.8
Lunar Rock 10017	1.84	Dolomite	4.69	Slate	5.39	Syenite	5.7	Periclase	9.69
Gjetost (Norway)	1.83	Limestone	5.06	Charnockite	6.15	Diorite	5.78	Spinel	9.91
Provolone (Italy)	1.75	Limestone	5.97	Gneiss	4.9	Oligoclase	6.40	Garnet	8.53
Romano (Italy)	1.75	Greywacke	5.4	Marble	6.02	Andesite	5.23	Quartz	6.05
Cheddar (Vermont)	1.72	Greywacke	6.06	Quartzite	5.6	Gabbro	5.8	Hematite	7.90
Emmenthal (Swiss)	1.65	Sandstone	4.90	Amphibolite	6.70	Gabbro	6.8	Olivine	8.42
Muenster (Wisconsin)	1.57			Eclogite	6.89	Norite	6.50	Trevorite	7.23
Lunar Rock 10046	1.25					Diabase	6.33	Lime	7.95