ridges faintly seen extending northward through both Figs. 8 and 9.

Differences between lunar and martian terrains lie in the seemingly more subdued relief of many martian craters, their flatter floors, fewer central peaks, more subdued debris blankets, absence of obvious secondary craters and rays, and possibly greater abundance of "ghost" craters. A striking double concentric "ghost," similar to prominent double concentric craters seen on the back side of the Moon is faintly visible in the western part of Fig. 8. A more facile isostatic adjustment of the martian crust could also be a contributing factor.

No sinuous rilles have yet been identified on the Mariner 6 photos. Furthermore, no distinctive Earth-like phenomena such as mountain ranges, tectonic basins, streamcut topographs, dune fields, playa flats, or other arid-region features have been recognized. On the other hand, a remarkable variety of albedo markings are apparent in the encounter photographs at high solar angle. Such albedo markings, however, are particularly susceptible to spurious effects in the present preliminary form, and their analysis must await reconstruction of the digital and analog data.

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3. Longitude measured eastward on Mars from the standard ephemeris zero meridian. Ephemeris longitude is measured westward from this meridian.
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Methane-Derived Marine Carbonates of Pleistocene Age

Abstract. In some calcium carbonate–bearing sandstones from the edge of the continental shelf off the northeast United States, the δC^{13} range is from −30 and −60 per mil for both aragonite and high-magnesium calcite. The δC^{13} of coexisting shells of Modiolus sp. is normal (+ 1.7 to − 2.7 per mil). The δO^{18} values of around + 3.5 per mil in all samples suggest deposition at temperatures around 0°C. Quaternary methane oxidized either chemically or microbiologically to carbon dioxide is the probable source of carbon in these carbonates.

Aragonite and high-magnesium calcite in sandstones dredged from five localities on the continental margin off the northeastern United States show stable isotope characteristics that (i) exhibit the largest negative values for δC^{13} yet reported for calcium carbonates; (ii) suggest a possible new mechanism of submarine lithification; (iii) confirm inorganic rather than biogenic precipitation of marine aragonite; (iv) confirm lowered sea temperatures during the last glacial maximum; and (v) exhibit the chemical aggressiveness of dissolved carbonates in corroding silicates and quartz and depositing carbonates in their place.

The aragonite-bearing rocks are slabs having irregular surfaces and numerous cavities lined with layers of clear aragonite in groups of radiating crystals (Fig. 1, top). Slightly agape valves of three specimens of *Modiolus* sp. with periostracum largely intact and a crab shell were enveloped and partially filled with such layers of aragonite.

Aragonite also occurs as masses, spherulites, or cementing matrix and accounts for as much as 50 percent of the total rock. Many feldspar and quartz grains are corroded or replaced by carbonates, and relic outlines of the original grain boundaries can be observed. Figure 1 (bottom) illustrates a common feature in which parts of the original grain persist; the twinning of the feldspar indicates the original continuity of the remnants.

Globorotalia truncatulinoides in sample 2715 (Table 1), the ostracode *Muellerina canadensis* (Brady) in sample 2689, and a C^{14} date of 20,000 years ago for the clear aragonite of sample 2715 indicate a Pleistocene age for these rocks.

The two samples containing high-magnesium calcite (about 14 mole percent $MgCO_3$) are from the northern part of Georges Bank; one, an irregularly shaped carbonate cemented sand, is from an unknown location in the northwest part of the bank; the other (AB4-67-12-174) is from the northeast part of the bank and is one of several flat (about 5 mm thick) concretion-like sandy plates, up to 10 cm in diameter. Neither sample has lined cavities like those of the aragonite-bearing rocks.

Distribution of particle sizes in the residue insoluble in acetic acid of two samples of gray sandy material from sample 2715 showed good sorting around a median size of about 0.35 mm for one sample, and poor sorting around a median size of about 0.2 mm for a sample containing clay. An x-ray analysis of the clay fraction showed dominant chlorite and mica with a trace of montmorillonite. The coarser fractions contained mainly quartz with about 10 percent feldspar.

Isotope data was obtained with a Nier-McKinney type of dual-collecting mass spectrometer (Nuclide Instrument). Carbon isotope data are reported as per mil deviation to the PDB_I—Chicago belemnite standard (*1*, *2*):

$$\delta C^{13} = [(R/R_{ST}) - 1] \times 1000$$

where *R* represents the ratio of C^{13} to C^{12} in the sample, and R_{ST} the ratio in the standard. Similarly δO^{18} is defined in terms of the ratio of O^{18} to O^{16}.

Our carbonate samples (Table 1) are depleted in C^{13} to about the same extent as certain carbonates associated with sulfur-evaporite domes (*3*) or oxidized hydrocarbons (*4*). Most methanes are more depleted in C^{13} than other natural compounds (*5*), although some methanes that have isotopically equilibrated with CO_2 at elevated temperatures show less depletion in C^{13}; the gases from hot springs in Yellowstone National Park represent such a case ($\delta C^{13} = -8$ to -28) (*1*). Methanes analyzed from marine and brackish deposits near Woods Hole have δC^{13} values between −55 and −60 per mil.

Figure 2 is based on more than 5000 analyses of carbon (*6*). Two characteristics are apparent: (i) carbonates extend over a wide range in δC^{13}; and (ii) the most oxidized carbon, that is, carbonates and the various CO_2 species, are enriched in C^{13} by comparison with reduced carbon, that is, kerogen, coal, crude oil, and natural gas. The only values that do not fit the pattern are from carbonates whose carbon is derived through biogenic or inorganic oxidation of organic matter and natural gases. This set of aragonites belongs to the latter category. Since the δC^{13} in the aragonites of stations 2583C and 2715 falls in the range of −50 to −60 per mil, methane appears to be the most likely source for the carbon because it represents the only material sufficiently depleted in C^{13}.

The primary factors that control the isotopic carbon variation in methane liberated from organic matter are determined by the strength of the terminal carbon-carbon bonds, the diagenetic temperature, and the maturity of the parent material (*5*). Below 100°C, the carbon-isotope fractionations in methane are considerable, namely, 60 to 80 per mil. These values are in the same range as data from the fractionation of CH_4 obtained during the bacterial fermentation of methanol (*7*). The rise in C^{13} for methane with geologic age is due to thermal degradation, a gradual depletion with time in the light carbon available for methane formation, and lack of reequilibration with a C^{12}-enriched carbon source (*5*).

If one assumes that a methane having a δC^{13} of −60 has been completely oxidized to CO_2 and water without any methane being left behind with which to reequilibrate, the CO_2 formed will be isotopically identical to its methane precursor. The subsequent fractionations occurring in the process of bicarbonate and eventually carbonate formation (*8*) will increase the C^{13} content in the final carbonate by several per mil (at room temperature); the actual increase will thereby depend on the efficiency of isotopic exchange between the CO_2 and its associated bicarbonate. In turn, a carbonate, having a δC^{13} of −60 per mil, should have a methane precursor in the range of about −60 to −70 per mil. Such light values for methane are commonly only observed in Quaternary marsh type or upper Tertiary (Pliocene and Miocene) crude oil deposits (Fig. 2).

The δC^{13} values for the samples of locality 2689 (Table 1) are less negative; they may have been derived a number of ways. Degradation of organic matter yields light methane and heavy CO_2. If this CO_2 is used in the carbonate formation, or if methane becomes oxidized to CO_2 and subsequently mixes with a heavy CO_2, a wide range of δC^{13} values can be obtained. Alternatively, a mixing with seawater bicarbonate may have caused the observed shift into the less negative range. The last suggestion appears to us to be the most straightforward explanation.

Shell material associated with the aragonite samples has a δC^{13} commonly found in marine biogenic carbonates. The δO^{18} values of the shells, however, are quite heavy and suggest either cold water conditions (about 0°C) or a lagoonal environment (evaporation) at the time the organisms deposited their carbonate. The fact that shells and aragonites are identical in δO^{18} (Table 1) indicates that waters highly enriched in dissolved CO_2 were probably discharged into the open ocean; CO_2 was released, and aragonite was formed in isotopic (O^{18}/O^{16}) equilibrium with the sea.

The C^{14} age of 20,000 years for the clear aragonite coating from sample 2715 indicates that a Pleistocene rather

Table 1. Analytical data on carbonate deposits from the eastern United States continental margin.

No.	Description	Minerals	δO^{18}	δC^{13}
		Station 2583 C (38°22.9′N; 73°29.4′W; 440 m)		
1.	Gray sandy matrix with shell fragments	Aragonite, quartz, feldspar, chlorite, mica, calcite	4.9	−49.1
2.	Clear aragonite layers	Aragonite, quartz (trace)	4.9	−56.0
		Station 2715 (38°47.5′N; 73°02.6′W; 320 m)		
3.	Dark gray, sandy matrix with some shell fragments	Aragonite, quartz, feldspar, chlorite, mica, Mg-calcite?	3.9	−52.1
4.	Dark gray, sandy matrix with some shell fragments	Aragonite, quartz, feldspar, chlorite, mica, Mg-calcite?	3.2	−56.7
5.*	Clear aragonite layers	Aragonite, quartz (trace)	3.2	−55.7
6.*	Clear aragonite layers	Aragonite, quartz (trace)	3.6	−56.3
7.*	Clear aragonite layers	Aragonite, quartz (trace)	2.9	−56.5
8.*	Clear aragonite layers	Aragonite, quartz (trace)	3.2	−59.4
9.*	Clear aragonite layers	Aragonite, quartz (trace)	3.2	−60.0
10.	*Modiolus* sp. shell		3.5	−2.7
11.	*Modiolus* sp. shell		3.2	−1.4
		Station 2689 (about 40°00′N; 69°30′W; 350 m)		
12.	Light brown, sandy matrix with some shell fragments	Aragonite, quartz, feldspar	3.4	−23.1
13.	Clear aragonite layers	Aragonite, quartz	3.4	−34.7
14.	Clear aragonite layers	Aragonite, quartz	3.3	−38.8
15.	Clear aragonite layers	Aragonite, quartz	3.6	−28.0
16.	Pelecypod shell		4.0	+1.7
		Locality unknown		
17.	Clear aragonite layers	Aragonite, quartz	3.5	−44.3
		Northwest part of Georges Bank		
18.	Calcium-carbonate-cemented sandstone	Mg-calcite, quartz, feldspar	1.2	−60.6
		Station AB4-67-12-174 (42°02′N; 66°56′W; 60 m)		
19.	Flat sandstone plates about 5 mm thick	Mg-calcite, quartz, feldspar	3.1	−53.6

* Carbon-14 age is 20,400 ± 800 years (W-2170, U.S. Geological Survey Laboratories, Meyer Rubin, analyst).

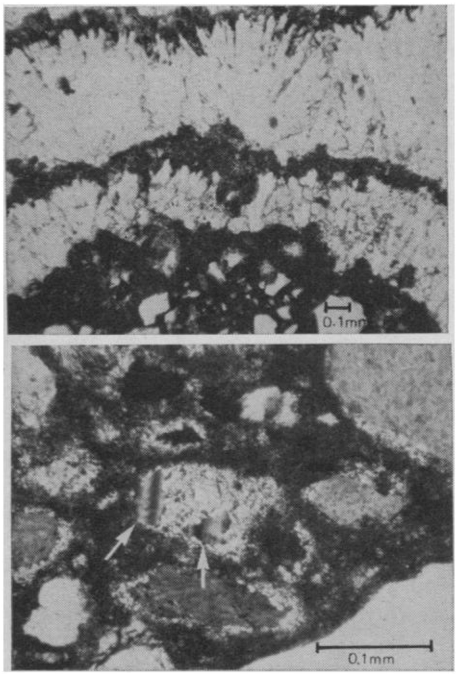

Fig. 1. Thin sections of aragonite-bearing sandstone (station 2715) from the edge of the continental shelf. (Top) Groups of radiating crystals of aragonite which coat sandstones cemented by a matrix of aragonite and clay minerals. Plain light. (Bottom) Quartz and feldspar replaced by aragonite. Twinning bands show optical continuity between two remaining feldspar areas (arrows). Other grains show corrosion. Crossed polarizers.

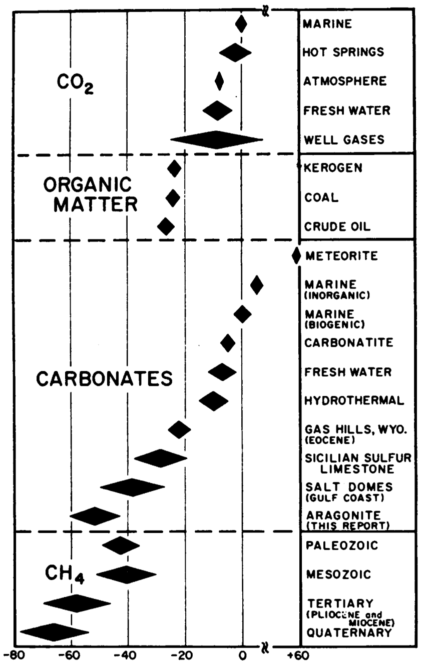

Fig. 2. δC^{13} ranges for various carbon-bearing materials. Width of diamond-shaped symbols equals 2 standard deviations for the data (*6*). The individual samples have been grouped into systematic classes of compounds and are plotted in form of cumulative frequency diagrams (range, 2 sigmas).

than a Tertiary source is likely for the carbon. Quaternary methane formed near the outer edges of the shelf in buried marsh deposits or marine sediments may have become oxidized chemically or, more probably by microorganisms, to CO_2:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (-\Delta F_{298^\circ K} = +195{,}000 \text{ cal})$$

The ΔF value suggests that this reaction is favored thermodynamically in low temperature environments. The CO_2 formed by this reaction then dissolved in water to form bicarbonate ions. Lowered sea level permitted groundwater charged with this bicarbonate to migrate seaward through aquifers (*9*) discharging into the sea roughly at the depths at which the samples had been dredged. Seawater provided the necessary calcium ions and raised the *p*H of the acidic water to the point where calcium carbonate precipitated. Alternatively, beds saturated with such water may have been exposed at their seaward edges by slumping or faulting, thus permitting the release of CO_2 and the precipitation of calcium carbonate. It is also conceivable that carbonates were deposited in interstices of the host rock in the spaces developed by the corrosion and removal of silicates. Such a reaction could produce beds of carbonate rock extending over wide areas. The presence of carbonate beds in the upper part of the geologic section of the continental shelf edge has been confirmed by dredges of the deep-submergence R.V. *Alvin*. Continuous seismic profiles suggest a considerable extent for these beds. Most of these carbonates are as unusual in isotopic composition as those reported here.

If sea level during the last glacial maximum is accepted as being 120 m below sea level at present (*10*), the carbonates (excluding the Georges Bank samples) formed at seawater depths of about 200 m, or at less depth if the samples dredged are talus that has moved downslope from the true outcrop position. The C^{14} date gives only the maximum date for the formation of the organic matter. The timing of the deposition of the carbonate at the height of the last glacial maximum is in accordance with the paleotemperatures near 0°C suggested by the distribution of oxygen isotopes. The temperature now at this location and depth is about 5°C (*11*).

An aragonite-bearing sample from a depth of 79 m in the vicinity of Wilmington canyon with δC^{13} values comparable to our values but of younger age has recently been found (*12*). The magnesium calcite–bearing samples from the top of Georges Bank may represent aragonite recrystallized to magnesium calcite under shallow water conditions (*13*); however, in view of their differences in physical appearance from the aragonite-bearing rocks, these samples may represent magnesium calcite precipitated directly by reaction with bicarbonate ions from the same type of source as the aragonite.

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