mentary strata beneath the pavement are rather flat lying and are discontinuous where cut by scour depressions.

The general tendency for manganese oxides to precipitate out of sea water was recognized by Murray (*1*). Recent summaries indicate that the geochemical precipitation of the manganese as nodules is not unusual (*5*). On the Blake Plateau, however, the Gulf Stream appears to be the special environmental factor that promotes the deposition of manganese oxide in the pavement form. Not only does the Gulf Stream replenish the sea bottom with a constant large volume of sea water, but its associated currents prevent the deposition of clastic sediments. Another factor which might be important in the formation of the manganese pavement is the presence of small, closely spaced phosphate nodules as solid nuclei which could initiate manganese deposition. However, this suggestion is weakened by the facts that an extensive area with phosphate nodules north of the pavement has no manganese and that most of the area of roundish manganese nodules south of the pavement has no phosphate. Also, extensive crusts of manganese oxide cover some of the New England seamounts (*6*) which have the same Gulf Stream environment but no phosphate nodules.

We conclude that the accretion of manganese oxide into the extensive pavement at the north end of the Blake Plateau is primarily the result of an environmental situation in which the impingement of the Gulf Stream currents against the sea bottom is an important factor.

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References and Notes

1. J. Murray and A. F. Renard, *Challenger Reports* (1891).
2. J. Murray, *Bull. Museum Comp. Zool. Harvard Coll.* **12**, 37–61 (1885).
3. J. R. Bartlett, *Proc. Amer. Ass. Advance. Sci.* **31**, 1–4 (1883).
4. T. R. Stetson, unpublished manuscript, Woods Hole Oceanogr. Inst. Ref. 61-35 (1961).
5. J. L. Mero, *The Mineral Resources of the Sea* (Elsevier, New York, 1965); H. W. Menard, *Marine Geology of the Pacific* (McGraw-Hill, New York, 1964); F. T. Manheim, *Occasional Publ. No. 3-1965*, Narragansett Marine Lab. (Univ. of Rhode Island, 1965), pp. 217–276.
6. R. M. Pratt and S. L. Thompson, unpublished manuscript, Woods Hole Oceanographic Inst. Ref. 62-40 (1962).
7. Work supported under contract 2196-6 with ONR and by the U.S. Geological Survey. Woods Hole Oceanographic Institution contribution No. 1473.

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Oxygen and Carbon Isotopic Composition of Limestones and Dolomites, Bikini and Eniwetok Atolls

Abstract. *Aragonitic, unconsolidated sediments from the borings on the Eniwetok and Bikini atolls are isotopically identical with unaltered skeletal fragments, whereas the recrystallized limestones exhibit isotopic variations resulting from alteration in meteoric waters during periods of emergence. Dolomites and associated calcites are enriched in* O^{18}, *perhaps because of interaction with hypersaline brines.*

The Cenozoic history of Bikini and Eniwetok atolls has been one of slow subsidence—more than 1200 meters since late Eocene time—interrupted by several prolonged periods of emergence during which the atolls stood above the sea as high islands (*1, 2*). The emergences are inferred from subsurface zones of vuggy, calcite-cemented limestone.

Petrographic evidence indicates that the limestone zones resulted from the partial solution of original skeletal material and the addition of crystalline calcite cement. This alteration of originally unconsolidated sediment to lithified rock is believed to have taken place through the agency of percolating meteoric water. Aragonite in these zones is largely or completely replaced by calcite. The zones of calcite-cemented limestone grade downward to unaltered aragonitic sediments; these zones are truncated and overlain with apparent unconformity by unaltered aragonitic sediments. The aragonitic sediments are considered to represent parts of the section that were not long exposed to meteoric waters. These unconformities, called solution unconformities by Schlanger (*2*), at depths of 90, 330, and 820 meters, were formed in Pleistocene, late Miocene, and early Miocene time. Dolomite occurred below the Miocene solution unconformities at Eniwetok (*2*); none was detected at Bikini (*1*).

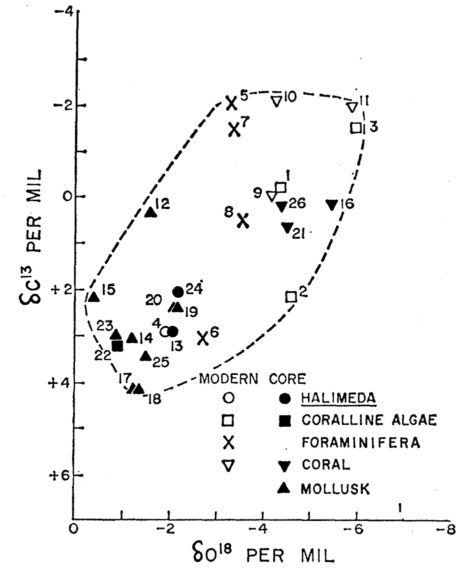

Fig. 1. Oxygen and carbon isotopic composition of skeletal fragments of the dominant carbonate-secreting organisms. The numbers are sample numbers.

The interpretation that the solution unconformities developed during periods of emergence is reinforced by the finding of fossil land snails of genera whose living representatives are usually found only on high islands, and of pollen that appears to be more closely related to present floras from high islands than to those from atolls (*3*).

We determined the oxygen and carbon isotopic composition of samples from the cores and cuttings (*4, 5*) in order to learn more about the processes causing lithification of carbonates in isolated, mid-ocean atolls, and in order to ascertain whether emergences of the atolls could be verified by the isotopic composition of the recrystallized limestone. The initial isotopic composition of the carbonate sediments was obtained by analysis of selected skeletal fragments of the dominant carbonate-secreting organisms now living in the area, as well as apparently unaltered skeletal fragments from the cores (Table 1 and Fig. 1). The results indicate little difference in the C^{13} and O^{18} contents of the skeletal fragments, except for the mollusks, from either source; no modern mollusks were analyzed.

The isotopic compositions of the recrystallized limestones, the altered skeletal fragments, and the coarsely crystalline calcites from the borings on the two atolls show striking variations in C^{13} content as compared to the unaltered skeletal fragments or to the unconsolidated sediments (Table 2 and Fig. 2). The unconsolidated calcareous muds (samples 28, 30, 32, 38) are well within the range of isotopic composition of the skeletal fragments and thus support the hypothesis that these aragonitic sediments have not been subjected to meteoric waters long enough to be recrystallized. Most recrystallized limestones (samples 27, 31, 33, 34, 36) show pronounced variations in C^{13} content, similar to those observed in the limestones in the Bermuda Islands (*6*). These isotopic variations result from the addition to the original sediment of calcite containing carbon derived from the gases of the soil zone ($\delta C^{13} \approx -25$ per mil), and possibly from isotopic exchange between the constituent grains and the interstitial waters when the atolls were emergent.

The variations in the O^{18} content of the recrystallized limestones are less striking, but they too can be explained as a result of solution of original carbonate and subsequent reprecipitation of calcite in meteoric waters. If the coarsely crystalline calcites (samples 29, 37, 41) formed in isotopic equilibrium with interstitial water at approximately 27°C (*7*), the δO^{18} value of the water must have been between -3.5 and -5.0 per mil (*8*).

A sample of sea water from Rongelap Atoll had a δO^{18} value of 0.0 per mil, whereas samples of meteoric waters (*9*) had values ranging from -3.8 to -5.8 per mil. These results are not conclusive, but they support the hypothesis that the coarsely crystalline calcites were formed in meteoric waters whose O^{18} contents were not appreciably different from present-day meteoric waters in the region.

The large variations in C^{13} content associated with alteration in meteoric waters are observed only in the samples (Table 2) from the upper portion of the borings on the two atolls. We believe that these variations are the result of the Pleistocene emergences. The variation with depth of the C^{13} content may be associated with the access of the meteoric waters to the limestones. Those samples altered near the surface would have the freest access to solutions that had become equilibrated with soil gases ($\delta C^{13} \approx -25$ per mil) and would therefore have the most negative δC^{13} values. Samples 100 to 200 meters below the surface would be exposed to solutions that had exchanged considerable amounts of carbon with the carbonates through which they passed, with the result that the δC^{13} values of these recrystallized limestones would differ lit-

Table 1. Oxygen and carbon isotopic and mineral composition of major sediment-contributing organisms.

Sample	Description	δO^{18} (per mil)	δC^{13} (per mil)	Calcite (%)	Aragonite (%)	Dolomite (%)
		Calcareous algae, Bikini atoll				
1	*Lithophyllum* sp.	−4.4	−0.2	100	0	0
2	*Porolithon craspedium*	−4.6	+2.2	100	0	0
3	*P. onkodes*	−6.0	−1.5	100	0	0
4	*Halimeda* sp.	−1.9	+2.9	0	100	0
		Foraminifera, Ifalik atoll				
5	*Calcarina spengleri*	−3.3	−2.0	100	0	0
6	*Marginopora vertebralis*	−2.7	+3.1	100	0	0
7	*Baculogypsina* sp.	−3.4	−1.5	100	0	0
8	*Amphistegina* sp.	−3.6	+0.5	100	0	0
		Coral, northern Marshall Islands				
9	*Acropora digitifera*	−4.2	+0.0	0	100	0
10	*Seriatopora hystrix*	−4.3	−2.0	0	100	0
11	*Porites lutea*	−5.9	−1.9	Trace	98+	0

Table 2. Oxygen and carbon isotopic and mineral composition of specimens from cores, Bikini and Eniwetok atolls. Trace, tr; crystalline, cryst.; recrystallized, recryst.

Sample	Description	Core No. (*1, 2*)	Depth (m)	δO^{18} (per mil)	δC^{13} (per mil)	Calcite (%)	Aragonite (%)	Dolomite (%)
			Skeletal fragments, Bikini					
12	Pelecypod	(2-1-2)	4.6	−1.6	+0.4	tr	98+	0
13	*Halimeda* sp.	(2-3-2)	16.8	−2.0	+2.9	3	97	0
14	Pelecypod	(2-11-1)	54.9	−1.2	+3.1	3	97	0
15	Pelecypod	(2A-20-1)	83.8	−0.4	+2.2	tr	98+	0
16	*Porites* sp.	(2A-32-1a)	193.5	−5.4	+0.2	3	97	0
17	Gastropod	(2A-36)	281.9	−1.3	+4.1	3	97	0
18	Mollusk	(2A-36-2)	281.9	−1.4	+4.1	0	100	0
19*	Pelecypod	(2A-1082)	329.8	−2.2	+2.4	0	100	0
20*	Pelecypod	(2A-1032)	329.8	−2.1	+2.4	0	100	0
			Skeletal fragments, Eniwetok					
21	Coral	(R-1-17)	0.9	−4.5	+0.7	0	100	0
22	*Lithophyllum* sp.	(R-1-24)	1.2	−0.9	+3.2	100	0	0
23	*Tridacna* sp.	(MU-7-3a)	4.6	−0.9	+3.0	0	100	0
24	*Halimeda* sp.	(RU-2-3)	9.8	−2.2	+2.1	20	80	0
25*	Mollusk	(F-1-830-840)	253-256	−1.5	+3.4	0	100	0
26*	Coral	(F-1-830-840)	253-256	−4.4	+0.2	0	100	0
			Limestone and matrix mud, Bikini					
27	Brown laminated limestone	(2-2-10)	15.2	−5.5	−10.0	100	0	0
28	Unconsolidated matrix mud	(2-3-2)	16.8	−3.9	−0.8	30	70	0
29	Coarsely cryst. calcite	(3-10-13)	25.0	−7.5	−10.0	100	0	0
30	Unconsolidated matrix mud	(2-7-3)	38.1	−5.2	−0.4	40	60	0
31	Recryst. limestone	(2-11-16)	56.4	−6.1	−6.7	100	0	0
32	Unconsolidated matrix mud	(2A-12-5)	59.4	−4.5	−1.1	40	60	0
33	Recryst. limestone	(2A-19-3)	82.3	−6.2	−7.8	100	0	0
34	Recryst. limestone	(2A-24-1)	95.1	−6.2	−6.1	95	5	0
35	Coral cast	(2A-26-8)	100.6	−5.4	−4.9	70	30	0
36	Chalky recryst. limestone	(2A-28-15)	135.6	−4.9	−2.7	100	0	0
37	Coarsely cryst. calcite	(2A-32-1b)	193.5	−6.3	−5.5	95+	tr	0
38	Unconsolidated matrix mud	(2A-37-15)	286.5	−4.2	−0.8	25	75	0 0
39*	Brown recryst. limestone	(2A-1135)	345.9	−5.1	−0.7	100	0	0
			Limestone and dolomite, Eniwetok					
40	Recryst. limestone	(K-1-253-258)	77.0-78.5	−5.9	−7.3	100	0	0
41	Coarsely cryst. calcite	(F-1-2-6)	183-190	−6.0	−7.3	100	0	0
42	Gastropod cast	(F-1-2-10)	183-190	−5.4	−2.7	100	0	0
43	Recryst. limestone	(F-1-3-17)	375-380	−2.7	−1.8	100	0	0
44	Recryst. limestone	(F-1-3-26)	375-380	−1.9	−0.2	100	0	0
45	Recryst. limestone	(F-1-6-21)	811-819	−0.8	−1.9	98+	0	tr(?)
46	Dolomite, calcitic	(F-1-12-7)	1315-1323	+1.1	+1.2	tr	0	98+
47†	Dolomitic limestone	(F-1-12-12)	1315-1323			55	0	45
47a	Calcite			0.0	+1.2			
47b	Dolomite, coexisting with calcite (No. 47a)			+2.9	+2.1			

* Indicates sample from cuttings. † Data from Schlanger (*2*, p. 1005).

tle from those of the unaltered carbonate sediments. An alternate explanation is that the deeper samples were altered during earlier Pleistocene emergences, and thus have had more time than the younger samples nearer the surface to approach isotopic equilibrium through reequilibration or recrystallization in the sea water that permeates the atolls (*7*).

With one exception, the samples of the limestones and dolomites affected by the postulated Miocene emergences are from Eniwetok. The one sample from Bikini (sample 39) associated with a Miocene solution unconformity retains no isotopic record of the alteration in meteoric water, which has been postulated to explain its petrographic character (*1*). The same is true of the recrystallized limestones from the Eniwetok borings (samples 43, 44, 45), but these contained small amounts of dolomite. Thus the isotopic variations of these recrystallized limestones from the deeper parts of the borings are distinctly different from those in the upper portion of the borings affected by Pleistocene emergence.

Dolomite (samples 46, 47b) and associated calcite (sample 47a) from the core are enriched in O^{18} (Fig. 2). These data are consistent with the hypothesis (*5, 10*) that dolomitization results from the reaction of carbonate sediment with hypersaline brines. Such hypersaline brines formed by the evaporation of sea water should also be enriched in O^{18}, and would result in the enrichment of O^{18} in the sediments with which they reacted. Perhaps this also accounts for the isotopic composition of the deeper recrystallized limestones (samples 43, 44, 45) from Eniwetok, which may also have been exposed to meteoric waters at some time in their history.

The coexisting dolomite and calcite exhibit an apparent fractionation (*11*) in δO^{18} of 3.7 per mil. These data are in reasonable agreement with the observed fractionation (corrected for differential acid fractionation) of 2.2 to 2.9 per mil between dolomite and coexisting carbonate sediment on Plantagenet Bank near the Bermuda Islands (*12*).

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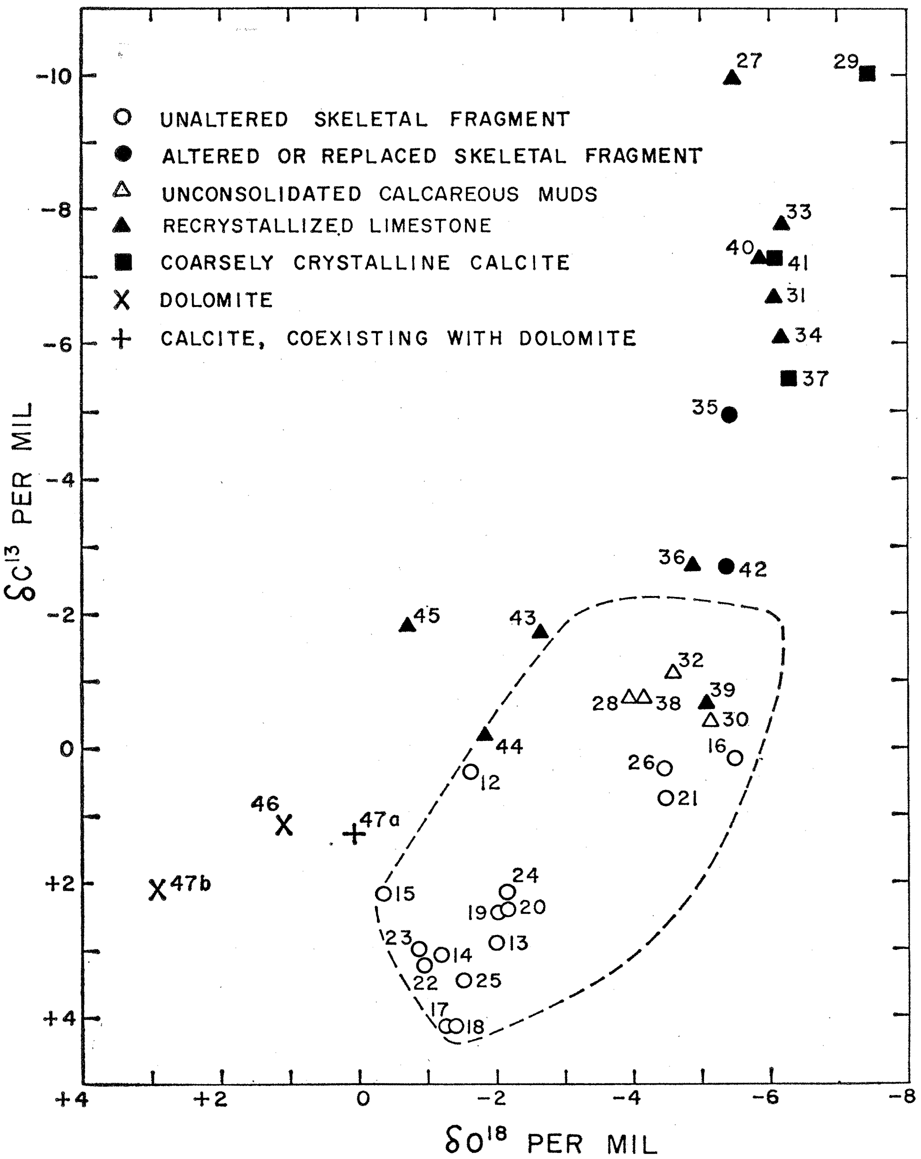

Fig. 2. Oxygen and carbon isotopic composition of carbonate cuttings and cores from the drill holes. The numbers are sample numbers.

References and Notes

1. K. O. Emery, J. I. Tracey, Jr., H. S. Ladd, *U.S. Geol. Surv. Profess. Papers 260-A* (1954), pp. 1–259.
2. S. O. Schlanger, Ed., *U.S. Geol. Surv. Profess. Papers 260-BB* (1963), pp. 991–1066.
3. H. S. Ladd and J. I. Tracey, Jr., *Deep-Sea Res.* **4**, 218 (1957).
4. Sediment samples were treated with phosphoric acid, and the CO_2 obtained was analyzed by mass spectrometer as described by J. M. McCrea, *J. Phys. Chem.* **18**, 849 (1950). Water samples were analyzed by the technique described by S. Epstein and T. Mayeda, *Geochim. Cosmochim. Acta* **4**, 213 (1953). The δO^{18} and δC^{13} values are relative to the PDB Chicago (Belemnite) standard; $\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1]\,10^3$, where R is the ratio of the heavy to light isotopes of either oxygen or carbon. The standard deviation of the analyses is 0.16 per mil in δO^{18} and 0.15 per mil in δC^{13}. The δO^{18} values for dolomite have been corrected for the differential acid fractionation of 0.8 per mil; see *5*.
5. R. A. Berner, *Science* **147**, 1297 (1965).
6. M. G. Gross, *J. Geol.* **72**, 170 (1964).
7. J. H. Swartz, *U.S. Geol. Surv. Profess. Papers 260-U* (1958), pp. 711–739.
8. S. Epstein, R. Buchsbaum, H. A. Lowenstam, H. C. Urey, *Geol. Soc. Am. Bull.* **64**, 1315 (1953).
9. Water samples, collected September 1961, were supplied by Dr. E. E. Held, Laboratory of Radiation Biology, University of Washington.
10. N. D. Newell, J. K. Rigby, A. G. Fisher, A. J. Whiteman, J. E. Hickox, J. S. Bradley, *The Permian Reef Complex of the Guadalupe Mountains Region, Texas and New Mexico—A Study in Paleoecology* (Freeman, San Francisco, 1953); J. E. Adams and M. L. Rhodes, *Bull. Am. Assoc. Petrol. Geologists* **44**, 1912 (1960); K. S. Deffeyes, F. J. Lucia, P. K. Weyl, *Science* **143**, 678 (1964).
11. In order to show that the apparent fractionation represents a true isotopic equilibrium fractionation, we would need to demonstrate that the two mineral species were formed at the same temperature in isotopic equilibrium with the same water having a constant O^{18} content. The available data do not permit this. Consequently we refer to the observed value as an apparent isotopic fractionation.
12. M. G. Gross, *Geol. Soc. Am. Bull.* **76**, 1283 (1965).
13. Supported by ONR contracts 477(10) and 477(37) project NR 083 012, and by the NSF (predoctoral fellowship to M.G.G. at the California Institute of Technology). We thank S. O. Schlanger, I. Friedman, R. A. Berner, P. K. Weyl, H. S. Ladd, and K. S. Deffeyes for comments on the manuscript, and S. Epstein for laboratory facilities. Contribution No. 380, Dept. of Oceanography, Univ. of Washington, Seattle.

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