

35. A COMPARISON OF THE STABLE OXYGEN AND CARBON ISOTOPE COMPOSITION OF EARLY CRETACEOUS AND LATE JURASSIC CARBONATES FROM DSDP SITES 105 AND 367

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ABSTRACT

Oxygen isotope data indicate that vein-filling carbonates begin to crystallize in approximate isotopic equilibrium with seawater. Pore waters in fracture systems which are partially isolated from seawater become isotopically lighter as the surrounding basalt weathers to clay minerals and zeolites. Vein formation continues at relatively low temperatures in water progressively depleted in O^{18} . Basalts at DSDP Sites 105 and 367 are believed to be extrusive because the sediments immediately overlying them do not have isotopic compositions indicative of high-temperature recrystallization.

Sediments at Site 367 are depleted in O^{18} relative to those from equivalent units at Site 105. This difference is due to the greater amounts of authigenic carbonate formed at higher temperatures, and possibly in the presence of lighter pore waters, at Site 367. The differences in isotopic composition and degree of recrystallization between the two sites are attributable to the thicker overburden at Site 367. Significant amounts of O^{18} must have been incorporated into authigenic silicate phases in order to explain the oxygen isotope composition at Site 367. The lowermost sediments at Site 367 are enriched in O^{18} relative to the sediments overlying them. Part of this enrichment is due to less recrystallization in these sediments. Oxygen isotope data suggest that recrystallization of these basal carbonates occurred early in the burial history of the sediments.

Nodular chert at Site 367 is associated with carbonates depleted in O^{18} . Present theories of chert formation do not account for this depletion. Clay content also exercises a large effect on the oxygen isotopic composition of carbonates. Carbonate-rich regions are depleted in O^{18} relative to associated clay-rich zones. This relationship suggests that carbonate-rich regions contain more authigenic carbonate formed at in situ temperatures than do clay-rich zones.

The carbon isotopic composition of carbonates from Site 367 varies systematically with depth, reflecting variations in the isotopic composition of dissolved inorganic carbon in the surface ocean. These variations are believed to reflect either changes in the amount of organic matter buried in sediments or changes in the ratio of C/P in organisms to that in deep ocean water.

INTRODUCTION

A sequence of Early Cretaceous and Late Jurassic carbonate sediments was penetrated at Site 105, Leg 11, in the western North Atlantic (Hollister et al., 1972). These sediments consist of over 100 meters of Tithonian limestones underlain by 60 meters of clayey limestone and calcareous claystone (Oxfordian to Kimmeridgian age) which rest on basalt at 620 meters subbottom. The Tithonian to Neocomian unit consists of light gray or white limestone interbedded with dark clayey limestone. The dark gray zones are much less lithified than are associated light gray or white layers (Lancelot et al., 1972). The underlying Oxfordian to

Kimmeridgian limestone and claystone are dominantly reddish-brown in color and are frequently interbedded with green zones. These deposits are quite similar to more or less coeval deposits exposed around the Mediterranean Sea (Bernoulli, 1972).

A strikingly similar section was encountered on Leg 41 at Site 367 in the eastern North Atlantic. Here, 250 meters of Early Cretaceous and Late Jurassic limestone overlies basalt at 1145 m subbottom. These rocks are described in some detail in the site report (Site 367, this volume). A comparison of the lithofacies present at Sites 105 and 367 is discussed at length by Jansa (this volume).

These sedimentary sequences contain similar constituents, and both have been lithified by burial under submarine conditions. The basic difference in the geologic history of the sediments at the two sites consists of the thickness of overburden to which each

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has been subjected. A comparison of the isotopic composition of carbonates from these sites offers an excellent opportunity for studying the effect of temperature and pressure, and associated diagenesis, on the isotopic composition of marine carbonates which have never been exposed to fresh water.

TECHNIQUE

Dried and ground samples were reacted with 100% phosphoric acid without further treatment according to standard procedures (McCrea, 1950). The resulting CO_2 was purified and analyzed on a dual-collecting, 60-sector, Nuclide mass spectrometer. Fractured surfaces of some specimens were mounted on aluminum stubs and coated with gold following 48 hours in a desiccator over osmium tetroxide (Pfefferkorn, 1970). These samples were examined using a Cambridge Mark II scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The results of the isotopic measurements are given in Table 1. All results except those marked with an asterisk are the averages of duplicate analyses. All data are reported relative to PDB (Craig, 1957). The oxygen isotope results are plotted versus depth in Figures 1 and 2. The carbon data are similarly plotted in Figures 3 and 4. The reproducibility of replicate analyses of "clean" carbonate is $\pm 0.1\text{‰}$. The reproducibility for oxygen on some of the samples which contained a relatively low percent carbonate was not as good, generally $\pm 0.2\text{‰}$. Reproducibility for carbonate from veins in basalt was very poor. A possible explanation for this is discussed below.

VEIN-FILLING CARBONATES

The isotopic composition of some carbonate veins in the basalt at Site 105 (Anderson, in preparation) and at Site 367 (this study) are listed in Table 1 and illustrated on Figures 1 through 4. Several veins at Site 105 have oxygen isotope compositions around 0. These veins must have formed at low temperatures, perhaps 15°C , or at higher (lower) temperatures in the presence of isotopically heavy (light) water. In these and all other cases discussed in this report, it is not possible to determine the exact temperature of recrystallization from the oxygen isotope data because the isotopic composition of the carbonate depends upon the isotopic composition of the ambient water and the ratio of water to carbonate as well as the temperature. Detail about both these variables is generally lacking. The temperature of bottom water during the Late Cretaceous is estimated to have been 10° to 15°C (Emiliani, 1954; Saito and van Donk, 1975; Savin et al., 1975) and these temperatures may have been characteristic of the Jurassic as well. These veins could easily have been formed at the ocean floor shortly after the basalt cooled, in equilibrium with ocean water at that time. Three of the veins at Site 105 have oxygen isotope compositions of -4.0‰ to -5.0‰ . These values indicate formation at higher temperatures or in equilibrium with isotopically light water.

Anderson and Lawrence (1976) present a model for vein generation from analyses of veins at Site 323. They

suggest that initial vein formation occurs at low temperatures in open communication with ocean water. These veins are isotopically heavy. As time progresses, basalt weathers to isotopically heavy clay minerals and zeolites (Muehlenbachs and Clayton, 1972). Pore waters in poor communication with the ocean become isotopically depleted in O^{18} . Later veins crystallize from this isotopically depleted water and are themselves isotopically light. This interpretation suggests that isotopically light veins form much later than isotopically heavy ones, exactly the reverse of an interpretation based on vein generation during cooling. Anderson (in preparation) will discuss the data from Site 105 in more detail with respect to this model, but one additional point in support of the model is worth discussing.

Samples 105-40-1, 104-105 cm (A) and (B) consist of two generations of carbonate. Sample A is fibrous calcite which in thin section can clearly be seen to be replacing the coarsely crystalline B. Sample A is 2.75‰ depleted in O^{18} relative to Sample B. If both calcites formed in equilibrium with water of the same isotopic composition, A would have formed at a higher temperature than B. This is incompatible with the thin section data. The model of Anderson and Lawrence reconciles this inconsistency. The replacement calcite formed in equilibrium with isotopically depleted water and thus lighter than the carbonate it replaced.

All of the veins analyzed from Site 367 have oxygen isotope compositions of -7.0‰ to -9.0‰ . These would be in equilibrium with modern ocean water at temperatures on the order of 50° to 60°C . Using the interpretations discussed above, these veins formed after considerable weathering of the basalt had occurred. This reasoning suggests that the basalt at Site 367 should be more weathered than the basalt at Site 105 or the fracture system at Site 105 provides more communication with the ocean, and prevents the formation of O^{18} depleted water.

Replicate analyses of vein carbonate from Site 367 gave very poor agreement (Table 1). The scatter in these values is much greater than analytical precision. The carbonate in these samples was physically separated from the host rock. In many cases, moderately large pieces of carbonate (0.5 to 2 mm in diameter) were obtained. Relatively few pieces of this size are needed to make up a sample for isotope analysis (0.01-0.02 g). If the isotopic composition of the carbonate veins is heterogeneous, then this variability might be expected to show up in replicate analyses. Such isotopic inhomogeneity would occur if vein carbonate initially began to form in equilibrium with normal ocean water and continued to form in equilibrium with progressively lighter water.

Nature of Basalts

The sediments from Site 105 show no significant trend in oxygen isotope composition with depth. Sediments from Site 367 tend to become more negative with depth down to about 1115 to 1120 meters sub-bottom. Samples taken between this depth and the underlying basalt are heavier than those immediately above. This data can be used to determine whether the basalts at these sites were intrusive or extrusive.

TABLE 1
Stable Isotope Composition of Cretaceous and Jurassic Carbonates From Sites 105 and 367

Sample (Interval in cm)	%CaCO ₃ ^a	δC ¹³	δC ¹⁸	Depth (m) ^b	Age ^c	Description
105-17-1, 75-76	65.9	+1.76	-1.32	404	Barr.-Haut.	Dark gray limestone
105-21-1, 53-54	50.2	+2.27	-1.26	449	Haut.-Val.	Gray-dark gray limestone
105-21-1, 62-63	83.1	+1.47	-1.82	449	Haut.-Val.	White limestone
105-25-1, 15-16	89.4	+0.90	-0.78	484	Val.-Tith.	White-gray limestone
105-28-3, 53-54	58.4	+2.02	-0.98	514	Val.-Tith.	Gray limestone
105-28-3, 59-60	64.0	+1.16	-1.08	514	Val.-Tith.	Light gray limestone
105-33-1, 100-101	88.4	+1.30	-2.24	559	Tith.-Kimm.	White limestone
105-33-4, 80-81	50.2	+1.53	-0.38	563	Tith.-Kimm.	Red, clayey limestone
105-33-4, 90-91	50.0	+1.32	-0.53	563	Tith.-Kimm.	Reddish tan, clayey limestone
105-35-3, 45-46	29.0	+2.09	-1.84	579	Kimm.-Oxf.	Red marlstone
105-35-3, 50-51	30.8	+2.24	-1.58	579	Kimm.-Oxf.	Red marlstone
105-38-2, 100-101	27.2	+1.98	-0.34	605	Kimm.-Oxf.	Tan-gray-green marlstone
105-38-2, 114-115	19.4	+2.30	-1.34	605	Kimm.-Oxf.	Red-brown marlstone
105-39-1, 100-101*	12.3	+2.33	-1.37	613	Kimm.-Oxf.	Red claystone
105-39, CC*	8.6	+1.73	-1.73	615	Kimm.-Oxf.	Red claystone
105-40-1, 104-105 (A)*		-1.34	-4.03	621		Fibrous calcite
105-40-1, 104-105 (B)*		+1.41	+0.28	621		Sparry calcite
105-40-1, 111-112*		-1.14	-2.06	621		Calcite vein
105-40-1, 118-119*		-1.80	-5.36	621		Calcite pod
105-41-1, 118-119*		-2.04	+0.63	625		Calcite vein
105-41-3, 45-46*		-1.82	+0.04	626		Network of calcite veins
105-41-3, 103-104*		+2.63	+0.09	627		Calcite vein
105-42-2, 81 (A)*		+2.47	+0.39	629		Clay-rich carbonate rock
105-42-2, 81 (B)*		+2.88	+0.16	629		Calcite vein
105-42-2, 129*		+1.54	-4.18	630		Coarse crystalline calcite
105-43-1, 102-103*		+1.96	-0.59	631		Calcite vein
367-25-1, 9-10	83.2	+0.62	-4.10	892	Neocomian	Hard gray limestone
367-25-1, 14-15	31.0	+2.04	-3.58	892	Neocomian	Dark gray marlstone
367-25-3, 59-61 (L)	79.0	+0.82	-3.55	895	Neocomian	Light gray limestone
367-25-3, 59-61 (D)	53.2	+1.26	-2.46	895	Neocomian	Dark gray marlstone
367-26-1, 50-51	89.5	+1.05	-3.81	911	Apt.-Barr.	Hard white limestone
367-26-1, 67-69 (GC)	55.0	+1.40	-2.88	911	Apt.-Barr.	Gray limestone
367-26-1, 67-69 (WC)	77.9	+1.09	-3.84	911	Apt.-Barr.	White limestone
367-27-2, 130-131	87.2	+1.39	-3.72	942	Neocomian	Hard white limestone
367-27-2, 137-139 (W)	77.8	+1.34	-3.84	942	Neocomian	White limestone
367-27-2, 137-139 (G)	41.6	+1.96	-2.26	942	Neocomian	Gray clayey limestone
367-27-3, 50-51	92.0	+1.42	-4.71	942	Neocomian	White limestone
367-28-1, 113-114	77.8	+1.98	-3.22	969	Neoc.-Val.	Gray clayey limestone
367-28-1, 134-136	91.3	+1.86	-3.74	969	Neoc.-Val.	Hard white limestone
367-28-3, 69-71	68.5	+2.38	-3.06	971	Neoc.-Val.	Dark gray marlstone
367-28-3, 108-109	89.2	+1.81	-5.18	972	Neoc.-Val.	Hard whitish limestone
367-29-1, 109-111 (UC)*	76.1	+2.56	-6.11	997	Berr.-Haut.	Chalk above chert
367-29-1, 109-111 (LC)	92.1	+2.60	-4.96	997	Berr.-Haut.	Chalk below chert
367-29-1, 137-139	94.6	+2.67	-5.00	997	Berr.-Haut.	Hard whitish limestone
367-30-1, 59-60	88.3	+1.96	-3.78	1026	Tithonian	White limestone
367-30-1, 72-73	51.8	+2.17	-3.32	1025	Tithonian	Black marlstone
367-30-1, 87	83.8	+1.98	-4.65	1025	Tithonian	Hard whitish limestone
367-30-1, 112-113	69.4	+1.95	-4.58	1026	Tithonian	Gray marlstone
367-30-1, 137-138	76.1	+1.96	-3.35	1026	Tithonian	Hard whitish limestone
367-30-2 97-99	89.0	+1.38	-4.31	1027	Tithonian	Hard whitish limestone
367-30-1, 139-140	93.4	+1.23	-5.31	1027	Tithonian	"Salt and pepper" limestone
376-31-1, 65-67 (C1)	79.2	+1.30	-6.42	1054	Tithonian	Chalk above chert
367-31-1, 65-67 (C2)	23.2	+0.91	-7.98	1054	Tithonian	Chalk below chert
367-32-3, 86-87 (WC1)	76.3	+1.22	-4.34	1085	Kimm. (+)	White limestone
367-32-3, 86-87 (GC1)	23.8	+1.27	-3.28	1085	Kimm. (+)	Green-gray marlstone
367-32-3, 86-87 (WC2)	79.9	+1.37	-4.40	1085	Kimm. (+)	White limestone
367-32-3, 86-87 (GC2)	37.8	+1.29	-3.90	1085	Kimm. (+)	Green-gray marlstone
367-32-3, 135-136	55.8	+1.30	-4.88	1086	Kimm. (+)	Hard white limestone
367-32-5, 50-51	85.8	+1.42	-5.72	1088	Kimm. (+)	Hard white limestone
367-32-5, 55-56	50.6	+1.41	-5.16	1088	Kimm. (+)	Hard pinkish limestone
367-32-5, 135-136	48.0	+1.44	-1.84	1089	Kimm. (+)	Red-brown marlstone
367-33-2, 67-69	83.8	+1.48	-3.45	1108	Kimm. (+)	Pink limestone
367-33-2, 75-77	37.8	+1.42	-3.05	1108	Kimm. (+)	Red-brown marlstone
367-33-3, 80-81	90.4	+1.03	-5.56	1109	Kimm. (+)	Hard white limestone
367-34-1, 105-106	18.4	+1.27	-2.70	1112	Kimm. (+)	Greenish claystone
367-34-1, 107-109	92.8	+1.63	-5.67	1112	Kimm. (+)	Hard white limestone
367-34-1, 137-139	90.0	+1.65	-4.72	1112	Kimm. (+)	Hard white limestone

TABLE 1 – Continued

Sample (Interval in cm)	%CaCO ₃ ^a	δC ¹³	δC ¹⁸	Depth (m) ^b	Age ^c	Description
367-34-3, 104-105 (W)	86.8	+1.70	-4.28	1115	Kimm. (+)	White limestone
367-34-3, 104-105 (R)	20.2	+1.54	-2.45	1115	Kimm. (+)	Red-brown claystone
367-34-4, 20-23 (W)	35.2	+1.55	-6.42	1116	Kimm. (+)	White chalk
367-34-4, 20-23 (G)	11.5	+1.62	-3.23	1116	Kimm. (+)	Green claystone
367-34-4 20-23 (R)	19.8	+1.60	-3.74	1116	Kimm. (+)	Red claystone
367-34-4, 124-125	48.8	+2.00	-1.77	1117	Kimm. (+)	Red marlstone
367-35-4, 51-53	6.4	+1.62	-2.13	1125	Kimm. (+)	Green-gray claystone
367-35-4, 61-63	88.1	+2.07	-4.16	1125	Kimm. (+)	Hard white limestone
367-35-4, 101-102 (DG)	15.4	+1.62	-1.62	1125	Kimm. (+)	Dark gray claystone
367-35-4, 101-102 (B)	17.2	+1.54	-1.64	1125	Kimm. (+)	Brown claystone
367-35-4, 101-102 (W)*	16.7	+1.69	-2.87	1125	Kimm. (+)	Gray-white claystone
367-36-3, 23-25 (G)	61.2	+2.26	-2.42	1131	Kimm. (+)	Gray-white limestone
367-36-3, 23-25 (P)	45.5	+2.36	-2.16	1131	Kimm. (+)	Pinkish marlstone
367-37-1, 67-69	44.6	+2.60	-1.98	1136	Kimm. (+)	Reddish marlstone
367-38-1, 143-144	33.4	+2.28	-2.50	1143	Kimm. (+)	Greenish-gray marlstone
367-38-1, 148-149	59.5	+2.40	-2.33	1144	Kimm. (+)	Greenish limestone
367-38-2, 9-10 (R)	22.0	+2.29	-2.18	1144	Kimm. (+)	Reddish marlstone
367-38-2, 9-10 (G)	40.8	+2.33	-1.68	1144	Kimm. (+)	Greenish marlstone
367-38-2, 35-36	54.6	+2.16	-3.80	1144	Kimm. (+)	Greenish limestone
367-38-2, 14*		+2.39	-7.74	1144		Calcite vein
		+2.30	-7.98			
367-38-3, 34*		-0.99	-6.34	1145		Calcite vein
		+0.56	-9.58			
		+1.68	-7.62			
367-38-3, 110-111*		+1.94	-7.38	1146		Calcite vein
		+1.17	-6.45			
367-39-1, 57-59*		+1.90	-6.83	1149		Calcite vein
		+1.58	-7.35			
367-39-2, 49-50*		+2.20	-6.94	1150		Calcite vein
		+2.00	-7.18			
367-40-1, 104*		+2.33	-6.16	1152		Calcite vein
		+1.21	-8.22			

^aBased on the amount of carbon dioxide liberated by acidification.

^bBased on length of drill string to top of core.

^cBased on preliminary shipboard analysis.

Note: * - see text for explanation. All isotope data relative to PDB. Data for Site 105, Cores 40-43 from Anderson (in preparation).

Drilling in the Caribbean on Leg 15 encountered carbonate sediments overlying a dolerite sill (Edgar et al., 1973). The heat from the sill must have produced a very high geothermal gradient in the overlying sediment. This submarine igneous activity stimulated the recrystallization and lithification of the overlying carbonates (Anderson and Schneidermann, 1973). Recrystallization at higher than normal temperatures produced a shift of several per mil in the oxygen isotopic composition of the sediments toward more negative values (Anderson and Schneidermann, 1973). This isotopic shift is observed for over 200 meters in the limestones above the sill.

The lack of any such shift in the sediments immediately overlying the basalt at Sites 105 and 367 strongly suggests that the basalts in these cases are extrusive or intruded a very thin sediment pile. Moore et al. (1973) show that basalt flowing into the sea raises the temperature of the surrounding water only 3°C due to the efficient convective transfer of heat. A thin sediment veneer would only slightly restrict this transfer and temperatures would be only slightly higher. Studies by Garrison et al. (1973) show that thin layers of sediment trapped within basalt pillows record

little isotopic evidence of high temperature recrystallization. A thick sediment pile slows down convective heat transfer and permits elevated temperatures to build up. This was not the situation at either Sites 105 or 367.

OVERALL OXYGEN ISOTOPIC TRENDS

Comparison of Figures 1 and 2 reveals that the oxygen isotopic composition of sediments from both units at Site 367 are more negative than sediments from the corresponding unit at Site 105. It seems unlikely that these sediments differed greatly in initial composition. If so, the differences seen now are due to differences in the degree of recrystallization, the temperature of recrystallization, the isotopic composition of the pore waters, the ratio of water to carbonate, or some combination of these factors. Lawrence et al. (1975) show that the weathering of the basaltic basement to authigenic clays or zeolites can produce pore waters depleted in O¹⁸ in the overlying sediments. Brenneke and Anderson (1975) suggest that this effect can be reflected in the sediments in the form of a slight negative shift in the oxygen isotopic composition. This is obviously not the case at Site 367

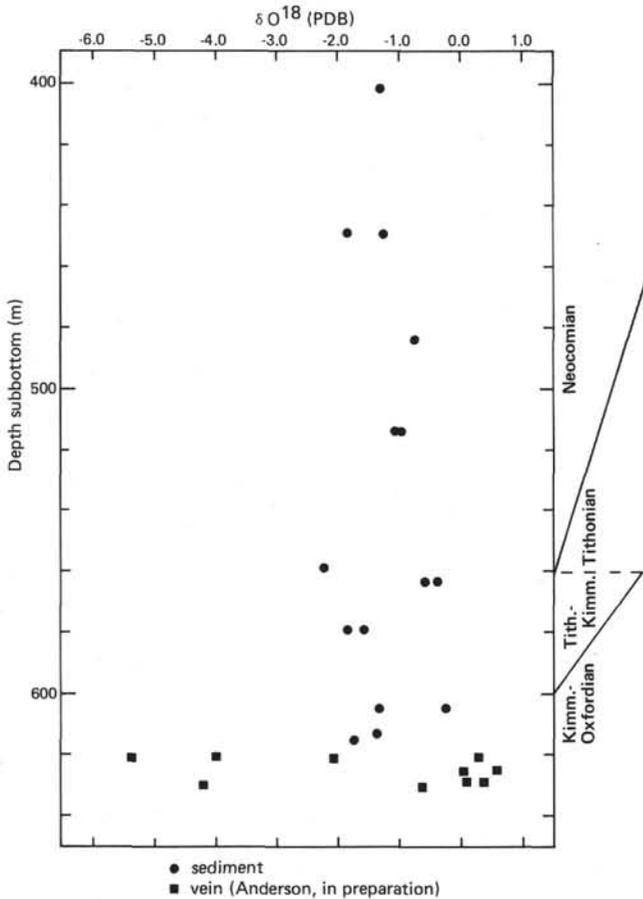


Figure 1. Oxygen isotope composition of Cretaceous and Jurassic carbonates from Site 105.

where the sediments immediately above the basalt are much heavier than those overlying them.

Perry et al. (1976) demonstrated that the alteration of volcanic debris to authigenic silicates can produce a similar effect on the pore water composition. Eade and Anderson (1975) and Anderson and Lawrence (1976) demonstrate that this can result in isotopically light carbonates. The difference in the oxygen isotopic composition between Sites 105 and 367 could be due to a greater amount of authigenic silicates at Site 367. Although simpler explanations for the isotope data are available, this possibility deserves to be examined in more detail.

Jansa et al. (this volume) shows that the sediments at Site 367 are more highly recrystallized than those at Site 105. This conclusion is confirmed by scanning electron microscopy done in conjunction with this study. Sediments from Site 105 contain a much higher percentage of recognizable nanofossil debris than do sediments from Site 367 (Plate 1). Oxygen isotope values are frequently -3‰ to -4‰ in sediments above 1120 meters subbottom at Site 367. Shackleton and Kennett (1975a) estimate that the isotopic composition of the ocean prior to the formation of continental ice sheets was -0.9‰ relative to the present ocean. This may have also been the initial composition of pore waters in oceanic sediments deposited prior to the formation of extensive continental ice masses. The

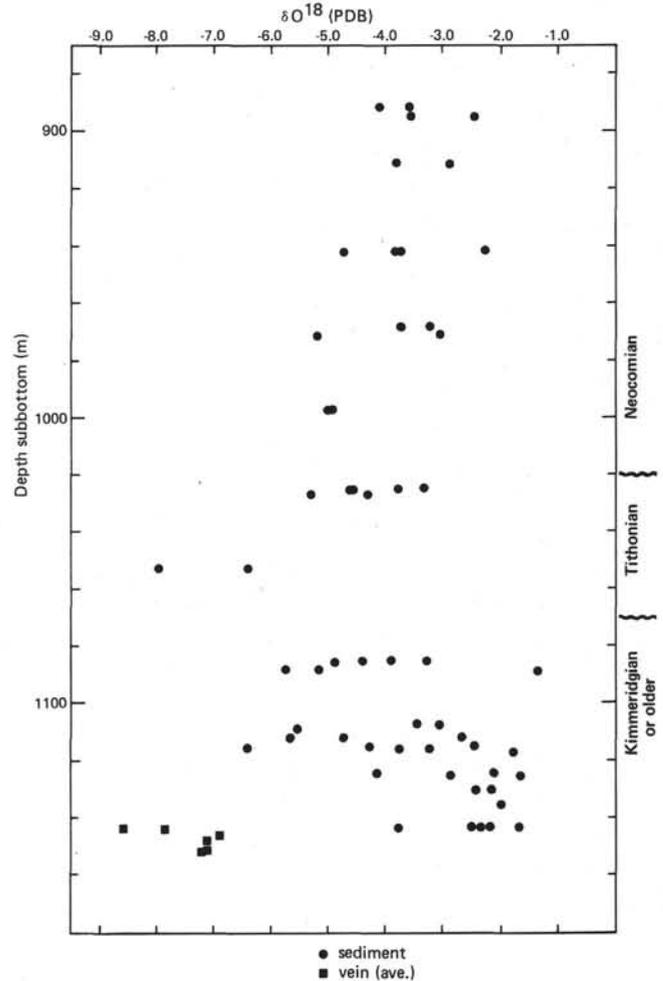


Figure 2. Oxygen isotope composition of Cretaceous and Jurassic carbonates from Site 367.

sediments at Site 367 would have been in equilibrium with pore water of that composition at 27° to 32°C (Craig, 1965). Assuming a geothermal gradient of $4^{\circ}\text{C}/100\text{ m}$ and a modern-day bottom temperature of 2°C , this corresponds to burial depths of 650 to 750 meters, slightly less than present-day burial depths. SEM examination of these sediments shows that they consist of a mixture of original material and authigenic carbonate. The isotopic composition observed is the product of a mixture of carbonate which crystallized at in situ temperatures and carbonate which formed at lower temperatures.

With the exception of Samples 367-29-1, 109-111 cm (UC), 367-31-3, 65-67 cm, and 367-34-4, 20-23 cm, (WC1) and (WC2) (discussed separately below), the most negative value obtained for the sediment was -5.7‰ for Sample 367-32-5, 50-51 cm. This corresponds to an equilibrium temperature of 45°C or a burial depth of about 1100 meters. This sample must have undergone essentially total recrystallization at, or very near, the present depth of burial or in the presence of isotopically light pore waters. These calculations assume that the ratio of oxygen in the pore water to oxygen in the carbonate is very large so that the isotopic composition of the pore water does not change

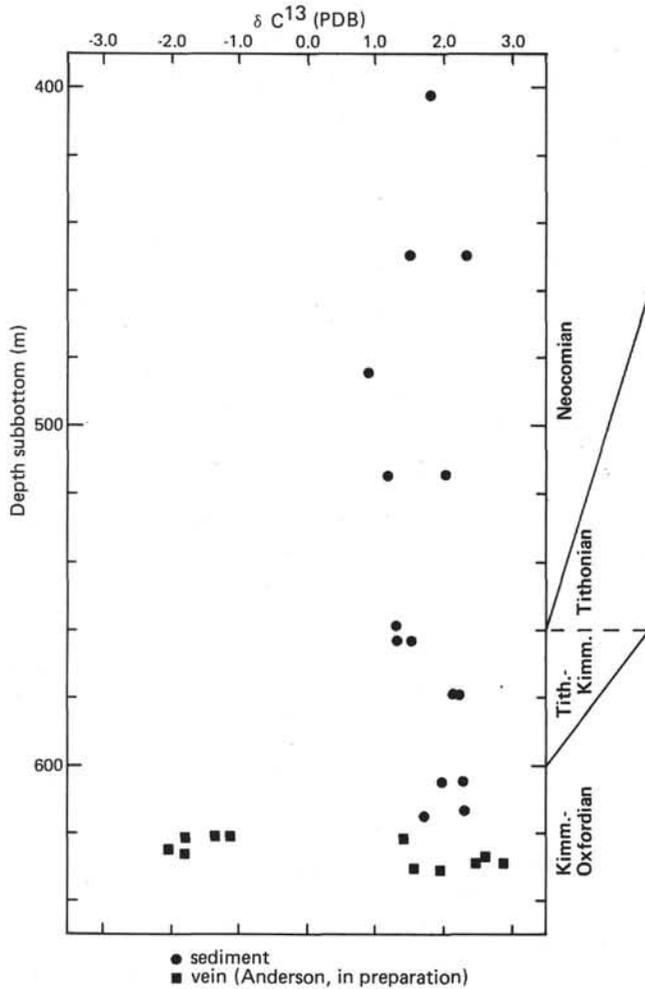


Figure 3. Carbon isotope composition of Cretaceous and Jurassic carbonates from Site 105.

significantly as it exchanges oxygen with the carbonate. Assuming a porosity of 40%, this ratio is only about 0.5, far smaller than required. In order to produce carbonate of the observed composition, the system must have been open to the flow of pore water or a source of O^{18} depleted water must have been available. The flux of pore water cannot be solely from compaction because water forced up through the sediment would have already exchanged oxygen with the underlying carbonate. Geochemical measurements on pore waters in the upper portions of other drill holes (Sayles and Manheim, 1974, and references therein) show no sign of ocean water percolation downward into the sediment column. Measurements of the isotopic composition of pore waters (see references below) also show no evidence of downward movement of water.

As discussed above, the isotopic composition of pore waters decreases due to the formation of authigenic silicates from volcanogenic precursors. Isotopic gradients of between 0 and $-1^{0}/_{00}/100$ m for calcareous sediments (Lawrence, 1973, 1974; Lawrence et al., 1975; Perry et al., 1976) and up to -3 and $-4^{0}/_{00}/100$ m for dominantly siliceous sediments (Gieskes and Lawrence, 1976) have been measured. The isotopic composition of

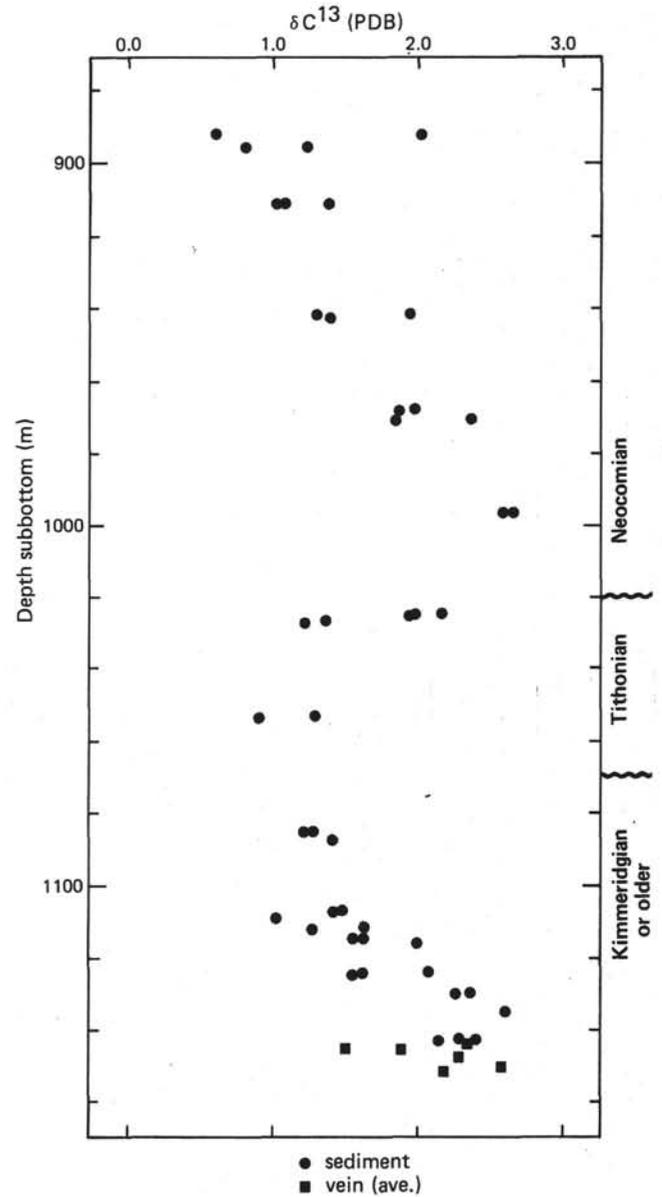


Figure 4. Carbon isotope composition of Cretaceous and Jurassic carbonates from Site 367.

the pore waters is sensitive to the ratio of authigenic silicate to authigenic carbonate and the depth at which the authigenic phases form. None of this information is available for these two sites.

The alteration of volcanogenic material to authigenic minerals takes up Mg^{++} and releases Ca^{++} as well as depleting the water in O^{18} (Lawrence et al., 1975; Perry et al., 1976; Gieskes and Lawrence, 1976). In all cases where significant isotopic gradients have been found in the pore waters, they have been accompanied by substantial increases in the Ca^{++} concentration and decreases in the Mg^{++} concentration of the pore water. These characteristic changes in Ca^{++} and Mg^{++} concentrations have never been observed at sites where measurement failed to reveal a depletion in the O^{18} content of the pore waters. In the upper 325 meters at Site 105, the Ca^{++} concentration doubles, but the Mg^{++} concentration shows little change (Sayles et al., 1972).

At Site 367 the Ca^{++} concentration increases from about 10 mmoles/l near the top of the sediment column to about 50 mmoles/l at 8000 meters subbottom. Mg^{++} concentrations show a much smaller change from slightly over 50 mmoles/l near the sediment-water interface to about 40 mmoles/l at 800 meters. The relation of these data to the pore water composition at much deeper depths is not clear, but the data above suggest that the pore waters at Site 367 are likely to be more depleted in O^{18} than the waters at Site 105.

As mentioned previously, bottom-water temperatures in the early Tertiary may have been 10°C higher than they are today. At the end of the Cretaceous, the sediment thickness at Site 367 amounted to at least about 600 meters (site report, this volume). Temperatures near the base of the sediment column were probably at least 35°C . Since the end of the Cretaceous, carbonate sediments at Site 367 have been exposed to conditions which could produce their approximate present isotopic compositions.

Sediment thickness at Site 105 at the end of the Cretaceous was about 350 meters (site report, Hollister et al., 1972). In situ temperature in the basal sediments should have been near 25°C , the same as today. Carbonate formed in equilibrium with these conditions (assuming a isotopic composition for pore water) would have an O^{18} value of about -3‰ . This is slightly lighter than the lightest sample (105-33-1, 100-101 cm) analyzed from this hole, which is not totally recrystallized (Plate 1, Figures 3 and 4). Even the lightest sample at Site 105 could be produced without the presence of O^{18} depleted pore water. Such pore water may have existed at this site, but the isotope evidence for its existence is lacking.

LOWERMOST SEDIMENTS AT SITE 367

Scholle (1976) presents data which suggest that lithification and recrystallization in deep-sea chalks and limestones is primarily due to pressure solution. An example of this phenomenon is illustrated in Plate 2, Figure 6. Pressure solution is driven by the change in solubility associated with the difference between the confining pressure of the pore fluid and the pressure at grain-to-grain contacts. Pressure solution would be expected to proceed faster at the greater pressure differentials in the more deeply buried sediments at Site 367. (Only the thickness of overlying sediment needs to be considered here as the weight of overlying water contributes equally to confining pressure and pressure at grain-to-grain contacts.) The higher temperatures associated with a greater sediment thickness may also be significant. Owen and Brinkley (1941) conclude that an increase in temperature decreases the effect of pressure on the solubility of weak electrolytes, but the increase in the rate of chemical reactions associated with higher temperatures may offset this. Perhaps more significantly, higher temperatures increase the rate of diffusion of ions. Weyl (1959) suggests that the rate limiting step in pressure solution is the diffusion of ions away from the point of grain contact in a thin film of water which is present between the grains. If Weyl's postulated mechanism is true, then the increased rate of diffusion at the higher

temperatures experienced at Site 367 should be significant.

In light of the above analysis, the isotopic data from the lowermost sediments at Site 367 (below 1120 m subbottom) are difficult to interpret. These sediments should be the most highly recrystallized and, correspondingly, have the most negative O^{18} values of any sediments analyzed, yet they are significantly heavier isotopically than the sediments immediately above (Figure 2). The isotopic data suggest that these lowermost sediments must be significantly less recrystallized than the overlying samples or they must have recrystallized at lower temperatures and therefore with a thinner overburden. Most probably the answer is a combination of the two factors. Jansa (this volume) reports that the occasional nannofossils in these lowermost sediments are well preserved although the matrix of the rock is a dense neomorphic calcite. Recrystallization in the lower sediments is clearly extensive enough that much of it had to occur at lower temperatures early in the burial history of the sediments.

EFFECT OF CHERT FORMATION

Samples 367-31-1, 65-67 cm (C1) and (C2) are from just above and below a small chert nodule. Sample C1 is from between 5 and 10 mm above the chert whereas Sample C2 is closer, perhaps 2 mm away. These two samples have the most negative oxygen isotopic compositions of any sediments analyzed from Site 367. Sample C2 (-8.0‰) would be in equilibrium with ocean water at a temperature of about 60°C . This would require a geothermal gradient of $6^{\circ}\text{C}/100\text{ m}$. Such a geothermal gradient would require an unreasonably high heat flow for crust of Jurassic age (heat flow data from Sclater and Francheteau, 1970; thermal conductivity data from Langseth, 1965, and Von Herzen et al., 1971). Even Sample C1 (-6.4‰) would require a geothermal gradient of $5^{\circ}\text{C}/100\text{ m}$. This suggests that recrystallization of these samples took place in the presence of water significantly depleted in O^{18} relative to ocean water.

The O^{18} depleted pore water apparently existed only around the chert nodule or recrystallization was concentrated there because this effect is evident only locally. Sample C2, which is from closer to the chert nodule and contains more silica itself, is isotopically lighter than C1. Water depleted in O^{18} would have formed if an authigenic phase rich in O^{18} formed from a precursor which was depleted in O^{18} . Heath and Moberly (1971), Heath (1973), and Wise and Weaver (1974) argue strongly that nodular chert forms by remobilization of biogenic silica. Biogenic silica ranges in oxygen isotope composition from $+2.4\text{‰}$ to $+6.3\text{‰}$ (Mopper and Garlick, 1971; Knauth and Epstein, 1975). Deep-sea cherts range in composition from $+0.5\text{‰}$ to $+6.0\text{‰}$ (Knauth and Epstein, 1975). At temperatures of 30°C and above, chert formed from a biogenic precursor enriches pore water in O^{18} rather than depletes it (Lawrence et al., 1975). Even at temperatures below 10°C , the O^{18} depletion of pore waters caused by this type of chert formation is very small (Lawrence et al., 1975).

Knauth and Epstein (1975) present data suggesting that opal-CT (the first step in chert formation) forms during shallow burial (less than 100 m depth). Opal-CT replaces the calcite matrix, releasing calcium carbonate which reprecipitates in the surrounding carbonate ooze (Wise and Weaver, 1974). Authigenic carbonate formed at this temperature (very shallow burial) should be relatively heavy, even if the pore water was somewhat depleted in O^{18} due to chert formation. The final step in chert formation is the inversion of opal-CT (disordered cristobalite) to microcrystalline quartz (Heath and Moberly, 1971; Wise and Weaver, 1974). This step normally takes place at elevated temperatures, either due to deep burial or a very high geothermal gradient (Heath and Moberly, 1971). Lancelot (1973) and Keene (1975) suggest that some quartz may form directly, without the opal-CT precursor. Knauth and Epstein (1975) report that microcrystalline quartz is depleted in O^{18} relative to co-existing opal-CT. Thus either the transition from opal-CT to quartz or the direct precipitation of quartz would enrich pore waters in O^{18} rather than deplete them.

If all of the above assumptions regarding the geothermal gradient, mode of chert formation, and isotopic composition of deep-sea chert and its precursors are correct, then the oxygen isotope data from Samples 367-31-1, 65-67 cm (C1) and (C2) are inexplicable. It is tempting to suggest that this chert nodule formed from a volcanic precursor. Volcanic ash typically has an oxygen isotope composition of about -23‰ relative to PDB ($+8\text{‰}$ SMOW, Garlick and Dymond, 1970). Formation of chert with an isotopic composition of $+3\text{‰}$ would produce pore waters immediately adjacent to the nodule which are greatly depleted in O^{18} . Such an explanation would not have to be universal because Knauth and Epstein found no such unusual values in carbonates associated with the cherts they analyzed, although the same effect appears present in Sample 367-29-1, 109-111. Unfortunately petrographic and SEM examination of 367-31-1, 65-67 cm failed to reveal any remnants of volcanic debris. The other alternative is that opal-CT replacement of the original carbonate and the resultant authigenic carbonate formation around the nodule occurred only after deep burial where the pore waters were already light. Clearly the question of chert formation and its effect on the isotopic composition of associated carbonates deserves more study.

Sample 367-34-4, 20-23 cm (W) is also very light (-6.4‰). Equilibrium precipitation of this sample in ocean water would require a temperature around 50°C . It seems unlikely that the geothermal gradient is that high ($5^\circ\text{C}/100\text{m}$) in these sediments. Although this sample appears in hand specimen to be a normal chalk, it contains only 35% carbonate. SEM micrographs (Plate 2, Figures 4 and 5) show grains comparable in appearance to silicates in other studies (Eade and Anderson, 1975, Plate 1, Figure 4). This authigenic silicate formation could have produced pore waters locally depleted in O^{18} .

Effect of Clay Content

When sampling material from Site 367, particular attention was given to small-scale lithology changes

within individual cores. Twenty pairs of samples from Site 367 taken within 40 cm of each other differed from each other by over 10% in carbonate content (Table 2). Another such pair had previously been sampled from Site 105. In 17 of the 21 cases examined, the sample which had the higher carbonate content was depleted in O^{18} , in some cases by up to 3‰ . Two of the other cases occurred very near basaltic basement and differed from each other only marginally in isotopic composition. The remaining two cases involve chert nodules and have been discussed above.

Variations in ocean conditions could induce primary isotopic variations in two ways. The isotopic composition of carbonate secreted by planktonic organisms could change because of changes in the temperature or isotopic composition of ocean water. Alternatively, selective dissolution could control the composition of the sediment as it is being deposited by preferentially dissolving a part of the sediment having some characteristic isotopic composition. Generally near-surface, warm-water forms are more susceptible to dissolution than the more robust, deeper living types (Berger, 1968).

Regular variations in the carbonate content of Quaternary cores have been documented by Arrhenius (1952), Hays et al. (1969), Hays and Perruzza (1972), Olausson (1971), and Gardner (1975) among others. These variations appear to coincide with glacial-interglacial cycles and are the result of changes in productivity and dissolution which are primarily caused by changes in circulation (Olausson, 1971; Ramsay, 1974) and changes in noncarbonate influx (Ruddiman, 1971; Gardner, 1975). Associated isotopic variations are primarily due to changes in the isotopic composition of ocean water caused by changes in the size of continental ice sheets (Shackleton and Opdyke, 1974). Jurassic sediments at Site 367, also present at Site 105 (Lancelot et al., 1972), are directly analogous to those observed in the Quaternary record because large-scale continental ice sheets did not exist at those times. Although glaciation was not widespread before the Oligocene or Miocene, carbonate cycles are

TABLE 2
Relationship Between Isotopic Composition and Carbonate Content

Sample (Interval in cm)	$\Delta\%CaCO_3$	$\Delta\delta O^{18}$	$\Delta\delta C^{13}$
105-21-1, 62-63 vs 105-21-1, 53-54	32.9	-0.56	-0.80
367-25-1, 9-10 vs 367-25-1, 14-15	52.2	-0.52	-1.42
367-25-3, 59-61 (L) vs 367-25-3, 59-61 (D)	25.8	-1.09	-0.44
367-26-1, 67-69 (WC) vs 367-26-1, 67-69 (GC)	24.7	-0.96	-0.31
367-27-2, 137-139 (W) vs 367-27-2, 137-139 (G)	36.2	-1.58	-0.62
367-28-1, 134-136 vs 367-28-1, 113-114	13.5	-0.50	-0.12
267-28-3, 108-109 vs 367-28-3, 69-71	20.7	-2.12	-0.57
367-29-1, 109-111 (LC) vs 367-29-1, 109-111 (UC)	16.0	+1.15	+0.04
367-30-1, 59-60 vs 367-30-1, 72-73	36.5	-0.46	-0.21
367-30-1, 87 vs 367-30-1, 72-73	31.5	-1.13	-0.19
367-30-1, 87 vs 367-30-1, 112-113	13.9	-0.07	+0.03
367-31-1, 65-67 (C1) vs 367-31-1, 65-67 (C2)	56.0	+1.56	+0.39
367-32-3, 86-87 (WC) vs 367-32-3, 86-87 (GC)	47.3	-0.88	+0.00
367-33-2, 67-69 vs 367-33-2, 75-77	46.0	-0.40	+0.06
367-34-1, 107-109 vs 367-34-1, 105-106	74.6	-2.99	+0.36
367-34-3, 104-105 (W) vs 367-34-3, 104-105 (R)	66.6	-1.83	+0.16
367-34-4, 20-23 (W) vs 367-34-4, 20-23 (G)	23.7	-3.19	-0.07
367-35-4, 61-63 vs 367-35-4, 51-53	81.7	-2.03	+0.45
367-36-3, 23-25 (G) vs 367-36-3, 23-25 (P)	15.7	-0.26	-0.10
367-38-1, 148-149 vs 367-38-1, 143-144	26.1	+0.17	+0.12
367-38-2, 9-10 (G) vs 367-38-2, 9-10 (R)	18.8	+0.50	+0.04
367-38-2, 35-36 vs 367-38-2, 9-10 (G)	13.8	-2.12	-0.17

common in early Tertiary and older sediments (Arthur and Roggenthen, 1976). The causes of earlier fluctuations are completely unknown. It is difficult, however, to explain why such primary variations in carbonate content should result in variations in the primary isotopic composition of the magnitude and direction observed.

Oldershaw and Scoffin (1967) suggest that clay-rich zones in limestone sequences can serve as important contributors of cement to surrounding regions. Arthur and Roggenthen (1976) report that although primary variations exist in carbonate content, these variations are enhanced by diagenetic effects. Clay-rich zones are regions of intense carbonate dissolution. The carbonate thus dissolved precipitates in the immediately adjoining, carbonate-rich, regions where void spaces (sites of low pressure) are more common. Weyl (1959) provides a theoretical basis for the catalytic effect of clay in his treatment of pressure solution. He suggests that water films between grains are much thicker when a layer of clay is also present. These thicker films should provide for faster diffusion of ions away from the sites of dissolution to the sites of reprecipitation. Clays may also produce chemical effects which would produce the same results.

Carbonate precipitated at the higher temperatures of deep burial should be depleted in O^{18} relative to original carbonate. The isotopic data would be explained if the clay-poor zones contain a substantially larger fraction of authigenic calcite formed at elevated temperatures than do the clay-rich zones. Clay-poor sediments near to a clay-rich zone should have more authigenic calcite than do clay-poor sediments further away from the clay-rich zone. Sample 367-34-1, 105-106 cm has a low carbonate content (18.4%). Sample 367-34-1, 107-109 cm is almost pure carbonate (92.8%) as is Sample 367-34-3, 137-139 cm (90.0%). The oxygen isotope composition of (107-109 cm) is much lighter than (105-106 cm) and slightly lighter than (137-139 cm) (Table 1). This pattern is consistent with the clay-rich zone serving as a source of carbonate for the surrounding region.

The explanation for the isotopic results given above is tentative and should be viewed with caution. The idea that clay zones undergo more intense dissolution explains the isotope data, but is difficult to reconcile with other facts. Preservation of the nannofossils at Site 105 is reported to be much better in the clay-rich zones than in clay-poor regions (Lancelot et al., 1972), and this phenomenon is common in deep-sea carbonates (Wise, oral communication, 1976). The preliminary results of SEM work on these samples is inconclusive (Plate 2, Figures 7-12) although Jansa (this volume) reports on the basis of his studies that diagenetic alteration is greater in limestones with lesser amounts of argillaceous material.

Lancelot et al. (1972), suggest that this differential preservation is because "the clay minerals prevent the minimum circulation required for the reprecipitation of calcite in intergranular spaces." If the clay-rich regions did not undergo recrystallization to as great an extent as carbonate-rich regions did, then the isotopic pattern illustrated by Table 2 would be explained. This

explanation seems incorrect for two reasons. First, there is no a priori reason for assuming any circulation is required for recrystallization, especially if recrystallization is driven by pressure solution. Second, Brenneke and Anderson (1975) observed this same isotopic relationship in other sediments from Leg 11. Some of the clay-rich zones in these sediments contain up to 50% authigenic dolomite. If ion mobility is sufficient to allow this amount of dolomite to form, calcite should be able to recrystallize.

The pressure solution explanation is not without difficulties either. Plate 2, Figure 9, shows half of a well-preserved coccosphere from a clay-rich zone at Site 367. The pore space within this coccosphere has not been filled by carbonate even though it is closer to the site of pressure solution than is the nearby carbonate-rich zone. Perhaps the best explanation is that clays affect the chemistry of the pore waters in some way not well understood.

Carbon Isotope Results

The relation of δC^{13} to carbonate content is not nearly as consistent as it is for δO^{18} (Table 2). In general, less deeply buried samples show a depletion in δC^{13} from clay-rich to carbonate-rich zones, whereas those samples more deeply buried exhibit the reverse.

The carbon isotopic compositions of sediments from Sites 105 and 367 are plotted against depth in Figures 3 and 4, respectively. Whereas too few samples were analyzed at Site 105 to show any small-scale variation with depth, it can be seen that the carbon values from Site 367 vary cyclically over a range of 2‰ . These variations seem independent of lithology or degree of recrystallization and are assumed to be primary. The carbon isotopic composition of biogenic carbonate depends upon the isotopic composition of dissolved inorganic carbon and various species-dependent "vital" effects (Shackleton et al., 1973; Savin and Douglas, 1973). Because bulk samples of carbonate were analyzed, it is assumed that any species-dependent fractionation was averaged out.

The isotopic composition of dissolved inorganic carbon in seawater varies with depth from about $+2\text{‰}$ at the surface to as low as -0.5‰ at the oxygen minima (Craig, 1970; Kroopnick et al., 1970; Kroopnick et al., 1972; Kroopnick, 1974b). Changes in the depth at which carbonate formed from very near the surface to the depth of the oxygen minima (400 to 500 m) could produce δC^{13} variations of the magnitude seen at Site 367. Much of the carbonate in the sediments from Site 367 is produced by calcareous algae (Coccolithophoridae) which must calcify within the photic zone, so that the preceding explanation is untenable. Therefore, the δC^{13} variations measured at Site 367 reflect variations in the isotopic composition of dissolved inorganic carbon in the near-surface waters of the ocean. These variations could be caused by either changes in the isotopic composition of the oceanic reservoir of carbon or by changing the partitioning of δC^{13} between surface and deep water.

The isotopic composition of dissolved inorganic carbon in the near-surface waters of the ocean is controlled by several processes: (1) a steady-state

quasi-equilibrium with the atmosphere (Kroopnick, 1974a,b); (2) the net flux of carbon to and from the surface zone in the form of organic matter; and (3) the equivalent net flux of carbon in the form of carbonate. Because the total net flux of carbon to and from the surface zone must be zero, processes (2) and (3) must be about equal in magnitude and opposite in sign (some CO_2 is also transported across the seawater-atmosphere interface).

The quasi-equilibrium between dissolved inorganic carbon and the atmosphere is a function of temperature, atmospheric PCO_2 , and the pH (or alkalinity) of the water (Kroopnick, 1974a). Local changes in any of these variables could produce local changes in the isotopic composition of dissolved inorganic carbon for perhaps as long as a few thousand years. Because the oceanic reservoir of carbon is 60 times as large as the atmospheric reservoir (Garrels et al., 1974), a world-wide change in any of the variables would have very little effect on the oceanic reservoir although the effect on the atmospheric reservoir could be quite large.

Such stability in the oceanic carbon reservoir would not be true if the composition of the atmosphere should continue to change for a long period of time. Terrestrial organic carbon is depleted in C^{13} relative to the atmospheric reservoir by about 18‰ (Craig, 1953). Silverman (1961, 1962) suggests that the evolution of land plants fixed sufficient light carbon to change the isotopic composition of the atmosphere and that these changes could explain trends in the $\text{C}^{13}/\text{C}^{12}$ ratio of petroleum with time. A change in the average net preservation resulting in the burial of an additional 2.5×10^{17} moles of fixed carbon would be sufficient to produce the variation of 2‰ in the oceanic reservoir observed at Site 367. This change in preservation could, for example, be due to the existence of very extensive coal swamps or to the rapid exposure and oxidation of previously buried organic matter which might accompany rapid uplift and accelerated erosion.

Variations in the net removal of organic carbon from the surface region could have as much effect on the isotopic composition of total CO_2 as variations in the preservation of terrestrial organic matter. Marine organic carbon is depleted in C^{13} relative to dissolved inorganic carbon by between 12 and 28‰ , depending upon environmental factors, with an average of around 20‰ (Degens, 1969). Carbonate carbon is roughly similar in isotopic composition to dissolved inorganic carbon (Kroopnick, 1974b). The isotopic composition of dissolved carbon is thus much more sensitive to the net flux of organic carbon than to the flux of carbonate carbon.

The net flux of organic carbon in the surface zone depends upon the rate of production of organic matter, the rate at which this organic matter is oxidized in the surface zone, the rate at which CO_2 from deep water is returned to the surface zone by upwelling, the fraction of CO_2 in deep water which is produced by the oxidation of organic matter, and the amount of CO_2 produced by the oxidation of organic matter (either recent or fossil) which is carried into the ocean by rivers. The same factors control the net removal of

carbon in the form of carbonate with the dissolution of carbonate substituting for oxidation of organic matter.

The individual processes which control the net removal of carbon are not independent. The rate of production of organic matter in the ocean depends principally upon the supply of nutrients, primarily phosphorous. The supply of P depends upon the rate of upwelling of nutrient-rich deep water and the rate of P influx from the land by river discharge. The amount of organic matter oxidized and contributed to the deep-water mass depends upon the rate of production of organic matter and on the amount of oxygen in the deep water. This latter depends upon the rate of formation of deep water, which, through conservation of mass, must equal the rate of upwelling.

An increase in ocean circulation would increase the supply of P to the surface zone and thereby increase the rate of production of organic matter. This would leave the dissolved inorganic carbon reservoir in the surface zone enriched in δC^{13} . This enrichment would be reflected in the isotopic composition of carbonate forming in this water. However, oxidation of the increased flux of organic matter would increase the CO_2 content of deep water and decrease its δC^{13} value. Oceanic circulation would carry this light CO_2 back up to the surface zone, shifting the surface reservoir back towards its original composition. It is likely that increased production of organic matter would be accompanied by an increase in carbonate secretion. The higher CO_2 content of the deep water would decrease its PH and increase the dissolution of carbonate.

All of the feedback in the ocean need not occur in one geographic locale. The increased amounts of oxidized organic carbon need not be returned to the surface by upwelling deep water at the exact locality where the increased organic production occurs. Local changes in the δC^{13} of the inorganic carbon in the surface ocean (about 1‰ , Kroopnick, 1971, 1974a). Most of this variation is across the Antarctic convergence where deep and surface waters mix freely. Although this is a region of extraordinarily high productivity, the influx of light carbon by upwelling is greater than removal by organic activity and the isotopic composition of dissolved inorganic carbon in this region is lighter than most of the rest of the ocean (Kroopnick, 1971, 1974a).

The net effect of a change in the oceanic mixing rate on the isotopic composition of dissolved inorganic carbon would depend upon changes in the amount of organic carbon preserved in the sediments. The dependence of the amount of organic carbon preserved on the mixing rate is not known, but the range of possible effects can be estimated by considering two limiting cases. In case 1 the *amount* of organic carbon preserved is assumed to be independent of the mixing rate. In this case the isotopic composition of dissolved inorganic carbon is also independent of the mixing rate. In case 2 the *fraction* of organic matter preserved is assumed to be independent of the mixing rate. With this assumption, it can be shown that doubling the oceanic mixing rate would increase the isotopic composition of the oceanic reservoir of carbon by about 1.2‰ (Brenneke, in preparation).

Broecker (1971,1974) stresses that the partitioning of δC^{13} between the deep and surface water masses is a function of the ratio of C/P in deep water to that in organisms. In case 1 above, this ratio is independent of the mixing rate. In case 2, however, doubling the mixing rate would raise the C/P ratio in deep water and decrease the enrichment of C^{13} in the surface ocean from the present 2 to 3‰ (Craig, 1970; Kroopnick et al., 1970; Kroopnick et al., 1972; Kroopnick, 1971, 1974b) to about 1.2‰ (Brenneke, personal communication).

The ratio of C/P in deep water to that in organisms could change in other ways. There is no a priori reason to believe that the C/P ratio in organisms has remained constant through time. If Broecker's analysis is correct, doubling the C/P ratio in organisms would double the isotopic difference between carbon in the surface and deep reservoirs. Halving the C/P ratio in organisms would halve the difference between the surface and deep reservoirs. Similar effects would result if changes in the rate of carbonate formation decreased or increased the carbon content of the ocean by 50%. The C/P ratio in the ocean is also sensitive to the rate of phosphorite formation. Large changes in the rate of P removal in this form, or large changes in the rate of P input by rivers due to varying erosion of phosphorites, would also change the isotopic difference between surface and deep water. In each case the carbon isotopic composition of deep-sea carbonates would reflect the changes in the isotopic composition of dissolved inorganic carbon in the surface waters.

Several other workers have noted the existence of periodic variations in the isotopic composition of marine carbonates. Jeffery et al. (1955), Compston (1960), Weber (1967), and Tappan (1968) all discussed variations based on average values for geologic periods. Thus the average carbon isotope composition of marine limestone of Cretaceous age is heavier than the average composition of similar limestone of Jurassic age (Weber, 1967). Because average compositions for each period were obtained from samples worldwide in distribution, resolution of variations on the time scale discussed here was not possible. In fact, the scatter over a given geologic period is so large (as can easily be visualized from Figure 4) that two co-authors, using the same data, reached opposite conclusions as to the actual existence of such variations (Keith and Weber, 1964; Weber, 1967). Explanations for these long-period fluctuations range from periodic diastrophism (Jeffery et al., 1955; Compston, 1960) to the evolution of land plants (Weber, 1967) to changes in nutrient supply from the continents because of topographic and climatic changes (Tappan, 1968). All of these explanations seem to require too long a time to operate to be responsible for the variations observed here.

Douglas and Savin (1973) and Shackleton and Kennett (1975a,b) have observed fluctuations in the δC^{13} of younger marine carbonates similar to those observed here. They also concluded that these variations reflect variations in the isotopic composition of dissolved inorganic carbon. They offered no explanation for these shifts. Fluctuations of much shorter duration have been found in Pleistocene cores by Sommer and Matthews (1975) and Anderson and Adelseck (unpublished data). Sommer and Matthews

suggest that these variations are worldwide in extent and suitable for stratigraphic purposes. If the variations found at Site 367 and those seen by Douglas and Savin (1973) and Shackleton and Kennett (1975a) are also found to be of worldwide extent, then they offer a new stratigraphic tool for older, relatively recrystallized cores which are difficult to date precisely by other methods.

CONCLUSIONS

1) Vein-filling carbonates begin to form at ocean-floor temperatures, in equilibrium with seawater, shortly after the basalt has cooled. Vein formation continues in the presence of isotopically light pore waters which are formed by the weathering of basalt to authigenic silicates. Poor communication between the pore water in the fracture systems and the ocean allows very light veins to form at relatively low temperatures.

2) The lack of any isotopic evidence of high temperature "baking" of the lowermost sediments at either Site 105 or Site 367 suggests that the basalts at both sites were extrusive or intruded only a very thin sediment pile.

3) Sediments from Site 367 are depleted in O^{18} relative to correlative sediments from Site 105 due to the greater degree of recrystallization at higher temperatures and possibly in the presence of lighter pore waters which has occurred at Site 367. The degree of recrystallization and temperature of recrystallization are both functions of the thickness of overburden. The lighter pore waters, if present, could be caused by greater amounts of authigenic silicates having been formed at Site 367.

4) The sediments immediately overlying the basalt at Site 367 are less recrystallized and isotopically heavier in oxygen than the sediments immediately above them. The isotope data suggest that much of this recrystallization occurred at relatively low temperatures and thus at relatively shallow burial depth. The cause of such early recrystallization and the reason why further recrystallization did not occur in these sediments are unknown.

5) Carbonates closely associated with two chert nodules at Site 367 tend to be depleted in O^{18} relative to all other sediments. No good explanation for these data is currently available. Present assumptions regarding the precursor of nodular chert or the timing of the onset of chertification may have to be revised.

6) The amount of clay in carbonate sediments significantly influences the oxygen isotope composition and degree of recrystallization of those sediments. Clays may produce these effects by their influence on pressure solution, pore water chemistry, or fluid movement.

7) The carbon isotopic composition of carbonates from Site 367 varies systematically with depth. These variations are believed to be primary and related to the isotopic composition of dissolved inorganic carbon in the ocean. These variations are presumably caused by changes in the amount of organic carbon buried in sediments or by changes in the C/P ratio in ocean water. Data from Site 105 are insufficient to test the possibility of using carbon isotope variations in Cretaceous and older deep-sea carbonates as a stratigraphic tool.

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PLATE 1

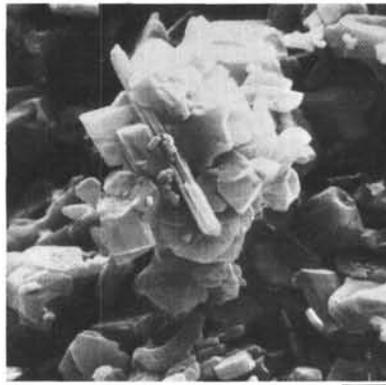
(All figures are scanning electron micrographs.)

- Figure 1 Sample 105-21-1, 62-63 cm. Recognizable coccolith debris abundant, overgrowths slight to moderate. Magnification $\times 5600$. Scale bar = 1 μm .
- Figure 2 Sample 105-21-1, 62-63 cm. Recognizable coccolith debris common. Blocky debris may be authigenic or overgrown fragments of larger microfossils. Magnification $\times 5600$. Scale bar = 2 μm .
- Figures 3,4 Sample 105-33-1, 100-101 cm. Recognizable coccolith debris still abundant, overgrowths slight to moderate. "Wispy" appearance due to presence of authigenic (?) silicates (see also Plate 2, Figures 1-5). Magnification $\times 3250$. Scale bar = 2 μm .
- Figure 5 Sample 105-38-2, 100-101 cm. Well-preserved coccolith inside a broken)calcsphere (?). Magnification $\times 2500$. Scale bar = 2 μm .
- Figure 6 Sample 105-38-2, 100-101 cm. Well-preserved coccolith beside broken fragment of calcsphere (?). Magnification $\times 1240$. Scale bar = 5 μm .
- Figure 7 Sample 367-31-1, 65-67 cm (C2). Rare coccolith still recognizable. Authigenic calcite abundant. Magnification $\times 1850$. Scale bar = 5 μm .
- Figure 8 Sample 367-31-1, 65-67 cm (C2). Higher magnification of another region of the same sample as Figure 7. Note crystal faces produced by overgrowths on coccolith in center. Magnification $\times 4700$. Scale bar = 1 μm .
- Figure 9 Sample 367-34-1, 107-109 cm. Authigenic calcite abundant. Magnification $\times 1300$. Scale bar = 5 μm .
- Figure 10 Sample 367-35-5, 51-53 cm. Well-preserved coccolith to right of center. Sample only 6% carbonate (see also Plate 2, Figure 9). Magnification $\times 2340$. Scale bar = 2 μm .
- Figure 11 Sample 367-35-4, 61-63 cm. Rare nannofossil debris (note edge of coccolith left of center). Authigenic calcite abundant. Sample is 84% calcite. Magnification $\times 2350$. Scale bar = 2 μm .
- Figure 12 Sample 367-35-4, 61-63 cm. Overgrown nannofossil debris. Authigenic calcite dominates. Magnification $\times 6000$. Scale bar = 1 μm .

PLATE 1



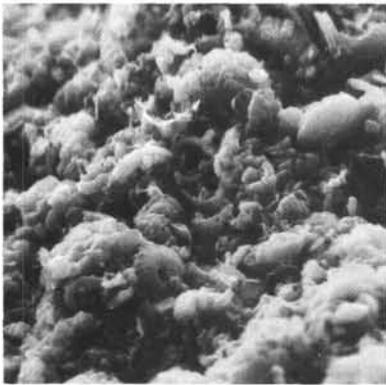
1 1 μm



2 1 μm



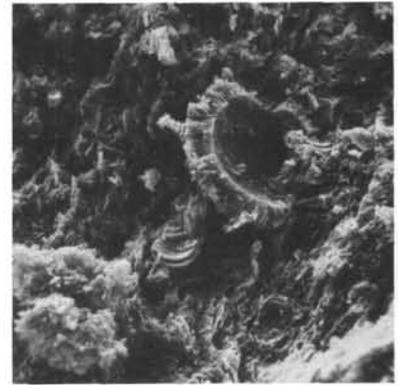
3 2 μm



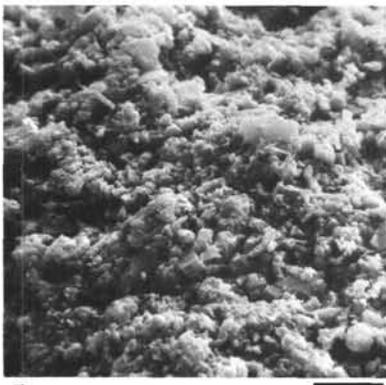
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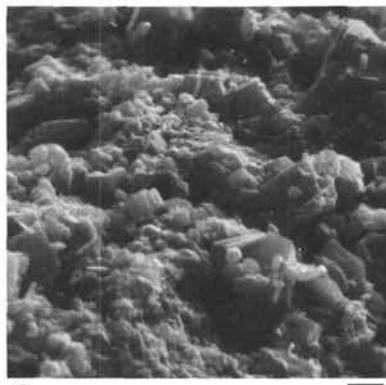
5 2 μm



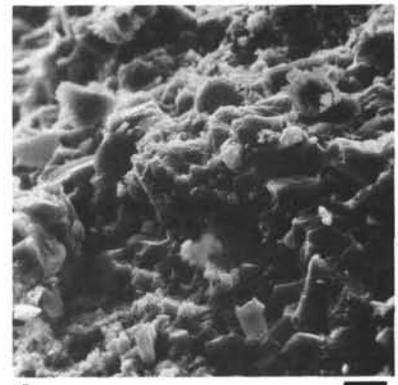
6 5 μm



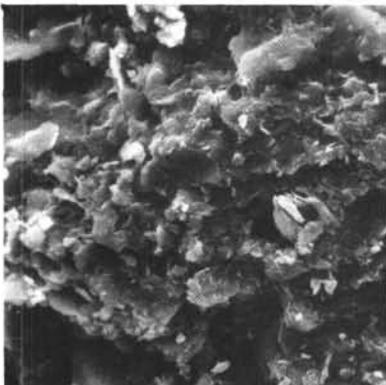
7 5 μm



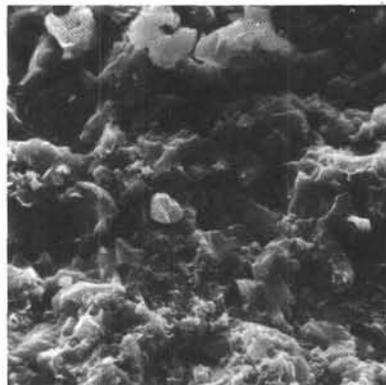
8 1 μm



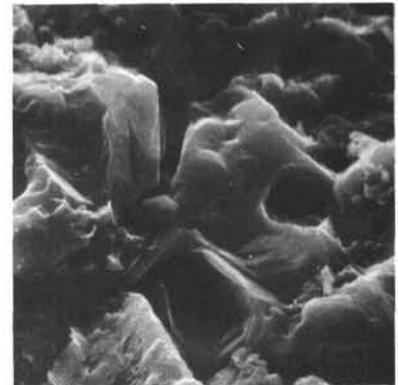
9 5 μm



10 2 μm



11 2 μm



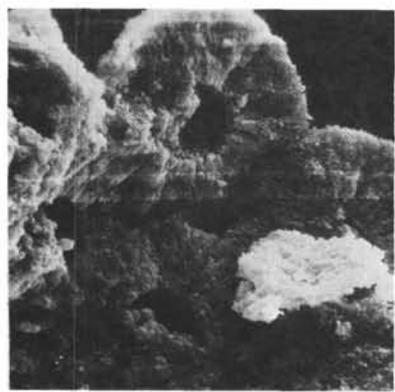
12 1 μm

PLATE 2

(All figures are scanning electron micrographs.)

- Figure 1 Sample 367-31-1, 65-67 cm (C2). Structure of chert nodule. Resembles view of "lepispheres" fig. 8b, Wise and Weaver (1974). Magnification $\times 1850$. Scale bar = $2 \mu\text{m}$.
- Figure 2 Sample 105-21-1, 62-63 cm. "Lepisphere" of cristobalite in fairly well preserved nanno-chalk (see also Plate 1, Figures 1 and 4; Plate 2, Figure 8). Magnification $\times 5600$. Scale bar = $1 \mu\text{m}$.
- Figure 3 Sample 105-38-2, 100-101 cm. Almost totally siliceous. Probably volcanic debris just above basalt. Magnification $\times 2475$. Scale bar = $2 \mu\text{m}$.
- Figure 4 Sample 367-34-4, 20-23 cm (W). "Wispy" appearance due to the presence of siliceous material (65% of sample). Authigenic calcite also common. Magnification $\times 2200$. Scale bar = $2 \mu\text{m}$.
- Figure 5 Sample 367-34-4, 20-23 cm (W). High magnification view of Figure 12, sample as Figure 4. Shows "wispy" nature of silicate-rich sample. Magnification $\times 5500$. Scale bar = $1 \mu\text{m}$.
- Figure 6 Sample 105-21-1, 62-63 cm. Coccolith clearly showing development of overgrowths which would eventually totally obscure it. Note pressure solution on u-per edge of coccolith. Magnification $\times 11,200$. Scale bar = $0.5 \mu\text{m}$.
- Figure 7 Sample 105-21-1, 53-54 cm. Clay-rich sample. No microfossils recognizable in sample. Magnification $\times 1360$. Scale bar = $5 \mu\text{m}$.
- Figure 8 Sample 105-21-1, 62-63 cm. Carbonate-rich sample. Nannofossils abundant and moderately well preserved (see also Plate 1, Figures 1 and 4; Plate 2, Figures 2 and 6). Magnification $\times 2250$. Scale bar = $2 \mu\text{m}$.
- Figure 9 Sample 367-35-4, 51-53 cm. Sample is only 6% carbonate, Jurassic in age, and buried over 1100 meters, yet this coccosphere is very well preserved. No overgrowths are observable. Magnification $\times 5700$. Scale bar = $1 \mu\text{m}$.
- Figure 10 Sample 367-34-4, 61-63 cm. Two nannofossils observable in center of the photo. Most of the sample appears to be authigenic. The sample is 88% calcite. Magnification $\times 2375$. Scale bar = $2 \mu\text{m}$.
- Figure 11 Sample 367-34-4, 20-23 cm & R) Sample is 20% carbonate. No recognizable nannofossils. Magnification $\times 2150$. Scale bar = $2 \mu\text{m}$.
- Figure 12 Sample 367-34-4, 20-23 cm (W). Sample is 35% carbonate. Most calcite appears authigenic but rare nannofossil fragments are present. Magnification $\times 2200$. Scale bar = $2 \mu\text{m}$.

PLATE 2



1 2 μm



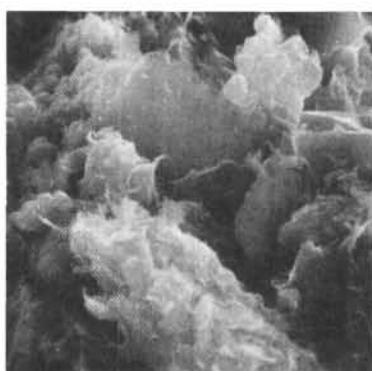
2 1 μm



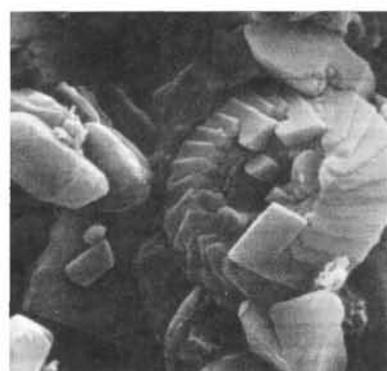
3 2 μm



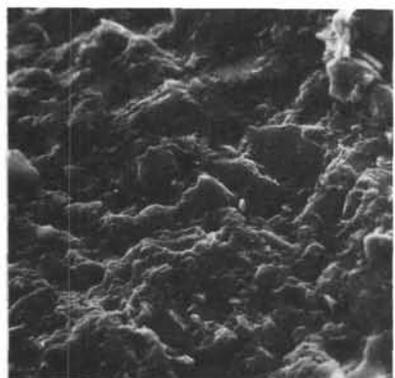
4 2 μm



5 1 μm



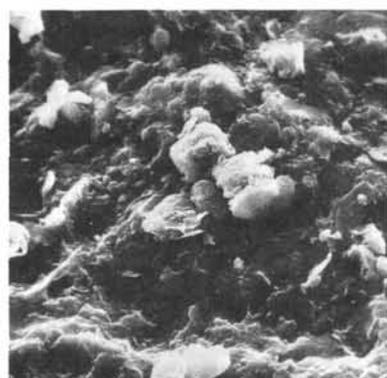
6 0.5 μm



7 5 μm



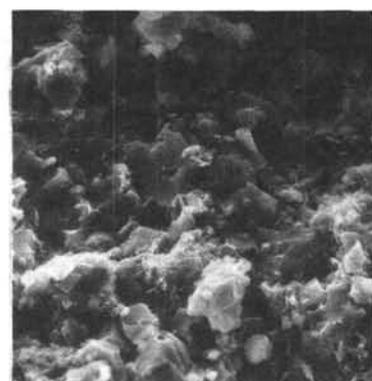
9 1 μm



11 2 μm



8 2 μm



10 2 μm



12 2 μm