

15. AUTHIGENIC CARBONATE NODULES IN THE NANKAI TROUGH, SITE 583¹

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ABSTRACT

Crystalline aggregates composed of calcium carbonate were recovered in the uppermost 50 m of Nankai Trough sediments during DSDP Leg 87A. These aggregates decomposed with time to masses of sandy calcite as determined by X-ray diffraction analysis. Petrographic and scanning electron microscopy revealed textures suggestive of a precursor phase prior to calcite, and this precursor has been tentatively identified as the mineral ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$. Stable isotope data suggest a large component of terrigenous organic matter as the carbon source, consistent with the appearance of these aggregates in highly reducing pyritic sediments containing abundant plant remains. We propose that these nodules formed in euxinic basins on the upper part of the Trough slope under normal seafloor conditions of pressure and temperature. Calculated temperatures of formation of this phase are not unusually low. The specimens from Site 583 are the first reported occurrences of ikaite in active margin sediments.

INTRODUCTION

Highly calcareous layers, ranging in thickness from a few millimeters to centimeters, were encountered at DSDP Site 583 in sediments from the Nankai Trough, during Leg 87A. Site 583 is located in the lowermost structural terrace on the western (landward) side of the Nankai Trough, approximately 15 km east of Site 298. The sediments, apparently free of biogenic carbonate remains, contained massive, white to yellowish brown, coarsely crystalline aggregates of calcium carbonate. Some of these aggregates (most notably, those from Holes 583, 583A, and 583C) occurred in the form of large (up to 5 cm in length) euhedral crystals in which calcite twinning and scalenohedral terminations were common (Figure 1).

A few of these large nodules were removed from the cores immediately after they were split in the shipboard core lab; pieces of the crystalline carbonates were impregnated with epoxy and cut into thin sections. Microscopic examination showed the samples to consist primarily of relatively large (10–50 μm), usually rhombohedral, and distinctly zoned crystals embedded in a porous groundmass composed of much finer-grained acicular calcareous material (see Figs. 2 and 3). Simultaneously, by X-ray diffraction of portions of these samples, we identified the mineral composition as a mixture of calcite and aragonite.

Significantly, even as the freshly split cores were being described, the crystals appeared to melt, changing luster and color to an opaque milky yellow in a matter of minutes. The crystalline form was gradually lost as they collapsed into a mass of minute crystals. Approxi-

mately 6 months later, when we re-examined the DSDP archive cores containing these nodules, the crystals had disappeared entirely, leaving only their molds and friable masses of pale yellow sand-sized fragments.

Subsequent consideration of this phenomenon suggests that the large aggregates seen on board the *Challenger* were crystals of the mineral ikaite (Pauly, 1963), a low-temperature hydrated calcium carbonate ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) that was discovered in the Ika Fjord, Greenland. We present here our analyses of the samples from the Nankai Trough as well as an explanation for the presence of this mineral in these sediments.

CARBONATE AGGREGATE MINERALOGY

X-ray diffraction analyses of the carbonate aggregates were performed on board ship within 24 hr. of core recovery from Site 583. Small samples were briefly ground in a mortar and mounted on glass slides before insertion in a Rigaku Miniflex X-ray diffractometer. As the crystalline aggregates were very soft and poorly consolidated, very little grinding was required to produce a powder that was sufficiently fine for a smear mount. The samples were analyzed at a scan rate of $1^\circ 2\theta/\text{min.}$, 1000 counts/s, with Cu $K\alpha$ radiation. These were the first X-ray diffractograms we obtained from these crystals, and, although these records suffice for the purpose of major mineral identification, the shipboard X-ray diffraction equipment does not produce high-quality traces. The resultant patterns were identified as almost entirely a mixture of calcite and aragonite, based on the presence of their major peaks at 29.36 and $26.18^\circ 2\theta$, respectively. The positions of the major aragonite peaks seen in these diffraction patterns correspond closely with those of the ASTM standard aragonite file; however, the peak intensities do not correlate well. One cause of this lack of correlation may be a preferred orientation in the smear mount; another possible cause may be that the mineral is something other than aragonite per se (e.g., a hydrat-

¹ Kagami, H., Karig, D. E., Coulbourn, W. T., et al., *Init. Repts. DSDP*, 87: Washington (U.S. Govt. Printing Office).

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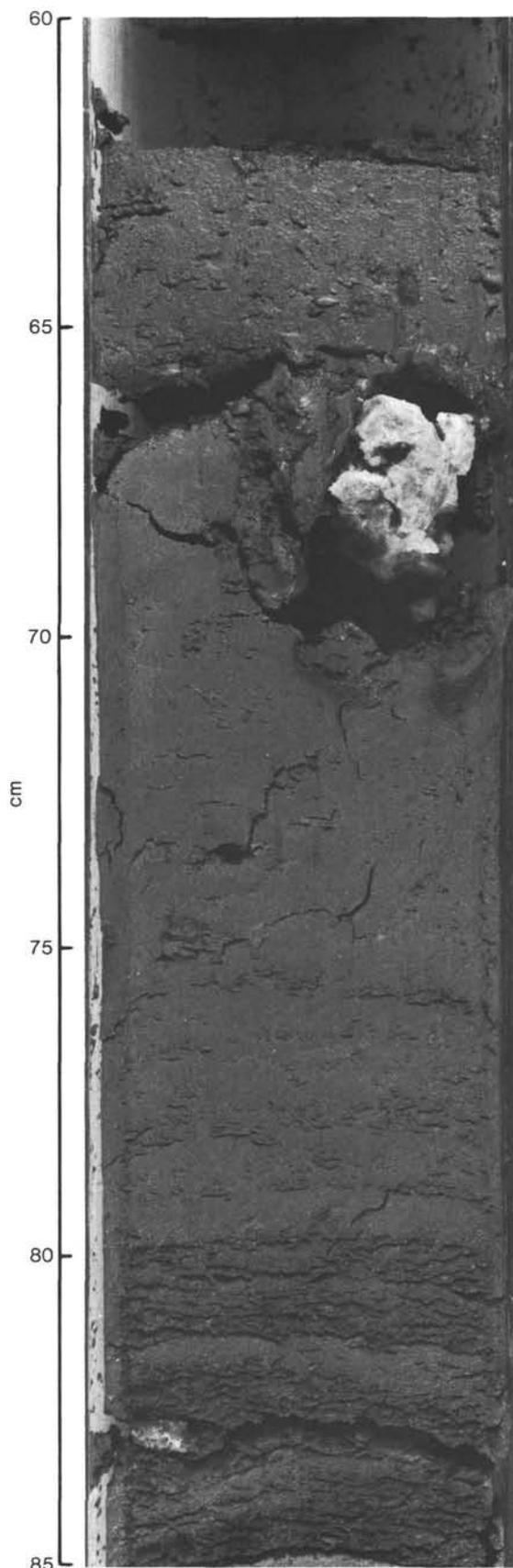


Figure 1. Appearance of carbonate nodules on freshly split core from 583A-3-3, 60-85 cm.

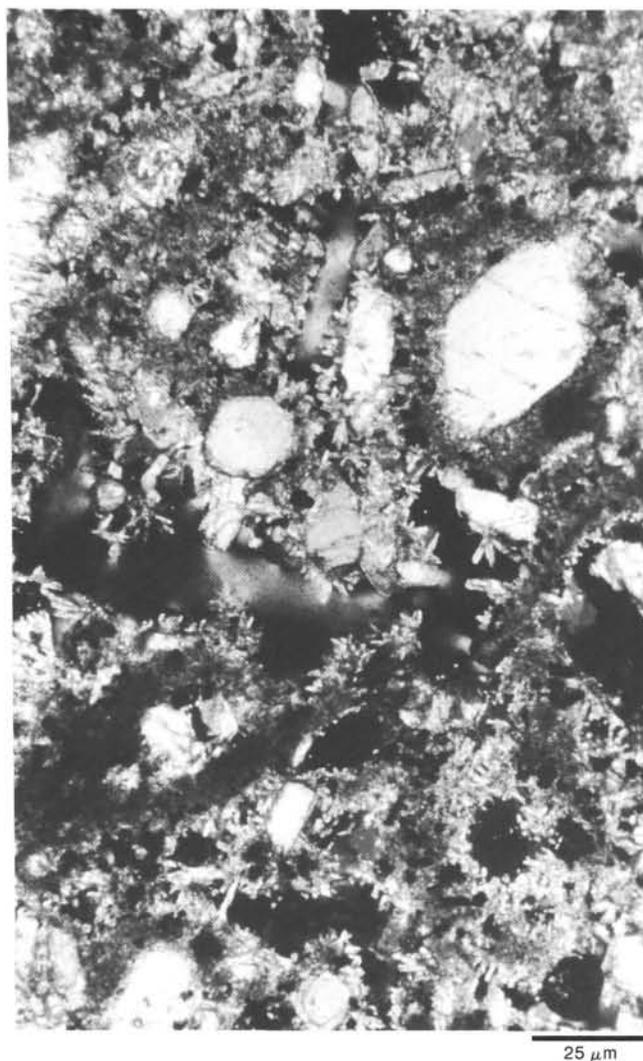


Figure 2. Thin-section photomicrograph showing carbonate rhombs in acicular matrix. Section 583C-2-2.

ed calcium carbonate form with a structure that very closely resembles aragonite).

OPTICAL PETROGRAPHY

In thin section, these nodules are composed of large (on the average, 10-50 μm), highly birefringent, rhombic crystals in an acicular groundmass. Frequently, the rhomb-shaped crystals grow in voids lined with the needlelike crystals. Moreover, the voids appear to display a preferred orientation with respect to the rhombs, suggesting *in situ* growth of the entire mass (Fig. 4). The X-ray diffraction data, together with the morphology of the individual crystals that compose these aggregates as seen in thin section, lead us to speculate that the acicular groundmass is composed of what we have tentatively identified as aragonite needles in which are embedded the larger calcite crystals.

Many of the larger rhombs clearly gave the appearance of being zoned in these thin sections (Fig. 5). However, when fragments of the decomposed nodules were examined much later by cathodoluminescence and the

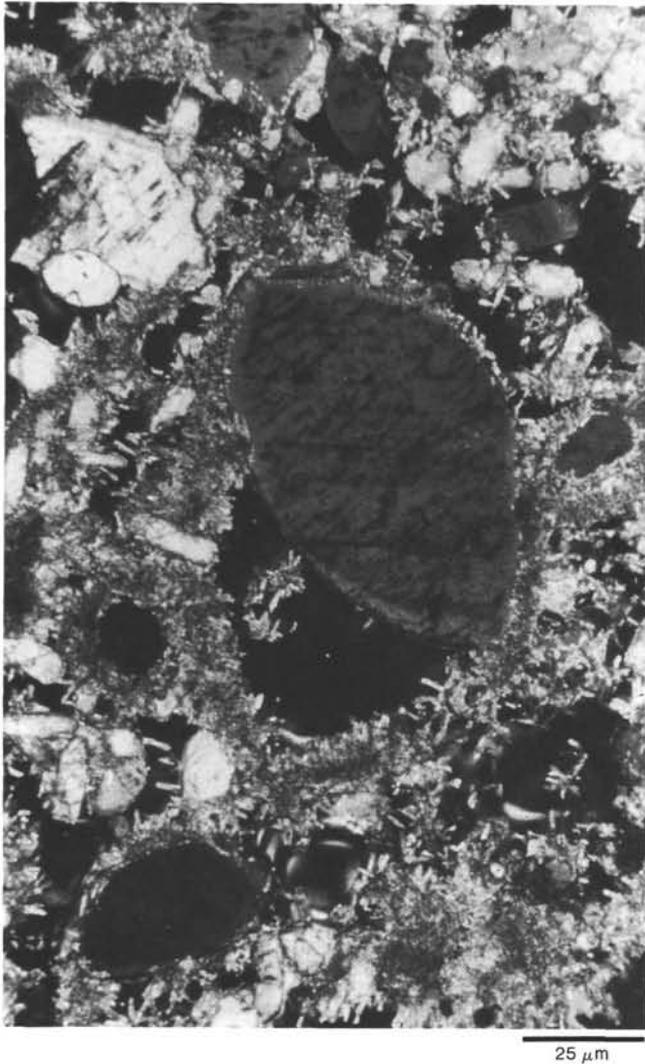


Figure 3. Thin-section photomicrograph showing carbonate rhombs in acicular matrix. Section 583C-2-2.

electron microprobe, no well-defined compositional zones were observed.

MICROPROBE ANALYSIS

Individual carbonate fragments were embedded in cold-mount epoxy for analysis by electron microprobe. The instrument used was a Cameca MBX electron microprobe X-ray analyzer with the Tracor-Northern automation package, operated under the Sandia-TASK program. Probe scans were run at 15 kV, 11 nA, count time = 33 s, with 1% standard deviation. Standard materials were run, as follows, with Bence-Albee correction BA-78 (Chambers, 1979): Ca, wollastonite; Mg, synthetic MgO; Fe, hematite (Elba); Mn, spessartine; and Sr, SrTiO₃.

Of these elements, only Ca and Mg were detected in significant quantities. The Mg content varied between less than 0.1 and 1.0 wt.%; these aggregates are virtually pure CaCO₃. The distribution of Mg is shown in Figure 6. The outer zone of the crystals shown in this photomicrograph contain on the order of 1 wt.% Mg, decreasing to approximately 0.1 wt.% in the center. This pattern could reflect either the original chemical zonation

or Mg-Ca exchange by diffusion from surrounding interstitial water that occurred some time after core recovery and storage. In any case, the Mg²⁺ concentration is insufficiently high to show distinct zonation when subjected to cathodoluminescence. In addition, at the time at which these crystal fragments were analyzed by the microprobe, they were observed to contain approximately 0.5 molecule of water (as determined by difference).

As a means of verifying the presence of excess water in the CaCO₃ crystal structure, we decided to x-ray one of these samples again on a high-resolution diffractometer and compare the results to the d-values and lattice parameters of standard calcite.

HIGH-RESOLUTION X-RAY DIFFRACTION

A smear slide was made of the crystalline residue from one of the Site 583 cores (583C-2-1, 71–72 cm) approximately 1 yr. after the core was recovered. High-resolution X-ray diffraction analyses were done using a Siemens D-500 automated powder diffractometer and Cu K α radiation at 40 kV and 30 mA. This diffractometer is linked to a DEC PDP11/34 RT11; SIEMAC, the program in use for X-ray identification, was used to scan the region between 20 and 96° 2 θ in 0.02° 2 θ steps. A least-squares program, developed by D. Appleman (USGS), was used to calculate the lattice parameters using the following (for a hexagonal primitive cell):

$$\begin{aligned} a \text{ and } b: & 4.99000 \quad \alpha, \beta = 90^\circ \\ c: & 17.00200, \quad \gamma = 120^\circ. \end{aligned}$$

Using these values for a standard calcite unit cell, we measured the lattice parameters on Sample 583C-2-1, 71–72 cm:

$$\begin{aligned} a \text{ and } b: & 4.96929; \text{ Std. error} = 4.09 \times 10^{-3} \\ c: & 16.92956; \text{ Std. error} = 3.60 \times 10^{-2}. \end{aligned}$$

In an attempt to rule out any possibility that the basic calcite structure of these crystals was distorted because of the presence of residual water molecules, we heated the slide to 75°C for 8 hr. and then x-rayed again. Using the same *hkl* and standard calcite unit cell parameters, the values for the heated sample were:

$$\begin{aligned} a \text{ and } b: & 4.97419; \text{ Std. error} = 4.28 \times 10^{-3} \\ c: & 16.96540; \text{ Std. error} = 5.56 \times 10^{-2} \end{aligned}$$

In summary, there seems to be little doubt that the mineralogy of this specimen is calcite. A comparison of the X-ray data on which this conclusion is based is presented in Table 1.

STABLE ISOTOPE ANALYSIS

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (relative to the PDB standard) values of selected samples (Table 2) were obtained using a Varian-Mat triple collector mass spectrometer and the standard analytical procedure (e.g., digestion of sample material by 100% phosphoric acid). The $\delta^{13}\text{C}$ values are all considerably lighter than expected for a marine carbonate; this anomaly and its implications for diagenesis

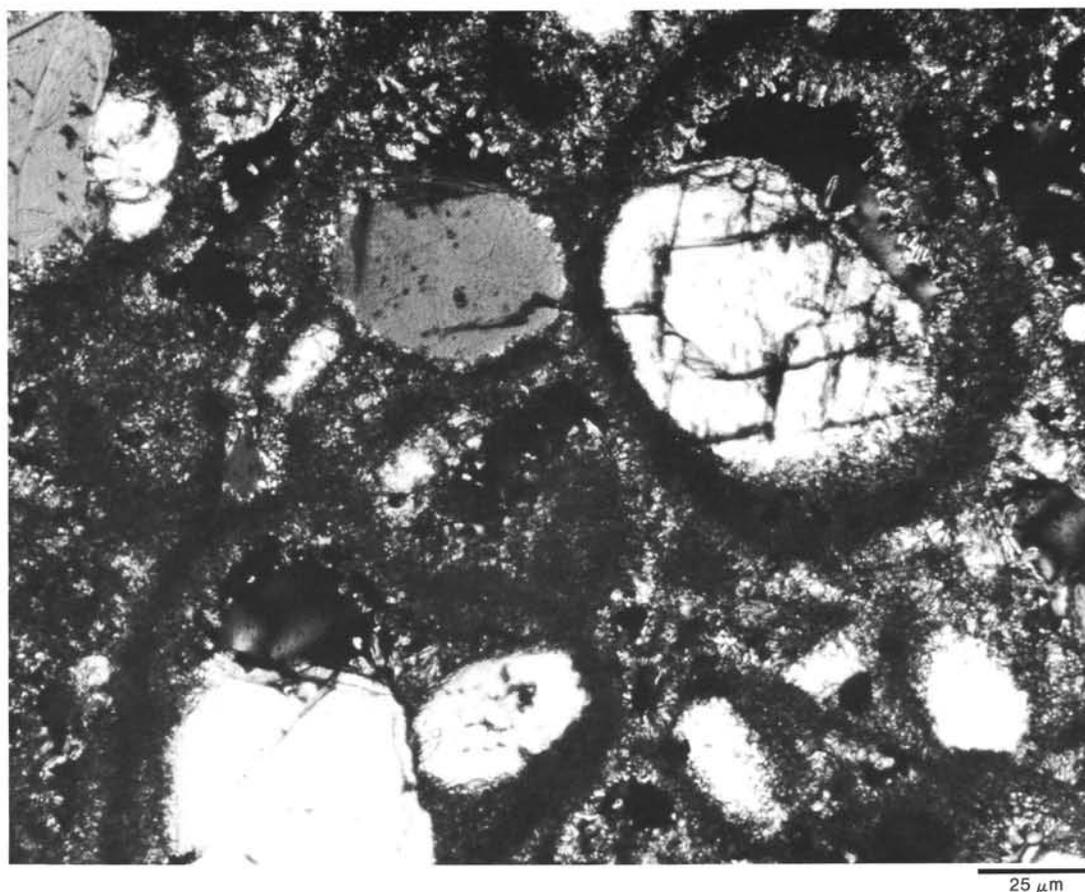


Figure 4. Geopetal(?) orientation of abundant voids in a thin-section photomicrograph. Section 583E-H1-2.

sis involving a terrestrial organic carbon source are discussed below.

Paleotemperatures for the formation of these nodules are calculated according to the equation of Epstein (in press) and are shown in Table 2. These temperatures, ranging from approximately 4.6 to 7.7°C, are within the range of normal seafloor conditions.

SCANNING ELECTRON MICROSCOPY

Finally, several fragments of the carbonate nodules were examined with a Hitachi S-500 scanning electron microscope, at an operating voltage of 25 kV. The photographs seen in Figures 7 and 8 display a variety of crystal forms. The gross morphology (e.g., Fig. 7) very closely resembles that of the "pseudogaylussite" first described by Trechmann (1901), the "thinolite" crystals in Dana (1884), and similar forms described by Boggs (1972), Kemper and Schmitz (1975; 1981), and Kaplan (1963).

At successively higher orders of magnification, however, these fragments appear to be composed of, or covered with, much smaller rhombohedral crystals (Fig. 8). There is virtually no evidence, as seen in the scanning electron micrographs, of the acicular masses seen in the thin sections that were made on board ship immediately after core recovery (Fig. 2, for example). The implication here is that, once the original nodules decomposed (or perhaps "melted" would be more accurate), the al-

teration of CaCO_3 was rapid and *in situ*, and took the form seen in Figure 8.

DISCUSSION

These nodules, composed of an apparently ephemeral calcium carbonate phase, changed rapidly in appearance, mineralogy, and structure from the time the original cores were first opened on board the *Glomar Challenger*. Based primarily on the admittedly circumstantial evidence consisting of the rapidity of alteration of these masses, their texture as seen in thin section, and the similarity to other reported occurrences of poorly defined calcium carbonate phases, we propose that these crystalline aggregates were originally composed of the mineral ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$. Furthermore, X-ray diffraction evidence, both aboard ship and after approximately 1 yr. in core storage, indicates a transformation from a highly hydrated phase to a mixture of calcite and aragonite to well-crystallized calcite according to the following scheme:

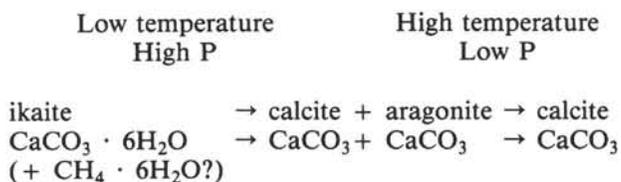




Figure 5. Thin-section photomicrograph showing distinctive concentric zoning in rhombic carbonate. Zonation was not, however, related to chemical composition. Section 583E-H1-2.

No other carbonate phases appear in this reaction; the resultant calcite is exceptionally pure, containing less than 1% MgO and no detectable quantities of strontium, iron, or manganese. Unlike the carbonates from DSDP Sites 438 and 439 in the Japan Trench (Legs 56 and 57; Matsumoto and Iijima, 1980), we found no evidence of either dolomite or ankerite in the aggregates described in this report.

The shipboard interstitial water profiles (Figs. 9–11) for calcium, manganese, and alkalinity are also consistent with an environment conducive to authigenic carbonate formation. At Site 583 these aggregates are exclusively associated with sandy pyritic sediments that contain abundant plant remains. The high sediment accumulation rates in the upper part of this section (225–315 m/Ma; site chapter, Site 583, this volume) undoubtedly contributed to the deposition of organic material and the subsequent formation of localized highly reducing environments. The most likely explanation for this is

a coupled reaction in which dissolved sulfate in interstitial waters is reduced in the presence of organic carbon from terrestrial plant material; the sulfide thus formed is precipitated as pyrite and the oxidized carbon as calcium carbonate.

The unusually light $\delta^{13}\text{C}$ values (Table 2) also support a significant contribution of organic carbon from terrestrial sources. The trends shown in the interstitial water profiles at Site 583 are quite similar to those from Sites 438 and 440 in the Japan Trench (Moore and Gieskes, 1980); Ca^{2+} increases linearly with depth, whereas both Mg^{2+} and alkalinity increase in the uppermost 50 m, then decrease steadily.

Two possibilities are suggested by the paleotemperatures calculated from the oxygen isotope data. One is that these temperatures (Table 2) are accurate for bottom-water conditions at the time of carbonate precipitation; perhaps, at this water depth, the pressure is sufficiently high for ikaite formation without suggesting ex-

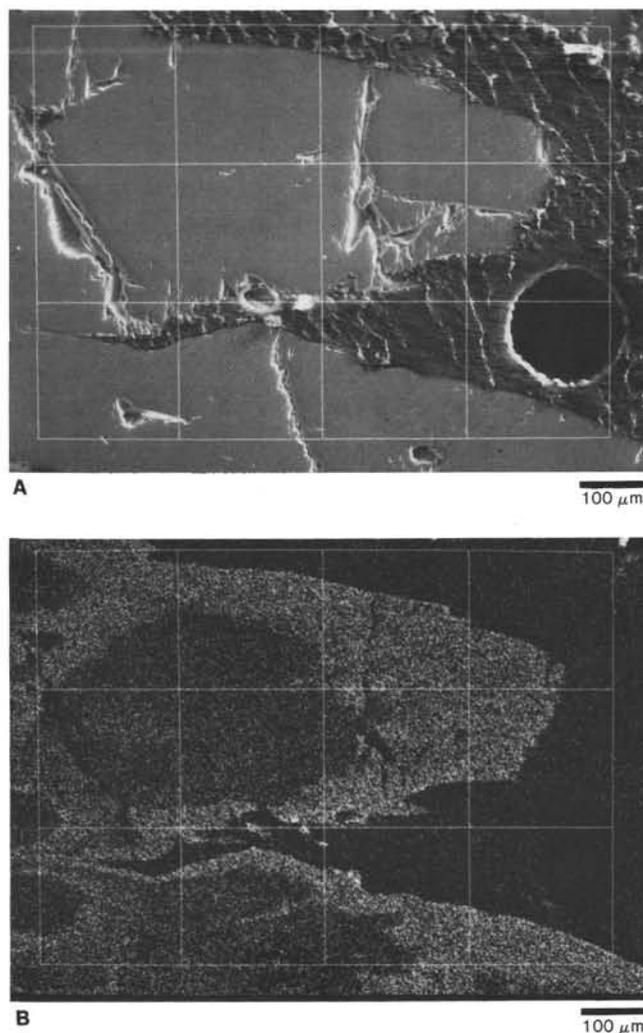


Figure 6. Microprobe photographs showing (A) carbonate fragments embedded in epoxy and (B) distribution of Mg^{2+} , with a maximum of 1% at the outer edges, probably resulting from post-recovery diffusion of interstitial water.

ceptionally low temperatures. A second possibility is that the ikaite crystals were initially formed at a time when bottom-water temperatures in the Nankai Trough were much lower and that they subsequently reequilibrated with warmer water some time after deposition.

We can only speculate on the presence of clathrates ($CH_4 \cdot 6H_2O$) within the calcareous aggregates. Organic matter is abundantly present in these sediments, so possibly sufficient methane was generated before sulfate reduction to coprecipitate with $CaCO_3 \cdot 6H_2O$. Although the pressure-temperature conditions at Site 583 were more than adequate for the formation of clathrates (Katz, 1971), we saw no direct evidence, other than the nodules, that a gas-ice mixture had been present.

Crystals similar to those seen on Leg 87A were recovered by the *Meteor* expedition to the Antarctic Ocean in 1980 (Suess et al., 1982). Apparently these samples also decomposed rapidly and were altered to calcite in the ship's laboratory; the identification made by the shipboard scientists was ikaite.

CONCLUSIONS

We speculate that the foregoing conditions—i.e., high organic carbon input, high sedimentation rates, high alkalinity, and reducing conditions—must have been extremely favorable for the precipitation of a calcium carbonate phase, probably ikaite ($CaCO_3 \cdot 6H_2O$) and possibly intergrown with clathrates ($CH_4 \cdot 6H_2O$). This conclusion is largely based upon the physical appearance of these crystals in freshly split cores, their subsequent disintegration, and their texture as observed in thin sections made immediately after core recovery. The similarity of the morphologies seen in the electron micrographs (Figs. 7, 8) also lend credence to this supposition, because these pseudomorphs (which are now composed purely of calcite) strongly resemble those of ikaite as discussed elsewhere in the literature. Temperatures of equilibration, as calculated from oxygen isotopic compositions, do not suggest unusually extreme climatic conditions. On the contrary, although these crystalline ag-

Table 1. X-ray diffraction data of standard calcite, calcareous nodule from Sample 583C-2-1, 71-72 cm, and the same sample after heating.

ASTM standard: calcite			Sample 583C-2-1, 71-72 cm (unheated)			Sample 583C-2-1, 71-72 cm (heated)		
Peak position (degrees 2θ)	d-spacing	Intensity	Peak position (degrees 2θ)	d-spacing	Intensity	Peak position (degrees 2θ)	d-spacing	Intensity
1. 23.02	3.861	12	1. 23.292	3.8189	9.2	1. 23.262	3.8237	5.6
2. 29.36	3.040	100	2. 29.676	3.0102	100.0	2. 29.614	3.0165	100.0
3. 31.37	2.849	3	3. 31.725	2.8204	3.6	3. 36.211	2.4806	8.1
4. 35.98	2.494	15	4. 36.261	2.4773	6.8	4. 39.627	2.2743	9.7
5. 39.44	2.283	20	5. 39.684	2.2711	14.7	5. 43.368	2.0856	6.5
6. 43.11	2.096	20	6. 43.436	2.0833	8.4	6. 47.340	1.9202	3.9
7. 47.13	1.927	5	7. 47.406	1.9177	3.5	7. 47.705	1.9063	11.5
8. 47.51	1.912	15	8. 47.745	1.9048	16.6	8. 48.717	1.8691	12.1
9. 48.48	1.876	15	9. 48.770	1.8672	16.4	9. 56.745	1.6222	2.6
10. 56.55	1.626	4	10. 56.828	1.6201	2.2	10. 57.592	1.6004	6.1
11. 57.36	1.605	8	11. 57.640	1.5992	17.9	11. 58.217	1.5847	3.1
12. 58.06	1.587	2	12. 58.312	1.5823	3.6	12. 60.863	1.5220	2.8
13. 60.70	1.524	5	13. 60.909	1.5209	3.5	13. 64.875	1.4372	28.3
14. 61.01	1.517	4	14. 61.255	1.5132	3.6	14. 65.763	1.4199	2.0
15. 61.32	1.511	3	15. 64.894	1.4368	20.5	15. 73.072	1.2949	2.1
16. 63.07	1.473	2	16. 65.048	1.4338	5.3	16. 83.945	1.1527	15.0
17. 64.63	1.441	5	17. 65.819	1.4189	3.4	17. 95.158	1.0443	4.4

Note: ASTM = American Society for Testing and Materials.

Table 2. Stable isotope data, Site 583.

Hole-Core-Section (interval in cm)	Sub-bottom depth (m)	Stable isotope data		Temperature (°C)
		δ ¹³ C	δ ¹⁸ O	
583A-2-3, 143-145	8.4	-28.88	+2.93	5.21
583A-3-1, 32-33	9.3	-25.26	+2.77	5.77
583-2-4, 44-45	10.4	-30.41	+3.12	4.57
583A-3-3, 125-128	12.2	-26.18	+2.67 ^a	6.12
		-26.09	+2.64 ^a	6.22
583A-3-4, 38-39	13.8	-28.06	+2.88	5.38
583A-6-2, 129-132	26.8	-29.24	+2.23	7.68
583C-2-1, 71-72	30.7	-31.42	+2.54	6.57
583C-2-2, 40-41	31.9	-28.48	+2.27	7.54

Note: δ¹³C and δ¹⁸O expressed in ‰ versus PDB standard.
^a Duplicate.

gregates may have been stabilized to some extent by the formation of methane hydrates (which are not at all uncommon at low seafloor temperatures and pressures of only a few hundred bars), their presence in Nankai Trough sediments suggests that this phase may in fact be much more widespread in the marine environment than has been previously supposed.

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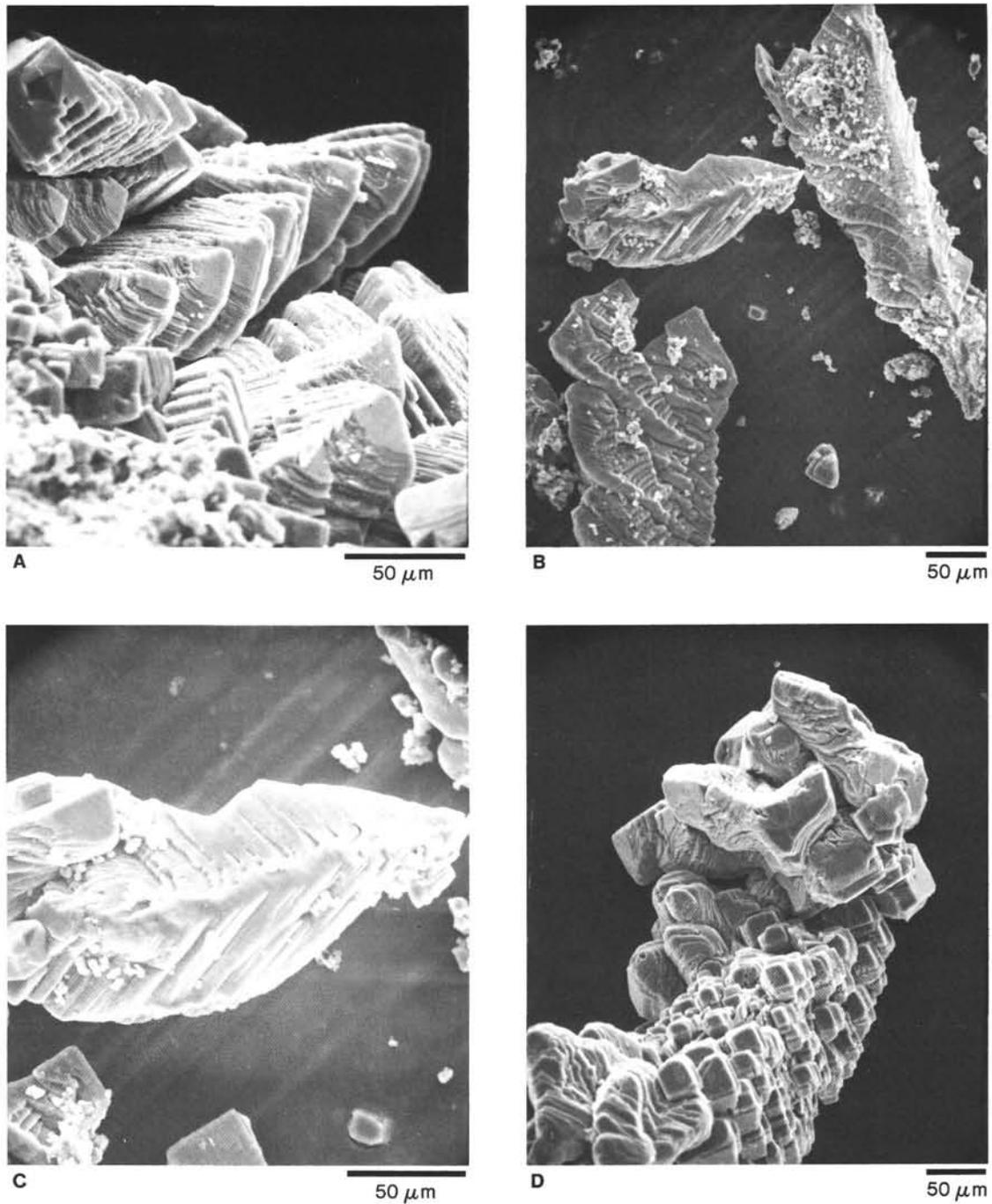
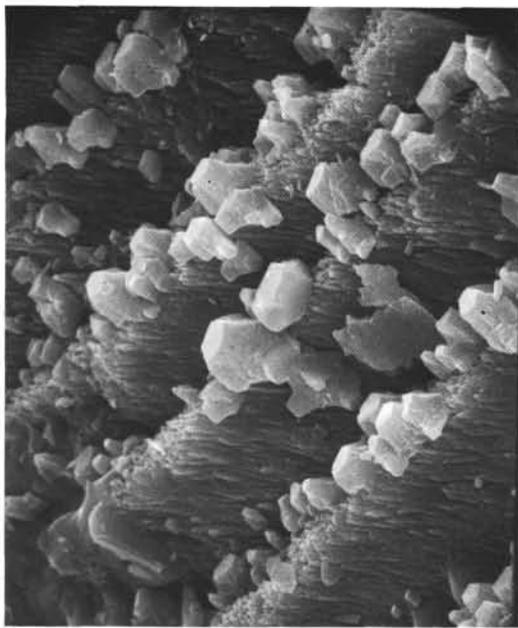


Figure 7. Scanning electron photomicrographs of carbonate fragments. A-C show what appear to be remnant scalenohedral forms similar to those reported in the early literature, although on a much smaller scale. D shows common rhombic texture, probably resulting from alteration of the original phase.



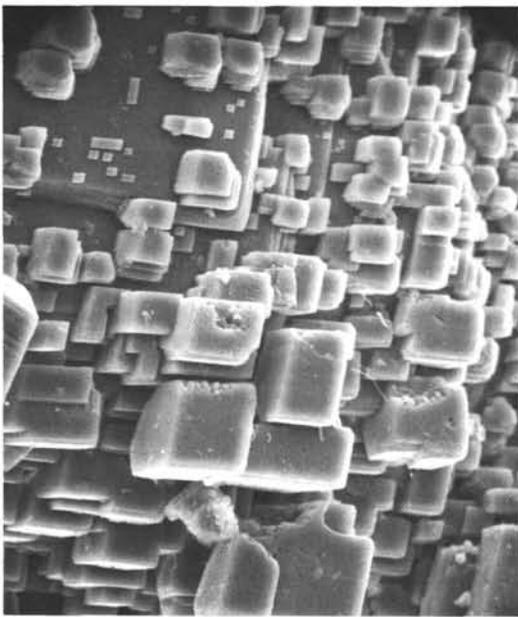
A

5 μm



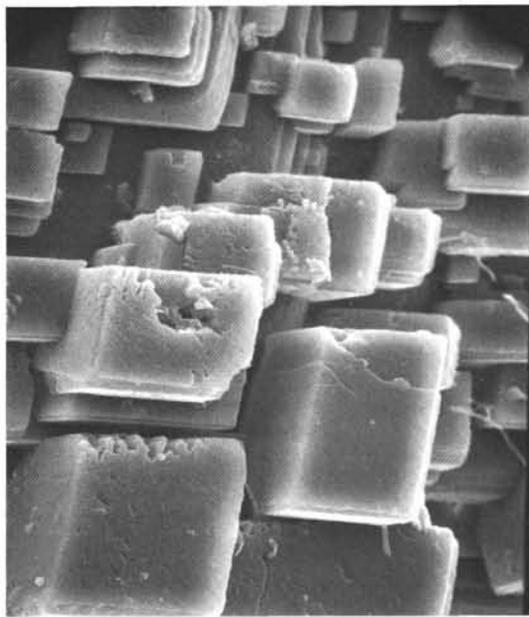
B

50 μm



C

50 μm



D

50 μm

Figure 8. Rhombic crystal surfaces of carbonate fragments. A shows prismatic, fibrous form as described in Boggs (1972). B-D show more common rhombic forms.

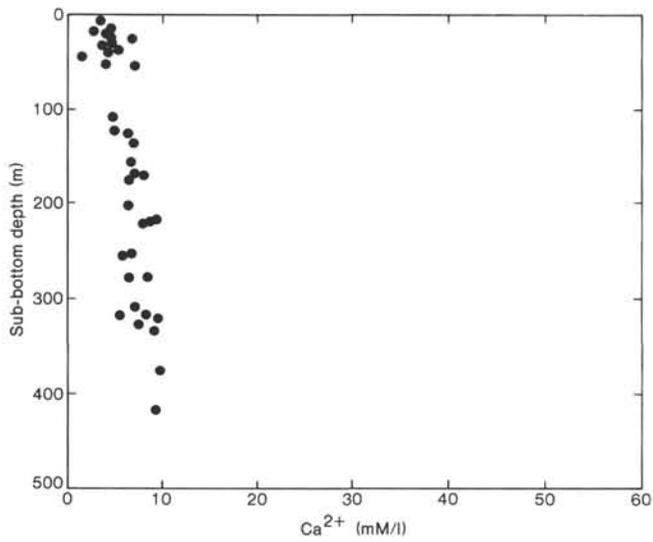


Figure 9. Pore water Ca^{2+} profile from Site 583.

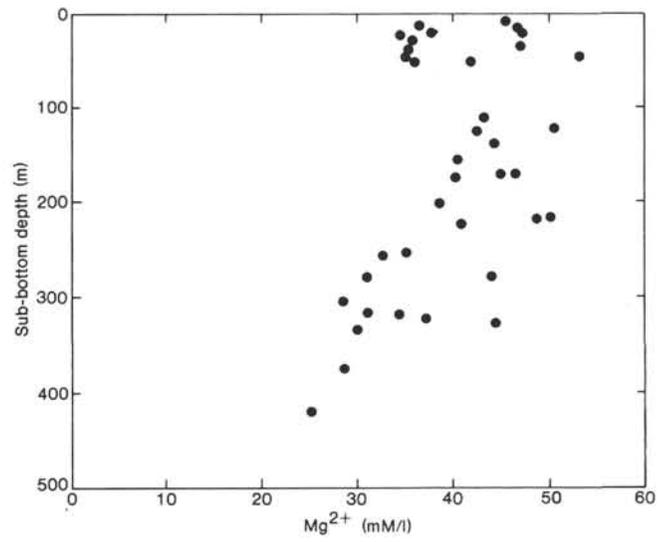


Figure 10. Pore water Mg^{2+} profile from Site 583.

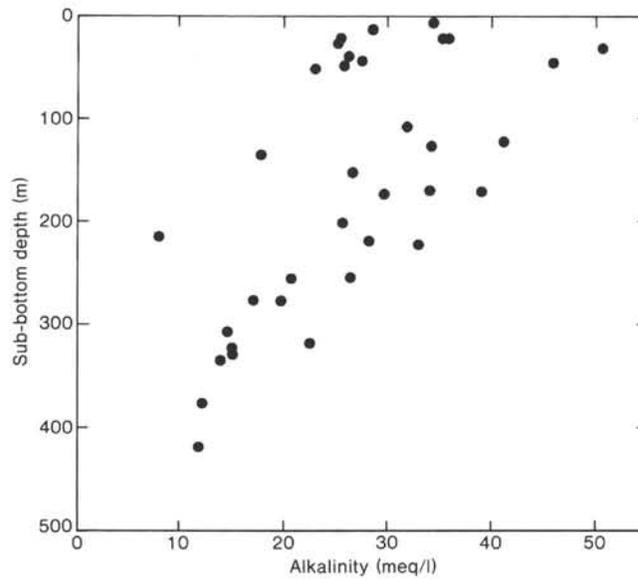


Figure 11. Pore water alkalinity profile from Site 583.