

## **Calcium Carbonate Hexahydrate from Organic-Rich Sediments of the Antarctic Shelf: Precursors of Glendonites**

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## Calcium Carbonate Hexahydrate from Organic-Rich Sediments of the Antarctic Shelf: Precursors of Glendonites

**Abstract.** Large euhedral crystals of calcium carbonate hexahydrate were recovered from a shelf basin of the Bransfield Strait, Antarctic Peninsula, at a water depth of 1950 meters and sub-zero bottom water temperatures. The chemistry, mineralogy, and stable isotope composition of this hydrated calcium carbonate phase, its environment of formation, and its mode of precipitation confirm the properties variously attributed to hypothetical precursors of the glendonites and thereby greatly expand their use in paleoceanographic interpretation.

Glendonites belong to a group of unusual calcitic pseudomorphs after original minerals of unknown composition. They are associated with glacial marine deposits of Permian to Recent age and are thought to have formed syngenetically from organic-rich muds at sub-zero temperatures in polar environments (1-3). Therefore, they may be important indicators of the regional distribution and temperature history of polar water masses (4).

We report here on what we believe is the first observation of a highly hydrated calcium carbonate mineral from anoxic, organic-rich sediments of the Bransfield Strait, Antarctic Peninsula, which has all

the attributes of the elusive glendonite precursor (5). This mineral phase is identical to synthetic  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ , known for over 100 years (6, 6a), and to the mineral ikaite from its single known occurrence in a carbonatite rock at the Ika Fjord, Greenland (7). The large euhedral single crystals from the Bransfield Strait sediments appear to be precipitated authigenically from  $\text{CO}_3^{2-}$  supplied from the early diagenetic decomposition of sedimentary organic matter and calcium from the interstitial seawater.

Crystal specimens of identical size and shape were discovered in two narrow zones at depths of 205 and 714 cm in a 12-m-long sediment core. The fresh minerals were initially amber in color and translucent; they occurred as elongate crystals with perfectly shaped bipyramidal terminations (Fig. 1). At laboratory temperature onboard ship, the interior became cloudy within hours and the mineral physically disintegrated into a mush of water and small whitish crystals, later identified as calcite. The terminations, edges of the bipyramids, and certain crystal fragments, however, remained intact for longer periods and could therefore be preserved by cold storage (8).

Subsamples of the hydrated crystals were analyzed for total calcium and total weight loss after ignition (9). With one exception, all analyses correspond to within  $\leq 1$  percent of the ideal composition of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  (in percentage by weight): CaO, 26.95;  $\text{CO}_2$ , 21.14; and  $\text{H}_2\text{O}$ , 51.92 (Table 1).

Prior to the analysis of hydrated specimens, dehydrated subsamples, stored at

Fig. 1. Single crystal of calcium carbonate hexahydrate from Bransfield Strait sediments. This is a hydrated phase of calcite which forms at sub-zero temperatures and elevated pressures from metabolic carbonate and seawater calcium. It is the first reported occurrence of this phase forming syngenetically in organic-rich, rapidly accumulating sediments. Its crystal structure is monoclinic and identical to that of synthetic  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ , and its chemical composition is similar to that of the mineral ikaite, reported from a carbonatite rock submerged in the Ika Fjord, Greenland. Scale, 1 cm.





room temperatures and pressures, were analyzed for phosphate, magnesium, calcium, and carbon in order to ascertain the gross composition and check for possible mixed phases (10). The dehydrated solid phase was essentially pure calcium carbonate with traces of sediment, mostly quartz and clays.

The very light  $\delta^{13}\text{C}$  values (Table 1) identify the carbonate as derived from organic matter. In contrast to calcium carbonate from skeletal components, the  $\delta^{13}\text{C}$  values of organic matter in recent marine sediments range from -10 to -30 per mil relative to the Pee Dee belemnite standard (PDB), frequently with values between -20 and -27 per mil (11). It is therefore common practice to trace formation of such isotopically light carbonates to organic matter as a source (12), whereby microbial decomposition and associated carbonate production, notably by sulfate reducers, transpose the stable carbon isotope signature of the organic matter to the solid calcium carbonate phase. The high metabolite contents of pore waters from the Bransfield Strait sediments leave little doubt that the  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  precipitation there is induced by such microbial carbonate production under anoxic conditions.

The  $\delta^{18}\text{O}$  value of +3.84 per mil relative to PDB (Table 1), for samples showing the least dehydration, indicates an equilibrium precipitation temperature of -0.6°C based on the "calcite" paleotemperature equation of Shackleton (13). This value is in good agreement with the measured bottom water temperature of -1.6°C at the sampling locality. However, it is not obvious why  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  and calcite should behave identically with regard to the isotope fractionation during precipitation from seawater, because effects of polymorphism on the oxygen isotope ratios have been observed elsewhere (14). Therefore, at this stage, inferences on geothermometry are tentative, particularly so in view of the changes of  $\delta^{18}\text{O}$  toward lighter values with increasing degree of dehydration.

Crystal structure and phase identification were determined by single-crystal (15) and random powder x-ray diffraction, respectively. Because of the much shorter time period required for the more accurate single-crystal measurements, no interfering calcite reflections from gradual dehydration were recorded. These data were used to index the reflections obtained from the random powder pattern (15). The most probable space groups of the hexahydrate phase are  $C2/c$  or  $Cc$ . Lattice constants and interplanar spacings ( $d$ -spacings) of the Bransfield Strait monoclinic  $\text{CaCO}_3 \cdot$

$6\text{H}_2\text{O}$  are, to our knowledge, the first obtained from the natural phase and are identical to those of synthetic products (6a). As far as we know, the structure of the mineral ikaite from Greenland has never been directly determined but instead was inferred from the very similar chemical composition of synthetic and natural phases.

In an optical examination at laboratory temperature, the progress of dehydration was easily observed. Hydrated crystal fragments of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  were colorless, showed no pleochroism or cleavage, had strong birefringence, were optically negative, and yielded a biaxial optical figure with strong dispersion of the bisectrix. The highest and lowest indices of refraction were  $n_\gamma = 1.542$  and  $n_\alpha = 1.482$ , respectively, and the intermediate one  $n_\beta = 1.530$ .

Extremely high metabolite concentra-

tions, in fact the highest ever reported for marine sediments, were measured in the pore waters of the Bransfield Strait sediments (Fig. 2). The increasing  $\text{NH}_3$  content reflects the continuously accumulating metabolites from the decomposition of organic matter by heterotrophic microbes. The total titration alkalinity, however, deviates from such a cumulative distribution by first increasing rapidly and then becoming constrained by the precipitation of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  at ~ 57 meq/kg. Concomitant with such a depth distribution of the major dissolved carbonate species, dissolved calcium decreases significantly.

We calculated the ion concentration product (ICP) between  $\text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$  from the alkalinity, pH, and calcium data for the in situ temperature of -1.6°C and a pressure of 1 atm, using published constants (16, 17). Such equilibrium

Table 1. Composition of hydrated and dehydrated subsamples.

Sample weight (mg)	Residue weight (mg)	Chemistry, hydrated sample				Stable isotopes			
		CaO (% by weight)		CO <sub>2</sub> * sample (% by weight)	H <sub>2</sub> O* sample (% by weight)	Hydrated subsample†		Dehydrated subsample	
		Residue	Sample			$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$
100.2	27.6	97.73	26.92	21.12	51.34	3.38‡	-22.88‡	2.08‡	-22.21‡
227.4	62.1	99.58	27.19	21.34	51.35	3.84§	-18.79§	0.95§	-18.94§
219.2	59.8	98.95	26.99	21.18	51.53				
145.1	39.2	100.20	27.07	21.24	51.56				
91.5	24.7	103.40	27.91	21.89	51.10				

\*Calculated from the total weight loss by partitioning CO<sub>2</sub> and H<sub>2</sub>O according to the measured CaO content (9). †For comparison, samples at various stages of dehydration were analyzed. Those designated "hydrated" showed evidence of only minimal dehydration. ‡Sample from *Meteor* cruise 56, station 278, 714 cm below the sediment surface. §Sample from *Meteor* cruise 56, station 278, 205 cm below the sediment surface.

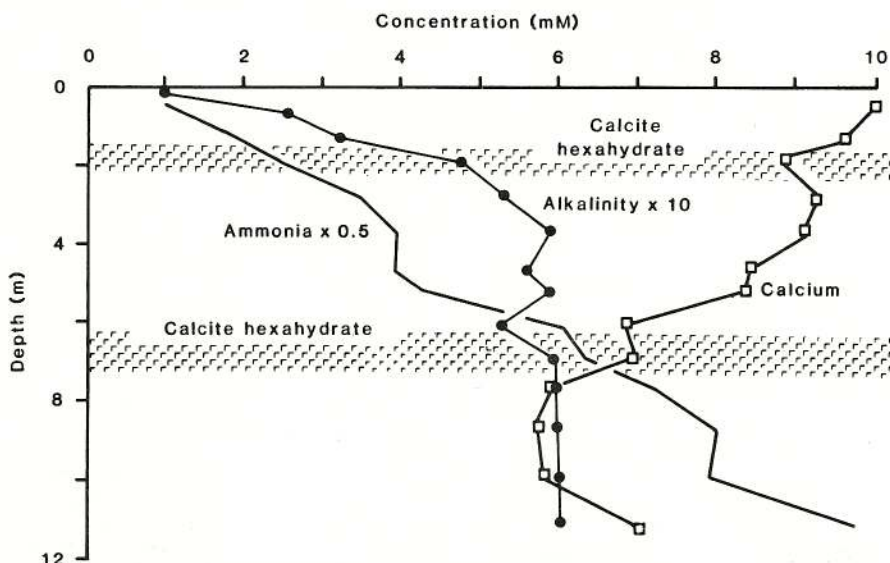
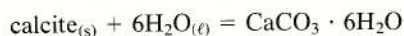


Fig. 2. Concentrations of dissolved metabolites and calcium in pore waters from Bransfield Strait sediments and depth intervals in the core where  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  occurred. The continuously increasing  $\text{NH}_3$  content with depth of up to 5 mM/kg results from the interstitial accumulation of bacterial metabolites with time. Alkalinity is also the result of metabolic activity; its concentration (of up to 60 meq/kg) and that of calcium (reduced to 6 mM/kg), however, become constrained by the precipitation of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  at these two depth intervals. For equilibrium modeling of the precipitation reaction, see (18).



modeling yields two maxima for the ICP, the first at 183 to 385 cm and the second at 700 to 714 cm. These are exactly the depth intervals at which solid-phase  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  was found. Averaging the results yields a mean value of  $1.62 \times 10^{-5}$  mole<sup>2</sup>/kg<sup>2</sup>. Using this value, we calculated the thermodynamic stability product at  $-1.6^\circ\text{C}$  (18) as  $^aK = 7.58 \times 10^{-8}$  or  $p^aK = 7.120$ . Recalculation of a solubility determination by Mackenzie (19) yields an activity product at  $2^\circ\text{C}$  and 1 atm of  $4 \times 10^{-8}$  to  $8 \times 10^{-8}$ . Using standard free energy data and the stability product (20), we calculate a Gibbs free energy of formation of  $-616$  kcal/mole. The hexahydrate is apparently unstable above  $0^\circ\text{C}$  at atmospheric pressure, its formation and persistence being favored by the magnesium content of seawater and certain additives, for example, Calgon, a mixture of polymetaphosphates and polyphosphates (6, 6a, 21), but it can also be prepared as a pure phase at  $0^\circ\text{C}$  (22). Because of a  $\sim 20$  percent decrease in volume accompanying the reaction



formation of ikaite appears favored at elevated pressures; indeed, above 6 kbar the hexahydrate forms spontaneously at the expense of both calcite and aragonite (6, 6a). All these conditions and stability relations for the formation of ikaite rather than calcite are met at the Bransfield Strait locality.

The data assembled here leave little doubt that  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  is an authigenic precipitate that forms at sub-zero temperatures from interstitial solutions of organic-rich sediments undergoing microbial decomposition. Its distribution in the geological record is probably diagnostic of high-latitude environments where organic-rich sediments accumulate rapidly in cold bottom waters.

A change from the original environment would cause rapid dehydration and conversion of monoclinic ikaite to orthorhombic calcite. This process would yield the long-known peculiar calcitic cryptocrystalline pseudomorphs (glendonites) in sedimentary rocks of all ages. Upon dehydration, the oxygen isotope signal would become lost because of reequilibration with the aqueous phase at a new temperature. The  $\delta^{13}\text{C}$  characteristics of the organic source material, on the other hand, would be preserved; for example, glendonites of Cretaceous age from the Upper Deer Bay Formation of Arctic Canada (23) show the same depletion in  $^{13}\text{C}$  as the Bransfield Strait ikaite; organic matter is thus identified as the carbon source.

The identification of ikaite from the Bransfield Strait sediments and the clarification of the relationship between this original phase and the pseudomorphs should further stimulate its application as a paleoclimate indicator, which was pioneered by Kaplan (2) and by Kemper and Schmitz (1). These investigators compiled and correlated patterns of glendonite distribution with other glacial marine indicators but did not know the identity of the glendonite precursors.

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5. The  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  crystals were recovered at  $62^\circ 16.5' \text{S}$ ,  $57^\circ 38.7' \text{W}$ ; water depth, 1951 m; temperature,  $-1.6^\circ\text{C}$  at a water depth of 1940 m; depth in the core, 205 and 714 cm; R.V. *Meteor* cruise 56, station 278, Geologisch Institut Kiel core 14882-2.
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8. Throughout transport, and the specimens were maintained at temperatures below the freezing point of water by storage either in Dry Ice or in a freezer.
9. Hereby the weight of  $\text{CO}_2 = 0.785 \times$  the weight of CaO (0.785 = molecular weight  $\text{CO}_2$ /molecular weight CaO). The weight of  $\text{H}_2\text{O}$  = the total weight loss - (0.785  $\times$  the weight of CaO). The total calcium of the residue was determined by standard atomic absorption spectroscopy.
10. The composition (in percent by weight) was as follows: calcium, 39.7; magnesium, < 0.08; phosphorus, < 0.03; carbon, 11.85  $\pm$  0.13; and organic carbon, 0.23  $\pm$  0.05. The solid phase resulting from spontaneous dehydration was rinsed, dried, and analyzed for calcium and magnesium by standard atomic absorption spectroscopy techniques, for total and organic carbon by a LECO induction-furnace procedure,

and for phosphate by the colorimetric molybdate method.

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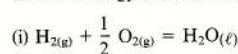
$$^aK = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} \cdot a_{\text{H}_2\text{O}}^6}{a_{\text{CaCO}_3 \cdot 6\text{H}_2\text{O}}} = \frac{\gamma_{\text{Ca}^{2+}} \cdot \gamma_{\text{CO}_3^{2-}} \cdot c_{\text{Ca}^{2+}} \cdot c_{\text{CO}_3^{2-}} \cdot a_{\text{H}_2\text{O}}^6}{a_{\text{CaCO}_3 \cdot 6\text{H}_2\text{O}}}$$

where  $c_{\text{Ca}^{2+}} \cdot c_{\text{CO}_3^{2-}} = 1.62 \times 10^{-5}$  mole<sup>2</sup>/kg<sup>2</sup>;  $\gamma_{\text{Ca}^{2+}}$  (35 per mil,  $-1.6^\circ\text{C}$ , 1 atm) = 0.25;  $\gamma_{\text{CO}_3^{2-}}$  (35 per mil,  $-1.6^\circ\text{C}$ , 1 atm) = 0.021;  $a_{\text{H}_2\text{O}}$  (35.07 per mil,  $-1.6^\circ\text{C}$ , 1 atm) = 0.981;  $a_{\text{CaCO}_3 \cdot 6\text{H}_2\text{O}}$  = 1 by definition ( $a$  is activity,  $c$  is concentration, and  $\gamma$  is the activity coefficient). The activities and temperature dependence are from: C. Mehrbach *et al.* (16); S. E. Ingle *et al.* (17); R. M. Garrels and C. L. Christ, *Solutions, Minerals, and Equilibria* (Harper and Row, New York, 1965); R. A. Robinson, *J. Mar. Biol. Assoc. U.K.* **33**, 449 (1954).

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20. For the reaction  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}_{(s)} = \text{Ca}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} + 6\text{H}_2\text{O}_{(l)}$ , the change in the Gibbs free energy of reaction ( $\Delta^R F$ ) can be calculated from the free energies of formation ( $\Delta^F F$ ) of the components:

$$\Delta^R F = -\Delta^F F_{\text{CaCO}_3 \cdot 6\text{H}_2\text{O}} + (\Delta^F F_{\text{Ca}^{2+}} + \Delta^F F_{\text{CO}_3^{2-}}) + 6\Delta^F F_{\text{H}_2\text{O}}$$

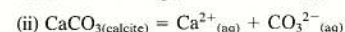
All free energy data were converted to  $273^\circ\text{K}$ .



$$\Delta^F F_{\text{H}_2\text{O}}^{273} = \Delta^R F_{\text{H}_2\text{O}}^{273} = \Delta^R H_{\text{H}_2\text{O}}^{298} - 273 \times$$

$$\Delta^R S_{\text{H}_2\text{O}}^{298} = -57.68 \text{ kcal/mole}$$

where  $H$  is enthalpy and  $S$  is entropy.



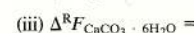
$$(\Delta^F F_{\text{Ca}^{2+}} + \Delta^F F_{\text{CO}_3^{2-}}) = \Delta^R F_{\text{diss}} + \Delta^F F_{\text{calcite}}$$

$$\Delta^R F_{\text{diss}}^{273} = -RT \ln ^aK = 10.42$$

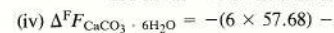
where  $R$  is the gas constant and  $T$  is the absolute temperature;  $^aK$  from R. L. Jacobson and D. Langmuir, *Geochim. Cosmochim. Acta* **38**, 301 (1974).

$$\Delta^F F_{\text{calcite}}^{273} = 271.50 \text{ kcal/mole}$$

$$(\Delta^F F_{\text{Ca}^{2+}} + \Delta^F F_{\text{CO}_3^{2-}}) = -261.08 \text{ kcal/mole}$$



$$-RT \ln ^aK = 8.89 \text{ kcal/mole}$$



$$261.01 - 8.89 = -616 \text{ kcal/mole}$$



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captain for able support at sea, N. Mülhan (Kiel) and P. Holler (Kiel) for valuable shipboard assistance, R. Wittstock (Kiel) for unpublished oceanographic data, E. Kemper (Hannover) for the glendonite samples, and J. S. Killingley (La Jolla) for assistance with the micro mass spectrometer. Support was also provided through a travel grant by the Oregon State University Foundation. Joint Research Program SFB95, University of Kiel; Contribution No. 383.

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