age size was 930 μm, with a range from 460 to 1210 μm (*9*). For comparison, Fig. 2b shows the crystals produced in the system without chloroform, which are needles 120 μm in average length. Microscopic examination showed that the agglomerate was composed of minute needle-like crystals. We anticipated that polymorphism or solvation might occur during the agglomeration process. However, we confirmed that this was not the case in the present system by means of an x-ray and spectrophotometric inspection. The agglomerate size was easily controlled by adjusting the agitation speed, temperature of the system, chloroform content in the system, and residence time. Agglomerate size decreased with increased agitation speed and with decreased chloroform content. Increasing the temperature difference between the ethanol solution and the mixture of chloroform and water resulted in a decrease in the agglomerate size.

The micromeritic properties of the agglomerates in Fig. 2a were investigated. The angle of repose (*10*) was 36° and the density of closest packing (*11*) was 0.488 g/cm³; the corresponding values for the crystals in Fig. 2b were 51° and 0.160 g/cm³. The agglomerated crystals could be formed into tablets by direct compression (*12*). It was not possible to compress the unagglomerated crystals because of their poor flowability. The hardness (*13*) and weight (*14*) values of the tablets formed from agglomerated crystals could meet the requirements for practical use.

In preliminary studies we found that other three-component systems such as benzene-ethanol-water, carbon tetrachloride–ethanol-water, and chloroform-acetone-water could be used instead of the present water-ethanol-chloroform system. This suggests that spherical crystallization might occur generally when a suitable mixture of three partially miscible liquids is employed as the crystallization solvent. Further, we expect that spherical crystallization may be adapted to a wide variety of drugs and chemicals.

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6. The contact angles of chloroform and water to salicylic acid were 0° and 105°, respectively.
7. Mixtures of ethanol, water, and chloroform in stoppered measuring cylinders (25 ml) were shaken and allowed to stand for 24 hours to determine the solubility of chloroform in ethanol-water mixtures with various proportions.
8. The proportions of the mixture of three solvents used are indicated by the open circle in Fig. 1.
9. Particle sizes were measured by sieve analysis, using the standard sieves specified in the Japanese Pharmacopeia.
10. The angle of repose was measured by pouring the powder onto a plate 10 cm in diameter.
11. The packing density was measured by tapping the powder into a measuring cylinder (50 ml).
12. Tablets were prepared with a single-punch machine (Erweka-GmbH, Frankfurt am Main, West Germany); their average weight and dimensions were 0.382 g, 10.05 mm in diameter, and 4.14 mm thick.
13. Hardness was measured diametrically by a moving plate hardness tester (Kyowa Seiko Co., Tokyo, Japan). The average value was 3.57 ± 0.63 kg.
14. The maximum difference from the mean tablet weight of 20 tablets was 2.56 percent.

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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 $CaCO_3 \cdot 6H_2O$, 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 CO_3^{2-} supplied from the early diagenetic decomposition of sedimentary organic matter and calcium from the interstitial seawater.

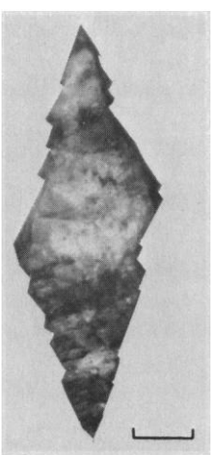

Fig. 1. Single crystal of calcium carbonate hexahydrate from Bransfield Strait sediments. This is a hydrated phase of calcite which forms at sub-zero temperatures and elevated pressures from metabolic carbonate and seawater calcium. It is the first reported occurrence of this phase forming syngenetically in organic-rich, rapidly accumulating sediments. Its crystal structure is monoclinic and identical to that of synthetic $CaCO_3 \cdot 6H_2O$, 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.

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 ≪1 percent of the ideal composition of $CaCO_3 \cdot 6H_2O$ (in percentage by weight): CaO, 26.95; CO_2, 21.14; and H_2O, 51.92 (Table 1).

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

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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 $\delta^{13}C$ values (Table 1) identify the carbonate as derived from organic matter. In contrast to calcium carbonate from skeletal components, the $\delta^{13}C$ 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 $CaCO_3 \cdot 6H_2O$ precipitation there is induced by such microbial carbonate production under anoxic conditions.

The $\delta^{18}O$ 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 $CaCO_3 \cdot 6H_2O$ 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 $\delta^{18}O$ toward lighter values with increasing degree of dehydration.

Crystal structure and phase identification were determined by single-crystal (*15*) and random powder x-ray diffractometry, 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 *C* 2/*c* or *C c*. Lattice constants and interplanar spacings (*d*-spacings) of the Bransfield Strait monoclinic $CaCO_3 \cdot 6H_2O$ 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 $CaCO_3 \cdot 6H_2O$ 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 concentrations, in fact the highest ever reported for marine sediments, were measured in the pore waters of the Bransfield Strait sediments (Fig. 2). The increasing 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 $CaCO_3 \cdot 6H_2O$ 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 CO_3^{2-} and Ca^{2+} from the alkalinity, *p*H, 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.

Chemistry, hydrated sample						Stable isotopes			
Sample weight (mg)	Residue weight (mg)	CaO (% by weight)		CO_2* sample (% by weight)	H_2O* sample (% by weight)	Hydrated subsample†		Dehydrated subsample	
		Residue	Sample			$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$
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_2 and H_2O 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.

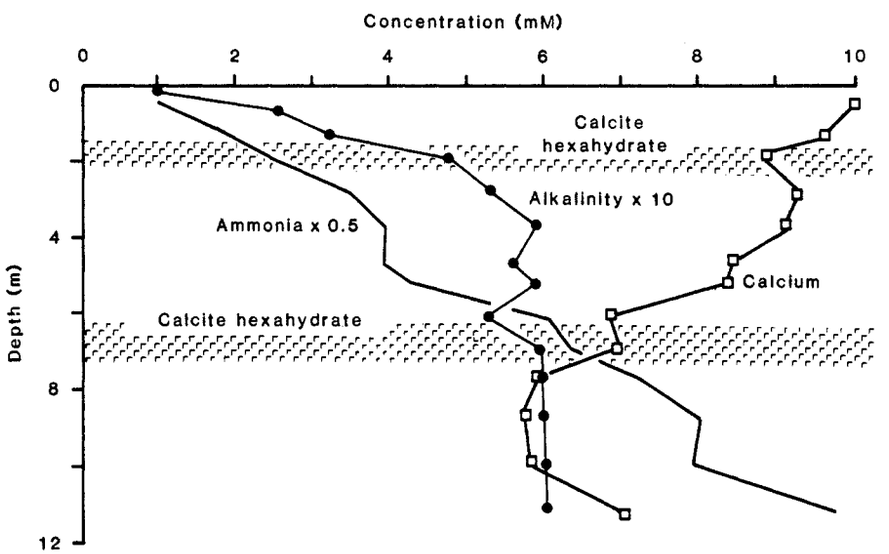

Fig. 2. Concentrations of dissolved metabolites and calcium in pore waters from Bransfield Strait sediments and depth intervals in the core where $CaCO_3 \cdot 6H_2O$ occurred. The continuously increasing NH_3 content with depth of up to 5 m*M*/kg results from the interstitial accumulation of bacterial 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 m*M*/kg), however, become constrained by the precipitation of $CaCO_3 \cdot 6H_2O$ 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 $CaCO_3 \cdot 6H_2O$ was found. Averaging the results yields a mean value of 1.62×10^{-5} mole^2/kg^2. Using this value, we calculated the thermodynamic stability product at −1.6°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°C and 1 atm of 4×10^{-8} to 8×10^{-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°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°C (*22*). Because of a ~ 20 percent decrease in volume accompanying the reaction

$$\text{calcite}_{(s)} + 6H_2O_{(\ell)} = CaCO_3 \cdot 6H_2O$$

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 $CaCO_3 \cdot 6H_2O$ 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 $\delta^{13}C$ 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}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 $CaCO_3 \cdot 6H_2O$ crystals were recovered at 62°16.5′S, 57°38.7′W; water depth, 1951 m; temperature, −1.6°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, 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 CO_2 = 0.785 × the weight of CaO (0.785 = molecular weight CO_2/molecular weight CaO). The weight of H_2O = the total weight loss − (0.785 × 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 ± 0.13; and organic carbon, 0.23 ± 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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18. $${}^aK = \frac{a_{Ca^{2+}} \cdot a_{CO_3^{2-}} \cdot a^6_{H_2O}}{a_{CaCO_3 \cdot 6H_2O}} = \frac{\gamma_{Ca^{2+}} \cdot \gamma_{CO_3^{2-}} \cdot c_{Ca^{2+}} \cdot c_{CO_3^{2-}} \cdot a^6_{H_2O}}{a_{CaCO_3 \cdot 6H_2O}}$$
where $c_{Ca^{2+}} \cdot c_{CO_3^{2-}} = 1.62 \times 10^{-5}$ mole^2/kg^2; $\gamma_{Ca^{2+}}$ (35 per mil, −1.6°C, 1 atm) = 0.25; $\gamma_{CO_3^{2-}}$ (35 per mil, −1.6°C, 1 atm) = 0.021; a_{H_2O} (35.07 per mil, −1.6°C, 1 atm) = 0.981; $a_{CaCO_3 \cdot 6H_2O_{(s)}} = 1$ by definition (*a* is activity, *c* is concentration, and γ 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 $CaCO_3 \cdot 6H_2O_{(s)} = Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} + 6H_2O_{(\ell)}$, the change in the Gibbs free energy of reaction (Δ^RF) can be calculated from the free energies of formation (Δ^FF) of the components:

$$\Delta^RF = -\Delta^FF_{CaCO_3 \cdot 6H_2O} + (\Delta^FF_{Ca^{2+}} + \Delta^FF_{CO_3^{2-}}) + 6\Delta^FF_{H_2O}$$

All free energy data were converted to 273°K.

(i) $H_{2(g)} + \frac{1}{2} O_{2(g)} = H_2O_{(\ell)}$

$$\Delta^FF^{273}{}_{H_2O} = \Delta^RF^{273}{}_{H_2O} = \Delta^RH_{H_2O}{}^{298} - 273 \times \Delta^RS^{298}{}_{H_2O} = -57.68 \text{ kcal/mole}$$

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

(ii) $CaCO_{3(calcite)} = Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$

$$(\Delta^FF_{Ca^{2+}} + \Delta^FF_{CO_3^{2-}}) = \Delta^RF_{diss} + \Delta^FF_{calcite}$$

$$\Delta^RF^{273}{}_{diss} = -RT \ln {}^aK = 10.42$$

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).

$$\Delta^FF^{273}{}_{calcite} = 271.50 \text{ kcal/mole}$$

$$(\Delta^FF_{Ca^{2+}} + \Delta^FF_{CO_3^{2-}}) = -261.08 \text{ kcal/mole}$$

(iii) $\Delta^RF_{CaCO_3 \cdot 6H_2O} = -RT \ln {}^aK = 8.89$ kcal/mole

(iv) $\Delta^FF_{CaCO_3 \cdot 6H_2O} = -(6 \times 57.68) - 261.01 - 8.89 = -616$ kcal/mole

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24. This work was supported by the Deutsche Forschungsgemeinschaft and the Office of Naval Research through grant N00014-79-C-0004, Project NR083-1026. We thank R.V. *Meteor*'s crew and 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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Stable-Carbon Isotope Ratios as a Measure of Marine Versus Terrestrial Protein in Ancient Diets

Abstract. *The stable-carbon isotope ratios for the flesh of marine and terrestrial animals from Canada's Pacific coast differ by 7.9 ± 0.4 per mil, reflecting the ~ 7 per mil difference between oceanic and atmospheric carbon. This difference is passed on to human consumers. The carbon isotopic values ($\delta^{13}C$) for human collagen thus yield direct information on the relative amounts of marine and terrestrial foods in prehistoric diets.*

In studies of the subsistence bases of prehistoric people, one may, by identifying faunal remains from archeological sites, determine the species of animals that were likely to have provided dietary protein. However, in those cases in which a population had access to two or more sources of protein, it is difficult to determine the relative amounts derived from each. It has been shown that stable-carbon isotope abundance ratios for human bone collagen can provide an estimate of the average fractions of the diet derived from C_3 and C_4 plants (C_3 plants fix carbon from ribulose diphosphate into a three-carbon acid, utilizing the enzyme ribulose-diphosphate carboxylase; in C_4 plants, CO_2 is first fixed into phosphoenolpyruvate to yield four-carbon acids, using the enzyme phosphoenolpyruvate carboxylase), because the C_3 and C_4 photosynthetic processes fractionate carbon by different amounts (*1*). In this report we show that a similar discrimination may be made between marine- and terrestrial-based diets on the coast of British Columbia and that this method can give a direct determination of the dietary adaptation of a population.

The purpose of this study was to determine whether the ~ 7 per mil difference observed between seawater bicarbonate and atmospheric CO_2 (*2*) is maintained through the various trophic levels, including human consumers, of the marine- and terrestrial-based food chains on the Pacific Coast. If such is the case, then a measurement of the $\delta^{13}C$ value,

$$\delta^{13}C = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000$$

where $R = {}^{13}C/{}^{12}C$, using the Pee Dee belemnite (PDB) standard for the bone collagen of a human consumer would give an estimate of the relative amounts of marine- and terrestrial-based carbon in the diet. The accuracy of this estimate will depend upon the variability in the $\delta^{13}C$ values for each food chain. If the variability introduced at each trophic level and in the collagen-forming process is large, it may obscure the difference between the two food chains.

Although the photosynthetic mechanisms may differ, marine phytoplankton fractionate carbon to approximately the same extent as terrestrial C_3 plants, that is, by about 19 per mil relative to their carbon source (*3*), thus maintaining the 7 per mil difference between air and ocean carbon at this trophic level. The plankton values do vary with ocean temperature but this variation is small (~ 0.35 per mil per degree celsius) (*4*), and we expect that for the study area considered here it will be negligible.

The fractionation between an animal's diet and the average $\delta^{13}C$ value for its whole body has been measured as 0.8 ± 1.0 per mil and is not species-specific (*5*). Therefore, the 7 per mil difference should persist between marine and terrestrial herbivores at this trophic level, without a great deal of variability being introduced. Furthermore, this small fractionation makes it possible to treat both plants and animals in a food chain as a single food source.

In this study the highest trophic level considered is man. For archeological studies, all isotope measurements should be made on bone collagen. This tissue reliably preserves its carbon isotope composition through time, as carbon replacement would result in the destruction of the protein. In living humans, bone collagen has a turnover of about 30 years (*6*), and so measurements will represent long-term average dietary intakes of individuals. This collagen is composed of amino acids which are derived from the food ingested. Dietary protein provides the essential amino acids, whereas the nonessential amino acids may be synthesized from carbohydrates or obtained from the protein. The diet on the Canadian Northwest Coast is reported (*7*) to have been very low in carbohydrate content, and so the human collagen would have been derived primarily from dietary protein. As this collagen results from the ingestion of a large number of animals and plants, it should therefore reflect the average $\delta^{13}C$ value for the food chain or chains upon which the diet is based. The $\delta^{13}C$ value for a consumer's collagen has been found to be ~ 5 per mil higher than that of its diet (*1*, *8*). The variability of this fractionation is not well known, but the limited available data suggest that it is ≤1 per mil (*1*, *8*).

Application of this technique will be

Table 1. Average $\delta^{13}C$ values relative to PDB for diet and consumer samples obtained from British Columbia and the Ottawa Valley, Quebec, and from the literature (*10*) (literature values are in parentheses). Variabilities are 1 standard deviation.

Description of samples	*N*	$\delta^{13}C$ (per mil)	Description of samples	*N*	$\delta^{13}C$ (per mil)
		Dietary materials			
Terrestrial mammals	27	−25.5 ± 1.5	Marine mammals	4	−17.5 ± 0.9
Terrestrial birds	15	−25.2 ± 1.5	Marine fish and shrimp	20	−17.5 ± 1.5
Freshwater fish	4	−28.8 ± 2.2	Littoral species	7	−18.7 ± 1.2
Population mean and error		−25.7 ± 0.3			−17.8 ± 0.3
		Human bone collagen			
(Northern European C_3 consumers	81	−19.6 ± 1.6)	(Greenland Eskimo	2	−12.8)
Ottawa Valley consumers	17	−19.6 ± 0.9	British Columbia consumers, coastal area	40	−13.4 ± 0.9
British Columbia consumers, interior area (N = 5) −15.4 ± 0.3					

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