Potential of ikaite to record the evolution of oceanic $\delta^{18}O$

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ABSTRACT

A challenge in the quest to understand the sensitivity of the climate system is the separation of the competing effects of ice volume or sea level, salinity, and temperature on foraminiferal $\delta^{18}O$. We present precipitation experiments on the mineral ikaite, a hydrated form of calcium carbonate found in organic carbon–rich deep-marine sediments, that show that the hydration waters within the ikaite crystal capture the $\delta^{18}O$ of seawater ($\delta^{18}O_{sw}$) with a fractionation factor of 1.0029 ($\pm$0.0002). The $\delta^{18}O_{sw}$ measures the volume of continental ice, with an overprint of local salinity. Isolation of $\delta^{18}O_{sw}$ by analysis of the hydration waters of sedimentary ikaite preserved at temperatures <4 °C could be exploited to create a record of sea level during the Pleistocene. Preliminary data of $\delta^{18}O_{sw}$ from hydration waters of ikaite at the Last Glacial Maximum agree with estimates from modeling of pore waters that Antarctic Bottom Water was +1.4‰ ± 0.2‰ heavier.

Keywords: Pleistocene, ikaite, sea level, ice volume, oxygen isotopes, climate.

INTRODUCTION

An independent history of ice volume relative to ocean temperature is key for the Pleistocene because the climate system response changed between ca. 900 and 600 ka, from a 40 k.y. beat to a larger amplitude 100 k.y. cycle, without a corresponding change in orbital forcing (Imbrie et al., 1993). Rapid sea-level changes may play a role in suborbital climate fluctuations of the last glacial cycle (Siddall et al., 2003). These two components of the climate system, sea level and ocean temperature, are united within the most prevalent proxy of the past ocean, $\delta^{18}O$ of foraminifera, which records the $\delta^{18}O$ of seawater ($\delta^{18}O_{sw}$), a function of continental ice volume and ocean salinity. In addition, fractionation of oxygen isotopes during precipitation of calcite is temperature dependent (Epstein et al., 1953). Independent measures of sea level range from dating corals and marine incursions into caves (e.g., Bard et al., 1990; Antonioli et al., 2004), to combining temperature proxies with $\delta^{18}O$ (e.g., Lea et al., 2002), to diffusion and/or advection models of sediment pore water $\delta^{18}O$ (Schrag et al., 1996; Adkins et al., 2002), and modeling combined with foraminiferal $\delta^{18}O$ (Siddall et al., 2003; Bintanja et al., 2005). Determining a quantitative record of sea level, independent of ocean temperature, over millennial time scales remains a challenge for assessing the sensitivity of the climate system to changes in atmospheric CO_2.

Here we present a novel temperature-independent methodology for reconstruction of the evolution of $\delta^{18}O_{sw}$. We propose that ikaite ($CaCO_3\cdot6H_2O$), a hydrated form of calcium carbonate comprising Ca-CO$_3$ surrounded by six water molecules, linked together by hydrogen bonds, captures and preserves the $\delta^{18}O_{sw}$ as hydration water within its crystal (Fig. 1; Lennie et al., 2004; Dickens and Brown, 1970). Ikaite is observed in nature at temperatures between −1.9 and 7 °C in highly alkaline waters rich in phosphate such as cold springs in the Ikka Fjord, Greenland (Pauly, 1963; Buchardt et al., 1997), and alkaline lakes such as Mono Lake, California (Council and Bennett, 1993). From the $CaCO_3$-H_2O phase diagram, ikaite should not exist at ocean temperatures and pressures (Marland, 1975; Bischoff et al., 1993). Nonetheless, ikaite crystals are found in organic-rich ocean sediments from the Bransfield Strait (Suess et al., 1982), Sea of Okhotsk (Greinert and Derkachev, 2004), the Laptev Sea (Schubert et al., 1997), the lower Zaire deep-sea fan (Jansen et al., 1987; Zabel and Schulz, 2001), the Nankai Trough (Stein and Smith, 1985), and the Gulf of Mexico (Hackworth, 2004). Ikaite can precipitate metastably, but its growth and survival are restricted to a limited environment.

It has been proposed that ikaite may grow near the sediment-water interface in the marine environment (Boggs, 1972; England, 1976), and so capture $\delta^{18}O_{sw}$. However, to reach ikaite saturation, a tenfold increase in alkalinity above seawater and an inhibition of calcite or aragonite crystallization by sulfate or phosphate are required (Burton, 1993; Bis-

choff et al., 1993). Within organic-rich sediments, diagenesis causes increased nutrients, dissolved inorganic carbon (DIC), and alkalinity. Conditions published for ikaite formation include ammonia ~5 mM, alkalinity of 25–75 mM, DIC 40 mM, and Ca^{2+} 6–9 mM (Suess et al., 1982; Stein and Smith, 1985; Zabel and Schulz, 2001). A compilation of ikaite $\delta^{13}C$ values ranging from −18.8‰ to −36.3‰ (mean −27.7‰ ± 3.7‰, n = 29) suggests that anaerobic oxidation of marine organic matter is a major, but not always the sole, carbon source (Suess et al., 1982; Jansen et al., 1987; Stein and Smith, 1985; Zabel and Schulz, 2001; Schubert et al., 1997). In most cases a proportion must derive from methane that has been oxidized to CO_2 during sulfate reduction.

Natural ikaite crystals decompose above 4 °C to form water and a mixture of vaterite and calcite (Lennie et al., 2004). The aim of this study is to synthesize ikaite in waters of varying $\delta^{18}O_{sw}$, and to determine whether the $\delta^{18}O$ of water trapped in the ikaite crystal structure ($\delta^{18}O_{ikaite-water}$) records the $\delta^{18}O_{sw}$. With preliminary data from the hydration waters of pristine crystals from sediments of the last glacial cycle, we confirm that ikaite has the potential to provide a record of $\delta^{18}O_{sw}$ and improve our understanding of Pleistocene ice-sheet dynamics and sea-level change.

METHODS

Batches of ikaite were synthesized from an adapted method of Marland (1975), using me-
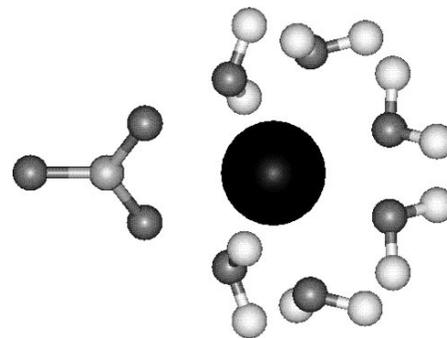
Figure 1. Ball and spoke model of ikaite to show Ca^{2+} coordinated by carbonate ion and six hydration waters.
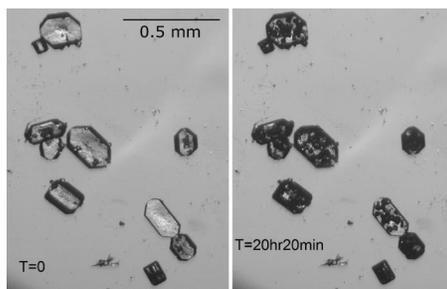
Figure 2. Pristine ikaite crystals under microscope, immediately after synthesis (A) and after 20 h and 20 min at room temperature (B).

$$\delta^{18}O_{medium} = -2.9(\pm0.2) + \delta^{18}O_{ikaite\ water}$$

Figure 3. Calibration of $\delta^{18}O$ of hydration waters of ikaite (filled circles and solid line) and $\delta^{18}O$ of calcite after decomposition of ikaite (open circles and dashed line), vs. $\delta^{18}O$ of medium, with residuals from least squares regression (x symbols). Arrow indicates $\delta^{18}O$ of added K_2CO_3.

dia with a range of $\delta^{18}O_{medium}$. The reactant solutions were prepared from volumes of water (18 MΩ) between 5 L and 1.5 L, and evaporated to 1 L on a hot plate at 40–50 °C.

We dispensed 100 mL of 0.3M $CaCl_2$ and 0.3M K_2CO_3 at a rate of 6.2 mL/h into a water-cooled insulated reaction vessel containing 600 mL of 0.045 M potassium hydroxide; the experiments ran for ~16 h. The vessel was stirred continuously and maintained at 2.1 ± 0.1 °C, with initial pH 13.35 decreasing to 13.25. Openings into the reaction vessel were covered to prevent condensation of air moisture. Equipment was cleaned with 2% HNO_3 for 24 h, rinsed, and dried prior to synthesis.

On completion of synthesis, the contents of the reaction vessel were poured into cooled polypropylene bottles and transferred to a cold lab (<4 °C). The contents were filtered, and a sample of the filtrate was frozen for isotopic analysis. The filtered ikaite crystals were rinsed with 250 mL of chilled (2 °C) demonized water and methanol, before centrifuging in a capped tube (6000 rpm, 21 °C, 45 min). The ikaite decomposed to form crystals (likely a mixture of vaterite and calcite) and water. The average yield of ikaite crystals was 91.5% (5.7 ± 0.25 g compared to an expected 6.23 g), and due to incomplete extraction of crystal

bound water during decomposition, we obtained 0.9–1.5 mL of hydration water, compared to an expected 3 mL, which was frozen for analysis. The crystal-bound water is insufficient to alter the $\delta^{18}O_{medium}$ during the experiment. The carbonate remaining after decomposition was analyzed for $\delta^{18}O$.

As a preliminary test of the ikaite approach, we have analyzed the hydration waters of two frozen crystals of sedimentary ikaite from contrasting sites: the Zaire Fan (GeoB 4914-3, water depth 4000 m, sediment depth 1125 cm; Zabel and Schulz, 2001), and the West Argentine Basin (GeoB 2809-4, water depth 3561 m, sediment depth 940 cm; Hensen et al., 2003). The ikaite crystals were allowed to decompose in capped tubes, and the hydration waters were frozen for analysis.

Oxygen isotope ratios of the water samples from crystal-bound water from natural and synthetic ikaite and the medium at the end of the experiment were analyzed, after off-line

equilibration with CO_2, using a Europa-PDZ Geo 20/20 isotope ratio mass spectrometer with a precision of ±0.06‰ and $\delta^{18}O$ calculated relative to the standard North Sea Water (0.132‰). The carbonate from decomposition of the experimental ikaite was analyzed online using a VG Isocarb device and a Prism mass spectrometer with a precision of ±0.1‰. A Carrera marble standard was run and used to calculate $\delta^{18}O$ and $\delta^{13}C$ relative to Peedee Belemnite (PDB).

RESULTS

The crystals produced from our precipitation experiments were euhedral and elongate, as large as 0.3 mm (Fig. 2), colorless under transmitted light, and decomposed at room temperature to yield the correct stoichiometry of $CaCO_3:H_2O$, which verified that ikaite had been synthesized. After decomposition, pore-like structures appeared in the crystal as described by Larsen (1994).

From a least squares linear regression, the $\delta^{18}O_{ikaite-water}$ (relative to standard mean ocean water, SMOW) of the hydration water in the ikaite crystal is linearly correlated with the $\delta^{18}O_{medium}$ (relative to SMOW) from which the ikaite precipitated (Fig. 3; Table 1), with an $R^2 = 0.993$. We obtain a calibration equation of:

$$\delta^{18}O_{medium}\ (‰) = -3.3\ (\pm0.3)$$
$$+ 1.04\ (\pm0.03)$$
$$\times\ \delta^{18}O_{ikaite-water}(‰). \quad (1)$$

Quoted errors on the intercept and slope are the standard error. The gradient is close to 1, and it is reasonable to assume that the gradient is 1, as it is unlikely that the fractionation factor ($\alpha_{ikaite-water}$) for isotopes between the ikaite-bound water and the medium water depends on the $\delta^{18}O_{medium}$. With this constraint, our calibration equation becomes:

$$\delta^{18}O_{medium}(‰) = -2.9(\pm0.2)$$
$$+ \delta^{18}O_{ikaite-water}(‰). \quad (2)$$

The $\delta^{18}O_{ikaite-water}$ is consistently enriched in $H_2^{18}O$ relative to the medium waters by an $\alpha_{ikaite-water}$ of 1.0029 (±0.0002).

By contrast, the $\delta^{18}O$ of the carbonate remaining after decomposition of the ikaite shows no dependence on the composition of the medium waters. The isotopic values for this carbonate are depleted considerably (−19‰ PDB) compared to marine carbonates.

DISCUSSION

Our experiment demonstrates that the $\delta^{18}O_{ikaite-water}$ records faithfully $\delta^{18}O_{medium}$ and is enriched relative to the medium by

TABLE 1. $\delta^{18}O$ VALUES OF MEDIUM WATERS AND IKAITE WATERS WITH STANDARD DEVIATIONS FOR REPLICATE ANALYSES OF THE SAME SAMPLES.

$\delta^{18}O$ medium (‰SMOW)	StDev (‰SMOW)	$\delta^{18}O$ ikaite water (‰SMOW)	St Dev (‰SMOW)	Fractionation factor $\alpha_{(ikaite-water)}$	$\delta^{18}O$ of $CaCO_3$ (‰PDB)	$\delta^{18}O$ of $CaCO_3$ (‰SMOW)
−3.6	0.021	−1.0	0.014	1.0026	−19.8	10.5
2.3	0.014	6.0	0.007	1.0037	−19.5	10.7
5.1	0.028	8.4	0.007	1.0033	−19.5	10.8
5.5	0.042	9.2	0.042	1.0036	−19.5	10.8
5.5	0.042	8.4	0.007	1.0029	−19.3	10.9
8.3	0.092	11.8	0.007	1.0030	−19.4	10.8
9.2	0.021	11.8	0.007	1.0026	−19.4	10.9
9.9	0.042	13.4	0.007	1.0035	−19.4	10.8
10.1	0.071	13.4	0.007	1.0033	−19.4	10.8
11.8	0.021	13.9	0.042	1.0021	−18.6	11.7
14.0	0.014	16.7	0.050	1.0027	−19.4	10.9
17.9	0.085	19.9	0.000	1.0020	−19.0	11.3

Note: The fractionation factor $\alpha_{(ikaite-water)}$ is calculated using: $\alpha_{(ikaite-water)} = (\delta_{ikaite} + 1000)/(\delta_{water} + 1000)$, where $\delta^{18}O_{ikaite}$ is the $\delta^{18}O$ of ikaite structural water and $\delta^{18}O_{water}$ is the $\delta^{18}O$ of water in the precipitating solution. $\delta^{18}O$ of calcite (relative to SMOW) is calculated using the formula $\delta^{18}O_{SMOW} = 1.03086\delta^{18}O_{PDB} + 30.86$.

2.9‰ ($\pm$0.2‰). Enrichment in H_2O^{18} is reasonable because the hydration of Ca^{2+} favors the heavier oxygen isotope of water.

The precipitation of ikaite takes place by the assembly of calcium-hydration spheres, $Ca(H_2O)_{7 \text{ or } 8}^{2+}$ (Naor et al., 2003), into a hydrogen-bonded crystallographic framework. Two coordinating oxygens of the Ca^{2+}-hydration sphere water molecules are displaced by two oxygens from a carbonate ion, and hydrogen bonding links these $CaCO_3.6H_2O$ moieties to form the ikaite crystal structure (Lennie et al., 2004). Oxygen isotopic fractionation during hydration ($\alpha_{\text{hydration sphere-water}}$) likely accounts for the entire 2.9‰ oxygen isotope enrichment in $\delta^{18}O_{\text{ikaite-water}}$ because there is a strong equilibrium fractionation of oxygen isotopes into the hydration shell of solvated cations relative to single H_2O molecules within liquid water. The oxygen isotope activity ratios of water in $CaCl_2$ solutions are lower than the composition ratios, which confirms that H_2O^{18} is preferentially incorporated into the hydration sphere of Ca^{2+} (Horita et al., 1993). By contrast, there is minimal fractionation during crystal assembly because the reduced mass difference between $Ca(H_2^{16}O)_{6 \text{ or } 7}(H_2^{18}O)^{2+}$ and $Ca(H_2^{16}O)_{7 \text{ or } 8}^{2+}$ is negligible.

Quantum and statistical mechanical models of the oxygen isotopic fractionation between water molecules and the hydration sphere of a cation ($\alpha_{\text{hydration sphere-water}}$) suggest that the isotope fractionation results from the influence of the field of the cation on the internal vibrational modes of the water molecules in the first hydration shell (Driesner et al., 2000). A simple model (Bopp et al., 1974) calculates $\alpha_{\text{hydration sphere-water}}$ and shows preferential enrichment of H_2O^{18} in the hydration waters of Li^+ and Na^+, and depletion for K^+ and Cs^+. Cations with a high charge/radius ratio interact with H_2O^{18} in preference to H_2O^{16} during hydration (Taube, 1954). We could find no literature value for $\alpha_{\text{hydration sphere-water}}$ for $Ca(H_2O)_{7 \text{ or } 8}^{2+}$, but the charge/radius ratio of 0.016 for Ca^{2+} in eightfold coordination is similar to that of Li^+ in fourfold coordination (0.014), which yields $\alpha_{\text{hydration sphere-water}}$ of ~1.005 at 4 °C (Bopp et al., 1974). This value is similar to $\alpha_{\text{ikaite-water}}$ of 1.0029, and $\alpha_{\text{gypsum-water}}$ for $CaSO_4.2H_2O$ of 1.003–1.0041 (Horita, 1989; Gonfiantini and Fontes, 1963). A critical point is that the $\alpha_{\text{hydration sphere-water}}$ is temperature independent (O'Neill and Truesdell, 1991). Our approach is the first direct measurement of the $\alpha_{\text{hydration sphere-water}}$ for calcium, and studies of mineral phases similar to ikaite [e.g., lansfordite ($MgCO_3.5H_2O$) and hellyerite ($NiCO_3.6H_2O$)] may validate quantum mechanistic models for the hydration of other divalent cations.

Kinetic control on isotopic fractionation is likely responsible for the $\delta^{18}O$ of the carbonate remaining after ikaite decomposition. If our carbonate system attained equilibrium with respect to CO_3^{2-} and water, at a pH of 13, the carbonate $\delta^{18}O$ values should be offset from the waters by ~18.4‰ (Usdowski and Hoefs, 1993). However, at this pH the oxygen isotopic equilibration time between CO_3^{2-} and water is >167 h (Zeebe and Wolf-Gladrow, 2001). Thus in our experiment, isotopic equilibrium is not achieved between CO_3^{2-} and water. The $\delta^{18}O$ of the K_2CO_3 used was −17.8‰ PDB (12.5‰ SMOW), and $\delta^{18}O$ values of decomposed carbonate are 1‰–2‰ depleted in ^{18}O by comparison. The light isotope partitions preferentially into the ikaite in accord with a kinetic control and <100% yield of ikaite.

$\delta^{18}O_{\text{ikaite-water}}$: A PROXY FOR OCEANIC $\delta^{18}O_{\text{sw}}$

Our experimental results demonstrate that the isotopic composition of the hydration waters captured within an ikaite crystal record the $\delta^{18}O_{\text{sw}}$ with an $\alpha_{\text{ikaite-water}}$ of 1.0029 ($\pm$0.0002). The ikaite approach, and our calibration, is ratified further by preliminary field data of $\delta^{18}O_{\text{sw}}$ from two ikaite crystals (Table 2). The change in $\delta^{18}O_{\text{sw}}$ ($\Delta\delta^{18}O_{\text{past-present}}$) is +0.2‰ $\pm$ 0.2‰ for GeoB4914-3, currently bathed by North Atlantic Deep Water (NADW), and +1.4‰ $\pm$ 0.2‰ for GeoB2809-4, currently bathed by Antarctic Bottom Water (AABW). The Zaire Fan ikaite is not directly dated, but derives from a sediment package containing ikaites from 36 ka to older than 49 ka, and the $\Delta\delta^{18}O_{\text{past-present}}$ is in the range of expected seawater values for the last glacial cycle (Siddall et al., 2003). The sample from the West Argentine Basin is dated as ca. 25 ka (^{14}C accelerator mass spectrometry), close to the Last Glacial Maximum (LGM) and the $\Delta\delta^{18}O_{\text{past-present}}$ of +1.4‰ $\pm$ 0.2‰ is identical to the LGM value of +1.3‰ $\pm$ 0.2‰ derived from modeling of pore waters at Ocean Drilling Program (ODP) Site 1093 in AABW (Adkins et al., 2002).

Our preliminary evidence of preservation of the full amplitude of the signal of the LGM $\delta^{18}O_{\text{sw}}$, using our $\alpha_{\text{ikaite-water}}$, lends confidence to our approach; in order to record $\delta^{18}O_{\text{sw}}$, ikaite must form near the sediment surface before the primary $\delta^{18}O_{\text{sw}}$ signal attenuates

(McDuff, 1985). While early precipitation of ikaite is also supported by the young ages of ikaites (ca. 2–3 ka) from around Antarctica, the timing of ikaite precipitation within the pore waters, as well as the source of carbon for the ikaite and the potential for postdepositional water exchange, are all important caveats that require further investigation.

The advantage of ikaite over the pore-water method is that, depending on its abundance within the sediment, it could allow reconstruction of $\delta^{18}O_{\text{sw}}$ and δD for time slices other than the LGM. Other potential sites for ikaite reconstruction of $\delta^{18}O_{\text{sw}}$ include (1) the Bransfield Strait, with ikaite at 2.05 and 7.14 ka, assuming typical sedimentation of 1 mm/yr (Suess et al., 1982), and (2) the Nankai Trough, with ikaites from ca. 35 to 140 ka, assuming sedimentation of 22.5 cm/k.y. (Stein and Smith, 1985). Discovery of <1 mm crystals throughout a Zaire Fan pelagic core (Jansen et al., 1987) begs the question of how prevalent small grains of ikaite that decompose before inspection may be within marine cores.

The concept of a mineral preserving the isotopic signature of $\delta^{18}O_{\text{sw}}$ is not exclusive to ikaite. An alternative crystalline solid, methane clathrate, which captures a methane molecule within a cubic lattice of water molecules, may be disadvantaged by its shallow occurrence (between ~300 and 1100 m), limited reconstruction of the deep ocean, its rapid decomposition upon recovery, and the danger of drilling in clathrate abundant areas. The hydration waters of ikaite are the optimal candidate for reconstructing a continuous evolution of $\delta^{18}O_{\text{sw}}$.

CONCLUSIONS

Laboratory precipitation experiments demonstrate a consistent $\alpha_{\text{ikaite-water}}$ (1.0029‰ $\pm$ 0.0002‰) between the $\delta^{18}O$ of the hydration water incorporated into the ikaite and the $\delta^{18}O$ of the medium. The crystal-bound water in the ikaite structure is enriched isotopically compared to the medium waters as a result of preferential incorporation of H_2O^{18} into the hydration sphere of the Ca^{2+} ion, which is locked into the ikaite crystal. The isotopic fractionation associated with the hydration process is comparably insensitive to temperature (~0.01‰/°C). The potential for the hydration waters of marine ikaite to record the

TABLE 2. PRELIMINARY DATA FROM THE HYDRATION WATERS OF PRESERVED CRYSTALS OF IKAITE

Core	Location	$\delta^{18}O_{\text{modern ocean}}$ (‰, GEOSECS)	$\delta^{18}O_{\text{ikaite water}}$ (‰)	$\delta^{18}O_{\text{past ocean}}$ (‰)
GeoB4914-3	Zaire Fan	0.13	3.3 $\pm$ 0.02	0.3 $\pm$ 0.16
GeoB2809-4	West Argentine Basin	0.02	4.3 $\pm$ 0.04	1.4 $\pm$ 0.17

Note: The GEOSECS data is taken from the closest stations. The range of $\delta^{18}O$ represents repeated analyses of different parts of the same crystal. The $\delta^{18}O_{\text{past ocean}}$ is calculated from the $\delta^{18}O_{\text{(ikaite-water)}}$

Pleistocene evolution of $\delta^{18}O_{sw}$ is confirmed by preliminary data from an LGM ikaite crystal that agree with pore-water reconstructions.

REFERENCES CITED

Adkins, J.F., McIntyre, K., and Schrag, D.P., 2002, The salinity, temperature, and $\delta^{18}O$ of the glacial deep ocean: Science, v. 298, p. 1769–1773, doi: 10.1126/science.1076252.

Antonioli, F., Bard, E., Potter, E.K., Silenzi, S., and Improta, S., 2004, 215-ka history of sea-level oscillations from marine and continental layers in Argentarola Cave speleothems (Italy): Global and Planetary Change, v. 43, p. 57–78, doi: 10.1016/j.gloplacha.2004.02.004.

Bard, E., Hamelin, B., and Fairbanks, R.G., 1990, U/Th ages obtained by mass spectrometry in corals from Barbados: Chemical Geology, v. 84, p. 157–158.

Bintanja, R., van de Wal, R.S.W., and Oerlemans, J., 2005, Modelled atmospheric temperatures and global sea levels over the past million years: Nature, v. 437, p. 125–128, doi: 10.1038/nature03975.

Bischoff, J.L., Fitzpatrick, J.A., and Rosenbauer, R.J., 1993, The solubility and stabilization of ikaite ($CaCO_3 \cdot 6H_2O$) from 0 to 25 °C: Environmental and paleoclimatic implications for thinolite tufa: Journal of Geology, v. 101, p. 21–33.

Boggs, S., 1972, Petrography and geochemistry of rhombic, calcite pseudomorphs from mid-Tertiary mudstones of the Pacific Northwest: U.S.A.: Sedimentology, v. 19, p. 219–235.

Bopp, P., Heinzinger, K., and Vogel, P.C., 1974, Calculations of the oxygen isotope fractionation between hydration water of cations and free water: Zeitschrift für Naturforschung. v. 29a, p. 1608–1613.

Buchardt, B., Seaman, P., Stockmann, G., Vous, M., Wilken, U., Duwel, L., Kristiansen, A., Jenner, C., Whiticar, M.J., Kristensen, R.M., Petersen, G.H., and Thorbjorn, L., 1997, Submarine columns of ikaite tufa: Nature, v. 390, p. 129–130, doi: 10.1038/36474.

Burton, E.A., 1993, Controls on marine carbonate cement mineralogy: Review and reassessment: Chemical Geology, v. 105, p. 163–179, doi: 10.1016/0009-2541(93)90124-2.

Council, T.C., and Bennett, P.C., 1993, Geochemistry of ikaite formation at Mono Lake, California: Implications for the origin of tufa mounds: Geology, v. 21, p. 971–974, doi: 10.1130/0091-7613(1993)021<0971:GOIFAM>2.3.CO;2.

Dickens, B., and Brown, W.E., 1970, The crystal structure of calcium carbonate hexahydrate at $\sim -120°$: Inorganic Chemistry, v. 9, p. 480–486, doi: 10.1021/ic50085a010.

Driesner, T., Ha, T.-K., and Seward, T.M., 2000, Oxygen and hydrogen isotope fractionation by hydration complexes of Li^+, Na^+, K^+, Mg^{2+}, F^-, Cl^-, and Br^-: A theoretical study: Geochimica et Cosmochimica Acta, v. 64, p. 3007–3033, doi: 10.1016/S0016-7037(00)00407-5.

England, B.M., 1976, Glendonites: Their origin and description: Mineralogical Record, v. 7, p. 60–68.

Epstein, S., Buchsbaum, R., Lowenstam, H.A., and Urey, H.C., 1953, Revised carbonate-water-isotopic temperature scale: Geological Society of America Bulletin, v. 64, p. 1315–1325.

Gonfiantini, R., and Fontes, J.R., 1963, Oxygen isotopic fractionation in the water of crystallization of gypsum: Nature, v. 200, p. 644–646.

Greinert, J., and Derkachev, A., 2004, Glendonites and methane-derived Mg-calcites in the Sea of Okhotsk, eastern Siberia: Implications of a venting-related ikaite/glendonite formation: Marine Geology, v. 204, p. 129–144, doi: 10.1016/S0025-3227(03)00354-2.

Hackworth, M., 2004, Mud volcanoes, gas hydrates, and carbonate formation at ''warm'' seeps in the northern Gulf of Mexico: Geological Society of America, Abstracts with Programs, v. 36, no. 5, p. 193.

Hensen, J., Zabel, M., Pfeifer, K., Schwenk, T., Kasten, S., Ridinger, N., Schulz, H.D., and Boetius, A., 2003, Control of sulfate pore-water profiles by sedimentary events and the significance of anaerobic oxidation of methane for the burial of sulfur in marine sediments: Geochimica et Cosmochimica Acta, v. 67, p. 2631–2647, doi: 10.1016/S0016-7037(03)00199-6.

Horita, J., 1989, Stable isotope fractionation factors of water in hydrated saline mineral-brine systems: Earth and Planetary Science Letters, v. 95, p. 173–179, doi: 10.1016/0012-821X(89)90175-1.

Horita, J., Wesolowski, D.J., and Cole, D.R., 1993, The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: I Vapor-liquid water equilibration of single salt solutions from 50–100 °C: Geochimica et Cosmochimica Acta, v. 57, p. 2797–2817, doi: 10.1016/0016-7037(93)90391-9.

Imbrie, J., Berger, A., Boyle, E.A., Clemens, S.C., Duffy, A., Howard, W.R., Kukla, G., Kutzbach, J., Martinson, D.G., McIntyre, A., Mix, A.C., Molfino, B., Morley, J.J., Peterson, L.C., Pisias, N.G., Prell, W.L., Raymo, M.E., Shackleton, N.J., and Toggweiler, J.R., 1993, On the structure and origin of major glaciation cycles. 2. The 100,000-year cycle: Paleoceanography, v. 8, p. 699–735.

Jansen, J.H.F., Woensdregt, C.F., Kooistra, M.J., and van de Gaast, S.J., 1987, Ikaite pseudomorphs in the Zaire deep-sea fan: An intermediate between calcite and porous calcite: Geology, v. 15, p. 245–248, doi: 10.1130/0091-7613(1987)15<245:IPITZD>2.0.CO;2.

Larsen, D., 1994, Origin and palaeoenvironmental significance of calcite pseudomorphs after ikaite in the Oligocene Creede Formation, Colorado: Journal of Sedimentary Research, v. A64, p. 593–603.

Lea, D.W., Martin, P.A., Pak, D.K., and Spero, H.J., 2002, Reconstructing a 350 ky history of sea level using planktonic Mg/Ca and oxygen isotope records from a Cocos Ridge core: Quaternary Science Reviews, v. 21, p. 283–293, doi: 10.1016/S0277-3791(01)00081-6.

Lennie, A.R., Tang, C.C., and Thompson, S.P., 2004, The structure and thermal expansion behaviour of ikaite, $CaCO_3.6H_2O$, from T=114 to T=293K: Mineralogical Magazine, v. 68, p. 135–146, doi: 10.1180/0026461046810176.

Marland, G., 1975, The stability of $CaCO_3.6H_2O$ (ikaite): Geochimica et Cosmochimica Acta, v. 39, p. 83–91, doi: 10.1016/0016-7037(75)90186-6.

McDuff, R.E., 1985, The chemistry of interstitial waters, Leg 86, in Initial reports of the Deep Sea Drilling Project, Volume 86: Washington, D.C., U.S. Government Printing Office, p. 675–687.

Naor, M.M., van Nostrand, K., and Dellago, C., 2003, Car-Parrinello molecular dynamics simulation of the calcium ion in liquid water: Chemical Physics Letters, v. 369, p. 159–164, doi: 10.1016/S0009-2614(02)01998-X.

O'Neill, J.R., and Truesdell, A.H., 1991, Oxygen isotope fractionation studies of solute-water interactions, in Taylor, H.P., Jr., et al., eds., Stable isotope geochemistry: A tribute to Samuel Epstein: Geochemical Society Special Publication 3, p. 17–25.

Pauly, H., 1963, Ikaite, a new mineral from Greenland: Arctic, v. 16, p. 263–264.

Schrag, D.P., Hampt, G., and Murray, D.W., 1996, Pore fluid constraints on the temperature and oxygen isotopic composition of the glacial ocean: Science, v. 272, p. 1930–1932.

Schubert, C.J., Nurnberg, D., Scheele, N., Pauer, F., and Kriews, M., 1997, ^{13}C depletion in ikaite crystals: Evidence for methane release from the Siberian shelves?: Geo-Marine Letters, v. 17, p. 169–175, doi: 10.1007/s003670050023.

Siddall, M., Rohling, E.J., Almogi-Labin, A., Hemleben, C., Meischner, D., Schmelzer, I., and Smeed, D.A., 2003, Sea-level fluctuations during the last glacial cycle: Nature, v. 423, p. 853–858, doi: 10.1038/nature01690.

Stein, C., and Smith, A.J., 1985, Authigenic carbonate nodules in the Nankai Trough, Site 583, in Kagami, H., et al., Initial reports of the Deep Sea Drilling Project: Washington, D.C., U.S. Government Printing Office, v. 87, p. 659–668.

Suess, E., Balzer, W., Hesse, K.F., Muller, P.J., Ungerer, C.A., and Wefer, G., 1982, Calcium carbonate hexahydrate from organic-rich sediments of the Antarctic Shelf: Precursors of glendonites: Science, v. 216, p. 1128–1131.

Taube, H., 1954, Use of oxygen isotope effects in the study of hydration of ions: Journal of Physical Chemistry, v. 58, p. 523–528, doi: 10.1021/j150517a003.

Usdowski, E., and Hoefs, J., 1993, Oxygen isotopic exchange between carbonic acid, bicarbonate, carbonate, and water: A reexamination of the data of McCrea (1950) and an expression for the overall partitioning of oxygen isotopes between the carbonate species and water: Geochimica et Cosmochimica Acta, v. 57, p. 3815–3818, doi: 10.1016/0016-7037(93)90159-T.

Zabel, M., and Schulz, H.D., 2001, Importance of submarine landslides for non-steady state conditions in pore water systems—Lower Zaire (Congo) deep-sea fan: Marine Geology, v. 176, p. 87–99, doi: 10.1016/S0025-3227(01)00164-5.

Zeebe, R.E., and Wolf-Gladrow, D., 2001, CO_2 in seawater: Equilibrium, kinetics, isotopes: Amsterdam, Elsevier Oceanography Series 65, p. 200–207.