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Ikaite Abundance Controlled by Porewater Phosphorus Level: Potential Links to Dust and Productivity

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ABSTRACT

Glendonites are pseudomorphs of the mineral ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) after loss of hydration water and occur in distinctive euhedral crystalline forms, sometimes clustered as rosettes of up to tens of centimeters in diameter. While it is generally accepted that organic-rich environments, methane seeps, and high phosphate levels are important for ikaite formation, glendonite occurrences in ancient sedimentary sequences are widely considered to reflect near-freezing temperatures, even at high latitudes during periods of greenhouse climates. To fully understand the paleoenvironmental significance of glendonites, a comprehensive examination of the modern ikaite setting is necessary. Temperature is the most important parameter that has been quantitatively constrained for the presence of ikaite. Low bottom-water temperature, while a required condition for formation of the mineral, is not adequate for its growth; other controls are necessary to explain the absence of ikaite in many cold environments. In this study, we discuss the control of carbonate chemistry on ikaite formation. Our compilation of geochemical data from sediment cores with well-preserved ikaite provide further evidence for the importance of phosphate. A phosphate concentration above $\sim 400 \mu\text{M}$ in shallow and cold porewater may be the requisite parameter for extensive ikaite precipitation. Thus, abundant glendonites in ancient successions mark past periods and regions of elevated porewater phosphorus concentrations, which may also be related to high surface productivity and/or iron fertilization.

Online enhancement: supplementary table.

Introduction

Temperatures below $4^\circ\text{--}7^\circ\text{C}$ are required to stabilize hydration water in the ikaite crystal structure (Pauly 1963; Stein and Smith 1986; Bischoff et al. 1993; Frank et al. 2008). Ikaite can form in the water column (Council and Bennett 1993; Buchardt et al. 1997), in sea ice (Dieckmann et al. 2008), and within the sediment column (Suess et al. 1982). Precipitation of authigenic ikaite in marine sediments is the focus of this study. On destabilization, ikaite crystals may release hydration water and form the pseudomorph called glendonite. The presence of glendonite has been documented in sed-

iments as old as the Neoproterozoic (James et al. 2005). An interpretation of the paleoenvironment from the geological record of glendonite occurrences relies on an understanding of the physical and biogeochemical controls in the modern ocean of the precipitation of the precursor ikaite. Because ikaite is known to form under cold conditions, glendonites are commonly interpreted as an indicator of near-freezing water temperatures (De Lurio and Frakes 1999; Price 1999; Swainson and Hammond 2001; Alley and Frakes 2003; Jones et al. 2006; Frank et al. 2008; James et al. 2009; Ivany and Runnegar 2010). However, bottom-water temperature cannot be the only factor controlling ikaite precipitation because temperature alone offers no coherent explanation for the modern spatial distri-

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bution of ikaite. For example, the Vega Drift offshore of the Antarctic Peninsula was reported to be an ikaite hotspot, where several cores contained multiple layers of ikaite in each core (Domack et al. 2007; fig. 1B). In sharp contrast, no ikaite has been found in any cores at similar water temperatures just southwest of the Vega Drift. Furthermore, mid- to low-latitude sites like the Zaire Fan (Zabel and Schulz 2001) and the Argentine Basin (Hensen et al. 2003), where ikaite was also found, apparently have bottom waters (2.4° and 2°C, respectively) warmer than those at the Antarctic nonikaite site Palmer Deep (0°C; fig. 1). To identify the paleoenvironment conducive to abundant glendonite deposits, it is critical to examine what additional factor(s) must contribute to the presence of ikaite in the modern (or recent) system.

In addition to cold bottom water, high levels of organic carbon, alkalinity, methane, and phosphate

are considered to favor ikaite/glendonite formation (Bischoff et al. 1993; Greinert and Derkach 2004; Dahl and Buchardt 2006). General consensus exists in the literature regarding the importance of these factors (Selleck et al. 2007), but there is a lack of comprehensive and quantitative comparison among these parameters at different ikaite sites from the modern ocean. It is not clear what the threshold levels of total organic carbon (TOC), alkalinity, or methane flux are to trigger ikaite precipitation and then produce an ikaite hotspot. Such a comparison may reveal common features in various sedimentary settings that induce the formation of ikaite, serving as a modern calibration for the paleoenvironmental significance of ancient glendonites. Here we compile both published and new geochemical data from six sediment cores containing well-preserved ikaite in differing abundances. This data set allows the identification of conditions additional to temperature that are critical for ikaite formation. Other sites reported to have fresh ikaite without sufficient analytical data for comparison (see the next section) are not included in this compilation. Because the occasional appearance of ikaite/glendonite indicates an environment not fully conducive to either precipitation or preservation of this mineral, we focus on sites consistently preserving ikaite in multiple layers and propose that the common conditions in such ikaite sites may also be representative of extensive ancient glendonite deposits.

Chemical Parameters for Ikaite Formation

While we acknowledge that physical parameters (e.g., sedimentation, lithology, and porewater seepage rates) may influence ikaite precipitation, we focus here on carbonate chemistry. Ikaite crystallization, like that of any mineral, is controlled by thermodynamics and kinetics. The direct thermodynamic controls on CaCO_3 precipitation include the concentrations of Ca^{2+} and CO_3^{2-} as well as the solubility product (K) of the carbonate mineral ($\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K$). The value of K is smaller at lower temperatures for ikaite, opposite to the solubility change with temperature of anhydrous calcium carbonate (Bischoff et al. 1993). We use bottom-water temperatures and geothermal gradients to estimate the precipitating temperature of ikaite. Porewaters with high alkalinity and dissolved inorganic carbon (DIC) are assumed to have high CO_3^{2-} concentrations. Organic matter degradation and methane oxidation contribute to DIC and thus indirectly control CO_3^{2-} . We compile porewater Ca^{2+} and DIC profiles to approximate the main thermo-

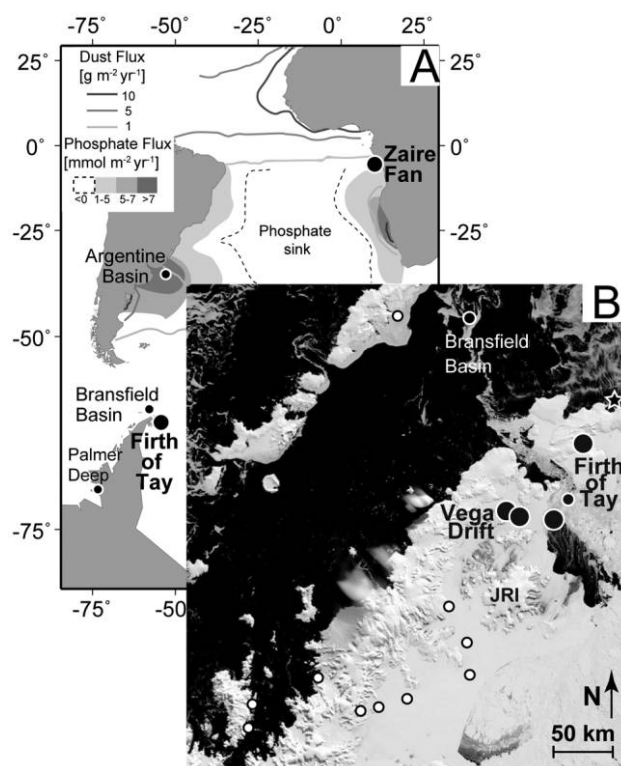


Figure 1. A, Locations of studied sites, with benthic phosphate fluxes and dust fluxes modified from Hensen et al. (1998) and Jickells et al. (2005). B, Satellite image of the Antarctic Peninsula. Large black circles with white rims represent sites with multiple ikaite layers, and small black circles with white rims represent sites with less than two ikaite horizons. White circles with black rims represent nonikaite sites. The Perseverance Drift, a newly discovered site, is shown by a star. JRI = James Ross Island. A color version of this figure is available online.

dynamic controls of ikaite precipitation, with sulfate and TOC as secondary factors influencing porewater DIC.

Kinetics control the crystallization rates of hydrated and anhydrous CaCO_3 minerals. When multiple minerals are supersaturated, there is a competition for porewater Ca^{2+} and CO_3^{2-} , and such a competition is controlled by crystallization rates. Phosphate is one of the strongest calcite inhibitors, significantly slowing down calcite precipitation rates (Berner and Morse 1974). High phosphate concentrations are commonly mentioned as an important condition for ikaite/glendonite formation (Bischoff et al. 1993; Selleck et al. 2007). This observation is largely based on a laboratory experiment, during which lake water with high phosphate concentration stabilized ikaite for about a year at 6°C (Bischoff et al. 1993). No chemical data from the natural environment, including marine sediment cores, have been used to confirm this suggestion. By inhibiting calcite formation, phosphate may very well promote ikaite growth. Therefore, porewater phosphate data are also compiled in this study.

Study Area, Sources of Data, and Analytical Methods

We have compiled data from four sites containing fresh ikaite (fig. 1), with both published and new geochemical data constraining the thermodynamic and kinetic controls on ikaite formation. They are the Bransfield Strait (JPC24, NBP0703) and the Firth of Tay (JPC2, NBP0703; Lu et al. 2012) offshore of the Antarctic Peninsula, the Zaire Fan (GeoB 4914-3, water depth of 4000 m) off the coast of Congo, and the Argentine Basin (GeoB 2809-4, water depth of 3561 m). These sites are located in drastically different oceanographic and sedimentary environments, ranging from a mid- to low-latitude deep-sea fan (water depth of up to 4000 m) to a shallow glacial fjord (the Firth of Tay). The abundance of ikaite is also very different among these sites. Ocean Drilling Program (ODP) site 1098 (Barker et al. 1999), at Palmer Deep west of the Antarctic Peninsula, is chosen as a nearby nonikaite reference site with cold bottom water. ODP site 1251 is located on Hydrate Ridge, off the coast of Oregon, United States (Tréhu et al. 2003), representing a setting with high phosphate levels in porewater but an absence of ikaite.

All downcore profiles used in this study are shown in figure 2. Data on the Zaire Fan (Zabel and Schulz 2001) and the Argentine Basin (Hensen and Zabel 2003) were obtained from the online database

<http://www.pangaea.de/>. The Palmer Deep (Barker et al. 1999) and Hydrate Ridge data (Tréhu et al. 2003) were downloaded from <http://www-odp.tamu.edu/>. Profiles for the Firth of Tay were published in Lu et al. (2012). Data on JPC24, in the Bransfield Strait, have not been previously published and are listed in table S1 (available online). At sites where DIC was not measured (e.g., the Argentine Basin), alkalinity and pH are used to calculate the DIC with equilibrium constants corrected by in situ temperatures (Zeebe and Wolf-Gladrow 2001). The Vega Drift, another site at the Antarctic Peninsula, is compared with these sites, but no specific geochemical data are available. The Vega Drift is in a hemipelagic and pelagic environment with organic rich (>1.5%) diatomaceous mud/ooze and postglacial sediments (Camerlenghi et al. 2001; Domack et al. 2007).

Site JPC24 (Bransfield Strait) was cored during US Antarctic Program cruise NBP0703. Porewater samples were collected from the core immediately after core recovery. They were stored in sealed glass ampoules for analysis of DIC and its carbon isotopic composition ($\delta^{13}\text{C}_{\text{DIC}}$), which are used to identify the ikaite-formation zone (IFZ) in the sediment column. The $\delta^{13}\text{C}_{\text{DIC}}$ values were determined on a Europa PDZ 20/20 mass spectrometer. The precision of analyses on Dickson-certified reference material batch 87 was $0.7\text{‰} \pm 0.2\text{‰}$.

Results

Downcore geochemical profiles are compiled in figure 2. No ikaite has been reported from Palmer Deep or Hydrate Ridge, and the ikaite abundances at the other sites range from one to two layers in the Argentine and Bransfield Basins to reportedly more than 10 layers in the Zaire Fan and the Firth of Tay. Bottom-water temperatures are all below 4°C at the chosen sites, and the in situ temperature increases with depth due to the geothermal gradient. Ca^{2+} concentrations (~10 mM) are similar at the sediment-water interface at all sites and decrease to various depths where authigenic carbonate minerals precipitated. DIC concentration profiles almost mirror Ca^{2+} profiles. Porewater Fe^{2+} concentrations are generally lower at the Zaire Fan and the Argentine Basin than at the two Antarctic ikaite sites, the Firth of Tay and the Bransfield Basin. PO_4^{3-} concentrations are highest at the Firth of Tay, with maximum values above 500 μM , where ikaite is the most abundant compared with all other sites. Maximum PO_4^{3-} concentrations at other ikaite-bearing sites are also >300 μM but are <200 μM at Palmer Deep, a nonikaite site. PO_4^{3-} concentrations

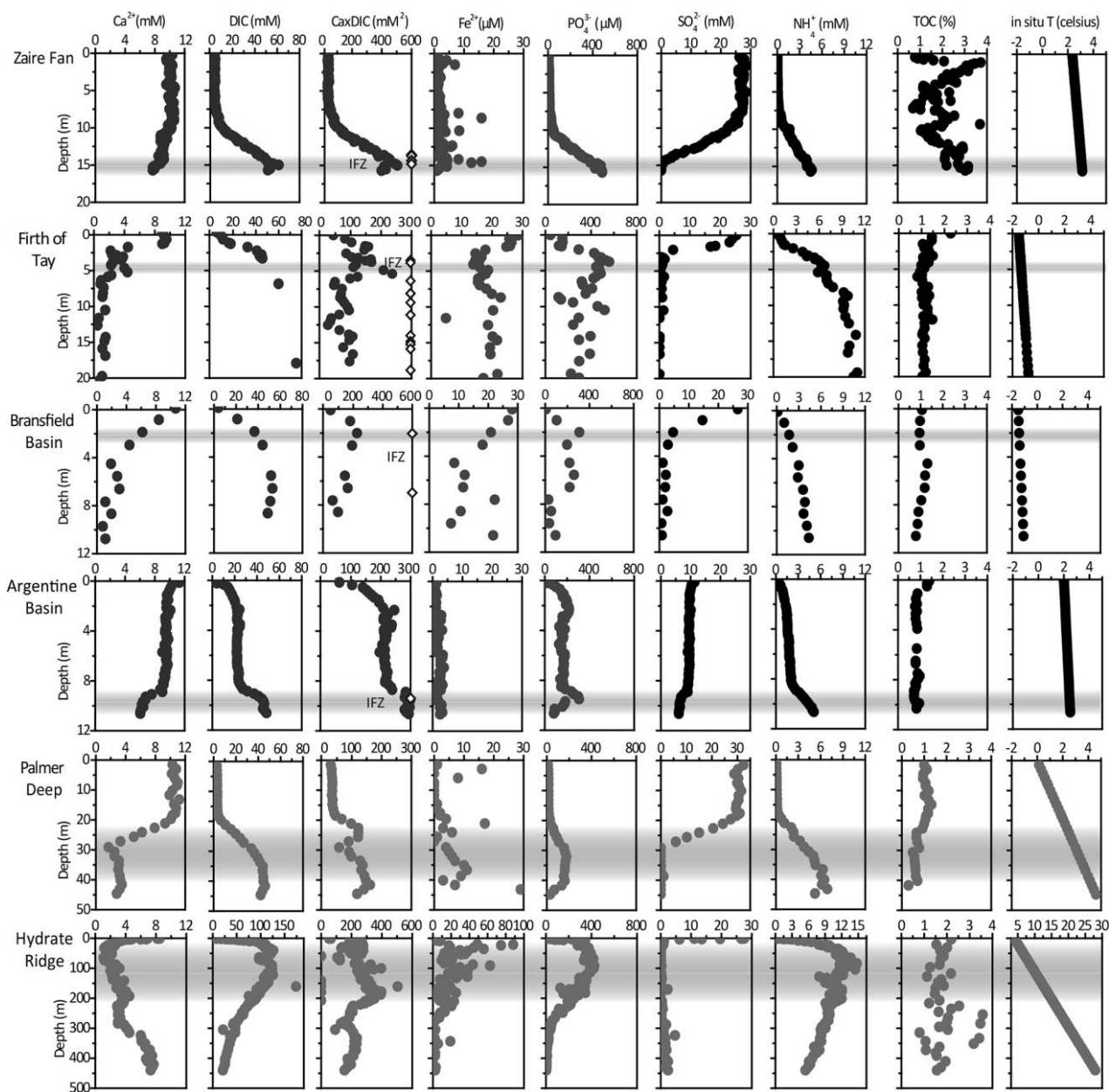


Figure 2. Downcore profiles of compiled parameters at all study sites. The depths for ikaite recovery are marked by diamonds in $\text{Ca}^{2+} \times \text{DIC}$ profiles. The ikaite-formation zones (IFZs) are defined by $\text{Ca}^{2+} \times \text{DIC}$, except for the Firth of Tay (Lu et al. 2012) and the Bransfield Basin (fig. 3), both defined by $\delta^{13}\text{C}$ values. T = temperature. A color version of this figure is available online.

at the other nonikaite site, Hydrate Ridge, are also high and are discussed later. Sulfate concentrations decrease from the sediment-water interface and are almost negligible at the IFZs in ikaite-bearing sites, except for the Argentine Basin. NH_4^+ increases with depth at all sites as a result of organic matter decomposition. The increased ammonia results from the interstitial accumulation of bacterial metabolites by decomposition of organic matter (Suess

et al. 1982). The Zaire Fan and Hydrate Ridge have relatively higher TOC values of up to 4%, compared with less than ~1% at other sites.

Discussion

Identifying the IFZs. To calculate precisely the saturation state of ikaite within a sediment core and identify the IFZs, it is necessary to have reliable

measurements of porewater pH, alkalinity, and Ca^{2+} concentrations as well as the solubility product K calculated for ikaite, corrected for the in situ temperature and salinity (Millero 1995; Papadimitriou et al. 2013). Complete data sets for these parameters are unavailable for all sites in this compilation. However, a rough approach may be sufficient to gauge where the ikaite originally formed within the sediment column. Because the ultimate goal of this study is to find the most important colimiting factor (along with temperature) for ikaite formation by comparing different sites, the uncertainty in our estimates for the IFZs will not bias our conclusion if the key parameter (e.g., phosphate) at prolific ikaite sites is significantly different from that at nonikaite sites.

The IFZs can be roughly estimated by inspecting the porewater Ca^{2+} and DIC profiles, since these are the most important thermodynamic (and kinetic) controls. An IFZ can be assigned to the depth where the decreasing Ca^{2+} downcore profile intersects with the increasing DIC profile, that is, where the $\text{Ca}^{2+} \times \text{DIC}$ value reaches a maximum in the core (fig. 2). The validity of this approach was supported by an independent IFZ prediction by projecting $\delta^{13}\text{C}$ values of ikaite crystals onto the $\delta^{13}\text{C}$ profile of porewater DIC at the Firth of Tay (Lu et al. 2012), assuming that $\delta^{13}\text{C}$ values of crystals record the DIC values of the porewater carbon pool. Additional $\delta^{13}\text{C}$ data from JPC24 in the Bransfield Basin (fig. 3) further confirm the earlier observation that ikaite recovered in the deeper layer was also formed in a relatively shallow IFZ close to the sulfate-methane transition zone. Ikaite $\delta^{13}\text{C}$ values reported at a nearby site in the same basin (Suess et al. 1982) are very similar to those of the JPC24. The IFZs assigned by carbon isotope values coincide with the highest $\text{Ca}^{2+} \times \text{DIC}$ values at both Antarctic sites. At the Zaire Fan and Argentine Basin sites, ikaite crystals were recovered within the depth ranges predicted by $\text{Ca}^{2+} \times \text{DIC}$ profiles. All of these observations suggest that the high $\text{Ca}^{2+} \times \text{DIC}$ value is generally a reliable way of identifying the IFZs, although paired $\delta^{13}\text{C}$ data for both porewaters and crystals provide the most precise constraints on the IFZ depths. Ikaite crystals found below the IFZs at the Firth of Tay and the Bransfield Basin were formed within the past 2000 yr and subsequently buried to deeper depths (Michalchuk et al. 2009; Barnard et al. 2014). They may not qualify as modern ikaite but can be regarded as subrecent.

Ikaite Abundances. The average and standard deviation of the measured geochemical parameters within our defined IFZs can be used to infer the in situ conditions of ikaite growth (table 1). These in

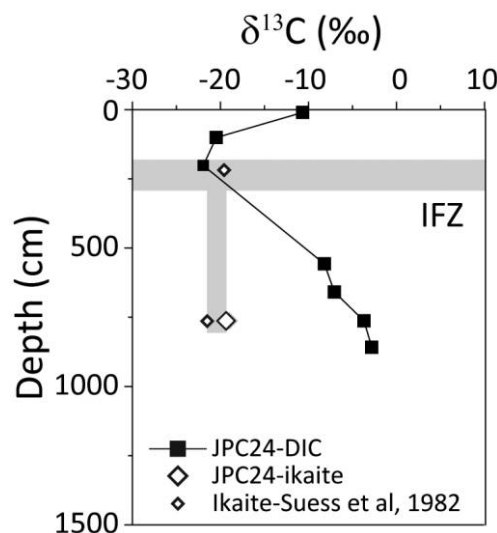


Figure 3. $\delta^{13}\text{C}$ values for porewater dissolved inorganic carbon (DIC) and an ikaite crystal at JPC24 (Bransfield Basin). Two additional $\delta^{13}\text{C}$ values from Suess et al. (1982) are also plotted for comparison. IFZ = ikaite-formation zone.

situ conditions then could be compared with some measure of the tendency for ikaite formation at a site. We can use the number of ikaite horizons as a measure of ikaite abundance (fig. 4), although ikaite horizons can serve only as a qualitative indicator because of the spatial heterogeneity of ikaite abundance that can be gauged only by coring multiple times within a small area.

Multiple crystals found in the same sedimentary layer are counted as a single horizon. The in situ conditions are plotted against the number of ikaite horizons. The purpose of such plots is not to search for any numerical trend among the data points but to identify the key parameter(s) that consistently and clearly separate extensive and persistent ikaite deposits from nonikaite sites. We interpret such key parameter(s) as the limiting control(s) on continuous ikaite precipitation and preservation in the marine environments (figs. 4, 5).

Key Geochemical Parameters. The temperatures at the IFZs are estimated from bottom-water temperatures (Jansen et al. 1987; Hensen et al. 2003; Science Party of NBP0703, 2008) and geothermal gradients (Macdonald et al. 1988; Manley and Flood 1989; Barker et al. 1999; Tréhu et al. 2003; Sultan et al. 2004; Loreto et al. 2011). Both in situ and bottom-water temperatures are below 7°C , the commonly assumed upper limit of ikaite stability (Bischoff et al. 1993). Within the ikaite stability field ($<4^{\circ}$ – 7°C), the temperature does not correlate with the presence or abundance of ikaite. The

Table 1. Summary of Chemical and Physical Parameters Examined

Site	SMT depth (m)	Bottom temperature (°C)	IFZ (m)	T (°C)	In situ conditions in IFZ					
					Ca (mM)	DIC (mM)	Fe (μM)	PO ₄ ³⁻ (μM)	NH ₄ ⁺ (mM)	TOC (%)
Firth of Tay	2.0	-1.5	2.6-3.8	-1.4	3.0 ± .7	43.8 ± 1.9	15.4 ± .8	491.6 ± 47.0	4.9 ± .8	1.3 ± .2
Bransfield Basin	3.0	-1.5	2.0-3.0	-1.4	5.3 ± 1.2	38.8 ± 3.1	19.5 ± 2.0	253.5 ± 78.0	1.9 ± .3	1.0 ± .1
Zaire Fan	14.3	2.4	13.5-15.7	3.1	8.3 ± .5	53.6 ± 3.4	5.3 ± 5.3	408.4 ± 63.3	4.2 ± .3	2.8 ± .4
Argentine Basin	9.3	2.0	8.9-10.7	2.5	6.8 ± .9	43.4 ± 5.3	2.2 ± .7	188.1 ± 85.4	4.1 ± .8	.8 ± .1
Hydrate Ridge	.3	4.0	.3-205.5	10.6	2.7 ± .9	109.4 ± 15.6	20.2 ± 13.7	328.3 ± 68.9	11.4 ± 1.3	1.7 ± .3
Palmer Deep	29.1	.0	22.7-43.2	3.4	3.7 ± 1.6	36.0 ± 10.4	7.2 ± 7.0	130.2 ± 42.9	4.7 ± 1.7	.6 ± .1

Note. DIC = dissolved inorganic carbon; IFZ = ikaite-formation zone; SMT = sulfate-methane transition; T = temperature; TOC = total organic carbon.

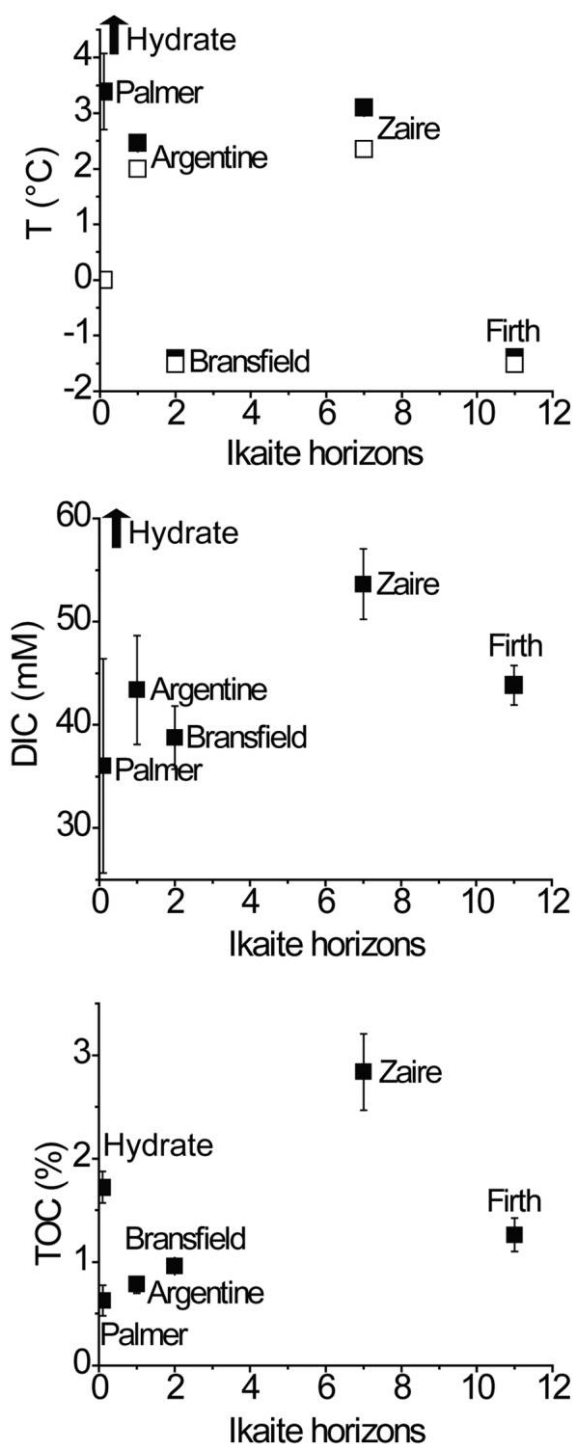


Figure 4. In situ conditions in ikaite-formation zones plotted against the number of ikaite horizons as closed squares. Open squares mark bottom-water temperatures. Both in situ temperature (T) and dissolved inorganic carbon (DIC) are much higher at Hydrate Ridge than at the other sites, as indicated by arrows. TOC = total organic carbon.

Bransfield Basin (approximately -1.5° to -1.1°C) is 3° – 4°C colder than the Zaire Fan (2.4° – 3.1°C), but the Bransfield Basin produces much less ikaite (two vs. seven layers). The Firth of Tay and the Vega Drift have water temperatures identical to that of the Bransfield Basin, but these two sites have substantially higher ikaite abundances (Domack et al. 2007).

DIC is not noticeably different among all the ikaite-bearing sites. The average DIC within the IFZs appears to be above ~ 40 mM. Such a DIC level is not significantly higher than levels at nonikaite sites, which precipitate anhydrous authigenic carbonates, indicating that alkalinity cannot be the determining factor for precipitating ikaite versus anhydrous carbonates.

Ikaite abundance generally increases with TOC level (fig. 4). However, only the Zaire Fan qualifies as truly organic rich, as it has a TOC level as high as 4%, and all the other ikaite sites have TOC values lower than 1.5%, a range common to many non-ikaite continental margins.

The Fe^{2+} profile behaves similarly at the Firth of Tay and the Bransfield Basin, being ~ 15 – 20 μM at the IFZs, but there are many more layers of ikaite at the Firth of Tay than at the Bransfield Basin (eleven vs. two). The IFZ Fe^{2+} is also similar at the Zaire Fan and the Argentine Basin, but the numbers of ikaite layers are distinctively different, suggesting that Fe^{2+} is not directly controlling ikaite presence.

The number of ikaite layers and phosphate concentration present a positive relationship (fig. 5). Phosphate concentrations reach their maxima at the IFZs, generally higher than 300 μM , but the maximum values vary among different sites. Phosphate levels are high at the Zaire Fan and the Firth of Tay, with ~ 10 ikaite layers. The Zaire Fan and the Firth of Tay attain levels of 400 – 500 μM phosphate at the IFZs, as high as double the concentrations found in the Bransfield Strait and the Argentine Basin (253 and 188 μM , respectively) with only one or two ikaite layers (Suess et al. 1982; Hensen et al. 2003). Most chemical profiles in the Firth of Tay and the Bransfield Basin are similar, but PO_4^{3-} and NH_4^+ concentrations are slightly higher at the Firth of Tay. The core in the Bransfield Basin is 22 m long, but we have chemical data only from the upper 12 m, where ikaite crystals were found (Barnard et al. 2014). There are notably more ikaite layers in the Firth of Tay than in the Bransfield Basin (eleven vs. two layers), likely due to higher phosphate concentrations inhibiting anhydrous calcite precipitation. Thus, a high phosphate concentration in porewater appears to be a common char-

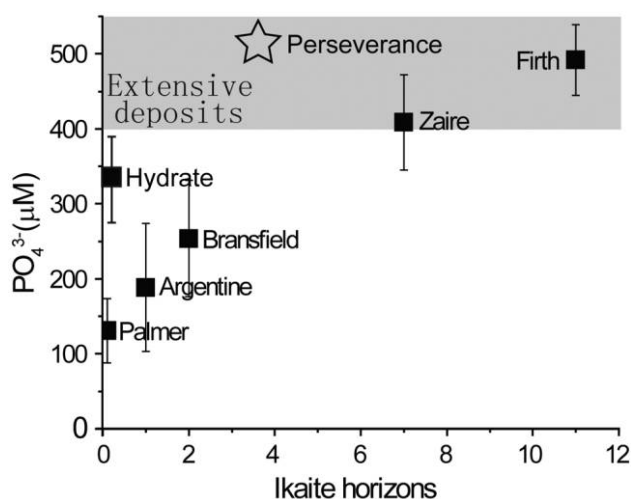


Figure 5. In situ phosphate concentrations in ikaite-formation zones plotted against ikaite horizons.

acteristic that leads to extensive and persistent ikaite deposits within the ikaite temperature stability field. A new site containing several layers of ikaite was recently discovered at the Perseverance Drift, a location very close to the Vega Drift and the Firth of Tay (fig. 1B). This new site also has phosphate concentrations in porewater (Science Party of NBP1203, 2013) on a par with the Firth of Tay and the Zaire Fan (fig. 5). Crystal mass data are available only for the Bransfield Basin, the Firth of Tay, and the Zaire Fan. Total weights of ikaite preserved at these sites are 11, 77, and 312 g, respectively, generally confirming that higher phosphate levels are favorable for producing more ikaite.

These observations suggest that a high phosphate concentration in porewater is a diagnostic feature of the marine environment that is capable of forming and preserving ikaite continuously through time. Although the phosphate concentrations of ~0.5 mM found in the extensive ikaite deposits are high compared with the sites in this compilation, they are still not close to the highest phosphate values (up to ~1 mM) reported from shallow marine subsurface porewaters, possibly related to phytoplankton blooms in Sachem's Head, Long Island Sound, where the temperature is too high (15°C) for ikaite formation (Martens et al. 1978; Ruttenberg 2003).

A closer look at sites with fewer ikaite layers further emphasizes the role played by phosphate in ikaite formation. The Argentine Basin site has only one layer of ikaite at ~9 m, coinciding with the maximum phosphate concentration, superimposed on an invariant downcore profile (fig. 2). The saturation state (as approximated by Ca^{2+} , DIC, and

temperature) is uniform across the phosphate peak, suggesting a relationship between ikaite formation and phosphate concentration of ~290 μM. The ikaite layers at the Bransfield Basin also appear to bracket the interval with the highest phosphate concentrations (fig. 2).

Nonikaite Sites. Both Palmer Deep and Hydrate Ridge are absent of ikaite. The temperature within the sediment column at Palmer Deep is comparable to that at ikaite-bearing sites. TOC is lower than 1% at Palmer Deep but is similar to that at the Argentine Basin site. Other parameters are not significantly different from the ikaite-bearing sites except that the phosphate concentration at Palmer Deep is lower than 200 μM. The low phosphate level is likely the reason that no ikaite was present at this site. Hydrate Ridge is well known for methane seeps, gas hydrates, authigenic calcite, and aragonite, but no ikaite has been reported (Luff and Wallmann 2003; Teichert et al. 2003). The TOC level at Hydrate Ridge is comparable to that at the Zaire Fan. The DIC at Hydrate Ridge is higher than that at all other sites (120 vs. 60 mM), due to a much longer drill core displaying the complete DIC profile in the sediment (fig. 2). The highest phosphate concentration determined for Hydrate Ridge is above 400 μM at ~100 mbsf at ODP site 1251 (Tréhu et al. 2003), close to our suggested range for extensive ikaite deposits. The absence of ikaite at this site may be due to high in situ temperatures. The bottom-water temperature is around 4°C, but the temperature rises to ~10°C at the depth with the maximum phosphate concentration (Tréhu et al. 2003; fig. 2). Even with the very high $\text{Ca}^{2+} \times \text{DIC}$ and phosphate levels at ~100 m (fig. 2), ikaite is not present. The higher ambient temperatures are likely the reason why ikaite is not present in sediments associated with high interstitial phosphate contents and early diagenetic phosphogenesis, for example, in upwelling regions offshore of Peru, Baja California.

Ikaite Distribution and Phosphate. Among the parameters examined in this study, phosphate concentration is the only one that unambiguously distinguishes sites with different ikaite layers (fig. 5). In summary, the results show a relationship between ikaite formation and high porewater phosphate and DIC but, critically, at relatively shallow burial depths before the geothermal gradient raises temperature beyond the ikaite stability field. We contend that it is the rarity of high phosphate and DIC at shallow depths (and therefore low temperature) within sediments that dictates the scarce presence of ikaite in global ocean sediments.

The mechanism for phosphate to enhance ikaite formation has been postulated only from the inhi-

bition effect of phosphate on calcite precipitation. Direct observations by scanning force microscopy suggest that phosphate can induce the formation of calcite nuclei with amorphous shapes during nucleation and disrupt the straight steps to form jagged steps during crystal growth (Dove and Hochella 1993). Atomistic computer simulation techniques have been used to model the adsorption energy of phosphonate ions on the planar vs. obtuse stepped surfaces of calcite (Ojo et al. 2002). The modeling results suggest that the incorporation of monophosphonate ions into the calcite obtuse step sites and kink sites may destroy the formation of potential kink sites and step assembly. Laboratory calcite synthesis experiments conducted under controlled pH and saturation states further confirm that CaHPO_4^0 inhibits calcite precipitation because it adsorbs on the surface and blocks the active crystal growth sites (Lin and Singer 2006). Similar approaches can be taken to investigate the adsorption and incorporation of phosphate within an ikaite crystal. The ikaite structure has already been simulated in a static atomistic computer model (de Leeuw and Parker 1998). Future studies utilizing molecular dynamic approaches may fundamentally unravel the relationship between phosphate and ikaite growth kinetics (Tang et al. 2009; Wolthers et al. 2013).

Dust and Productivity. One of the main motivations for this study is to address why such extensive ikaite deposits have been uniquely found in one small area around Antarctica, where bottom waters are ubiquitously cold. The answer to this question—the role played by porewater phosphate—has critical implications for glendonites in ancient deposits. It is now possible to reconcile the seemingly sporadic distribution of ikaite in the Atlantic and Southern Oceans (fig. 1), considering the high porewater phosphate levels common to extensive ikaite deposits. The Zaire Fan and Argentine Basin sites are both located in or near regions with high fluxes of phosphate from sediment to seawater (fig. 1A; Hensen et al. 1998). Such benthic fluxes were calculated on the basis of porewater phosphate profiles near the sediment surface with a resolution of up to 0.5 cm (Hensen et al. 1998). At the Antarctic Peninsula, the strong preference of ikaite to grow at the Vega Drift and the Firth of Tay may be related to the dusty glacial environment. A satellite image of the entire peninsula shows that the northeast side of James Ross Island is the only area with obvious dusty ice covers and reported ikaite occurrences (fig. 1B). The absence of ikaite southwest of James Ross Island is possibly correlated with the dust-free glacial ice, while the plume of dust on the opposite side of the island appears to extend toward the Vega Drift. Iron

oxides may serve as a powerful phosphorus pump, adsorbing phosphate when settling through the water column and releasing phosphate to porewater during iron reduction in the sediment (Slomp et al. 1996; Atkins and Dunbar 2009).

Although ikaite formation at the Firth of Tay is more likely the result of phosphorus adsorption/desorption on iron oxides, productivity- and organic matter-induced high phosphate levels in the sediments may be found in other Antarctic regions. It is reported that iron fluxes from terrigenous sediments are transported across sea ice and released to the ocean during melt, triggering and regulating phytoplankton blooms in iron-limiting areas, such as the Ross Sea, East Antarctica, and the Southern Ocean (Sedwick and DiTullio 1997; Sedwick et al. 2000, 2011; Reddy and Arrigo 2006; Lannuzel et al. 2007; Raiswell et al. 2008; Tagliabue et al. 2011; Boyd et al. 2012). A significant amount of Fe is found in the aeolian sediments in southern McMurdo Sound, and a considerable fraction is bioavailable, possibly causing phytoplankton blooms (Atkins and Dunbar 2009; Chewings et al. 2014).

Porewater phosphate concentrations at the Zaire Fan are more likely raised by organic matter decomposition as a consequence of dust-induced iron fertilization causing high surface productivity along the African coast (fig. 1A; Jickells et al. 2005). Organic matter is also a major sink for phosphorus in the sediments (Froelich et al. 1982; Rittenberg 1990). Decomposition of organic matter could thus generate high phosphorus fluxes to porewater. Porewater iron concentrations at the Firth of Tay are about three times higher than those at the Zaire Fan (fig. 2), while the TOC level is substantially higher at the Zaire Fan, supporting the notion of different mechanisms for strong phosphate enrichment at tropical and polar ikaite hotspots. There may be a causal link between dust fluxes and ikaite persistence, which is connected by inorganic and/or organic phosphorus recycling. However, the regenerated phosphate, promoting ikaite formation, may not necessarily return to the overlying water as a strong benthic flux. Ikaite/glendonite, therefore, probably cannot be used to infer the ultimate fate of recycled phosphorus because, for example, the porewater phosphate may remain trapped in the sediment column for an extended period of time.

Implications for the Paleoenvironment with Extensive Glendonite Deposits. The general term “extensive glendonite deposits” is used to differentiate sites with abundant ikaite crystals deposited in multiple layers over extended sedimentary sequences from sites where the crystals are restricted to one or two layers. On the basis of the observations at ikaite-

bearing sites, we propose that elevated porewater phosphate levels (~0.5 mM) can be inferred from extensive glendonite deposits, marking important locations and periods of increased phosphate recycling in the top 20 m of sediments. Such a phosphate indicator is particularly relevant to glendonites deposited under greenhouse conditions. However, this study does not challenge the fact that glendonites can form only at low temperatures, and the Hydrate Ridge site supports the notion that ikaite cannot easily form or survive when the ambient temperature is higher than 10°C, even with high phosphate concentrations. Therefore, both low temperature and high phosphate concentrations are required for ikaite formation.

Paleocene-Eocene strata at Svalbard, in the Arctic Ocean, are well known for abundant glendonites (Spielhagen and Tripathi 2009). However, the Cenozoic long-term cooling did not produce increasingly more glendonite deposits of younger ages (Glendonkov et al. 2000), regardless of the possibility that glendonites are not well known and recognized precisely. It could indicate that the Early Cenozoic glendonites are related to persistently strong phosphorus regeneration at Svalbard. Similar scenarios were proposed for the Eocene Fur Formation of Denmark (Huggett et al. 2005). A recent article by Foellmi (2012) reviewing the Cretaceous climate found glendonite-based evidence suggesting that cooling might be controversial, while at least some of the Jurassic and Cretaceous glendonites have been recovered within or around periods of global ocean anoxia (Foellmi 2012; Teichert and Luppold 2013). Glendonites have also been found in Cretaceous polar regions, such as the Deer Bay Formation of Arctic Canada in the Upper Valanginian (Kemper and Jeletzky 1979), Svalbard in the Upper Hauterivian and the Aptian (Price and Nunn 2010; Rogov and Zakharov 2010), and Arctic Russia in the Valanginian and the Hauterivian (Rogov and Zakharov 2010). Glendonites are common in glacial deposits during the Permian in eastern Australia, ranging from temperate to polar latitudes (Jones et al. 2006; Thomas et al. 2007; Frank et al. 2008; James et al. 2009). It is possible that ex-

tensive glendonite deposits in greenhouse conditions were related to climatic transitions that had in situ temperatures sufficiently low (probably <10°C) for ikaite formation and biological productivity and/or iron oxide deposition favorable for phosphorus regeneration in sediments at the same time.

Conclusions

In modern to subrecent ikaite occurrences, the bottom-water temperature and the in situ temperature are both below 4°C. The presence of glendonite may indicate bottom-water paleotemperatures below 10°C, on the basis of the observations at Hydrate Ridge. By comparing the available geochemical data from different sites, high porewater phosphate concentration at shallow sediment depths before the geothermal gradient increases the in situ temperature is the only feature that clearly distinguishes extensive ikaite deposits from all other sites. Within the appropriate temperature range, ikaite precipitation at high phosphate levels helps explain the distribution of ikaite-bearing sites in modern oceans. Phosphate concentrations in porewater may rise because of different mechanisms at low/high-latitude ikaite hotspots. Large glendonite deposits in past greenhouse climates, especially when associated with poor oxygenation conditions, likely indicate relatively cold bottom water and strong sedimentary phosphorus cycling and may also signify dusty environments and/or high productivity.

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