Spatial and temporal distribution of ikaite crystals in Antarctic glacial marine sediments

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Summary We report on the distribution of ikaite crystals (calcium carbonate hexahydrate, $CaCO_3 \cdot 6H_2O$) in Antarctic glacial marine sediments based upon the examination of over 100 high resolution Holocene sediment cores now recovered from most portions of the Antarctic margin. Ikaite crystals occur systematically throughout Holocene age sediments only in portions of the NW Weddell Sea and Eastern Bransfield Basin. The most contiguous deposystem with abundant ikaite includes the Vega Drift, a large (614 km^2) mud accumulation found in the Erebus and Terror Gulf and adjacent portions of the Prince Gustav Channel. The spatial pattern we define reflects the outflow of cold (< -1.9 ^oC) Weddell Sea derived shelf water which circulates out of the Weddell Sea gyre and around the northern tip of the Antarctic Peninsula and Joinville Archipelago into the eastern Bransfield Basin. The association of ikaite with very cold waters of NW Weddell Sea is coupled with regional patterns of high productivity as revealed by both satellite (SeaWifs) images and the regional distribution of organic rich (> 1.5% TOC) diatom muds and oozes found on the continental shelf, within which the ikaite crystals reside. There is also a temporal variation of ikaite crystal abundance and geochemistry with highest abundance limited to within the middle to early late Holocene (from 5 to 2 ka BP) and a trend toward more positive $\delta^{13}C$ values through to the modern. Ikaite crystals are not found on other portions of the Antarctic margin with any regularity, the only other occurrence known to us are in early Holocene muds of the Palmer Deep. We have not observed ikaite in the Ross Sea or within the sediments of the East Antarctic shelf. The cold outflow from the Weddell Sea inherits its thermal character from contact with the Ronne-Filchner and Larsen Ice Shelves and this along with the organic rich (seasonally open marine) nature of the hosting sediment has paleoenvironmental significance for ancient occurrences of ikaite (glendonite) as now commonly reported from Late Paleozoic and Neoproterozoic glacial marine sequences.

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Introduction

The association of ikaite crystals and their pseudomorph calcite forms, known as glendonites, with glacial marine sediments has been know for some time (Kaplan, 1979; Suess et al.,1982; Shearman and Smith, 1985; DeLurio and Frakes, 1999; Collings, et al., 1998; Halverson et al., 2004; James et al., 2005). While other, non glacial marine, conditions do allow for the formation of ikaite crystals, the common element in their formation is cold water and high levels of biotically available organic matter which favors high pore water alkalinity and elevated dissolved phosphorous levels, the later of which suppress alternate carbonate phases from forming out of the alkaline solutions. Disassociation of methane hydrate may also provide a suitable geochemical, pore fluid, habitat for the formation of $CaCO_3 \cdot 6H_2O$ (Grienert and Derkachev, 2004). While the observation of ikaite formation in the Eastern Bransfield Strait (Suess et al., 1982; Fig. 1) was fundamental to our understanding of ikaite occurrence in glacial marine settings in the Antarctic, there have been no published reports of ikaite occurrence in Antarctic glacial marine sediments until our observations in 2000 (Camerlenghi, et al., 2001). Since then we have been: 1) compiling a growing data base of high resolution Holocene marine sediment records from the continental shelf surrounding Antarctica (Fig. 2) and, 2) observing the spatial and temporal pattern of ikaite abundance and geochemistry. We report herein on the results of this survey and provide preliminary geochemical data from a suite of ikaite crystals.

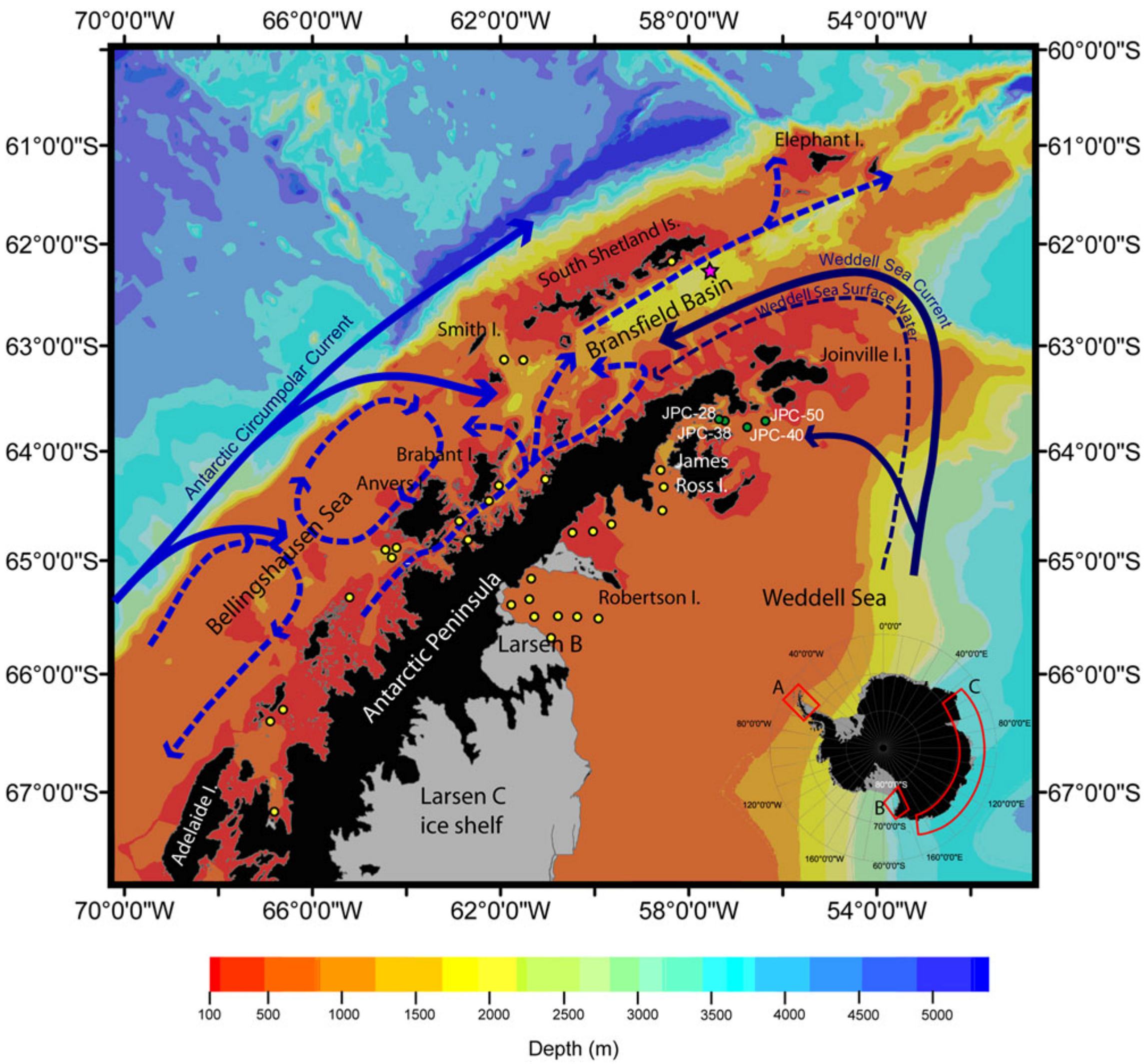

Figure 1. Map of the northern Antarctic Peninsula showing locations of cores with ikaite (green dots), without ikaites (yellow dots), and the original observation of ikaite by Suess et al. (1982) pink star. Oceaongraphic circulation demonstrated by blue lines and dashed lines (after, Shevenell and Kennett, 2002). Antarctic map insert shows location of the detailed map (A) and locations in the Ross Sea (B; Domack et al., 1999) and along the East Antarctic Margin (C: Leventer et al., 2006) where we have also examined numerous cores for ikaite, with no results.

Methods

Our observations on sediment cores include material collected during seven separate cruises including: NBP 95-2, ODP Leg 178; NBP 99-03, NBP 00-03, NBP 01-01 & -07, LMG-05-2, and NBP 06-3. Samples of ikaite were either removed as unaltered crystals from freshly examine cores (on board ship) or were sampled from the archived cores at the Antarctic Marine Geology and Research Facility of Florida State University. In these cases both unaltered ikaite crystals and dehydrated $CaCO_3$ granules were sampled and observed within the freshly opened cores. Our observations of ikaite crystals include the typical morphologies of: a) squared off prismatic crystals of 3-4 cm dimension, b) smaller pyramidal habits of smaller dimension 2-3 cm, and more commonly c) sigmoidal, square prismatic forms 3-4 cm with twinned terminations or canted pyramid faces (Swainson and Hammond, 2001).

Stable carbon and oxygen analyses were conducted on only the residual $CaCO_3$ grains after degradation and dehydration of the ikaite (Table 1). In addition some radiocarbon analyses were also completed on the residual calcium carbonate (Table 1). Dehydrated ikaite (calcite) grains were first picked and crushed, then analyzed for carbon and oxygen isotope ratios on a Fisons Optima dual inlet, gas source mass spectrometer using an Isocarb automated carbonate preparation system. Analytical (1D) error is better than 0.05‰ for $\delta^{13}C$ and 0.1‰ for $\delta^{18}O$.

Table 1. Results of isotopic analysis on $CaCO_3$ residues derived from ikaite crystals.

Cruise: Core Depth (cm)	**$\delta^{13}C$**	**$\delta^{18}O$**	**Radiocarbon Age**
NBP 00-03 JPC 38 226-227	-3.3	na	1,986 +/- 40
JPC 38 240-241	-2.6	na	1,957 +/- 38
JPC 38 552-	0.9	na	3,580 +/- 44
JPC 38 861-864	-17.2	na	4,610 +/- 55
NBP 01-07 JPC 40 525-529	-13.46	2.71	na
JPC 40 991-993	-15.14	2.74	na
JPC 40 1704-1705	-17.89	3.19	na
JPC 40 1828	-18.11	2.78	na

Discussion

Our observations clearly indicate that there is a distinct spatial limitation to the distribution of ikaite across the Antarctic continental shelf (Fig. 1). Although the entire margin has yet to be sampled for high resolution sequences we have surveyed a significant portion of the shelf in both the Ross Sea, along the East Antarctic margin, and on both sides of the northern Antarctic Peninsula (Fig. 1). In many of these cases we have penetrated the entire post glacial record (the entire Holocene epoch) with stratigraphic thickness of 26 to 108 m (Palmer Deep).

The spatial limitation of ikaite distribution is obviously associated with the region of the Erebus and Terror Gulf a broad gulf positioned between James Ross Island, the Trinity Peninsula, and the Joinville Archipelago. Within this region there is a large sediment drift (Vega Drift) within which all of the cores containing ikaite are to be found (Fig. 2). The Vega Drift consists of a hemipelagic and pelagic deposystem with organic rich biosiliceous (diatom) mud, ice rafted debris and variations of volcaniclastic sand, derived as ash falls, ice rafting, or meltwater plums (Camerlenghi et al., 2001; Backman and Domack, 2003; Fig. 2). Total organic carbon contents within these muds often exceed 1.5 % throughout the cores. Outside of the Vega Drift deposystem ikaite crystals are reported from the hemipelagic muds of the Bransfield Strait (Fig. 1; Suess et al., 1982) and the bay south of Joinville Island (J. Wellner, personal communication, 2007). One other occurrence of ikaite is reported (isolated degraded crystal) and that is from the basal (early Holocene) section of the Palmer Deep core (ODP Leg 178, site 1098; Barker et al., 1999).

Why are ikaite crystals isolated to the Vega Drift deposits of the Erebus and Terror Gulf? We propose that the very cold waters emanating out of the Weddell Sea (core temperatures of -1.9 ^{o}C; Fig. 1) are in part controlling the ikaite formation since the stability field of ikaite is favored by temperatures near 0 °C. However, ikaite does form in other regions where the temperatures are a few degrees warmer than the Erebus and Terror Gulf (Suess et al., 1982; Grienert and Derkachev, 2004) and we do not find ikaite south of James Ross Island where temperatures are equally cold or colder. Neither do we find ikaite along the western Antarctic Peninsula where temperatures are warmer (due to the influence of Circum-Polar Deep Water; Fig. 1) but not in excess of other environments where ikaite is forming (refs as above). The other parameter involved must be the geochemical facies within the sediments of the Vega Drift. These sediments are organic rich and the region is typically a high productivity realm during the austral summer, as revealed by maxima in chlor-a concentrations shown in numerous SeaWifs images (personal observation). Hence the high organic carbon content of these sediments may also be a contributing factor, as diagenetic alteration changes the pore fluids to favor ikaite genesis. Elevated decomposition of organic matter by anaerobes within the sediment would favor high [HCO_3], [SO_4] and [PO_4] resulting in ikaite genesis over other carbonate phases (Grienert et al., 2004). The maintenance of ikaite deep within the sediment column (at least to 25 mbsf) would suggest that once ikaite forms in the muds of the Vega Drift it remains stable for some time. This observation along with the preliminary $\delta^{13}C$ measurements (Table 1) indicates that the carbon source of ikaite formation is derived from the surrounding organic matter, as it is metabolized by the microbial ecosystem as opposed to a methane derived source (such as biogenic methanogensis or clathrate disassociation). The later would be expected to yield more negative $\delta^{13}C$ values (Greinert and Derkachrv, 2004; Kodina et al., 2003; Schubert et al., 1997) and, would for the clathrate case, lead to down core decomposition of the ikaite to residual calcite (Greinert and Derkachev, 2004). It is possible that the deposits of the Vega Drift are in the earliest stages of methane seepage and therefore have not progressed to the point of ikaite recystallization described by Greinert and Derkachev, 2004).

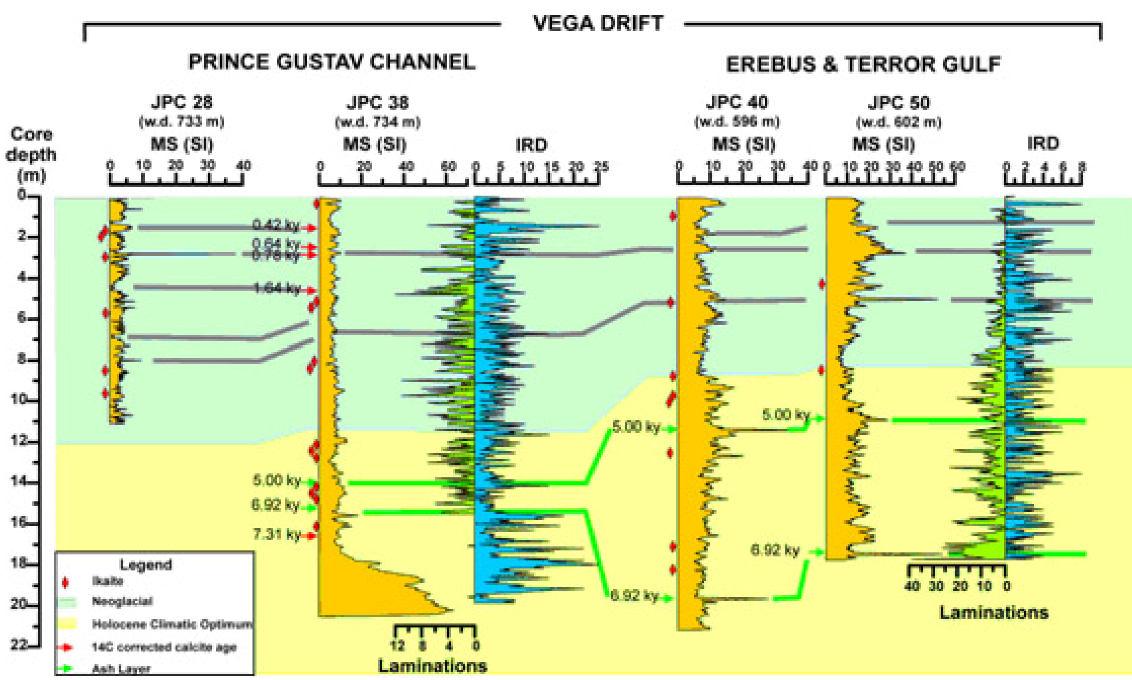

Figure 2. Stratigraphic fence diagram of key Jumbo Piston Cores (jpc) that contain ikaite crystals (shown as red diamonds). We also provide corrected calcite radiocarbon ages (red arrows), volcanic ash layers (green lines as correlated by Willmott et al., 2006), and correlations based upon physical properties (gray lines). Superimposed are paleoenvironmental periods such as the middle Holocene optimum (light yellow) and Neoglacial (light blue). JPC -28 is from LMG-05-02, JPC-38 from NBP-00-03, and JPC 40 & 50 from NBP 01-07. Other cores from and near these sites (kasten cores) with ikaite crystals are not shown in this diagram.

A key question remains however and that is why other organic rich muds found on the Antarctic continental shelf (Fig. 1) that are in temperatures well within the ikaite stability field are not yielding evidence of ikaite genesis? The answer may lie in the nature of the organic matter derived by primary production in the Erebus and Terror Gulf. The region has several other unique features including proximity to abundant glacial (sediment laden) meltwater plumes which aid in sedimenting organic particulates via flocculation (personal observation via water column video surveys). Future work needs to concentrate on the nature of primary production in this region, the fate of particulate matter through the water column (both biogenic and terrigenous), and the early diagenetic biogeochemistry of the sediment column. All of this work is currently underway (http://www.hamilton.edu/news/exp/antarctica/2006/week3.html).

Summary

Ikaite formation in Antarctic glacial marine muds is spatially limited to regions of the NW Weddell Sea (Vega Dift) and Eastern Bransfield Basin. The conditions providing this limited occurrence are related to the high regional productivity and very cold outflow of waters derived from the Weddell Sea. Early diagenetic conditions contributing to the formation and preservation of abundant Ikaite in the Vega Drift are as yet unknown although preliminary geochemical indices on degraded ikaite (calcite) indicate that alternate carbonate phases (other than ikaite) are not yet stable to depths of 10's of meters and the alkalinity is derived from microbial degradation of organic matter within the surrounding sediment, rather than methanogenesis at depth.

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