THE FATE OF THE SUBMARINE IKAITE TUFA COLUMNS IN SOUTHWEST GREENLAND UNDER CHANGING CLIMATE CONDITIONS

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ABSTRACT: Ikaite is considered a metastable mineral forming and stable only at low temperatures and therefore an indicator of low-temperature carbonate precipitation often associated with cold marine seeps. It is found world-wide but most spectacularly in Ikka Fjord in southwest Greenland as submarine carbonate tufa columns. Here, ikaite is formed as a result of submarine spring water mixing with cold seawater. As ikaite disintegrates at temperatures above 6–7°C, it has been speculated that global warming could endanger this unique habitat as well as other sites. In Ikka Fjord *in situ* water chemistry in and around an ikaite column measured continuously over two years showed that the column water is alkaline (pH > 9–10) throughout the year with temperatures of −1.3–6.0 °C and conductivities of 5.7–7.9 mS cm^{-1}, favoring year-round growth of columns at 4–5 cm per month. Short-term *in situ* measurements with needle micro sensors from both older dehydrated and calcified parts and more recently formed solid parts of an ikaite tufa column showed similar pH and temperature values, including a temperature variation over the tidal cycle. In the uppermost, recently deposited ikaite matrix, spring water escaping at the top causes passive drag of seawater into the porous ikaite matrix, leading to a mixing layer several centimeters thick that has pH values intermediate to the spring water in the column and the surrounding seawater. We conclude that the main part of the columns, consisting of fossilized ikaite (inverted to calcite) partly sealed by calcifying coralline algae and with year-round flow of alkaline freshwater through distinct channels, are resistant to warming. In the more diffuse top part of the columns, the formation of ikaite, and thus column growth, will be limited in the future due to increased fjord water temperature during the < 3 summer months a year.

INTRODUCTION

Ikaite is a rare low-temperature mineral, a metastable hexahydrate of calcium carbonate ($CaCO_3 \cdot 6H_2O$), which has been reported from contrasting environments such as high-latitude marine sediments at Bransfield Strait, Antarctica (Suess et al. 1982), the Sea of Okhotsk, Eastern Siberia (Greinert and Derkachev 2004), Mono Lake in California (Shearman et al 1989), in two spring outflows at Expedition Fiord on Axel Heiberg Island in the Canadian High Arctic (Omelon et al. 2001), and more recently as directly precipitated grains in sea ice in the Weddell Sea, Antarctica (Dieckmann et al. 2008; Dieckmann et al. 2010). There is strong evidence that ikaite, as a metastable mineral, represents a world-wide indicator of unique geochemical conditions for carbonate precipitation under low temperature.

The Ikka Fjord in Southwestern Greenland is the type locality for ikaite formation. Here, conspicuous submarine tufa columns rise high above the fjord bottom (Pauly 1963). The basic geochemistry of the columns and the surrounding zoology, botany, and microbiology has been described (Buchardt et al. 1997), on which basis the Greenland Home Rule issued a special protection for this unique habitat in 2000 due to the diverse marine habitats associated with the submarine tufa columns.

Ikka Fjord is a threshold fjord 13 km long and 1.6 km wide with two distinct parts: a deep outer fjord with a maximum depth of 175 meters

and a shallow inner fjord up to 25 meter deep. A hydrographical sill at 15 m depth separates and protects the inner part of Ikka Fjord from larger icebergs that commonly are seen in the outer fjord. Several rivers and springs discharge into the fjord and influence the surface water. The inner part of Ikka Fjord (the Ikka Column Garden, Fig. 1) harbors more than 700 individual tufa columns > 1 m tall within an area of 3 km × 0.5 km (Buchardt et al. 1997; Buchardt et al. 2001). The columns are rooted in muddy sediments and typically occur in clusters, forming structures up to 18 m tall that range from a few centimeters to several meters in diameter (Seaman and Buchardt 2006). The older basal parts of the columns are encrusted by coralline red algae (*Clathromorphum* spp. and *Lithothamnion* spp.) stabilizing the column structures. Around the base of the columns, talus cones of tufa debris are formed. These talus cones may be several meters in diameter and are frequently cemented into hard buildups by secondary mineralization and encrusting organisms. Older parts of the columns are partly or completely recrystallized into calcite and monohydrocalcite (Dahl and Buchardt 2006).

The ikaite tufa columns form when alkaline submarine spring water seeps through the fjord sea bottom sediment and mixes with cold seawater (Buchardt et al. 1997). The spring water has been characterized (Buchardt et al. 2001) as a sodium-bicarbonate–carbonate brine with high alkalinity (150–175 mmol l^{-1}), high pH (10.2–10.5), high molar Mg/Ca ratios
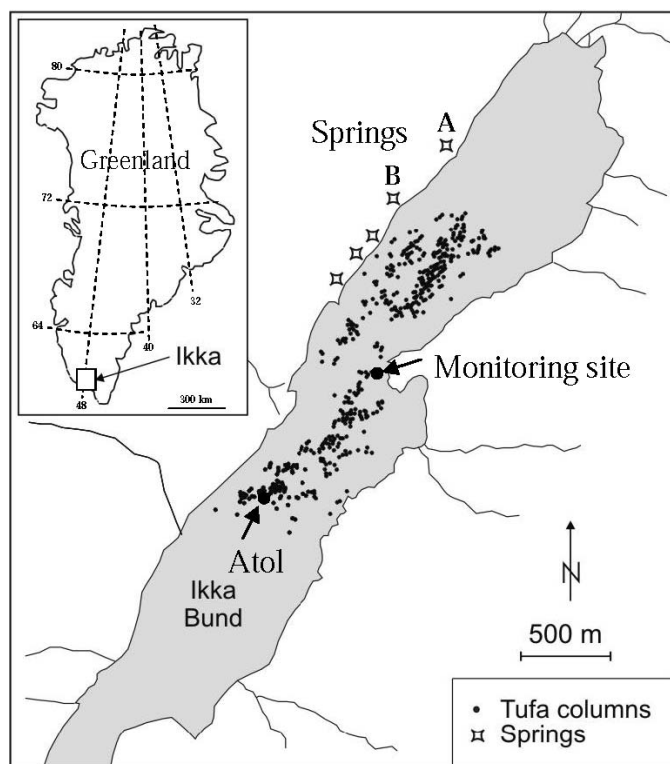
FIG. 1.—Map of Ikka Fjord and surrounding areas, and the distribution of major tufa columns in the Ikka Column Garden and springs in Ikka Fjord. Inset shows the location of the focus area in southwest Greenland.

($>$ 12), and elevated PO_4^{3-} (25 ppm) as compared to the local fjord water (alkalinity: 2.1 mmol l^{-1}, pH: 7.9, PO_4^{3-} < 1 ppm). Supersaturation with regard to ikaite, calcite, and aragonite develops where spring water and seawater mix, and neutral $CaCO_3^\circ$ ion pairs are incorporated into a clathrate structure bound by hydrogen bonds (Buchardt et al. 2001). Ikaite precipitation is favored by low temperatures and high phosphate ion concentration in the spring water, which is known to inhibit crystallization of calcite and aragonite and thereby favoring the precipitation of ikaite (Shearman et al. 1989; Bishoff et al. 1993).

The submarine spring water is of meteoric origin (Buchardt et al. 2001) and is generated from deep aquifers developed in the surrounding 1300 Ma Grønnedal Ika igneous complex, an elongated body of carbonatite and nepheline syenite intruded into Archean gneisses (Blaxland et al. 1978). The carbonatite is composed of calcite and siderite with apatite (P_2O_5 up to 3.6% weight) as a minor component (Pearce et al. 1997). The peculiar chemistry of the submarine spring water is most likely related to dissolution of secondary Na-carbonate minerals formed within the complex, where Na has been derived from dissolution of nepheline (Buchardt et al. 2001).

The mineral ikaite is stable only at temperatures below 6–7°C (Marland 1975; Bischoff et al. 1993; Buchardt et al. 2001) and recrystallizes rapidly to calcite or other carbonate minerals above this temperature (Dahl and Buchardt 2006). The presence of > 1000 individual ikaite tufa columns in Ikka Fjord (Seaman and Buchardt 2007) suggest that water temperatures in the fjord generally are below these temperatures. However, model calculations on future effects of global warming in the southern Greenland region point to increasing summer water temperature (Christiansen et al. 2007), which raise concern over the stability and fate of the tufa columns in the future. Therefore, a monitoring project initiated in 2006 detailed physical–chemical parameters over a full-year cycle in the Ikka fjord, in the fjord water, and inside the columns themselves. Visits to the fjord had previously been limited to the summer months (June to August).

This study reports data from three summer expeditions (2007–2009), one fall expedition in October 2007, and the first winter expedition to the fjord in April 2008. We hypothesized that water flow through the columns is reduced during winter time, causing seasonality in their formation rates, and that future ikaite formation may therefore be limited depending on summer to winter formation rates. This paper describes the results of the first *in situ* full year monitoring program (over two years) and the first winter observations of the fjord system, along with first *in situ* microsensor measurements of temperature and pH in different parts of the columns during short-term deployments over tidal cycles. Integration of these new data with earlier results and observations motivate a conceptual model of water flow and growth in ikaite tufa columns that has implications regarding their susceptibility to climate change.

METHODS

Temperature Data

Air temperatures in Ikka Fjord were measured in two hour intervals from August 2006 to August 2007 at a coastal station close to the Camp Field site (coordinates 61° 11.76′ N; 48° 01.27′ W) using a Tinytag Plus high-resolution zero-off calibrated temperature data logger (Gemini Data Loggers, Ltd., UK). For comparison, air temperature data for 2006, 2007, and 2008 from the climate station at the Danish naval base at nearby Grønnedal (less than 10 km away) were obtained from Greenland's Kommando (GLK). The two sets of air temperatures were correlated on a monthly basis (August 2006 to August 2007) to produce regression equations for the period. Incomplete air temperatures from the nearby abandoned mining town of Ivittuut were available for a longer period (1958 to 1997, Danish Meteorological Institute DMI, Cappelen et al. 2001). Combining the data from Ikka Fjord, Grønnedal, and Ivittuut, we estimated the monthly and mean annual air temperatures for Ikka fjord over a period from 1961 to 2008. Finally, the air temperatures from Ikka Fjord for 2007 and 2008 were correlated with water temperatures from the reference station at the Camp Field site. By correlating observed air and water temperatures from Ikka Fjord and the above described estimated monthly air temperatures for Ikka Fjord (1961–2008), monthly mean values of water temperatures in Ikka Fjord were estimated for the period from 1961 to 2008.

Ice Cover

The winter ice cover of Ikka Fjord was monitored during the winter 2006–2007 using a custom automatic digital camera (see Christiansen 2001) that collected photos on a daily basis. The pictures were used to estimate when solid ice was established in autumn 2006 and when it broke up in summer 2007. Ice thickness was measured at six different locations in a transect across the inner part of Ikka Fjord during the winter expedition in April 2008.

Hydrographical Data

Temperature and salinity profiles were measured at six positions in the inner fjord (Ikka Bund, Fig. 1) during the summer expedition in July 2007 using a calibrated conductivity, temperature and depth (CTD) instrument (CTD-Diver, Van Essen Instruments, Germany). Two temperature profiles were measured during winter (April 5, 2008) near the Atoll complex and in the outer fjord using calibrated temperature–light data loggers (HOBO Pendant, ONSET, MA, USA). Conductivity readings were converted to salinity using standard algorithms (Fofonoff and Millard 1983).

Analysis of Terrestrial Spring Water

Values of pH (SenTix 41, pH meter 315i; Wissenschaftlich-technische Werkstätten, Germany) and conductivity (con 325, cond340i; Wissenschaftlich-technische Werkstätten, Germany) were measured directly in two terrestrial springs (A and B, Fig. 1). The temperature was monitored at two-hour intervals from August 2006 until July 2007 using autonomous temperature loggers (Tinytag Plus high resolution data logger, Gemini Data Loggers, Ltd., UK).

Long-Term Underwater Measurements

Temperature, conductivity, and pH of the column spring water was monitored inside a tufa column (7.3 m high and 0.35 m wide at the insertion height of sensors) standing approximately 20 meters from the coastline at a water depth of 9.5 m at the Camp Field site (Fig. 1). The monitoring was done automatically with a three-hour interval using an underwater data logger system (Data logger 3660, Aanderaa Data Instruments, Norway) and calibrated sensors (Conductivity/Temperature Sensor 4119, pH-Sensor 3264; Aanderaa Data Instruments, Norway).

Holes (5 cm in diameter) were drilled into the column with a pneumatic drill and the sensors were placed in the holes pointing towards the center of the column at a height of $\sim$ 1 m above the seafloor. The fitted sensors were sealed into the ikaite matrix using linseed oil putty. A seawater reference station was placed $\sim$ 2 m from the column with sensors mounted $\sim$ 1 m above the seafloor. All sensors were connected with waterproof cables to the data logger, which was placed in a watertight metal cylinder on the bottom of the fjord. Data were stored on a data storage unit (DSU 2990; Aanderaa Data Instruments, Norway), which was changed during each field campaign. Non-steady measurements related to the disturbance of the internal flow system due to sensor installation were noted. During the first nine months (July 2007 to April 2008), the pH value increased steadily from 9.84 to 10.23 but remained stable between 10.23 and 10.25 for the following 15 months (April 2008 to July 2009). A CTD-sensor (Schlumberger Water Services, UK) logging every hour from July to October 2007 was placed at the reference station for monitoring tidal effects.

Short-Term in situ Measurements

A column on the Atoll site (Fig. 1) was selected for detailed monitoring of temperature and pH in the ikaite matrix at different heights above the column base, i.e., in the solid fossilized base of the column, in the relatively new ikaite higher up on the column, and in the freshly forming ikaite in the column top. Small holes ($\sim$ 17 mm diameter) were drilled with an underwater pneumatic drill at each depth horizon, and a 20-cm-long nylon cylinder (15 mm inner diameter) was inserted into each hole. The cylinder acted as a guide for the needle pH and temperature underwater microsensors (Unisense A/S, Denmark), which were inserted until a silicone rubber ring on the sensor shaft sealed the cylinder with the sensor tip briefly inserted into the central ikaite column matrix. Additional sealing around the insertion point of the cylinder used linseed-oil putty. Subsequent visual inspection showed no leakage of low-salinity spring water into the surrounding seawater. Additional point measurements of pH were collected by gently pushing the pH needle microsensor into the porous freshly formed ikaite on the column top and taking readings at $\sim$ 2 cm and $\sim$ 5–6 cm depth.

The temperature and pH microsensors and an Ag/AgCl reference electrode were connected via water-tight connectors to a diver-operated underwater data logger (UW-Meter, Unisense A/S, Denmark). Prior to deployment, the temperature microsensor was linearly calibrated in water at different temperatures as monitored with a calibrated electronic thermometer (TermoTesto 110, Testo AG, Germany), and the pH microsensor mV signal was linearly calibrated from readings in standard pH buffers (pH 4, 7, and 10) showing a nearly Nernstian response of 53–57 mV per pH unit. Initial *in situ* tests were done with an underwater cable connection to the surface, where sensor signals were recorded on a battery-operated strip-chart recorder (Servogor 110, Gossen-Metrawatt, Austria) placed on the dive platform, which was anchored above the site. Sensor signals during later deployments were monitored by the diver on the display of the underwater meter and communicated to the surface line-holder via a diver phone. Before insertion into the guiding cylinders, a reading of sensor signals in the surrounding seawater was recorded, and once a stable sensor reading was obtained after insertion to the column the data logger was deployed, recording at 1 min intervals for a period of 8–20 hours depending on the actual battery capacity of the meter.

Tufa Column Water Flow and Growth Rates

The flow rate of the submarine spring water was estimated on three active columns near the Atoll complex (Fig. 1). One column was cut at 8 m depth approximately one meter above the base, while the two others were kept intact. Twenty-liter plastic bags were placed over the columns and sealed from the surrounding seawater. Within 48 hours the bags were filled, mainly with water of lower density than the surrounding seawater. The bags were sealed and brought to the surface, where the amount of water in each bag was determined. The water was later identified as a mixture of alkaline fresh water (spring water) and seawater. Seawater admixture was estimated from the oxygen isotopic composition of the water (Buchardt et al. 2001). The rate of ikaite formation over winter was monitored over a period of nine months from July 2007 to April 2008 by cutting the top part of the Atoll column and subsequently measuring the vertical growth. This measure is considered a potential growth rate rather than an actual growth rate in that the cutting minimized the flow resistance in the column. Samples collected from columns were all kept frozen and transported to Copenhagen for further analysis. The presence of ikaite was identified using X-ray diffraction on frozen samples that were ground and mounted in the freezer (according to the method described by Dahl and Buchardt 2006).

RESULTS

Climatic Trends

Because no continuous air-temperature records exist for Ikka Fjord except for the years 2007 and 2008, we estimated the long term temperature trends in the fjord area by integration with other temperature data sets as discussed above. Our estimates suggest that the mean annual air temperature in Ikka Fjord from 1961 to 2008 ranged from -1.9 °C (1972) to $+2.9$ °C (1985). A trend line based on annual mean air temperatures for the three warmest months (June to August) in the area from 1961 to 2007 (Fig. 2) suggests roughly an increase in summer air temperature of $\sim$ 0.3°C per decade ($R^2 = 0.65$). Based on the relation between observed air and fjord water temperatures in Ikka Fjord in 2007 and 2008, this increase would be equal to a fjord water summer temperature increase close to 0.1°C per decade since 1961. These estimates are very rough numbers and should not be used to document climate changes in the region.

Terrestrial Springs

The terrestrial springs at sites A and B are homothermal with mean annual water temperatures close to 3.4°C (Fig. 3). Temperatures in 2007–2008 varied from 0.9°C to 5.9°C in spring A and from 2.2°C to 4.1°C in spring B. Three distinct temperature cooling events were recorded in both springs on 23 January, 20 March, and 3 April 2008, immediately after positive air temperatures. These warm events may have caused cold melt water from the surroundings to affect spring temperatures. Both springs
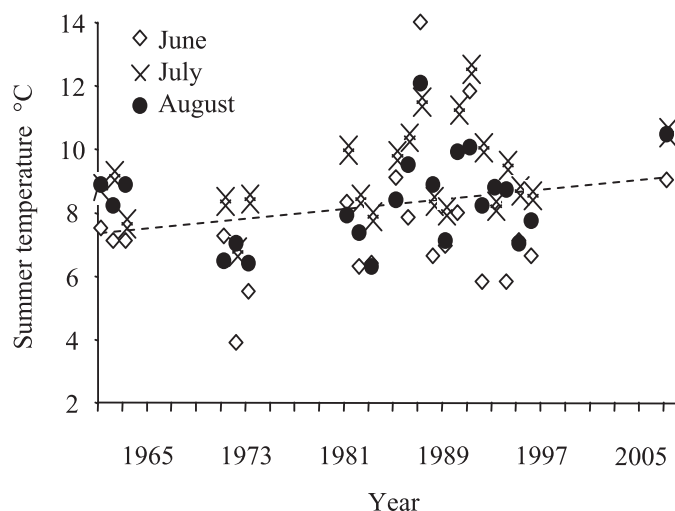
F<small>IG</small>. 2.—Plot of mean air temperature in the warmest three months of the year between 1961 and 2008. The dashed line represents the trend for the month of July.

were analyzed during the winter expedition, on 5 April 2008. These chemical analyses of the spring water showed low values of conductivity and neutral pH values (Table 1).

Hydrography of Ikka Fjord

Hydrographical observations from July 2007 at six stations in the fjord confirmed earlier data (Buchardt et al. 2001) indicating that the fjord is stratified during the summer months into three main horizontal water bodies (Fig. 4): (1) a thin brackish surface water layer ∼ 2 m deep (zone 1) with relatively high temperatures, (2) a thicker thermocline and halocline layer ∼ 4 m deep (zone 2), with dramatic change in temperature and salinity, and (3) the underlying sea-water body (zone 3) with high salinity and slowly decreasing temperatures with depth. Highest and lowest water temperatures measured in July 2007 were 13.2°C in zone 1 and 3.5°C in zone 3. Correspondingly, salinity increased from < 5‰ in zone 1 to 32.8‰ in zone 3. The brackish-water body is a result of river runoff, mainly in the innermost part of the fjord, whereas sea water originates in the Davis Strait with influence from the East Greenland current.

During the winter of 2006–2007, the first ice was observed on October 14, 2006 and the inner Ikka Fjord was ice covered for 172 days from October 23, 2006 to April 12, 2007. The inner fjord was completely ice covered during the winter expedition in April 2008 and the ice thickness was measured to between 53 and 90 cm. A marked halocline between fresh and salt water was found about one meter below the ice. Observed temperatures dropped from 0.0°C in the top layer to around −0.8°C at 4 m depth.

Column Characteristics

During the 2007 and 2008 expeditions, visual underwater inspection of columns was restricted to two areas in the fjord: the Atoll complex and

the Camp Field site (Fig. 1). Detailed and repeated visual *in situ* inspections of selected columns and analyses of column fractions cut off as part of the flow measurements (Atoll site only) showed rather contrasting column conditions with height (Fig. 4). The cemented base of the monitoring column could be followed more than 0.5 m below the sediment surface and became more than twice as wide as at the sediment–water interface. The lower third of the exposed column was completely covered by crustose coralline red algae. Laboratory investigations of a similar column fragment showed that the stability and structure were unaffected after 14 days in seawater at 16.3°C with a mass loss of < 1%. Half way up on the monitoring column coralline algae were less dominant and clean mineral surfaces occur. Analysis of a mid-fragment from a nearby column revealed that the stability and structure remained the same after 14 days in seawater at 16.3°C and with a mass loss of < 1%. The uppermost ∼ 30% of the columns were generally free of coralline algae, probably as a result of the grazing action by abundant sea urchins (*Strongylocentrotus* sp.), and appeared completely white. Samples of the column top incubated for 14 days were either completely or partly decomposed when incubated at 9°C or 7.5°C, respectively. X-ray diffraction analyses of a freshly formed part of a column apex revealed the dominance of ikaite with only traces of calcite. New column tops growing over the cutting surfaces also consisted of pure ikaite.

Temporal Trends in Seawater and the Monitoring Column

Seawater temperature, salinity, and pH measured at the reference station (Camp Field site, 8.5 m depth) during a two-year period from 2007 to 2009 exhibited seasonal temperature variations over the year. In contrast, measurements of water chemistry in the base of the monitoring column over two years (Fig. 5) showed that the conductivity and pH inside the column remained constant and were not influenced by changes in the surrounding water. The mean pH value (± standard deviation) in the column was pH 10.1 (± 0.05), and pH 8.1 (± 0.1) at the reference station. No correlations were evident between pH measured in the column and those in the surrounding fjord water. Water in the column had a conductivity of 6.7 (± 0.5) mS cm^{-1}, whereas the fjord water had a mean conductivity of 27.5 (± 1.1) mS cm^{-1}. The mean annual water temperature inside the column was similar to the surrounding sea water, i.e. 1.8 (± 2.0) °C.

Column Water Chemistry Based on Microelectrodes

Short-term *in situ* microsensor measurements of pH and temperature in a tufa column showed some differences between the basal part with distinct flow channels in a fossilized ikaite matrix sealed off from the seawater, and the upper part consisting of a porous and looser layer of fresh ikaite (Fig. 6). While pH showed a constant high value of ∼ pH 9.8 in the upper part, pH fluctuated between pH 9 and pH 10 in the more basal part of the column, possibly reflecting non-steady-state conditions after insertion of the pH sensor. Temperature in the tufa column varied from 3–5°C in the lower parts and from 6–8°C in the upper parts following the overall temperature profile in the surrounding water. Highest temperatures were observed during incoming tides, whereas
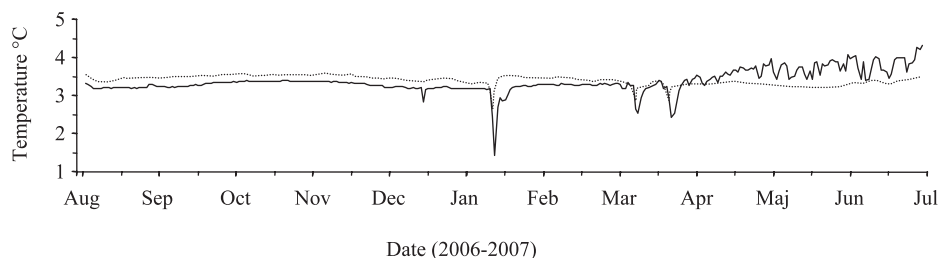

F<small>IG</small>. 3.—Data illustrating spring water temperature measured at site A (black line) and site B (dashed line) (see Fig. 1) between 15 August 2006 and 9 July 2007.

TABLE 1.— *Water-body characteristics in Ikka Fjord.*

Type of water	Spring	Spring	Column	Sea	Sea
Area	Intrusion	Intrusion	Fjord	Fjord	Fjord
Locality	Spring A	Spring B	Camp	Camp	Mid fjord
Avg. temperature, °C	3.4	3.4	2.9	2.7	–
Max. temperature, °C	4.3	3.6	10.4	8.1	13.2
Min. temperature, °C	1.4	2.6	−1.3	−1.3	0.8
Conductivity, mS cm^{-1}	0.11	0.15	6.9	27.9	0–32.3
pH	7.4	7.5	10.3	8.2	–
Salinity, ‰	–	–	–	–	0–32.8

lowest temperatures were measured during outgoing tides in the Ikka Fjord. Manual pH measurements in the uppermost porous ikaite matrix showed pH 9.3 ± 0.2 (mean ± st.dev.; n = 5) about 2 cm below the tufa surface, and pH 10.2 ± 0.4 (mean ± st.dev.; n = 4) about 5–6 cm below the tufa surface, thus indicating the presence of an outer zone in the ikaite matrix where mixing of seawater and spring water occurs.

Flow and Growth Rates

Column apexes showed outflow of low-density water at a flow rate strong enough to create water turbulence that was visually evident. Underwater inspection of the top sections of several columns indicated that all had an internal vertical channel system. The flow of water through column 2 (the one being cut) measured by the plastic bag method was estimated to be 112 cm^3 per hour. Repeated visits during the four expeditions in 2007 and 2008 showed that column 2 grew at an almost constant rate of 4–5 cm vertical height per month (Fig. 7), i.e., 50–60 cm per year, with a mass growth of ~ 61 g per month (a total of 2133 g over 174 days). Calculating the mass growth as carbonate (in CaCO$_3$ · 6H$_2$O), the mass of ikaite equals 10.25 moles of carbonate per year, i.e., about 7% of the total amount of carbonate released from the column (assuming 112 cm^3 water being released per hour year round with a mean carbonate concentration of 153 mM according to Buchardt et al. 1997).

DISCUSSION AND CONCLUSIONS

Climate Change and Fjord Water Temperature

Our estimated air-temperature variations in Ikka Fjord (1961–2008) are in line with the general climate variations observed in West Greenland (Box 2002). The increasing summer temperature (June, July, and August) of approximately 0.3°C per decade, and the corresponding estimated summer temperature increase in the fjord water of 0.1°C per decade, will eventually influence ikaite formation. Average water temperature at 8 meter depth was 2.7°C in 2007 and 2008 and 3.2°C in 2008 and 2009, which is far below the critical temperatures for ikaite of 6–7°C. Effects of increasing summer fjord water temperatures above the critical temperature for ikaite formation will be noted first in columns within the upper 6 m of the water column. However, large uncertainties exist on how much increasing air temperature will influence fjord water temperature as compared to the influence of salt water from large scale circulation and cold melt water from land.

Sensitivity to Climate Changes and Conclusions

Once steady-state conditions were established after drilling, *in situ* water conductivity, pH, and temperature inside the column were constant over two years, in contrast to the conditions in the fjord water. These
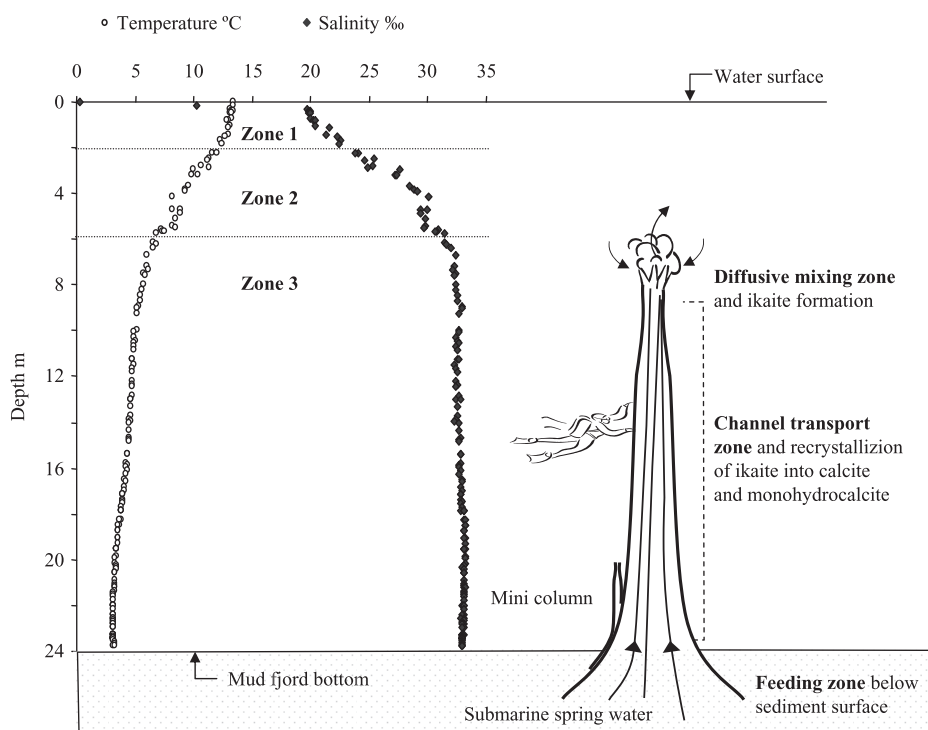

FIG. 4.—Conceptual model for the zones of an ikaite tufa column. The spring water is more buoyant than seawater and flows upwards in flow channels inside the column. Ikaite is precipitated in the mixing zone at the column apex where spring water mixes with seawater. Lowermost parts of the column are stabilized over time due to recrystallization of ikaite forming calcite and monohydrocalcite as well as growth of crustose coralline algae on the columns (the diver is not to scale).
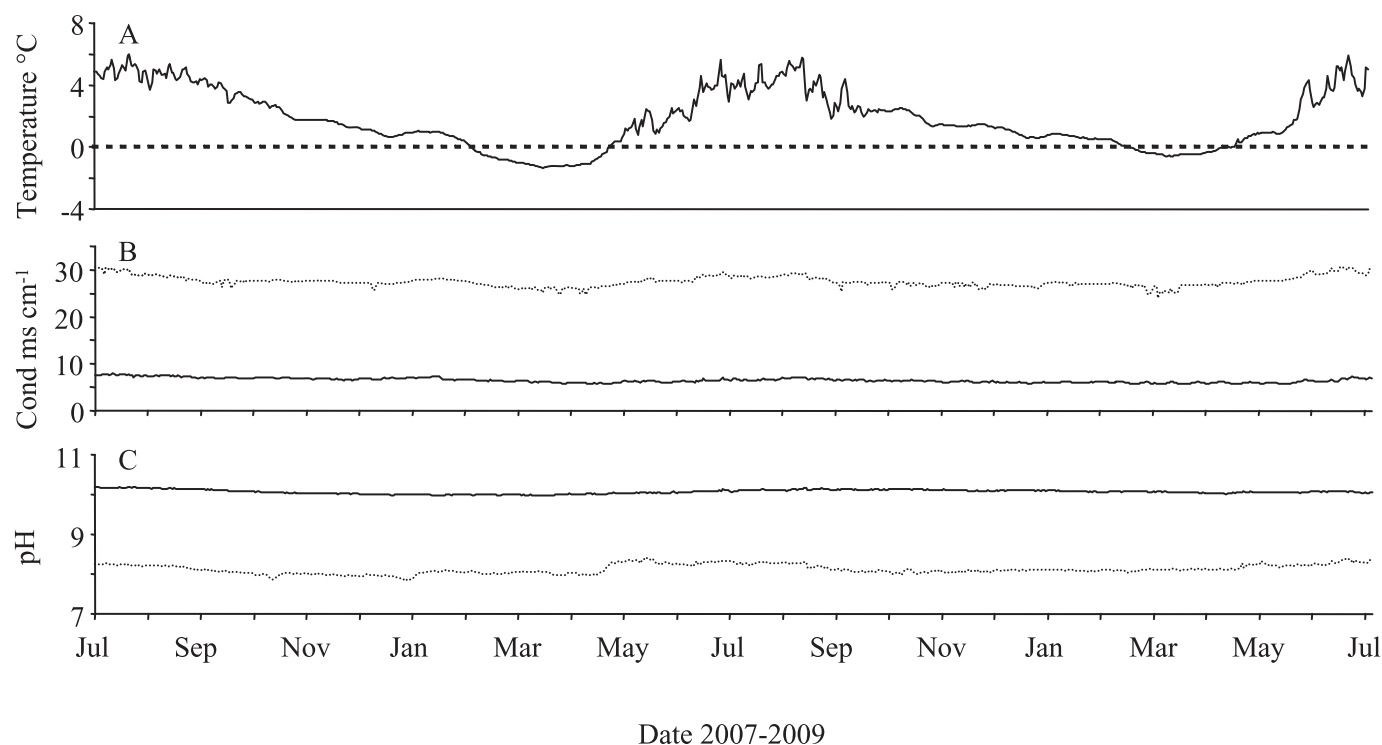
FIG. 5.—Characteristics (daily means) of fjord water (dashed lines) and Ikka column water (solid lines) measured at 8.7 m depth over two years starting July 2007. **A)** Temperature, **B)** conductivity, and **C)** pH.

observations suggest a continuous flow of water inside the tufa columns year round, consistent with measurements of column growth rates suggesting that columns grow continuously at a nearly constant rate of 4–5 cm month^{-1}. This implies that also the spring water feeding into the base of the ikaite columns is running almost constant year round. In fact, terrestrial homothermic springs were observed to run throughout the year; however, these or similar terrestrial homothermic springs are not

considered the main source for the water feeding into the base of the ikaite columns due to contrasting chemistry of the terrestrial homothermic springs and the water collected from the ikaite columns.

Short-term *in situ* measurements with needle microsensors inserted into older parts of an Ikka column showed generally similar pH and temperature values over the two-year period. Coarse-scale pH profiling in the uppermost fresh ikaite matrix showed pH values between those of
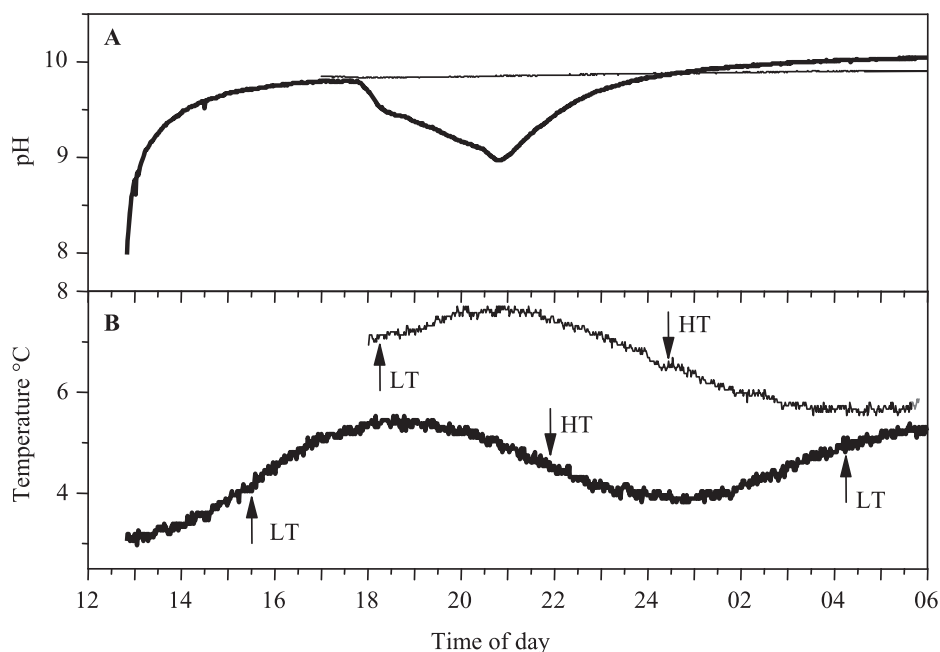

FIG. 6.—Short-term *in situ* measurements of pH and temperature with needle microsensors inserted into the base (thick lines, measured on July 7 and 8, 2008) and upper part (thin lines, measured on July 10 and 11, 2008) of an Ikka column. Arrows indicate time of low tide (LT) and high tide (HT) in Ikka fjord on the measuring days.

Fig. 7.—Photos showing time steps in the column growth experiment. **A)** the original column prior to the cut in July, 2007, **B)** the base of the column after cutting July 6, 2007, **C)** the newly formed ikaite cut away after 100 days, and **D)** the newly formed ikaite cut away after another 173 days. A well-defined flow system remains open within the column, as seen from the edges after cutting.

spring water and seawater in the outermost 2 cm of the matrix, whereas the pH 5–6 cm below the outer surface reached spring-water pH values. We speculate that spring water escaping at the apex of the tufa columns causes passive flow of seawater into the outer porous ikaite matrix, facilitating a mixing of seawater and spring water. This process would thereby enhance rapid ikaite formation and fast vertical growth rates of the tufa columns (Fig. 3).

An average potential growth rate of half a meter per year measured at several cut columns is similar to earlier estimates based on growth from cut surfaces (Buchardt et al. 2001). Growth of unaffected tufa columns may be considerably lower due to more restricted flow and interaction with seawater, but even with a 10 times slower growth rate a column 2 m high would have a maximal age of 40 to 50 years, during which time the lowermost two thirds of the column becomes stabilized due to encrustation and replacement of ikaite. Columns with such fast growth rates should have reached the surface of the water if not for the combined action of sea ice and tides during winter that erode the top of the longest columns. Such column erosion by fjord ice was observed directly during winter 2008.

The spectacular submarine carbonate tufa columns formed by carbonate precipitation of ikaite in the Ikka Fjord are protected by law due to their uniqueness of marine biodiversity associated with the tufa columns. In the light of recent and predicted climatic changes in the Arctic, it is crucial to evaluate the resilience of the columns and their highly temperature-sensitive growth. The evaluation presented here combines new techniques and provides a unique high-resolution data set with respect to *in situ* water chemistry in and around ikaite columns. Results document that the main part of the columns are resistant to warming as they consist mainly of fossilized ikaite, which is not sensitive to temperatures. Nonetheless, the formation of ikaite in the more diffuse top of the columns could be limited in the future due to increasing summer fjord water temperature, but only during the short summer where water temperatures may increase to levels above critical for ikaite formation. Winter ikaite formation thus seems to be important for ongoing column formation and the unique biogeochemical environment that harbors an extreme and partly endemic microbial community (Schmidt et al. 2006).

Ikaite has been identified as an indicator mineral for carbonate precipitation at low temperatures worldwide and in contrasting environments. The presence of ikaite indicates very recent formation and/or continuous low temperatures after formation. This has several implications, as shown by Mikkelsen et al. (1999), e.g., ikaite can be formed on a short-term basis as white spots in the shells of frozen shrimp during storage and within hours transform into a mixture of anhydrous calcium carbonate forms after being kept at room temperature. Similarly, at Mono Lake ikaite is formed during the cold winter time at the lake shore line but disappears during spring time (Shearman et al 1989). In both cases rapid disintegration after warming have destroyed the physical, chemical, and isotopic evidence of formation, and alters the geochemical record as for the frozen shrimp (Mikkelsen et al. 1999). In Ikka Fjord in Greenland, our observations suggest that Ikaite will be formed year-round but that ikaite formed in the upper part of the water column most likely will degrade under warmer climate conditions as current water temperatures are near the threshold temperatures during the summer. Thus, ikaite formation will be followed by disintegration in an annual cycling (similar to present day shore line at Mono Lake). At greater water depths in Ikka Fjord, formed ikaite will be kept year-round below the threshold temperature and, therefore, slowly recrystallize to form calcium carbonate, consequently leaving pseudomorphs of the primary precipitate. This has important implication for other sites, e.g., in the Mono Lake basin, where Pleistocene and Holocene tufas may originally have been precipitated as ikaite.

Future investigations on metastable mineral formation as ikaite at near threshold temperatures require high-resolution temporal water-chemistry data as presented here, in order to quantify the importance of mineral formation on a seasonal basis. In Ikka Fjord as other places, the presence of rare low-temperature minerals may increasingly rely on formation during the cold season.

REFERENCES

BISCHOFF, J.L., STINE, S., ROSENBAUER, R.J., FITZPATRICK, J.A., AND STAFFORD, T.W., 1993, Ikaite precipitation by mixing of shoreline springs and lake water, Mono Lake, California, USA: Geochimica et Cosmochimica Acta, v. 57, p. 3855–3865.

BLAXLAND, A.B., VAN BREEMEN, O., EMELEUS, C.H., AND ANDERSON, J.G., 1978, Age and origin of the major syenite centres in the Gardar province of South Greenland: Rn-Sr studies: Geological Society of America, Bulletin, v. 89, p. 231–244.

BOX, J.E., 2002, Survey of Greenland instrumental temperature records: 1873–2001: International Journal of Climatology, v. 22, p. 1829–1847.

BUCHARDT, B., SEAMAN, P., STOCKMANN, G., VOUS, M., VILKEN, U., DÜVEL, L., KRISTIANSEN, A., JENNER, C., WHITICAR, M.J., KRISTENSEN, R.M., PETERSEN, G.H., AND THORBJØRN, L., 1997, Submarine columns of ikaite tufa: Nature, v. 390, p. 129–130.

BUCHARDT, B., ISRAELSON, C., SEAMAN, P., AND STOCKMANN, G., 2001, Ikaite tufa towers in Ikka Fjord, Southwest Greenland: their formation by mixing of seawater and alkaline spring water: Journal of Sedimentary Research, v. 71, p. 176–189.

CAPPELEN, J., JØRGENSEN, B.V., LAURSEN, E.V., STANNIUS, L.S., AND THOMSEN, R.S., 2001, The observed climate of Greenland, 1958–99 with climatological normals, 1961–90: Danish Meteorological Institute, Technical Report 00-18, 152 p.

CHRISTENSEN, J.H., HEWITSON, B., BUSUIOC, A., CHEN, A., GAO, X., HELD, I., JONES, R., KOLLI, R.K., KWON, W.-T., LAPRISE, R., MAGAÑA RUEDA, V., MEARNS, L., MENÉNDEZ, C.G., RÄISÄNEN, J., RINKE, A., SARR, A., AND WHETTON, P., 2007, Regional Climate Projections, *in* Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., and Miller, H.L., eds., Climate Change 2007: The Physical Science Basis: Contribution of Working Group I, Fourth Assessment Report, Intergovernmental Panel on Climate Change, Cambridge, U.K., Cambridge University Press, p. 847–940.

CHRISTIANSEN, H.H., 2001, Snow-cover depth, distribution and duration data from northeast Greenland obtained by continuous automatic digital photography: Annals of Glaciology, v. 32, p. 102–108.

DAHL, K., AND BUCHARDT, B., 2006, Monohydrocalcite in the arctic Ikka Fjord, SW Greenland: first reported marine occurrence: Journal of Sedimentary Research, v. 76, p. 460–471.

DIECKMANN, G.S., NEHRKE, G., PAPADIMITRIOU, S., GÖTTLICHER, J., STEININGER, R., KENNEDY, H., WOLF-GLADROW, D., AND THOMAS, D.N., 2008, Calcium carbonate as ikaite crystals in Antarctic sea ice: Geophysical Research Letters, v. 35, L08501.

DIECKMANN, G.S., NEHRKE, G., UHLIG, C., GÖTTLICHER, J., GERLAND, S., GRANSKOG, M.A., AND THOMAS, D.N., 2010, Ikaite ($CaCO_3 \cdot 6H_2O$) discovered in Arctic sea ice: The Cryosphere, v. 4, p. 227–230.

FOFONOFF, P., AND MILLARD, JR., R.C., 1983, Algorithms for computation of fundamental properties of seawater: UNESCO, Technical Papers in Marine Science, v. 44, 53 p.

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.

MARLAND, G., 1975, The stability of $CaCO_3 \cdot 6H_2O$ (ikaite): Geochimica et Cosmochimica Acta, v. 39, p. 83–91.

MIKKELSEN, A., ANDERSEN, A.B., ENGELSEN, S.B., HANSEN, H.C.B., LARSEN, O., AND SKIBSTED, L.H., 1999, Presence and dehydration of ikaite, calcium carbonate hexahydrate, in frozen shrimp shell: Journal of Agricultural Food Chemistry, v. 47, p. 911–917.

OMELON, C.R., POLLARD, W.H., AND MARION, G.M., 2001, Seasonal formation of ikaite ($CaCO_2 \times 6(H_2O)$) in saline spring discharge at Expedition Fiord, Canadian High Arctic: assessing conditional constraints for natural crystal growth: Geochimica et Cosmochimica Acta, v. 65, p. 1429–1437.

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

PEARCE, N.J.G., LENG, M.J., EMELEUS, C.H., AND BEDFORD, C.M., 1997, The origins of carbonatites and related rocks from the Grønnedal–Ika Nepheline Syenite complex, South Greenland: C-O-Sr isotope evidence: Mineralogical Magazine, v. 61, p. 515–529.

SEAMAN, P., AND BUCHARDT, B., 2006, The morphology and distribution of ikaite tufa column in Ikka Fjord, southwest Greenland: Meddelelser om Grønland, Geoscience, v. 44, 38 p.

SCHMIDT, M., PRIEMÉ, A., AND STOUGAARD, P., 2006, Bacterial diversity in permanently cold and alkaline ikaite columns from Greenland: Extremophiles, v. 10, p. 551–562.

SHEARMAN, D.J., MCGUGAN, A., STEIN, C., AND SMITH, A.J., 1989, Ikaite, CaCO₃ × 6H₂O, precursor of the thinolites in the Quaternary tufas and tufa mounds of the Lahontan and Mono Lake basins, Western United States: Geological Society of America, Bulletin, v. 101, p. 913–917.

SUESS, E., BALZER, W., HESSE, K.F., MULLER, P.J., AND WEFER, G., 1982, Calcium carbonate hexahydrate from organic-rich sediments of the Antarctic Shelf: precursor of glendonites: Science, v. 1216, p. 1128–1131.