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MONOHYDROCALCITE IN THE ARCTIC IKKA FJORD, SW GREENLAND: FIRST REPORTED MARINE OCCURRENCE

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ABSTRACT: **Monohydrocalcite (MHC) has previously been known only from fresh-water and terrestrial environments. However, as documented in the present paper, MHC is a common mineral (up to 55%) in debris fragments from submarine ikaite ($CaCO_3 \cdot 6H_2O$) tufa columns in the cold marine Ikka fjord, SW Greenland. The columns form where alkaline fresh water from submarine springs mixes with cold seawater and precipitates ikaite. Petrographical and geochemical data indicate that MHC represents a transitional diagenetic phase in the recrystallization process of metastable ikaite to final calcite. The stable-isotope data ($\delta^{13}C$ and $\delta^{18}O$) document a closer relationship of MHC with the precursor ikaite than with calcite. Replacement of ikaite by MHC is suggested to take place by dissolution and precipitation in a semi-closed pore-water system dominated by alkaline spring water and with only limited access of seawater. In this environment, nucleation of calcite is inhibited by phosphate ions. Apart from calcite, aragonite and hydrous Mg carbonates were also observed in the tufa debris. The Mg carbonates represent late diagenetic phases, probably formed from recrystallization of MCH in normal seawater environments.**

INTRODUCTION

Monohydrocalcite ($CaCO_3 \cdot H_2O$) is a common mineral found in talus cones around tufa columns in the marine Ikka Fjord, SW Greenland. The mineral is well known from fresh-water deposits but has not previously been described from marine environments. Ikka Fjord is the type locality of the metastable calcium carbonate hexahydrate ($CaCO_3 \cdot 6H_2O$) ikaite, which forms spectacular columnar tufa buildups in the fjord (Pauly 1963a, 1963b). Danish and British surveys were carried out in Ikka Fjord in the summers of 1995 to1997 (Buchardt et al. 1997; Seaman 1998; Buchardt et al. 2001; Seaman and Buchardt 2006). During field work, divers collected tufa fragments from talus cones surrounding the tufa columns. Ten samples of tufa debris fragments were screened for mineral composition, and all ten contained monohydrocalcite (in the following abbreviated to MHC) and calcite as the major minerals. In this paper we document this unique occurrence of MHC by XRD, petrography, and mineral density separation. In addition we present a model for the formation of MHC from decomposition of ikaite in a semi-closed pore-water system.

MONOHYDROCALCITE

Mineralogy

Naturally occurring calcium carbonate monohydrate was named monohydrocalcite by Semenov (1964). Later the name hydrocalcite was suggested by Marschner (1969), but this name had previously been used for $CaCO_3 \cdot 3?H_2O$ (Fleischer 1964). Similar to calcite (space group R3c, class 3/m uniaxial, negative), MHC belongs to the rhombohedral subclass (trigonal) of the hexagonal system, but the space group is $P3_112$, class 32 and uniaxial positive (Roberts et al. 1990). Unit-cell parameters are a = 10.566 Å and c = 7.573 Å compared to calcite a = 4.989 Å and c = 17.062 Å. Infrared absorption spectrometry performed by Catherine et al. (1977) and Řídkošil et al. (1991) has shown that the carbonate ion exhibits lower site symmetry than in calcite. In comparison with calcite and aragonite the birefringence is low (δ = 0.045), giving third-order green in a 30 µm thin section. The density of MHC is 2.38 g/cm^3, which is 12% and 19% smaller than calcite (2.71 g/cm^3) and aragonite (2.94 g/cm^3), respectively, facilitating identification of the minerals on back-scattered electron (BSE) images.

Stability

MHC is metastable with respect to calcite and aragonite at all pressures and temperatures (Hull and Turnbull 1973). The mineral seems to be relatively stable below 100°C (Taylor 1975), and ^{14}C dating from the deepest MHC layer found at 8.5 m depth in a sediment core from Lake Kivu (Central Africa) showed an age of 9750 years (Stoffers and Fischbeck 1974). Exposed to air, the mineral can exist at room temperature for several years, but heating accelerates decomposition. In boiling water the transformation to calcite occurs within a few hours. Under dry conditions, dehydration to calcite takes place instantaneously at temperatures above 120°C (Stoffers and Fischbeck 1974).

Solubility

Solubility for MHC has been determined only at 25°C ($K_s = 10^{-7.60}$; Hull and Turnbull 1973). At this temperature, MHC is less soluble than ikaite ($K_s = 10^{-6.62}$; Bischoff et al. 1993a) but more soluble than calcite and aragonite ($K_s = 10^{-8.48}$ and $10^{-8.34}$, respectively; Plummer and Busenberg 1982). Solubility of ikaite decreases with lower temperatures in contrast to calcite and aragonite (Bischoff et al. 1993a), while nothing is known about the behavior of MHC at low temperatures.

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Occurrence

In nature, MHC has typically been found in lacustrine environments, but it also occurs in caves, as weathering products, and in living organisms. It was first discovered in nature by Sapozhnikov and Tsvetkov (1959) in Lake Issyk-Kul in Kirgizia, where it forms calcareous encrustations and contributes up to 40% of the upper 85 cm of the sediment column (Giralt et al. 2001; Ferronskii et al. 2003). Occurrences of MHC have subsequently been described from Lake Kuvi in Central Africa (Stoffers and Fischbeck 1974), from Lake Fellmongery and Lake Butler in South Australia (Taylor 1975), from East Basin Lake in Victoria, Australia (Last and De-Deckker 1990), and from Walker Lake in Nevada (Bischoff et al. 1991), all characterized by hypersaline waters. MHC has also been found in Solar Lake, Egypt, where it probably precipitated under saline conditions (Stoffers and Fischbeck 1975) and from Bainbridge Crater Lake on the Galapagos Islands (Riedinger et al. 2002).

MHC has been reported as a constituent of speleothems in limestone caves (Fischbeck and Müller 1971; Fischbeck 1976; Polyak et al. 1994; Onac 2001) and as precipitates from biochemical processes in the so-called moonmilk assemblage, a soft, white, plastic substance normally composed of calcite, hydromagnesite, and organic filaments found in caves (Broughton 1972). MHC has also been identified as a constituent in speleothems in a Hawaiian basaltic cave (Léveillé et al. 2000a, 2000b). MHC is known as a secondary mineral formed under certain weathering conditions. Řídkošil et al. (1991) found MHC precipitated as coatings and crusts on polymetallic veins in the Vrančice ore deposit, Czechoslovakia, and suggested it was a product of vadose solutions, catalyzed by the presence of copper ions. From Greenland, MHC has previously been described as a common secondary mineral in the Sarfartôq Carbonatite Complex (Petersen and Secher 1993), probably related to surface weathering.

Lowenstam and Weiner (1983) listed Monera, Mollusca, and Chordata as groups of organisms able to precipitate monohydrocalcite biominerals. MHC has been found as a component of vertebrate otoliths (Carlström 1963), in a guinea-pig bladder stone (Catherine et al. 1977), and as precipitates from bacteria located in saline soils (Rivadeneyra et al. 1993; Rivadeneyra et al. 1998). MHC has also been found in the upper sediments from abandoned Maasai settlements in Kenya and Tanzania, which is most likely derived from livestock dung (Shahack-Gross et al. 2003). Decay-induced biomineralization of saguaro cacti has also included MHC (Garvie 2003).

In the laboratory, mixing natural seawater with highly soluble carbonates, e.g., Na_2CO_3 (Kinsman and Holland 1969) and $(NH_3)_2CO_3$ (Towe and Malone 1970), has resulted in precipitation of MHC. As a result of this experiment Kinsman and Holland (1969) determined the distribution coefficient of Sr in MHC to be $k_{sr} = 0.064$ from seawater precipitation at 16°C (535 ppm Sr by weight, as used in the following). MHC spherulites from artificial seawater were precipitated by adding Na_2CO_3 (Dejehet et al. 1999). Another experiment performed by Babcân et al. (1992) showed that MHC was precipitated from supersaturated solutions (0.05 M with ionic strength at 0.03 mol/L) at 25°C when changing the Ca/Mg ratio in solution. By adding Ca and Mg carbonate in 1:1 and 1:3 molar solutions MHC was coprecipitated with barringtonite and nesquehonite (hydrous Mg carbonates), respectively. In a simulation experiment of carbonate diagenesis with nesquehonite and supernatant brine (25%), MHC, dolomite, and huntite were formed (Davies et al. 1977). The formation of MHC in various nonmarine environments is generally ascribed to inhibition of calcite and aragonite nucleation by high levels of Mg^{2+} or PO_4^{3-} ions (Stoffers and Fischbeck 1974; Hull and Turnbull 1973) or to biological activity (Lowenstam and Weiner 1983).

Chemistry

A compilation of chemical data from MHC in lacustrine environments (Taylor 1975; Stoffers and Fischbeck 1974; Hull and Turnbull 1973; Sapozhinikov and Tsvetkov 1959) indicates that MHC has a simple chemistry: Sr concentrations range from 0.34×10^3 to 3.4×10^3 ppm, Na from 1.2×10^3 to 5.2×10^3 ppm, Mg from 0.13 to 1.5%, Fe from 0.23 to 1.7×10^3 ppm, and K concentration is around 0.6×10^3 ppm. PO_4^{3-} is present in the range from 0.4×10^3 to 5.0×10^3 ppm.

GEOLOGICAL SETTING

The Ikka Column Garden in the inner part of Ikka Fjord (Fig. 1) contains more than 700 individual ikaite tufa columns higher than 1 m and covers an area of 3 × 0.5 km (Buchardt et al. 1997; Seaman 1998; Buchardt et al. 2001; Seaman and Buchardt 2006). Columns are rooted in muddy, noncalcareous sediments and occur as clusters in water depths from a few meters to 25 m. They form structures up to 18 m high with diameters from a few centimeters to several meters. Growth direction is vertically up, and the growth rate is high; cut columns revisited a year later showed vertical growth of up to 0.5 m. Light penetration in the fjord is good, and the columns are often encrusted by the coralline red algae *Clathromorphum* and *Lithothamnion* down to the bottom. Around the base of columns, talus cones of tufa debris are formed, possibly as a result of bio-abrasion by borrowing organisms (e.g., bivalves) and by collisions with ice floes. These talus cones may be several meters in diameter and are frequently cemented into hard buildups by secondary mineralization and encrusting organisms.

Ikka Fjord is connected to the David Strait through the 500-m-deep Arsuk Fjord. A hydrographic sill at 15 m depth separates and protects the inner part of Ikka fjord from larger icebergs which commonly occur in the outer fjords. Discharge from rivers during the summer results in stratification of the upper 1–3 m of the water column with maximum temperatures of 10–12°C and a salinity below 20‰. Below the halocline, the water column is well mixed and oxygenated due to a tidal range of 2–3 m; its temperature in the summer is 1–3°C, and its salinity around 33‰. In the winter period, the conditions of the ice-covered fjord are uncertain, but complete mixing of the water column is expected.

The ikaite tufa columns form when submarine spring water (subsequently referred to as Ikka water) enters through the fjord bottom and mixes with cold seawater (Buchardt et al. 1997). The Ikka water is described by Buchardt et al. (2001) as a sodium-bicarbonate–carbonate brine characterized by high alkalinity (150–175 mmol/L), high pH (10.2–10.5), high molar Mg/Ca ratios (> 12), and elevated PO_4^{3-} (0.26 mmol/L) compared to local seawater (alkalinity: 2.1 mmol/L, pH 7.9, $PO_4^{3-} < 0.01$ mmol/L). Supersaturation with regard to ikaite, calcite, and aragonite develops where spring water and seawater mix. Ikaite precipitation is favored by low water temperature and high phosphate ion concentration, which is known to inhibit crystallization of calcite and aragonite (Shearman et al. 1989; Bishoff et al. 1993a; Council and Bennett 1993). The Ikka water is of meteoric origin (Buchardt et al. 2001) and is generated from aquifers developed in the 1300 Ma igneous Grønnedal–Ika complex, which is an elongated body of carbonatite and nepheline syenite intruded into foliated Achaean gneisses (Emeleus 1964; Emeleus and Upton 1976; Blaxland et al. 1978). The carbonatite is composed of calcite and siderite with apatite (P_2O_5 up to 3.6% by weight) as a minor component (Pearce et al. 1997). Major fault zones are oriented SSW–NNE and compose the overall control of the tufa column distribution along lineaments in the fjord (Seaman 1998). The peculiar chemistry of the 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).

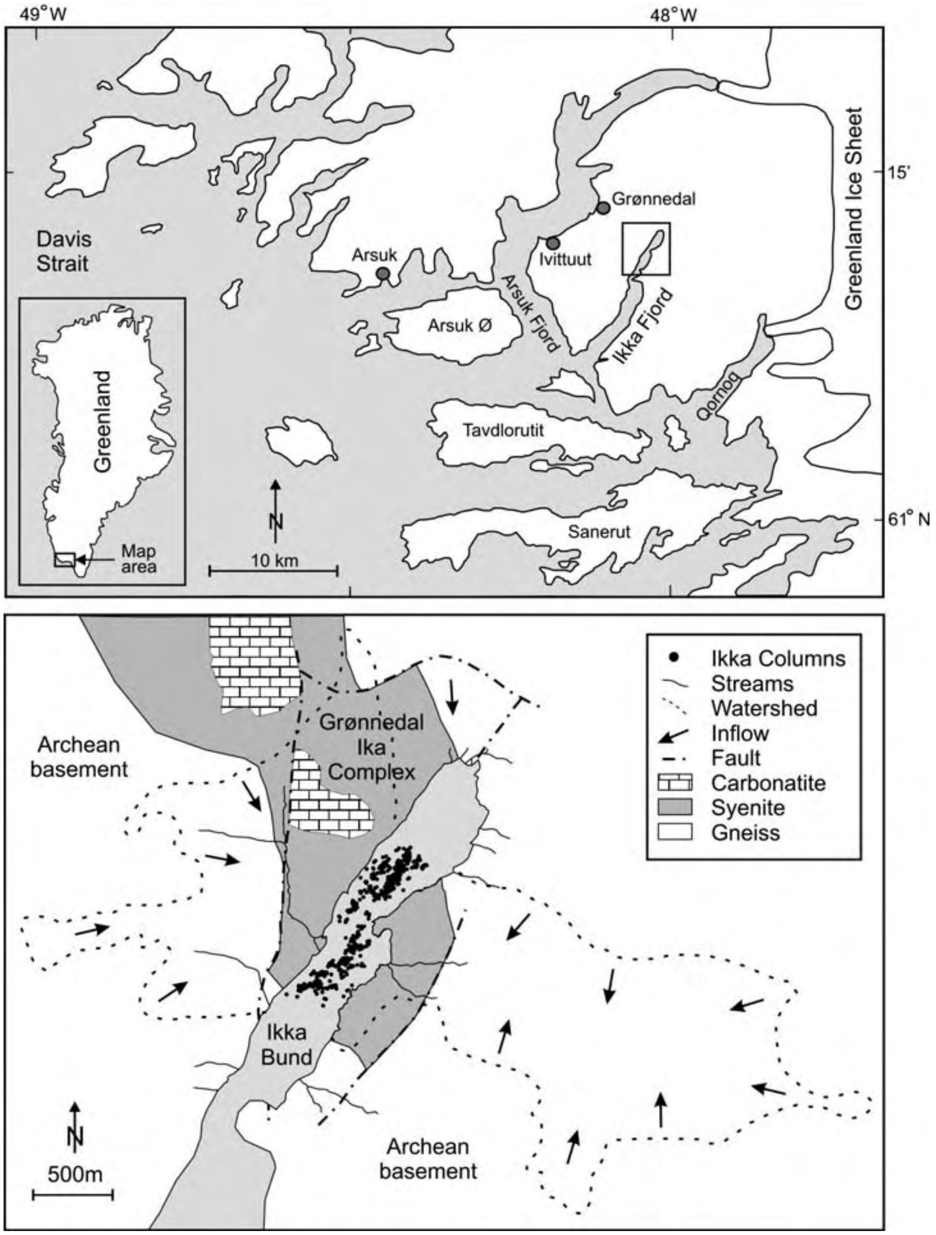

FIG. 1.—Ikka Fjord. **A)** Location map of the Ikka Fjord and surrounding areas in southwest Greenland. **B)** Relationship between the Ikka Column Garden and the Grønnedal–Ika igneous complex. Geological map from Emeleus (1964). Both figures modified from Buchardt et al. (2001).

SAMPLES AND METHODS

Sample Collection and Storage

Divers collected tufa debris fragments at the fjord bottom. Fragments containing ikaite were kept frozen; others were stored at room temperature. The tufa debris fragments range from being quite massive to very porous and constitute a variety of habits from columns and tubes to highly irregular rock debris in a size range from 5 to30 cm (Fig. 2). The surfaces of the fragments have been exposed to bio-abrasion (burrows) and are partly covered by coralline algae, bryozoans, gastropods, and barnacles, and some samples contain gravel-size dropstones. Two out of ten investigated samples, which all contained MHC, were selected for the more detailed studies presented here. Tufa sample 201 (Fig. 2A, B) is very porous, light gray to white, with a few burrows 1–2 mm wide and attached bivalves. Sample 205 is massive, cream-colored, and full of small and large burrows 10–30 mm wide. It is partly covered by *Clathromorphum*, and bivalves overgrown by tufa are common.

Ikaite was sampled directly from the tufa columns; it was immediately frozen and kept at −18°C. Newly formed ikaite tufa is white and porous with no attachment of biota. The framework is uniformly composed of an interlocking mass of 0.1–2 mm euhedral, transparent ikaite crystals. Five samples of ikaite tufa were investigated. Sample 230 is a newly formed (1996) column top from the major ikaite skerry, representing induced growth above a cutting surface from 1995. Samples 231 and 233 are naturally formed ikaite from the same locality collected in 1995. Sample 232 (induced growth) and 240 (naturally precipitated) are from localities close to the skerry. A sample list is shown in Table 1.

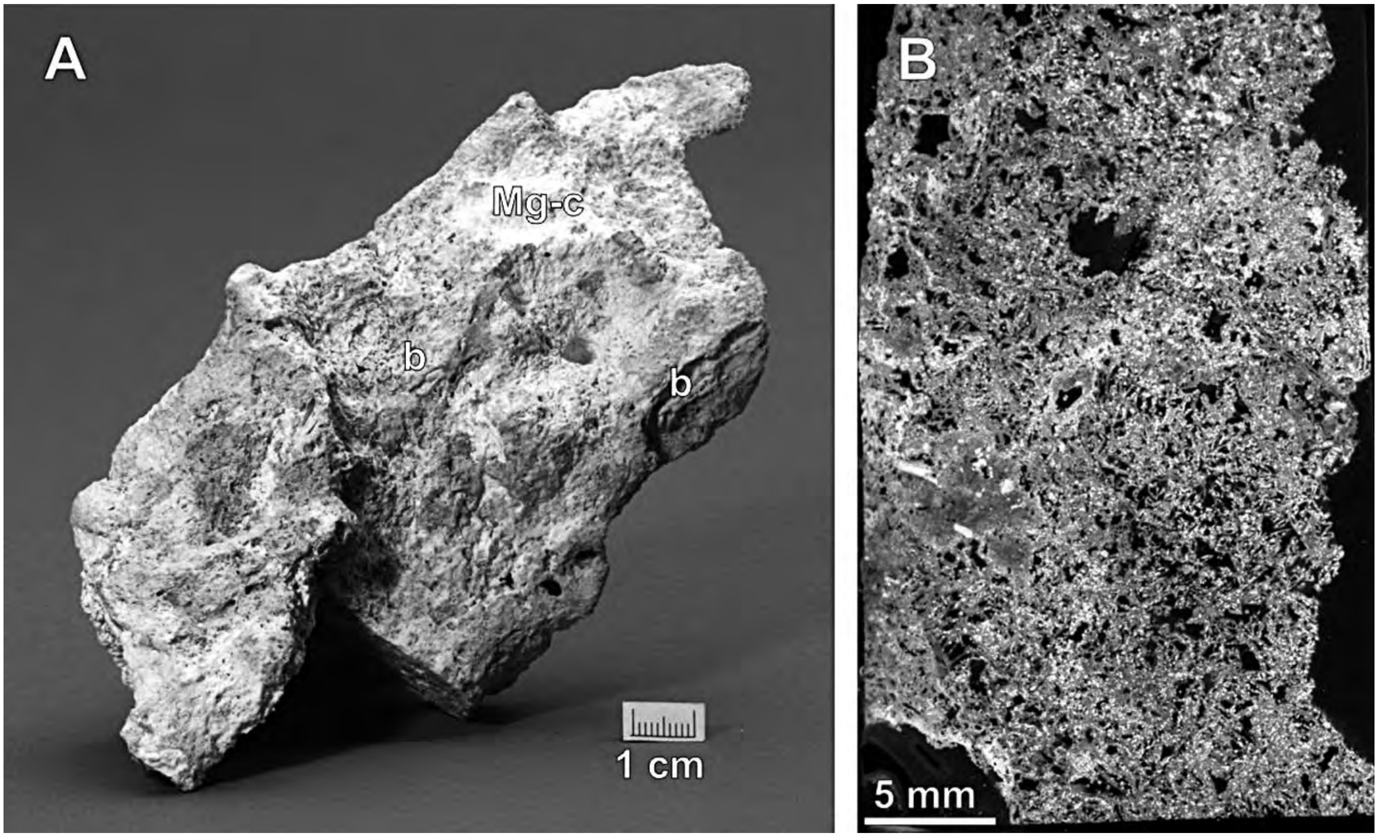

FIG. 2.— Tufa debris fragment 201 collected from the bottom of Ikka Fjord. **A)** Photo of whole fragment. The sample appears very heterogeneous and includes fragments of bivalves (b). The white color is associated with the Mg carbonate (Mg-c); see Figure 6A. A few 1–2 mm burrows occur. **B)** Photomicrograph of a thin section showing highly heterogeneous tufa rock with variable pore size and interparticular porosity.

Sample Preparation

Tufa Debris.—Heavy-liquid mineral separation was performed in order to determine and separate the mineral components of two tufa debris fragments (samples no. 201 and 205). For this purpose we sampled 20–30 g from the tufa fragments, manually crushed the rock in a mortar, and used the 63–123 μm fraction for the mineral separation. To obtain clear separations the heavy liquid-mineral suspension was centrifuged to accelerate the settling rate. All sample treatments were performed at room temperature inclusive drying. The utilized liquid was tetrabromoethane (2.96 g/cm^3) diluted with dipropyleneglycol (1.02 g/cm^3). The gravity separation resulted in five fractions: (I) density $>$ 2.8 g/cm^3, (II) density from 2.5 to 2.8 g/cm^3, (III) density from 2.3 to 2.5 g/cm^3, (IV) density from 2.1 to 2.3 g/cm^3, and (V) density $<$ 2.1 g/cm^3; see Table 2.

Ikaite.—Approximately 5 g of frozen ikaite from storage at -18°C were sampled and gently crushed in a chilled mortar. Further preparation for mineralogical and chemical analysis took place at 0°C. In order to clean the samples for adherent seawater and prevent recrystallization, a solution of phosphate in distilled water adjusted to 0.21 mmol/L with KH_2PO_4 was cooled down to 0°C with ice cubes of distilled water in a refrigerator. The frozen ikaite was then placed in the solvent for 1 hour to obtain temperature equilibrium and rinsed three times in the mixture and a final time in distilled water to remove the phosphate. Excess water was removed in the fridge with filter paper. Further attempts were not made to dry the samples using acetone or ethanol as performed by Pauly (1963a) and Ito (1998). Finally, the samples were refrozen. Total time for the preparation at 0°C took approximately 1½ hours. Before chemical analysis the ikaite samples were freeze-dried. This process causes collapse

TABLE 1.—*Samples and treatment.*

Sample	Location	Rock type	Mineralogy	Storage	Methodology
201	Fjord bottom	Tufa debris	Calcite, MHC, Mg carbonate	Room	DS[1], XRD[2], AAS[3], MS[4]
205	Fjord bottom	Tufa debris	Calcite, MHC	Room	DS, XRD, AAS, MS
230	Top of column	Induced growth	Ikaite	Freezer	XRD, AAS, MS
231	Top of column	Induced growth	Ikaite	Freezer	XRD, AAS, MS
232	Top of column	Induced growth	Ikaite, aragonite (trace)	Freezer	XRD, AAS, MS
233	Top of column	Induced growth	Ikaite	Freezer	XRD, AAS, MS
240	Part of column	Natural growth	Ikaite, MHC, calcite	Freezer	XRD

[1] Density separation in heavy liquid. [2] X-ray diffraction. [3] Atomic absorption spectrometry. [4] Mass spectrometry.

TABLE 2.—*Mineral separation of tufa debris samples.*

Density, g/cm^3	Sample 201[1] grams	Sample 201[1] %	Sample 205 grams	Sample 205 %
Fraction I, $x > 2.8$	0.034	0.83	0.029	0.22
Fraction II, $2.5 < x < 2.8$	1.377	33.95	11.558	87.66
Fraction III, $2.3 < x < 2.5$	2.236	55.15	1.590	12.06
Fraction IV, $2.1 < x < 2.3$	0.283	6.98	0.008	0.06
Fraction V, $x < 2.1$	0.125	3.09	0.001	0.01
Σ	4.055	100	13.186	100

[1] Due to the fragile character of sample 201 a large amount of dust (80% of the fraction between 63 and 125 μm) was generated and adsorbed to the larger particles. To remove the dust ultrasonic treatment was performed.

of the ikaite structure and formation of calcite but preserves ikaite morphology (Buchardt et al. 2001).

Analytical Methods

The tufa debris samples were investigated for weight loss due to heating. The fractions were analyzed after mineral separation by X-ray diffraction (XRD), atomic absorption spectrometry (AAS), spectrophotometry, and mass spectrometry. Thin sections of tufa debris were examined in optical and scanning electron microscopes. Clean frozen ikaite samples were analyzed by XRD and after freeze-drying by AAS, spectrophotometry, and mass spectrometry. XRD was performed on all fractions by a Phillips PW3710 X-ray diffractometer with Cu tube (wavelength α_1 = 1.54056 Å, wavelength α_2 = 1.54439 Å, intensity ration $\alpha_2/\alpha_1 = 0.5$, receiving slit 0.2, generator current 30 mA, and voltage 40 kV). The scan was run from 2 to 70° 2θ with step size 0.03° 2θ and measuring time per step of 1.2 seconds. The crushed ikaite was placed in frozen frames, and the scan was run from 7 to 35° 2θ with step size 0.05° 2θ and 1.0 second measuring time per step with a receiving slit at 0.45. This allowed the strongest peaks of the calcium carbonate hydrates (ikaite and monohydrocalcite) and anhydrous polymorphs (calcite, aragonite, and vaterite) to be identified, and prevented recrystallization during measurement. The minerals were identified with help of the ICDD (International Centre for Diffraction Data) powder diffraction database.

Determination of Ca, Mg, Na, K, Fe, Mn, and Sr contents by AAS was performed with a Perkin-Elmer PE-5100 instrument. A 200 mg sample was dissolved in 5 ml of 20% HCl, heated for 1 hour at 80°C, and then diluted with distilled water to 50 ml. Detection limits are 5 ppm for Mg and around 10 ppm for the other elements. Relative standard deviations of Fe and Mg are 2%, Ca and Sr 3%, and Mn 6% deduced from repeated measurements of a limestone.

Determination of PO_4^{3-} as molybdenum blue complex was performed with a Perkin-Elmer 55E spectrophotometer. After dissolution of the sample in HCl, 1 ml solution was diluted with 9 ml H_2O and to oxidize all the phosphorus to PO_4^{3-}, 2 droplets of 30% H_2O_2, and 4 droplets of pure H_2SO_4 was added. The sample was then evaporated almost to dryness and finally diluted with H_2O to 10 ml and molybdate acid was added. Ascorbic acid was the reducing agent to form molybdenum blue. All numbers for the carbonate minerals are reported as parts per million (ppm) by weight.

The carbon and oxygen isotope determinations were carried out following the method described by McCrea (1950) with the use of a Finnigan MAT 250 triple-collector mass spectrometer. Five milligrams of carbonate were allowed to react with 100% phosphoric acid at 50°C for 15 min. Results are given as δ values relative to V-PDB, and reproducibility is better than ± 0.04‰ for $\delta^{13}C$ and $\delta^{18}O$.

Optical microscopy was performed on uncovered standard thin sections of tufa debris. Gold-coated fracture samples of debris were studied in secondary electron-mode (SE-mode) and carbon-coated thin sections in backscattered electron mode (BSE mode) with a Philips 515 scanning electron microscope. Operating conditions were 25 kV with a spot-beam size of 200 nm.

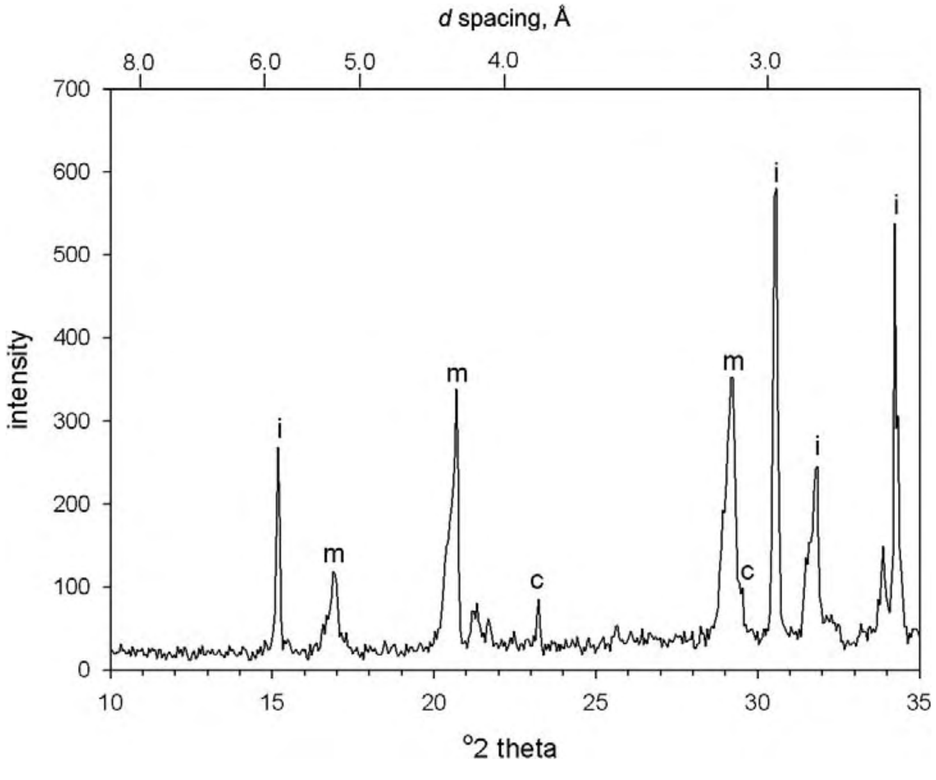

FIG. 3.—Powder X-ray diffractogram of column fragment 240 showing coexisting ikaite, monohydrocalcite, and calcite. Diagnostic diffraction lines are indicated as (i) ikaite, (m) monohydrocalcite, and (c) calcite.

TABLE 3.—*XRD results of mineral fractions of sample 201 and 205. Relative peak[1] intensities in % of major reflections.*

		Sample 201[2]			Sample 205		
	Fractions	Calcite	MHC	Aragonite	Calcite	MHC	Aragonite
Density, g/cm^3	Fraction I, $x > 2.8$	32	20	100	47	n.d.	100
	Fraction II, $2.5 < x < 2.8$	100	27	24	100	6	13
	Fraction III, $2.3 < x < 2.5$	6	100	2	16	100	11
	Fraction IV, $2.1 < x < 2.3$	trace	100	3	19	100	4
	Fraction V, $x < 2.1$	n.d.	100	n.d.	7	9	n.d.
Grain size	Fraction > 125 µm	57	100	20	100	46	49
	Fraction 63 < x < 125 µm	50	100	11	100	36	31
	Fraction < 63 µm	42	100	10	100	18	6
	Ultra sonic treatment	35	100	10	-	-	-
	Bulk	40	100	9	100	11	4

[1] Major peaks used have the *d* values in Å: 3.03 for calcite, 4.33 for MHC, and 3.38 for aragonite, n.d. not detected. [2] Fraction II, III, VI and V have been placed in silicone-impregnated sample holders due to low friction of the Mg carbonates.

RESULTS

Mineralogy

The newly formed ikaite tufa sample 230 consisted of pure ikaite both before and after cleaning. This confirms that recrystallization did not occur during either storage for more than four years at −18°C or subsequent cleaning. Three of the naturally grown tufa samples also consist of pure ikaite and traces of aragonite, while one sample (240) showed coexistence of ikaite, MHC, and calcite (Fig. 3). Decomposition of ikaite was investigated at room temperature (20°C) by repeated scans of a single sample. Complete recrystallization to calcite occurred after 300 minutes, and neither vaterite nor MHC were observed in the end product.

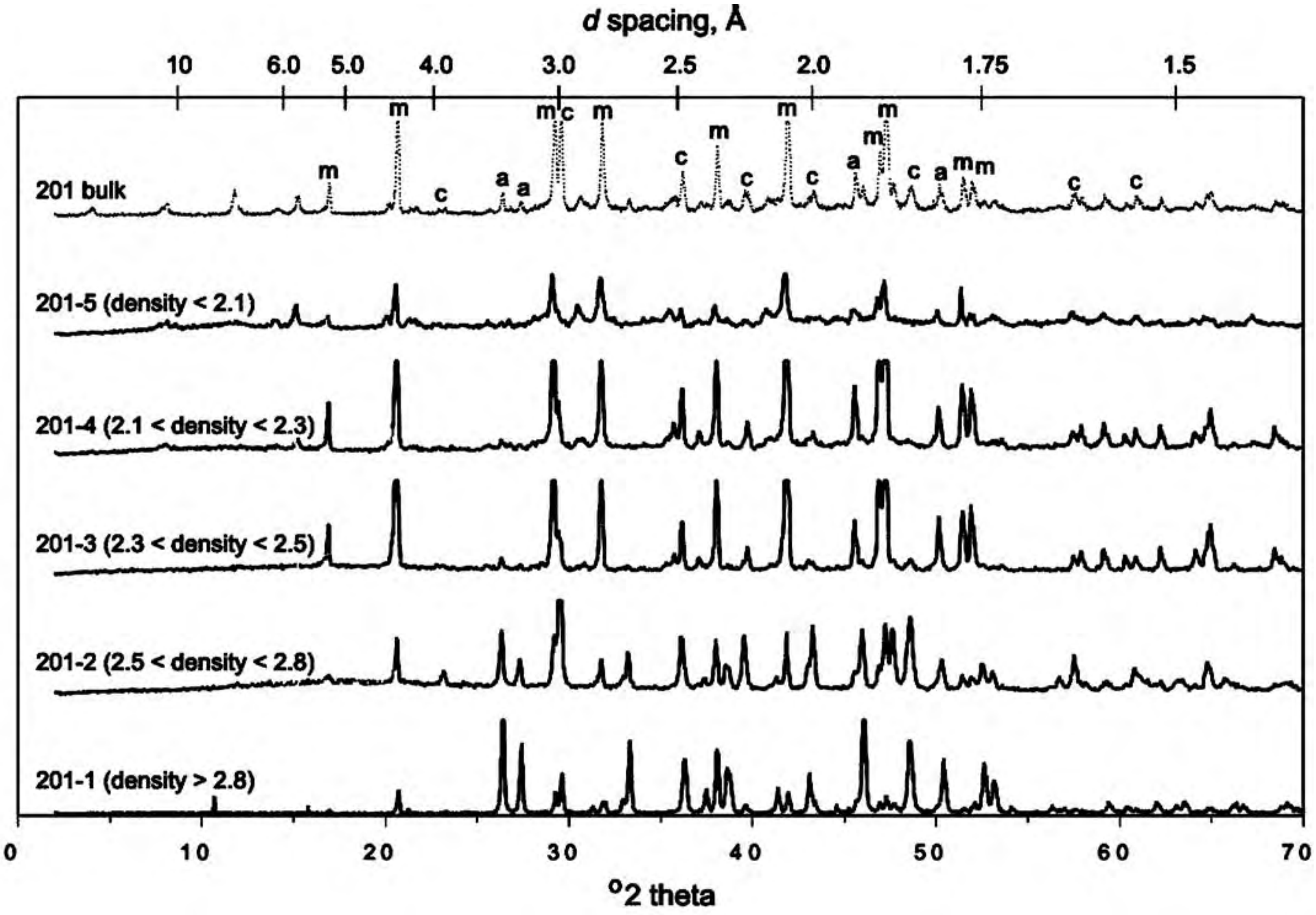

FIG. 4.—X-ray powder diffraction diagrams of the five density fractions obtained from mineral separation of sample 201. All samples contain MHC. Fraction 1 contains aragonite as dominating mineral, in fraction 2 calcite and fraction 3 and 4 MHC dominate. The Mg carbonates are seen in fractions 4 and 5 as non-indicated peaks. Diagnostic diffraction lines are indicated as (a) aragonite, (m) monohydrocalcite, and (c) calcite.

The samples of tufa debris contain calcite, MHC, and minor amounts of aragonite and hydrous Mg-carbonates (Table 3, Fig. 4). In sample 201, MHC is the dominating mineral. Heating at 230°C for 24 hours showed a complete transformation to calcite, while the hydrous Mg-carbonates changed to hydromagnesite and 17.5% of the weight was lost. The heaviest fraction (> 2.8 g/) constitutes < 1% weight of the total sample, and aragonite (2.94 g/cm^3) is the dominating mineral. Calcite (density 2.71 g/cm^3) dominates in the 2.5–2.8 g/cm^3 fraction together with small amounts of MHC and aragonite. The 2.3–2.5 g/cm^3 fraction is dominated by MHC (density 2.38 g/cm^3) with minor amounts of calcite and hydrous Mg minerals. The 2.1–2.3 g/cm^3 fraction is again dominated by MHC and hydrous Mg carbonates. The lightest fraction (< 2.1 g/cm^3) also contains MHC. Other peak lines in this fraction are not in accordance with the ICDD data of known hydrous Mg carbonates, which otherwise would be reasonable suggestions inasmuch as the mineral dehydrates to hydromagnesite. The peak search revealed a good match of 2θ values for dypingite (e.g., *d* value 5.86, 4.20, 3.07, 2.93), but the 2.15 g/cm^3 density is a bit high. The small shifts for higher *d* values compared to dypingite data (Raade 1970) in the pattern may reflect differences in composition.

In sample 205, the major carbonate phase is calcite, which occurs in all fractions. MHC is the dominating mineral in the density ranges from 2.3 to 2.5 g/cm^3 and from 2.1 to 2.3 g/cm^3. Similarly to sample 201, the heavy fraction (> 2.8 g/cm^3) is dominated by aragonite but constitutes only < 0.2% weight. The lightest fraction has peaks from MHC and calcite, but the dominating peaks have not been identified.

Petrology

The debris fragments have a pure carbonate composition with an insoluble residue (albite, quartz) below 1%. The framework is similar to fresh tufa, and larger euhedral carbonate crystals of 0.5–2 mm size are common in some of the samples. In thin sections, MHC is identified by a low birefringence and low intensity (density) recorded by the BSE detector and is present in three different habits in the tufa debris (Fig. 5): (1) spherules, (2) subhedral to euhedral crystals, and (3) zoned euhedral crystals. Spherules (1) have a diameter of 10–200 μm and show centered conoscopic figures. The samples appear light brown to brown in color (probably due to inclusions of organic matter) and are composed of radial acicular crystals (Fig. 5A). Subhedral to euhedral crystals (2) up to 80 μm are often situated between the spherules. Crystal faces towards the pore spaces are common, and partial replacement of the spherules occurs occasionally. The crystals are clear and transparent, lacking inclusions of organic material. In BSE mode, the density of the spherules is lower than that of the surrounding euhedral crystals (Fig. 5B), possibly reflecting a close association between the spherules and organic material. Rare zoned euhedral crystals (3) have a size of 50 μm (Fig. 5C). The individual zones are separated by vugs, and intracrystalline porosity is common, possibly due to dewatering of ikaite. The crystals show similarities to thinolitic pseudomorphs described by Shearman and Smith (1985), Bischoff et al. (1993b), and Larsen (1994).

Sample 201, partly composed of hydrous Mg minerals, shows moldic porosity, and the 1–2 mm neoformed grains appear cryptocrystalline (Fig 6A). In thin section the crystal walls appear opaque and are covered by very thin acicular crystals. When observed in BSE mode the walls are composed of radiating acicular crystals (Fig. 6C). In SEM the crystals have a flaky structure and the thickness of the crystals is about 0.5 μm, while the length can exceed 200 μm (Fig. 6A, B). The morphology is similar to figures of protohydromagnesite shown by Davies and Bubela (1973).

Chemistry

The trace-element distribution of the various mineral phases in the two investigated tufa debris fragments can be determined with reasonable

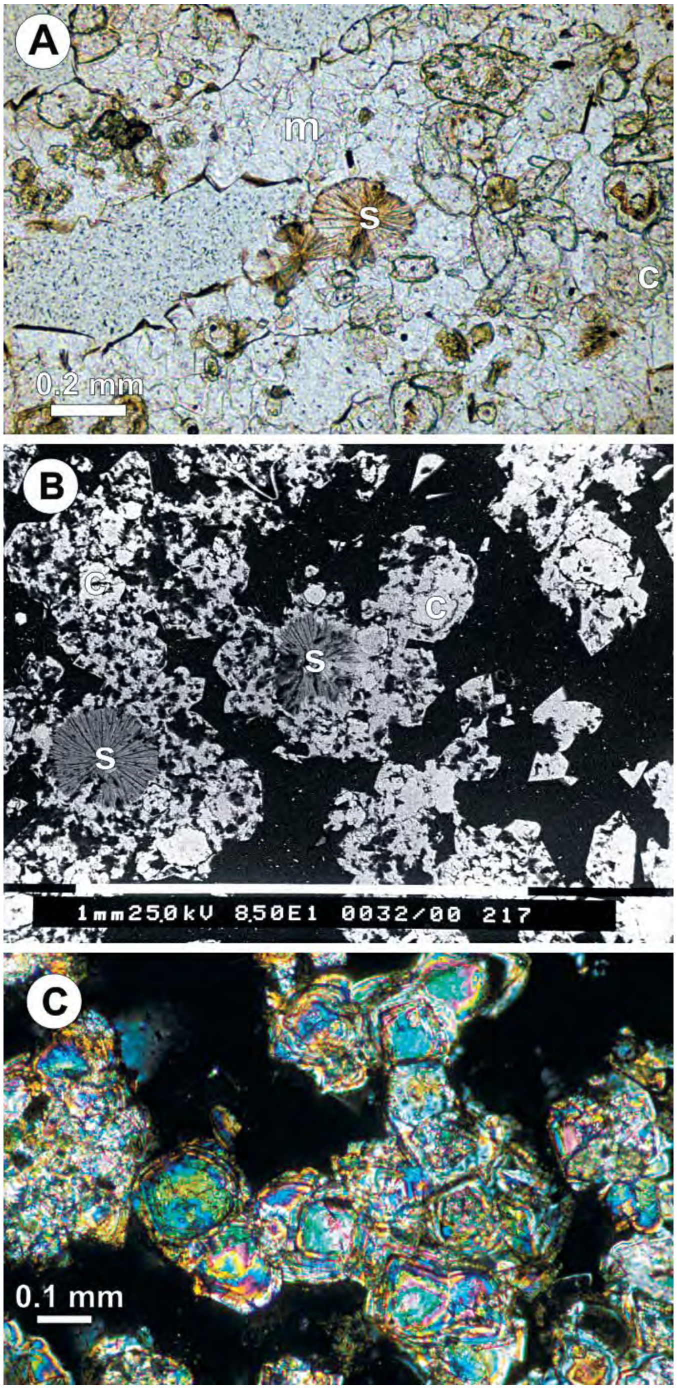

FIG. 5.—Monohydrocalcite in tufa debris from Ikka Fjord. **A)** Spherules (s) of MHC composed of radiating needles. The surrounding matrix consists of MHC (m) and calcite (c). MHC contains inclusions of calcite and exhibits crystal faces exposed to the pore space. The calcite is anhedral and characterized by high relief and birefringence. Calcite has common inclusions of probably algae-derived material. Transmitted light, scale bar 0.2 mm. **B)** Back-scattered electron image, where the darker areas correspond to lower density. Spherules are characterized by lower density compared to euhedral crystals of MHC. Adjacent euhedral crystals of MHC host larger inclusions of subhedral calcite (high density). **C)** Zoned porous euhedral crystals of MHC. The individual zones are separated by vugs (observed from BSE). Crossed polars, scale bar 0.1 mm.

accuracy from the chemical analyses of the density fractions (Table 4). Na and Sr are highest in fraction II, composed of calcite, while Fe and to a certain degree K and PO_4 are concentrated in fraction III, composed of MHC. Mg is low in both fractions and shows no preference. Mn is low in all minerals, indicating precipitation in well-oxygenated water. The Mg-carbonate-rich fractions have the largest concentration of K, Fe, Mn, and PO_4 and are low in Ca and Sr. The original composition of ikaite has been calculated from the AAS analyses of freeze-dried ikaite samples (now calcite), using a water content in ikaite of 51.9%. Results show little difference in chemical compositions between individual samples (Table 4) except for sample 230, which probably was contaminated by seawater before cleaning. Ikaite is low in Sr (average 1800 ppm by weight) and Mg (average 0.13% by weight). However, the molar ratios of Sr/Ca and Mg/Ca are significantly higher in ikaite (0.005 and 0.013) than in calcite (0.004 and 0.005) and MHC (0.003 and 0.005). Fe, Mn, Na, and K contents are all low compared to the coexisting calcite and MHC. Phosphate is highly variable (300 to 1700 ppm).

Carbon and oxygen isotope compositions of ikaite and the density fractions are given in Table 4 and shown in Figure 7. Ikaite is constant in both $\delta^{13}C$ and $\delta^{18}O$ values (average −6.4‰ and −10.8‰, respectively). The fractions containing calcite and MHC have almost identical carbon isotope compositions ($\delta^{13}C$ values from −5.3‰ to −5.1‰), while the Mg-enriched fractions have more positive $\delta^{13}C$ values (−4.7‰ and −3.5‰). A similar distribution is seen in the oxygen isotope compositions, but with a larger scatter between calcite (fraction II) and MHC (fraction III).

DISCUSSION

Our study demonstrates that large amounts of MHC (up to 55% by weight) occur in tufa debris fragments from the bottom of Ikka Fjord together with calcite and Mg carbonates. The majority of the samples have been stored at room temperature, and post-sampling modifications leading to formation of MHC cannot be excluded. However, the coexistence of MHC, ikaite, and calcite in a column sample (240) stored at −18°C directly after sampling indicates that MHC is of natural origin and not an artifact from storage. Moreover, none of the investigated tufa debris fragments contained ikaite at the time of sampling, and later recrystallization of ikaite crystals can be excluded as a source for the MHC. Newly formed tufa is composed of pure ikaite without traces of MHC, and the coexistence of ikaite and MHC in the older tufa sample suggests that MHC grew from *in situ* decomposition of ikaite. Our chemical and petrographical data support this hypothesis.

Seawater in Ikka Fjord is undersaturated with respect to both ikaite and MHC (Buchardt et al. 2001), and precipitation of MHC must be restricted to pore-water environments with modified seawater chemistry. Temperatures inside the columns and at the fjord bottom never exceed 3°C (Buchardt et al. 2001), thus defining a stable, cold-water environment for all MHC-precipitating processes. Moreover, the columns are host to a complex pore-space biota of bacteria, algae, and meiofaunal organisms (Sørensen and Kristensen 2000), which probably has a profound influence on mineral stability and mineral precipitation in the column environment.

Generally, MHC occurs with three different morphologies: spherules, massive euhedral crystals, and zoned euhedral crystals (Fig. 5). Dominating in the investigated tufa debris fragments are spherules and massive crystals, while the zoned euhedral crystals are rare. Petrographic relationships show the spherules to be formed before the massive crystals, which occupy the pore space between the former. Two processes of ikaite transformation to MHC can be proposed from the morphology of the MHC crystals: (1) *in situ* replacement and (2) dissolution and reprecipitation. The *in situ* replacement of ikaite by MHC results in formation of the zoned euhedral crystals. This process is related to dissolution and reprecipitation at a small scale at low water/rock ratio and is a process commonly resulting in fabric preservation (Bathurst 1975). The void-containing fabrics of some of these MHC crystals show the character of glendonites (Larsen 1994; Brandley and Krause 1997), which have been suggested to be ikaite pseudomorphs (Shearman and Smith 1985). This fabric reflects the dehydration and shrinking following ikaite recrystallization.

A first step in the formation of spherules and massive euhedral crystals of MHC must be a progressive dissolution of the primary ikaite phase leading to supersaturation in the pore water with respect to other carbonates. Even though the highly metastable ikaite is surprisingly stable in the Ikka column systems, dissolution at a large scale must take place in the fjord water environment, inasmuch as none of the tufa debris fragments contained any ikaite. Time as well as the gradual pore-water modification from a highly alkaline spring-water composition to seawater probably mediates this process. Additionally, decomposition of biofilm envelopes protecting the individual ikaite crystals (see Buchardt et al. 2001, their fig. 5) also accelerates the dissolution. The dissolution of ikaite crystals must be gradual, because the overall structures of the columns are preserved even in ikaite-free fragments.

The close association between organic material and MHC spherules observed in thin sections suggests a biogeochemical origin probably related to algae and/or bacteria. Concentric spherulites of MHC have previously been described by Davies et al. (1977) as often containing an organic (algal) fragment as a nucleus. Their experiment indicated that humic acids delay the onset of any carbonate precipitation, but MHC was the first precipitate when the threshold was exceeded. The spherulites from Lake Kivu are also associated with organic activity (Stoffers and Fischbeck 1974). In general, the origin of calcified spherulites has been ascribed both to bacterial and cyanobacterial precipitates. Investigations by Rivadeneyra et al. (1998) showed an evolution in three stages of spherulites caused by bacteria. Spherulites evolve from calcified chains or filaments of bacteria, randomly oriented in circular forms. The next stage is the formation of more or less compacted discs that were succeeded by a three-dimensional body with an internal radial structure. However, we believe that the delicate radial structure observed in the spherules from the tufa debris is not obviously related to any formation involving randomly orientated calcified chains. A formation due to cyanobacterial activities is more likely. Verrecchia et al. (1995) precipitated spherules in experiments with purified cyanobacteria and compared them to spherulites developed in calcrete crusts and both types show fibro-radial and concentric structures. Despite the fact that the formation of MHC spherules in the Ikka talus debris appears to be associated with organic activity, the $\delta^{13}C$ values indicate that most of the carbon is of inorganic origin.

The cation ratios of ikaite reflect seawater ratios (Buchardt et al. 2001). MHC has an average molar Sr/Ca ratio of 0.0034, which is more than halfway between that of ikaite (0.0049) and a normal low-temperature, marine calcite (0.0028; Kinsman and Holland 1969; Veizer 1983). The tufa calcite in Ikka Fjord is enriched in Sr (Sr/Ca ratio of 0.0041) compared to low-temperature marine calcite. This can be explained by a fast transformation of ikaite to calcite, because calcite precipitation experiments have shown a positive correlation between Sr in calcite and the rate of precipitation (Tesoriero and Pankow 1996; Watson 1996). The Na/Ca molar ratio is 0.0022 in ikaite, 0.0098 in MHC, and 0.0128 in calcite. The large uptake of Na during recrystallization is probably also a consequence of the fast transformation of ikaite to MHC or calcite. Investigation of calcite precipitation by Busenberg and Plummer (1985) showed that the amount of Na incorporated is a function of the rate of crystal growth, which induces crystal defects. The values of other elements, Fe, Mn, and K, are low in ikaite compared to MHC and calcite, and the elements are extracted from seawater.

MHC is a common by-product in laboratory experiments investigating carbonate precipitation and diagenesis from supersaturated solutions

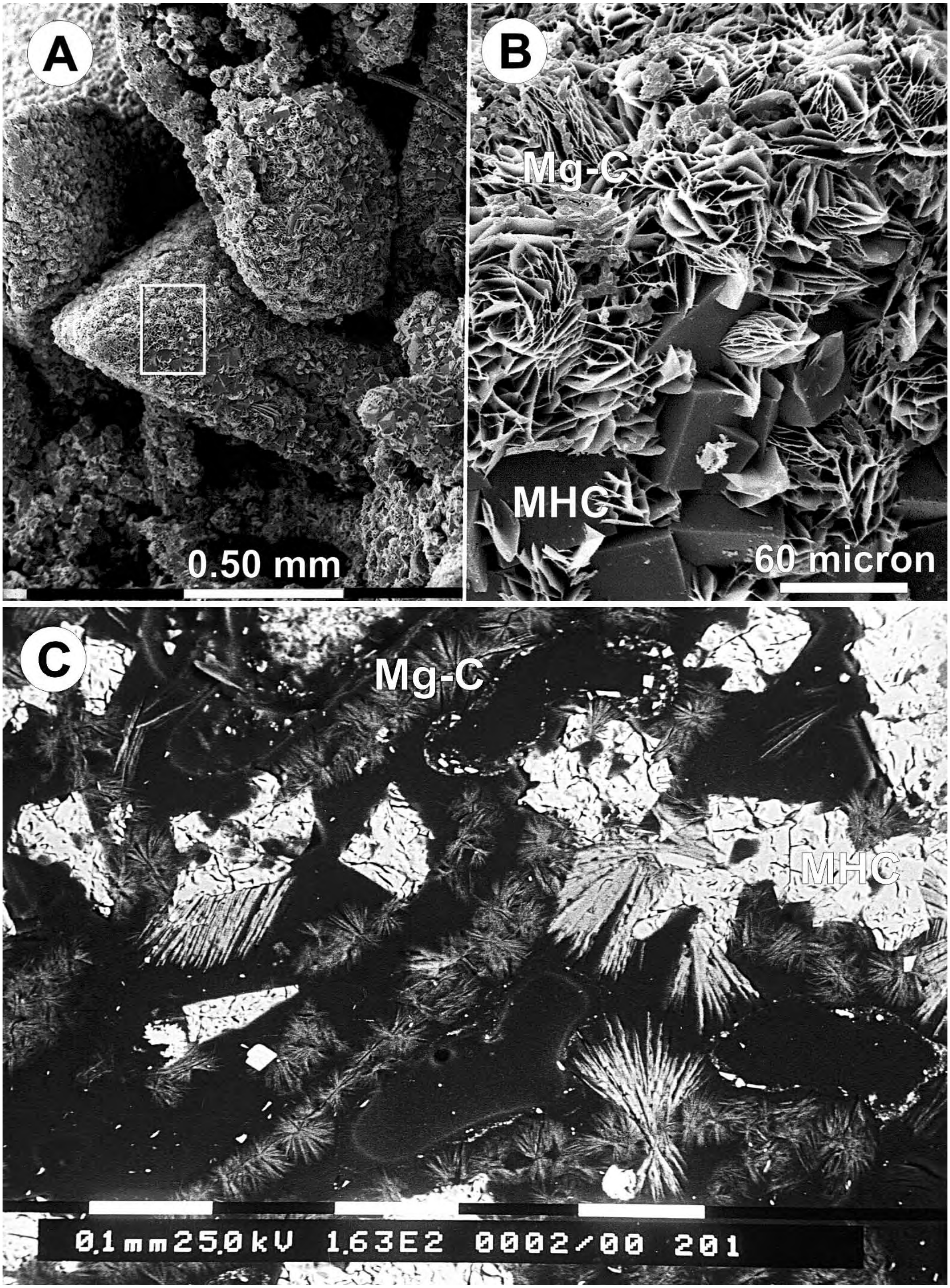
A
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Table 4.—*Chemical and stable-isotope data from density fractions of tufa samples and from pure ikaite.*

Density fraction	Sample	Ca %	Mg %	Na ppm	K ppm	Fe ppm	Mn ppm	Sr ppm	PO_4^{3-} ppm	$\delta^{13}C$ ‰ V-PDB	$\delta^{18}O$ ‰ V-PDB
II (calcite)	201-II	35.3	0.67	2650	103	283	15	3200	1674	−5.28	−6.15
	205-II	36.6	0.11	2475	70	190	15	3225	4014	−5.27	−7.86
III (MHC)	201-III	31.2	0.97	1475	128	495	15	2525	2988	−5.13	−7.31
	205-III	32.6	0.09	2100	95	423	18	2250	4230	−5.19	−8.20
IV (Mg carbonate)	201-IV	21.5	6.14	1932	520	2131	31	2102	3927	−4.67	−6.73
V (dypingite?)	201-V	5.26	15.19	2566	783	2270	39	855	6770	−3.54	−4.37
Ikaite[1]	230-IR	16.21	0.22	2954	127	55	4	1621	2732	−6.32	−10.88
	231-IR	16.16	0.13	366	27	42	5	1751	1660	−6.32	−10.95
	230-IC	16.45	0.15	202	19	29	5	1659	1744	−6.24	−10.79
	231-IC	16.59	0.13	208	18	33	6	1816	325	−6.37	−10.99
	232-IC	16.59	0.13	212	17	34	7	1768	1287	−6.41	−10.76
	233-IC	16.55	0.11	221	16	21	7	1792	1082	−6.44	−10.62
	Average[2]	**16.55**	**0.13**	**211**	**18**	**29**	**6**	**1759**	**1109**	**−6.37**	**−10.79**

All percent and ppm values are calculated by weight. [1] Ikaite was analyzed as calcite and recalculated to ikaite (water content 51.9%). R marks unclean samples. C is samples cleaned in 25 ppm PO_4^{3-} solution, [2] average only refers to ikaite samples, derived from values of cleaned samples.

(Kinsman and Holland 1969; Towe and Malone 1970; Davies et al. 1977). It is well known that many dissolved species (e.g., organic molecules, phosphate ions, and magnesium ions) inhibit the already sluggish nucleation of calcite and aragonite crystals (Bischoff 1968). Aragonite nucleation is also impeded by low water temperatures (Kinsman and Holland 1969; Rao 1981; Rao et al. 1998). The initial stability of ikaite in the mixing zone between spring water and seawater in Ikka Fjord has been ascribed to the high concentrations of phosphate ions (up to 0.26 mmol/L) in the spring water (Buchardt et al. 2001), some of which is incorporated into the ikaite crystals ($PO_4^{3-} \approx 1100$ ppm). During ikaite dissolution, phosphate is released into the pore water, thereby favoring the precipitation of MHC over calcite and aragonite.

The concentration of magnesium ions is high in the Ikka Fjord water but low in the spring water (> 45 mmol/L and < 1.7 mmol/L, respectively; Buchardt et al. 2001), and any inhibiting role of magnesium, therefore, must involve admixture of seawater to the pore-water system. As seen from Figure 7, this influence is aptly reflected in the carbon and oxygen isotope composition of the various tufa minerals. Mollusk shells formed under isotopic equilibrium conditions in the cold fjord water away from the columns have $\delta^{13}C$ and $\delta^{18}O$ values between +1 and +3‰, defining the marine end member of a mixing curve between ikaite and seawater carbonate. A rough estimate from this curve suggests that MHC formed at 20 to 25% seawater admixture and the Mg carbonates at 30 to 50% seawater, the "dypingite" phase showing the greatest seawater influence.

The combined petrographic, chemical, and isotopic data leads us to the conclusion that most of the growth of MHC took place in a pore-water environment still dominated by the spring water, probably in the tufa columns. Older columns are thereby stabilized not only by encrustations but also by formation of the less soluble MHC in outer parts closest to seawater. The tufa debris fragments are dominated by MHC and calcite because all primary ikaite have dissolved from contact with the phosphate-free seawater. Formation of MHC can also take place in the talus pile as long as the local pore water is still dominated by high phosphate concentrations due to ikaite dissolution.

The occurrence of the hydrous Mg carbonate (dypingite?) should be further investigated. Usually the hydrous Mg carbonates are found as alteration or weathering products of serpentinites, dunites, or Mg containing carbonates (Langmuir 1965; Raade 1970; Matsumoto 1992) and as evaporite minerals precipitated from hypersaline waters with high Mg concentrations and Mg/Ca ratios. High alkalinity is also favorable for the formation of hydrous Mg-carbonates (Canterford and Tsambourakis 1984; Bâbcan et al. 1992). The Mg/Ca molar ratio in the spring water is above 12, but the overall Mg concentration is low. Samples of Ikka water diluted with seawater show a rising Mg content and a constant Ca content with increasing seawater addition, indicating that only Ca ions are precipitated when the waters mix (Buchardt et al. 2001). The Mg carbonate is then a secondary mineral formed when the debris fragments are exposed to seawater, and so are interpreted as a product of marine diagenesis, perhaps associated with alteration of MHC. The process of concentrating Mg from seawater could be related to the presence of opal, which is known to be a scavenger of Mg (Hurd 1973). A source of opal is spicules from sponges, which are common in Ikka Fjord.

MHC has not previously been encountered in marine environments. The occurrence of the mineral in tufa debris from Ikka fjord gives some guidelines to predict where it could be found. Ikaite is the unstable calcium carbonate mineral which acts as a precursor of MHC in Ikka Fjord. Thus, wherever ikaite is formed, transformation to MHC is possible. Marine ikaite is described from organic-rich bottom deposits in near-freezing environments, where phosphate ions and organic compounds inhibit calcite and aragonite nucleation; such environments could also be favorable to MHC formation.

CONCLUSION

The tufa debris fragments collected from the bottom of Ikka Fjord in SW Greenland provide a unique opportunity to study modifications of carbonates in a marine, cold-water environment. From the study of tufa debris and primary ikaite we can conclude that:

1. Monohydrocalcite (MHC) is a common mineral in tufa debris collected at the base of the ikaite tufa columns and is also found in column fragments together with ikaite.

←

Fig. 6.—Mg carbonate in tufa debris sample 201. **A)** Hydrous Mg carbonate replacing 1–2 mm rhombs of MHC/calcite. Scanning electron image. **B)** Enlarged image of white frame from part A. The Mg carbonate plates are up to 200 µm long and 0.5 µm thick and replace the larger euhedral crystals of MHC and calcite. Scanning electron image. **C)** Thin section, back-scattered electron image. The euhedral crystals with higher light intensity are MHC or calcite. The hydrous Mg carbonate (low density = dark) composes the walls of the replaced rhombs. When observed in light microscope the Mg carbonate is opaque.

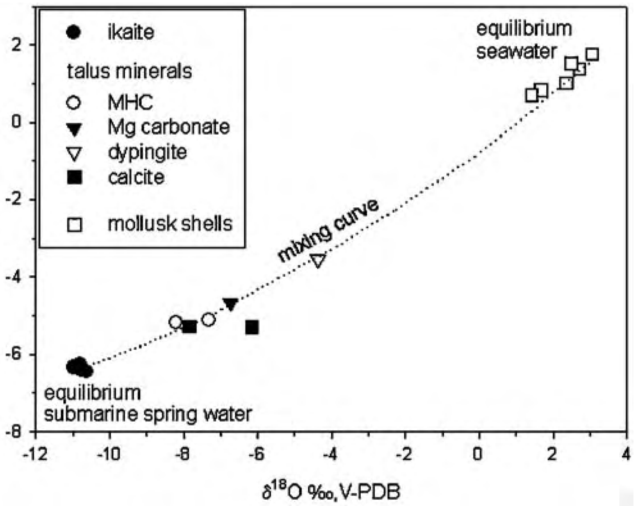

FIG. 7.—Carbon and oxygen isotope compositions of ikaite and of the density fractions dominated by monohydrocalcite, calcite, Mg carbonate, and "dypingite" in Ikka Fjord as given in Table 4. Ikaite data are similar to those reported by Buchardt et al. (2001) and represent isotopic equilibrium values for the cold (3°C) spring water. Data on mollusk shells are from Buchardt et al. (2001). These mollusks grew their shells in the cold seawater (1–2°C, 32% salinity) in Ikka Fjord away from the ikaite columns and represent seawater isotopic equilibrium values. The shape of the mixing curve defined by these two end members reflects the larger water–rock ratios with regard to oxygen than to carbon.

2. MHC forms from decay of ikaite in the tufa columns by admixture of minor amounts of seawater into the pore fluid. The decay reflects the high solubility and mineralogical instability of ikaite.
3. Precipitation of MHC is favored over calcite and aragonite because of inhibition by phosphate ions of the nucleation of the latter minerals. Organic molecules may also play a role in the precipitation of MHC, because spherulitic crystal aggregates of MHC contain organic matter.
4. Mg carbonates occur as secondary carbonate minerals in tufa debris fragments, probably as a result of marine diagenesis of MHC on the seafloor after disruption of columns.
5. To our knowledge this is the first reported occurrence of MHC in a marine environment. Ikaite is a relatively common mineral in cold-water seafloor environments with high phosphate concentrations from organic decay, and MHC may be found in such environments as well.

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