minerals

MDPI

Article

Mineral Changes to the Tufa Columns of Ikka Fjord, SW Greenland

Gabrielle J. Stockmann [1,*], Paul Seaman [2], Tonci Balic-Zunic [3], Mark Peternell [4], Erik Sturkell [4], Bengt Liljebladh [4] and Richard Gyllencreutz [5]

1 Institute of Earth Sciences, University of Iceland, Sturlugata 7, 102 Reykjavík, Iceland
2 2 Mill Steadings, Mawcarse, Kinross-shire KY13 9SN, UK
3 Department of Geosciences and Natural Resource Management, University of Copenhagen, 1350 Copenhagen K, Denmark
4 Department of Earth Sciences, University of Gothenburg, 413 20 Gothenburg, Sweden
5 Department of Geological Sciences, Stockholm University, 106 91 Stockholm, Sweden
* Correspondence: gabrielle@hi.is

Abstract: The submarine tufa columns of Ikka Fjord in Southwest Greenland have been studied during multiple field campaigns since 1995. The fjord contains close to thousand columns previously shown to consist of the metastable carbonate mineral ikaite ($CaCO_3 \cdot 6H_2O$), which requires near-freezing conditions to remain stable over longer periods of time. During a field campaign to Ikka Fjord in the summer of 2019, seawater temperatures of 6–9 °C and visual physical changes to the columns were observed. These are the highest recorded seawater temperatures measured in Ikka Fjord in over three decades of research. In response, three selected columns at three different locations were sampled at their bases, middle, and top sections for mineralogical analysis. These samples were supplemented by a four further column samples and an extensive hydrographical campaign during fieldwork in the summer 2021. Here, we report the results of the mineralogical analyses performed by X-ray diffraction and μ-Raman Spectroscopy on these column samples. The results show that the columns analysed now consist of the less hydrated carbonate minerals, monohydrocalcite ($CaCO_3 \cdot H_2O$), aragonite, and calcite ($CaCO_3$). One of the columns has completely altered into monohydrocalcite, whereas the other columns have crusts of ikaite and cores of monohydrocalcite ± aragonite and calcite. This change is interpreted as a dehydration reaction and mineral alteration from ikaite to monohydrocalcite continuing to aragonite ± calcite in response to being bathed in warming seawater. Hydrographic profilers and static dataloggers recorded seawater temperatures of 4–8 °C in the column-containing fjord areas during June–August 2021. The upper parts of the columns are particularly exposed to temperatures > 6 °C, considered to be the long-term stability threshold of ikaite in Ikka Fjord. The mineral dehydration reactions are irreversible. It is therefore predicted in a warming Arctic, ikaite will only appear as new growth on the columns for a short period, and that with time, the columns of Ikka Fjord will change mineralogy into mainly monohydrocalcite.

Keywords: ikaite; monohydrocalcite; mineral alteration; seawater; Ikka Fjord; tufa columns

check for updates

Citation: Stockmann, G.J.; Seaman, P.; Balic-Zunic, T.; Peternell, M.; Sturkell, E.; Liljebladh, B.; Gyllencreutz, R. Mineral Changes to the Tufa Columns of Ikka Fjord, SW Greenland. *Minerals* **2022**, *12*, 1430. https://doi.org/10.3390/min12111430

Academic Editor: Huifang Xu

Received: 29 September 2022
Accepted: 8 November 2022
Published: 10 November 2022

1. Introduction

The marine Ikka Fjord in Southwest Greenland (Figure 1) has been subject to a multitude of scientific expeditions since 1995 thanks to the existence of nearly one thousand submarine tufa columns in the shallow inner part of the fjord (Figure 2) e.g., [1]. These were identified by mineralogist Hans Pauly to consist of a previously unknown mineral of the chemical formula $CaCO_3 \cdot 6H_2O$ [2,3]. The compound calcium carbonate hexahydrate had long been known by chemists from laboratory experiments e.g., [4]. Following his discovery of the compound as a new mineral, Hans Pauly decided to name it 'ikaite' after the fjord, using its old spelling of Íka Fjord [2], which was in use at the time. A sampling campaign of columns and their abundant and diverse biological life by biologist Henning Thing and divers from the naval base Grønnedal in 1994, kicked off a biological-geological expedition from the University of Copenhagen in 1995 simultaneously with a geophysical expedition from Imperial College in London, UK [5]. From 1996 onwards, all expeditions and research on the columns has been carried out as a joint venture called the 'IKKA project'. The multi-disciplinary research conducted in Ikka Fjord over the years has included zoology, botany, microbiology, hydrology, sedimentology, marine geophysics, geochemistry, isotope geology, petrology, mineralogy, and oceanography. Several parameters have been studied on regular intervals over the 27 years of research within the IKKA project, including the number and distribution of columns, mineral composition, and temperature and salinity profiles of Ikka Fjord, combined with a substantial archive of photo and video records of the columns e.g., [1,6–11]. The temporal datasets allow observations and conclusions to be made regarding changes to the columns over almost three decades. The work presented here focuses on the observed mineralogical and physical changes to the columns, and changes in seawater temperature. With Arctic regions already experiencing a warming by a factor 4 compared to the rest of the globe [12], and with ikaite columns being protected under Greenland legislation [13], a future scenario concerning the fate of the columns in a warming climate is included in this work.

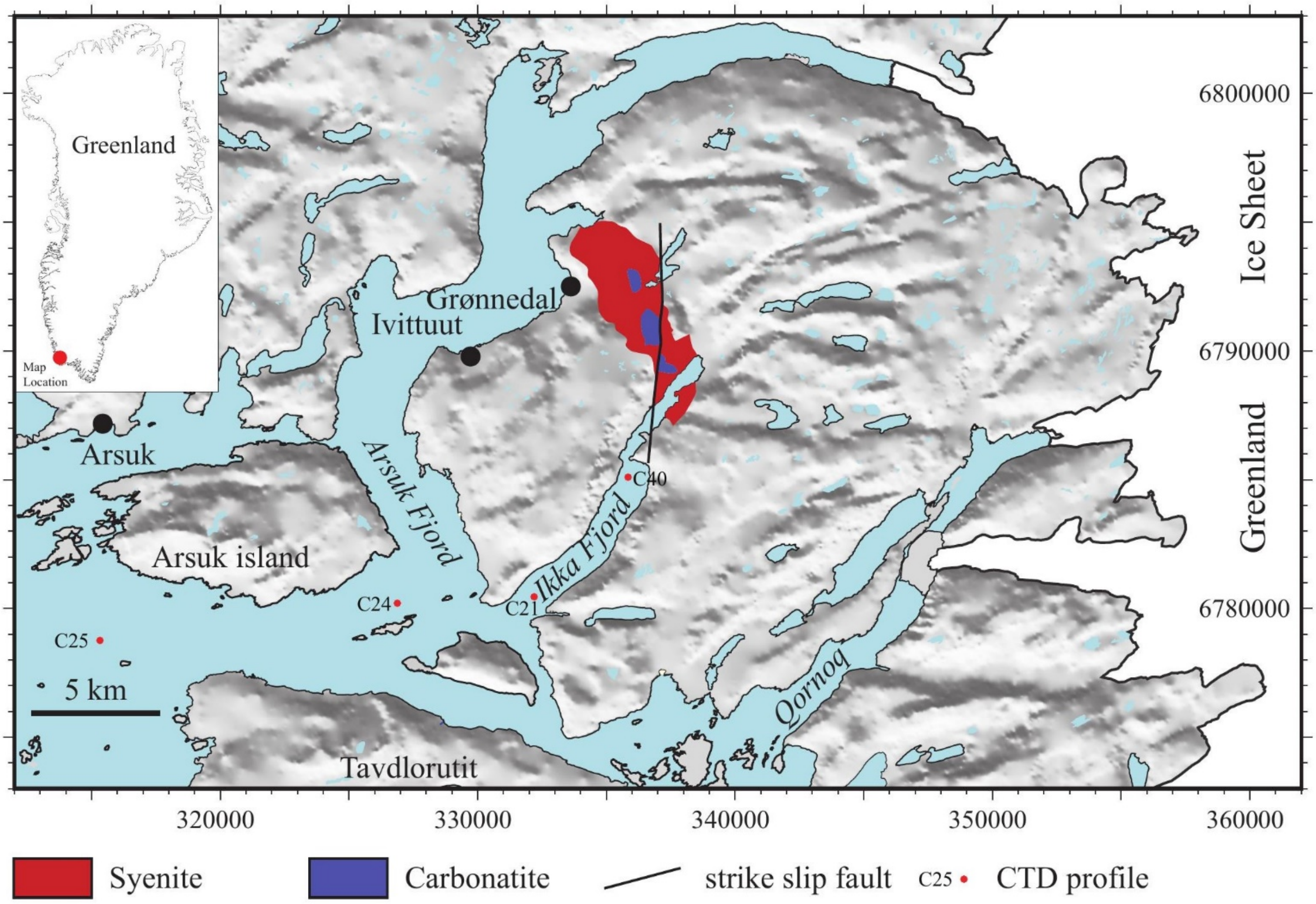


Figure 1. Location of Ikka Fjord in Greenland. Red and blue-coloured areas mark the Grønnedal-Íka igneous complex, and grey areas consist of old Archean gneissic rocks.

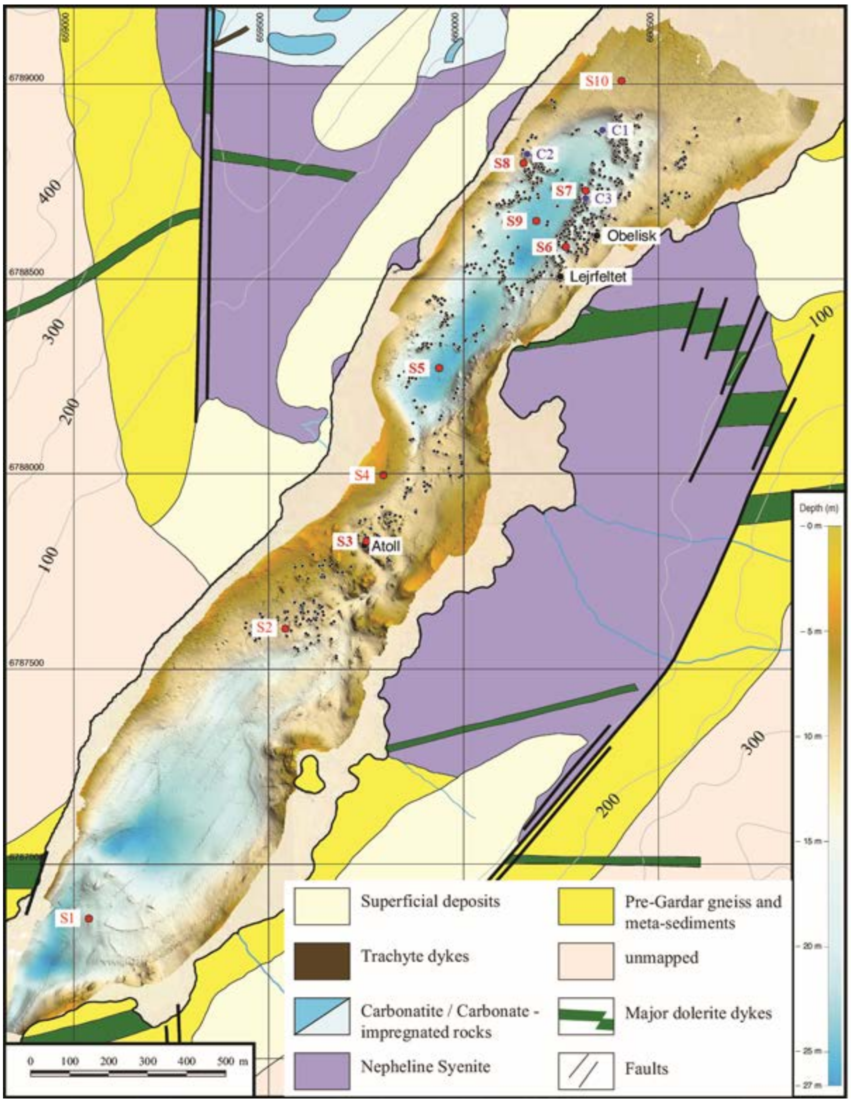


Figure 2. Bathymetric map of Ikka Fjord showing all positions of columns and marks the three areas where column samples were taken in 2019, plus the positions of the ten HOBO dataloggers, and of the Atoll and the Obelisk column areas.

2. Mineralogical and Geological Background

Ikaite has been shown through experiments to have a stability field at kbar-high pressures and low temperatures [14], i.e., P-T conditions that are not met on Earth. When encountered in nature, it is always as a metastable phase that formed in place of the thermodynamically more stable anhydrous calcium carbonate minerals ($CaCO_3$), calcite, aragonite, and vaterite e.g., [15,16]. Various parameters have been identified to energetically favour precipitation of ikaite over calcite, which can vary from one setting to another. In the case of Ikka Fjord, the main parameters are identified to be (1) low water temperatures < 6 °C, (2) Mg in seawater inhibiting calcite, (3) supersaturation with respect to ikaite, (4) dominance of $CaCO_3^0$ ions in solution, and (5) possibly the assistance of bacteria aiding, enhancing, or protecting ikaite growth [6,17–20]. The proposed model for the formation of ikaite in Ikka Fjord (Figure 3) involves a mixing of (1) Ca^+ ions from seawater with (2) pH 10–11 groundwater of sodium bicarbonate-carbonate composition providing the CO_3^{2-} ions leading to ikaite saturation and precipitation [1,6,18]. The alkaline groundwater stems from fluid-rock reactions inside the Grønnedal-Íka igneous complex (Figure 1) by dissolution of Na-rich nepheline syenites and Ca- and Fe-rich carbonatites [21–23]. Mapping of the columns illustrate how the distribution of the columns in Ikka Fjord is constrained by the outcrop of the Grønnedal-Íka complex [8,11,24], with no column growth detected where the bedrock beyond changes to old Archean gneisses (Figure 2). Several faults and dikes cut the Grønnedal-Íka complex and one major fault is considered to run down the centre of Ikka Fjord [25]. Early-on, Pauly (1963) [2,3] suggested the columns were forming over springs seeping through fractures in the seabed of Ikka Fjord. As no glaciers are calving into Ikka Fjord and with several subsurface thresholds preventing icebergs from entering the fjord, the sedimentary cover of the floor of the fjord is relatively thin and permeable and is punctuated by rock outcrops, which further allow groundwater to seep through (Figure 3) [8]. Indeed, both groundwater and air are seen to escape from the columns (Figure 4a), and when cut, large volumes of groundwater stream out and new growth of ikaite starts to form almost immediately (Figure 4b) [1,6]. As the groundwater has a lower density than seawater, the growth is upwards, enabling columns to grow up to the halocline, some being 2–3 m below sea surface (Figure 3), where brackish water no longer supplies sufficient Ca^+ ions [1,6] for ikaite formation. In total, 938 columns of size 0.5 to 20 m tall were mapped from a multibeam sonar survey (Figure 2) providing GPS position, depth, and height of all individual identifiable columns as they appeared in 2019 [11]. Columns have been observed to grow up to 0.5 m per year (Figure 4b) and are therefore likely to be continuously growing and/or changing shape [6]. Column water was sampled from the two column areas, the Atoll and Lejrfeltet (Figure 2) [6], and other columns have been monitored with probes for O_2, light, and pH [9,10]. The temperature of the sampled column water is stable around 3–4 °C [9]. At in-situ temperatures, the Atoll column water had pH 10.5 and Lejrfeltet column water had pH 10.2 reflecting minor variations in sodium concentration and alkalinity [6,18,19]. The presence of minor concentrations of orthophosphate in the column water (<25 ppm) was previously speculated to be the controlling factor inhibiting calcite [6,18,19] formation. However, Tollefsen et al. (2018) [20] showed that it was in fact Mg in seawater that has the controlling role of inhibiting calcite growth in the Ikka Fjord system. There is clear line between calcite and ikaite growth as a function of Mg concentration and pH, with 5–30 mmol/kg Mg and high pH > 9 favouring ikaite in experiments at 5 °C [20]. The long-term stability temperature of ikaite is difficult to establish due to its metastable character and the various factors that can affect the kinetics favouring ikaite. In summers of 1995–1997, seawater temperatures never surpassed 6 °C, and the actively growing columns were found to consist of 98–100% ikaite [1,6]. In contrast, the broken-off pieces of columns lying on the seabed in 1995–1997 were identified to consist of mainly monohydrocalcite (MHC) with minor aragonite, calcite, and Mg-carbonates [7]. Ikaite has been shown in laboratory experiments to nucleate up to 35 °C [26], but it is the long-term stability of ikaite at elevated temperatures that is of concern for the columns of Ikka Fjord. Visual inspections of physically altered columns in 2018 and a field campaign with divers in the summer-autumn of 2019 reaffirmed these concerns. Water temperatures of 6–9 °C were measured from bottom to top among the columns both in June and September 2019 [11], i.e., above the previously established temperature stability threshold for ikaite in Ikka Fjord. For how long the warming of the seawater in the fjord has taken place is uncertain. Hansen et al. (2011) [9] reported normal low seawater temperatures in Ikka Fjord during 2007–2009, whereas Trampe et al. (2016) [10] registered a mean temperature of 7.5 °C and a max. temperature of 9.4 °C at the top of a selected column during a seven-day campaign in August 2013.

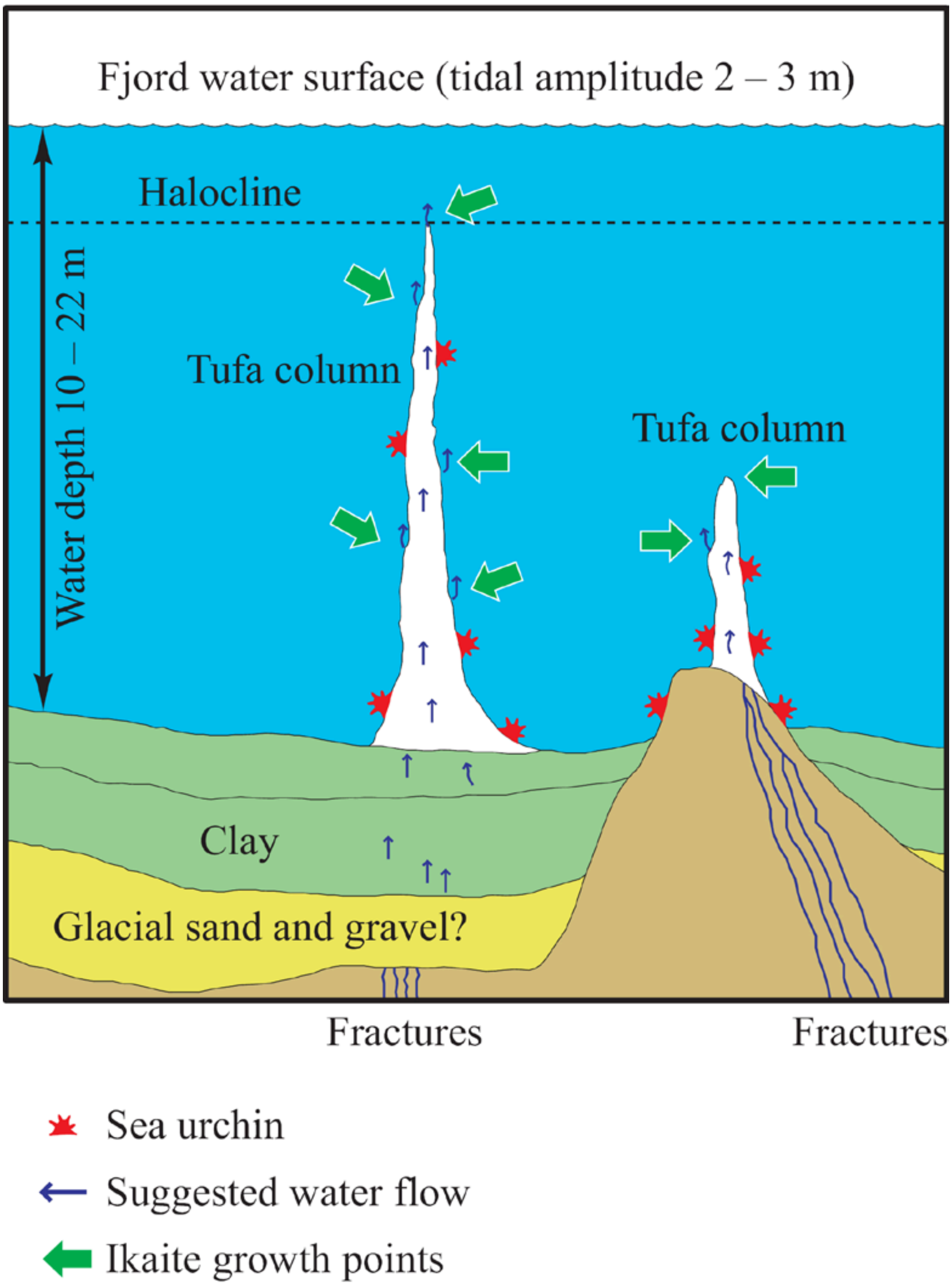
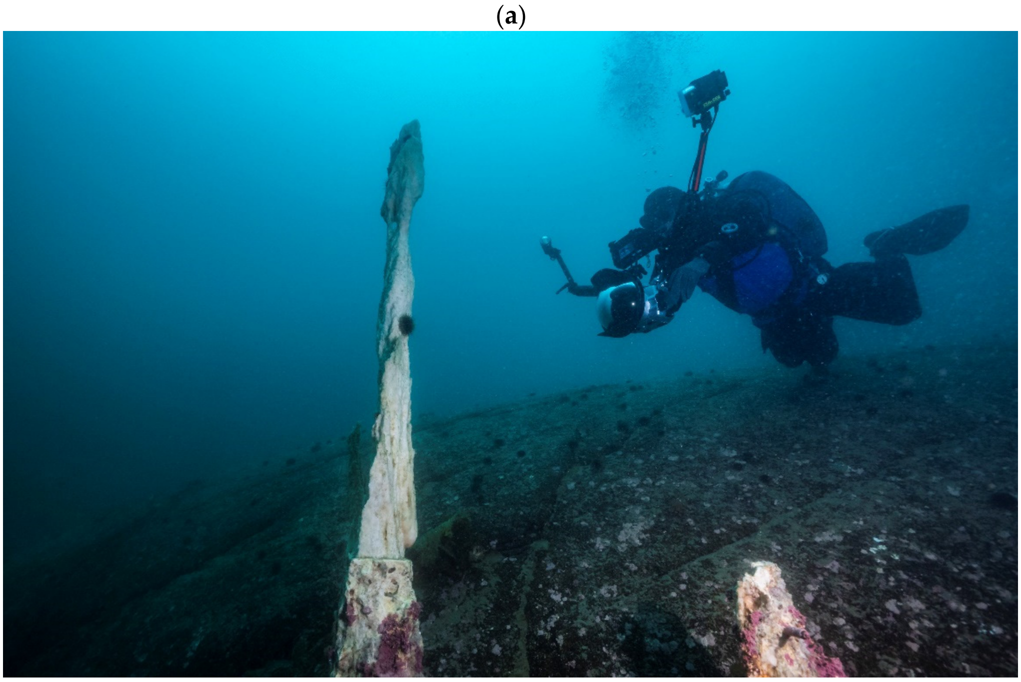


Figure 3. Proposed model for the formation of tufa columns over submarine springs in Ikka Fjord.

(a)

(**a**)



(**b**)

Figure 4. (**a**) Photo showing the air bubbles and groundwater escaping from the columns in 2022, and (**b**) the new growth of ikaite on a column that was last cut in 1997. Photo credits: Bengt Liljebladh (**a**) and Uli Kunz (**b**).

3. Methods

3.1. Column Sampling Process

Column sampling in Ikka Fjord was performed by Royal Danish Navy divers on 22–23 June 2019 and by professional divers from SUBMARIS during 12–22 August 2021. In the 2019 sampling campaign, the divers cut off 20 cm to 80 cm long pieces of three columns at three locations in Ikka Fjord (C1–C3 in Figure 2) (see GPS positions in Seaman et al., 2022 [11]). The divers collected samples from the bottom, middle, and top sections of the three columns, adding up to nine samples in total. They were instructed to look for the most freshly white parts of the columns to check if new growth still consisted of ikaite. Seawater temperature and depth was recorded by the divers at each of the nine sampling sites together with video recording of the sampling process. The samples were carried in nets to a Rigid-Hulled Inflatable Boat (RHIB) at the surface and immediately stored in a cool box. After sampling each column, the cool box containing the column samples were transported back to the Danish navy vessel F360 HVIDBJØRNEN and transferred to a −18 °C freezer. The freezer stayed onboard HVIDBJØRNEN under supervision of the navy crew until arrival in Reykjavík port in July 2019, where the freezer with columns was transported to the University of Iceland. Selected samples were taken out and kept frozen in a cool box during transportation by Icelandair Cargo to the University of Copenhagen in Denmark for mineral analysis.

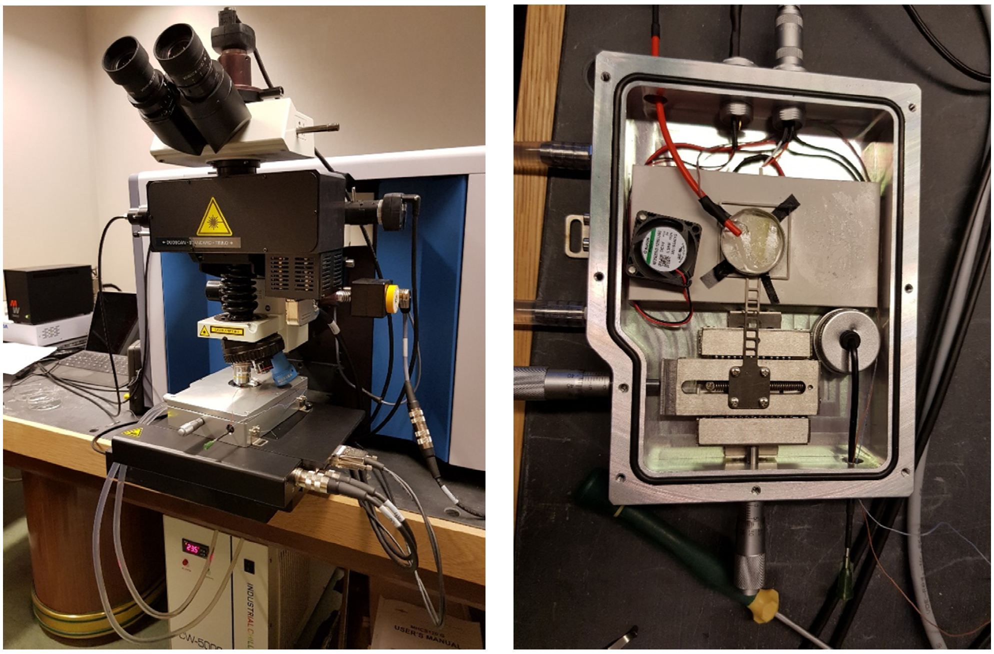
The column sampling conducted during August 2021 was performed by marine biologist Uli Kunz and maritime archaeologist Florian Huber, both professional divers and underwater photographers from the company SUBMARIS. The aim was to collect potential new growth on the column sampling points from 2019. However, this turned out difficult because none of the sampling points were marked for future reference on collection nor were easily recognizable two years later. In the end, four 20–70 cm length column pieces were sampled from the approximate column sampling areas of 2019 (Figure 2). Column 1-2021 was taken at 12 m water depth from the C2 area of 2019, column 2-2021 was sampled at 4.5 m water depth from the C3 area of 2019, and column 3-2021 was sampled at 13 m water depth at the C1 area of 2019. Finally, column 4-2021 was taken at 14–15 m water depth at the C3 area of 2019 (see map in Figure 2). The columns were transported in a cool box with frozen cooling blocks to a freezer at the nearby military Station Grønnedal. From here they were transported as frozen goods by Royal Arctic Line to Aarhus University in Denmark, where they were stored in a −20 °C freezer until further mineral analysis in 2022.

Note that the depths recorded by divers at the time of sampling and that the tidal water in Ikka Fjord could be up to 2–3 m different to tidal datum depth. In 2019, columns 1 and 3 were sampled at high tide, whereas column 2 was sampled as the tide was dropping. The sampling in 2021 was performed during rising tide with an increase of maximum 0.5 m sea level during the sampling time.

3.2. Mineral Analysis

In order to identify the minerals present in the nine column pieces collected in 2019 and the four column pieces collected in 2021, powder X-ray diffraction (XRD) patterns for the samples were measured at the University of Copenhagen with a Bruker-AXS D8 Advance diffractometer equipped with a Cu X-ray tube, a primary beam Ge111 monochromator (wavelength 1.54059 Å) and a silicon-strip LynxEye detector with an opening of 3.3°. The measurements were made in reflection mode, employing the Bragg-Brentano technique, with a fixed divergence of the primary beam (0.25°), a measuring step of 0.2° 2θ, and a time per step of 0.5 s. Measurements ranged between 10°–45° 2θ using a rotating sample holder. The quantitative analysis was made with the use of Rietveld refinement [27,28]. The program used for the Rietveld refinement was Topas version VI [29]. In calculations, the scale factors, unit cell parameters, and preferred orientation parameters (for ikaite and calcite) were refined. The starting crystal structure data for minerals were taken from the ICSD database [30]. As ikaite is known to be sensitive to high temperatures, the samples were kept in a freezer until immediately before analysis. In addition, the sample holders from the XRD instrument were kept in the freezer until analysis. Short analytical runs of approximately 16 min from 10° to 45° were used to minimize the risk of transformation of ikaite during analysis. This approach proved to be an efficient method to study ikaite samples in previous XRD studies [18].

Laser-induced µ-Raman measurements were carried out at defined temperatures on a slice of column 1-2021 at 21 ± 1 °C and selected pieces of the 2019 columns at −20 ± 0.1 °C using a Horiba (Jobin Yvon) LabRam HR Evolution Raman spectrometer at the Earth and Environmental Science Department of the University of Gothenburg. The samples were exited with an air-cooled frequency-doubled 532 nm NdYAG laser utilizing an Olympus 10× objective. The lateral resolution of the unpolarized confocal laser beam was on the order of 10 µm. Spectra were generated in the ranges of 50–1300 cm^{-1} and 3000–3600 cm^{-1} utilizing an 1800 grooves/cm grating and a thermoelectric cooling electron multiplier CCD including a front illuminated 1600 × 200 pixel chip. Spectral resolution on the sample is in the order of 1 cm^{-1}. The wavenumber calibration was done using the 520.7 cm^{-1} Raman band on a polished silicon wafer with a wavenumber accuracy usually better than 0.5 cm^{-1}. Minor samples for Raman analysis were stored in a fluid-cooled cold stage kept at −20 °C (Figure 5) to ensure no alteration was taking place during analysis. A MHCS120G cold stage from Microptic® with a MDTC600 temperature controller and MCH-6L water chiller for cooling was used. Frozen seawater attached to the columns was chipped off in a cool room, melted, and then poured into the container holding the sample. The surface was polished and kept free of ice. The lid of the fluid-ice container was made of a CaF_2, Raman grade polished window (Crystran Ltd., Poole, UK) allowing the transmission of the Raman laser beam (Figure 5b).



(**a**) (**b**)

Figure 5. (**a**) Setup of Raman analysis of column samples at the University of Gothenburg using (**b**) a fluid-cooled container to maintain a temperature of −20 °C during analysis.

3.3. *Seawater Measurements*

Seawater measurements in June and September 2019 were performed by the divers from the Royal Danish Navy on the vessel F360 HVIDBJØRNEN and their SCUBAPRO Digital 330 M diving computers with ±1 °C accuracy. Before diving in September 2019, the diving computer was calibrated against a laboratory thermometer with ±0.1 °C accuracy. For further description see Seaman et al. (2022) [11].

Oceanographer Jesper Sano Højdal of HydroCharting Aps, conducted a total of 78 CTD profiles from inner Ikka Fjord along its entire 13 km length into the larger Arsuk Fjord (Figure 1) during the period 26–30 June 2021 (Supplementary Material S1). A Valeport Swift SVD Conductivity-Temperature-Depth (CTD) probe was used for this study with an accuracy of ±0.05 mS/cm for conductivity, ±0.01 °C for temperature, and ±0.005 bar for pressure (depth). In addition, ten HOBO ONSET dataloggers were deployed du-ring the CTD profiling operation at ten different positions in Ikka Fjord (S1–S10 in Figure 2). The dataloggers measure temperature with an accuracy of ±0.53 °C at 30 min intervals. Five of the dataloggers were retrieved and their depth of deployment recorded by the SUBMARIS divers on 20–21 August 2021, of which four dataloggers were running normally and their data downloaded. The remaining five dataloggers will be retrieved in summer 2023.

4. Results

A total of 41 samples extracted from the 2019 and 2021 column pieces were analysed by X-ray diffraction (XRD) (see Table 1). New sample pieces were cut from the 2019 columns for μ-Raman spectroscopy analysis to obtain high-resolution spectra of columnar ikaite, monohydrocalcite (MHC), aragonite, and calcite, and to compare with the previously obtained XRD data. The raw data of the 78 CTD profiles and the four HOBO datalogger data are provided in Supplementary Materials S1 and S2, respectively. All four column samples collected in 2021, and the top and mid-section of column 3 collected in 2019 were photographed with the 3D-program Scaniverse. The six 3D-photograph files are provided in Supplementary Material S3. Selected data of the minerals identified by XRD analysis are provided in Supplementary Material S4, and raw data from all the Raman analyses in Supplementary Material S5.

Table 1. XRD Results of tufa column samples from Ikka Fjord *. Relative proportions in wt%.

Sample ID	Depth (m)	Temp. (°C)	Ikaite	Monohydrocalcite	Calcite	Aragonite
2019-1-1A	13.3	6	68.5 (7)	29.4 (7)	2.2 (5)	
2019-1-1B	13.3	6	77.4 (7)	22.6 (7)		
2019-1-2A	10.3	8	93.3 (4)	6.7 (4)		
2019-1-2B	10.3	8	100			
2019-1-2C	10.3	8	99.9 (5)		0.1 (5)	
2019-1-2D	10.3	8	100			
2019-1-3A	6.0	7	100			
2019-1-3B	6.0	7	100			
2019-1-3C	6.0	7	100			
2019-1-3D	6.0	7	99.8 (3)		0.2 (3)	
2019-1-3E	6.0	7	100			
2019-1-3F	6.0	7	100			
2019-2-1A	10.0	7	100			
2019-2-1B	10.0	7	100			
2019-2-1C	10.0	7	100			
2019-2-2A	6.5	7		95.4 (4)		4.6 (4)
2019-2-2B	6.5	7		79.6 (5)	0.5 (2)	19.9 (5)
2019-2-2C	6.5	7	100			
2019-2-3A	2.7	9	100			
2019-2-3B	2.7	9	100			

Table 1. *Cont.*

Sample ID	Depth (m)	Temp. (°C)	Ikaite	Monohydrocalcite	Calcite	Aragonite
2019-2-3C	2.7	9	99.8 (5)		0.2 (5)	
2019-2-3D	2.7	9	95.7 (8)	2.3 (8)	2.0 (3)	
2019-3-1A	13.3	8	98.2 (6)	1.8 (6)		
2019-3-1B	13.3	8	99.1 (2)	0.6 (2)	0.3 (1)	
2019-3-2A	10.1	8	99.7 (1)		0.3 (1)	
2019-3-2B	10.1	8	99.3 (1)	0.5 (1)	0.2 (1)	
2019-3-2C	10.1	8	99.8 (1)		0.2 (1)	
2019-3-2D	10.1	8	100			
2019-3-2E	10.1	8	100			
2019-3-2F	10.1	8	100			
2019-3-3A	3.9	9	94.9 (3)	4.7 (3)	0.4 (1)	
2019-3-3B	3.9	9	95.5 (4)	1.7 (1)	0.9 (1)	1.9 (4)
2019-3-3C	3.9	9	99.4 (1)		0.6 (1)	
2019-3-3D	3.9	9	98.2 (5)		0.2 (1)	1.6 (5)
2022-1a-r	12.0	n.d.	100			
2022-1b-c **	12.0	n.d.		99.9 (8)	0.1 (8)	
2022-2a-r	4.5	n.d.	99.2 (2)		0.8 (2)	
2022-2b-c	4.5	n.d.	73.4 (2)	26.6 (2)		
2022-3a-r	13.0	n.d.		93.7 (4)	3.9 (4)	2.4 (3)
2022-3b-c	13.0	n.d.		87.0 (5)	1.6 (2)	11.4 (5)
2022-4a-r	14–15	n.d.	100			

* Sample ID with -r: sample from rim, and -c: sample from centre of column, n.d.: no data registered. The number in parentheses are standard deviations referring to the last digit. ** Contains some minor unidentified phase(s).

4.1. X-ray Diffraction

Table 1 shows the results of the 2019 and 2021 columnar mineral analysis with XRD. For the 2019 columns, the number of analyses reflects the size of the column sample with more analyses being carried out on the larger samples. Aim was made at analysing areas with visual differences with respect to colour and structure, bearing in mind the divers were instructed to sample the 'freshest'-looking mineral growth. For the 2021 columns, analysis was carried out on slices of the columns with one sample from the rim (crust) and one from the centre, respectively. Results of the fresh-looking 2019 columns show most of the samples to consist of ikaite with a few exceptions. In column 1, an altered part of mixed ikaite and MHC was found at the bottom corresponding to 13.3 m water depth (Table 1). The mid and top sections were pure ikaite. In column 2, the middle part from 6.5 m depth was the most altered with the presence of 80–95 wt% MHC together with 5–20 wt% ara-gonite, whereas the bottom section consisted of pure ikaite. The top section from 2.7 m depth had minor MHC and calcite. Column 3 had a bottom and a mid-section made of ikaite. The top section from 3.9 m depth had ikaite as the main mineral constituent (95–100 wt%) together with minor MHC (2–5 wt%), aragonite (<2 wt%), and calcite (<1 wt%) (Table 1). Results of the 2021 columns illustrate that whereas the outer rim (crust) of the older columns can still consist of 100% ikaite, core parts in these columns were either partly or completely altered into MHC (27–100 wt%) ± aragonite (≤11 wt%) and calcite (≤4 wt%). In the oldest looking column 3, based on its coverage by coralline algae (see 3D-photo in Supplementary Material S3), no ikaite was detected. Its rim (crust) was mainly MHC and the core a mix of MHC, aragonite, and calcite in subsequent order based on amount (Table 1). Representative XRD powder diagrams and Rietveld quantitative phase analysis of pure ikaite and monohydrocalcite, and mixed phases including aragonite and calcite are provided in Supplementary Material S4.

4.2. Raman Spectrometry

With the availability of XRD results of the different mineral phases in columns 1–3 of 2019, new samples were taken from the same areas of the mid and top sections of column 3 and analysed with a µ-Raman spectrometer. The mineral ikaite was not included in the Raman mineral database, therefore our own spectra of ikaite were obtained and compared with literature results e.g., [31]. Through this, high-quality spectra were obtained of ikaite, MHC, and aragonite (Figure 6a–c). Monohydrocalcite and aragonite spectra were included in the Raman mineral database and thus could be identified by matching against these database references. To obtain a pure calcite of columnar origin, a piece of the column was taken out and left to dry at room temperature with no fluids present. This ensured a 100% conversion into calcite within a couple of days (Figure 6d).

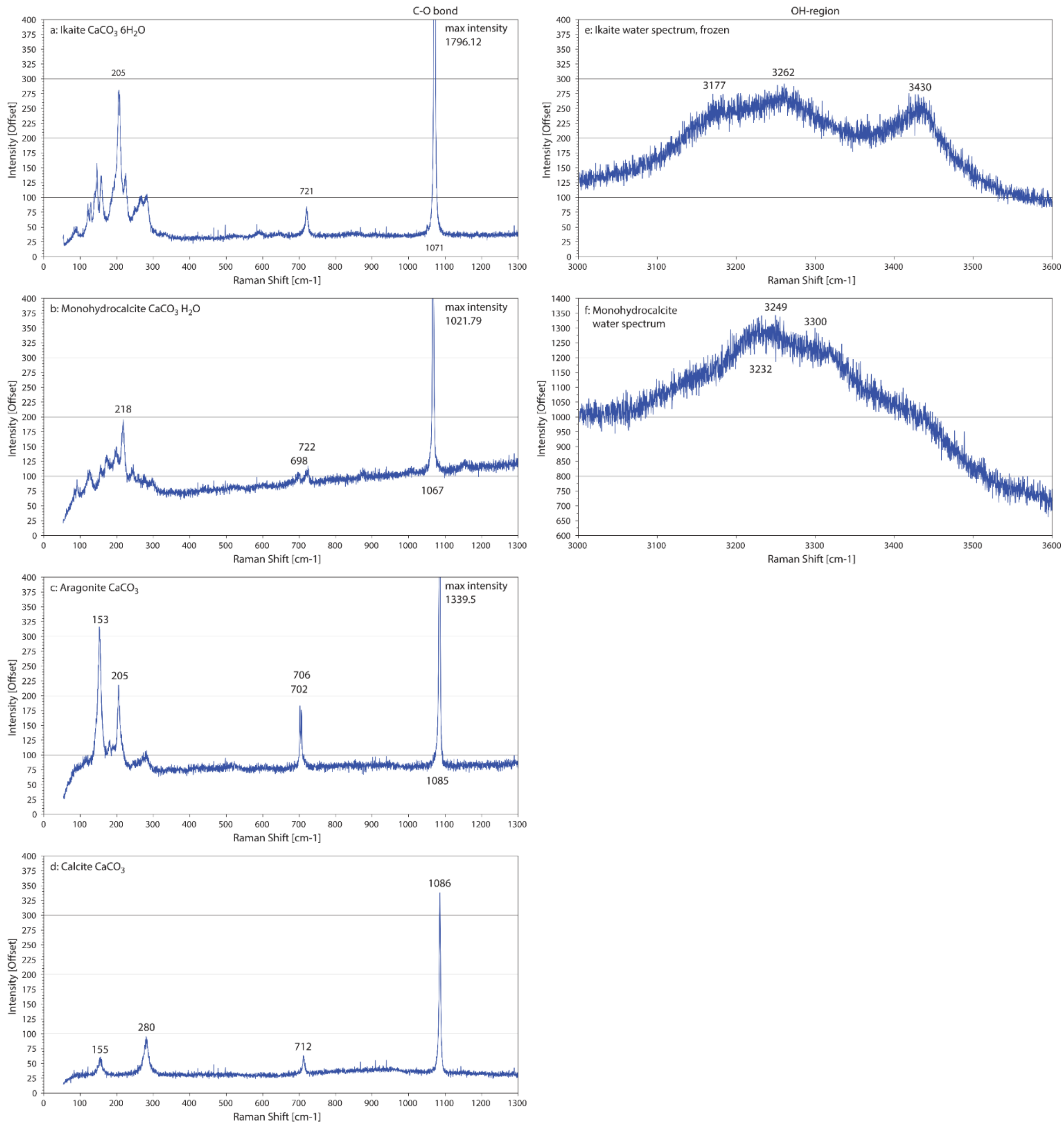


Figure 6. Results of Raman analysis of minerals of columnar origin from Ikka Fjord of (**a**) ikaite, (**b**) monohydrocalcite, (**c**) aragonite, (**d**) calcite, and the OH-region of (**e**) ikaite, and (**f**) monohydrocalcite.

Samples were run until sufficient statistics were recorded showing how the different peaks (e.g., lattice peaks, C-O bond, and peaks in the OH-region) are shifted between columnar ikaite, MHC, aragonite, and calcite, respectively (see Figure 6a–d). As an example, the C–O bond shifted position from c. 1071 cm^{-1} to 1067 cm^{-1} from ikaite to MHC, and from 1085 cm^{-1} to 1086 cm^{-1} from aragonite to calcite (Figure 6a–d). Peaks in the OH-region of 3000–3600 cm^{-1} were only present for the hydrated minerals, ikaite and monohydrocalcite. Ikaite had three peaks at c. 3180, 3260, and 3430 cm^{-1}, respectively, for a frozen sample (Figure 6e), whereas monohydrocalcite had a broader peak area between c. 3200 and 3300 cm^{-1} (Figure 6f) for an unfrozen sample. Text files (.txt) with the raw data for all six spectra can be found in Supplementary Material S5.

The analysis then progressed onto column 1 sampled in August 2021. Instead of spot samples, seven points across a cut slice of the column were investigated (Figure 7). The cutting of the columnar slice of column 1-2021 took place in a −18 °C cold laboratory, and the column slice was frozen together with seawater from Arsuk Fjord, the neighbouring fjord of Ikka Fjord (Figure 1), and photographed before analysis (Figure 7). As no cooling options were possible for this size of sample during Raman analysis, the analysis time was kept to two hours. From visual inspection, there were two differently coloured areas of the column (Figure 7). One encompassed a more greyish part found only at the rim, whereas a white more massive-looking part encompassed the main column (Figure 7). In addition, greenish areas were found throughout the column, which are assumed to be biologically coloured by algae and bacteria. As observed by spot analysis by XRD, the grey rim consisted of ikaite, whereas the central part was made up of MHC with an estimated distribution of 5–10 vol% ikaite and the remaining 90–95 vol% consisting of MHC (Figure 7). To date, only column 1 of the 2021 columns has been analysed by µ-Raman spectrometry. The raw data of the Raman analysis of these seven points including the OH-region are provided as text files in Supplementary Material S5.

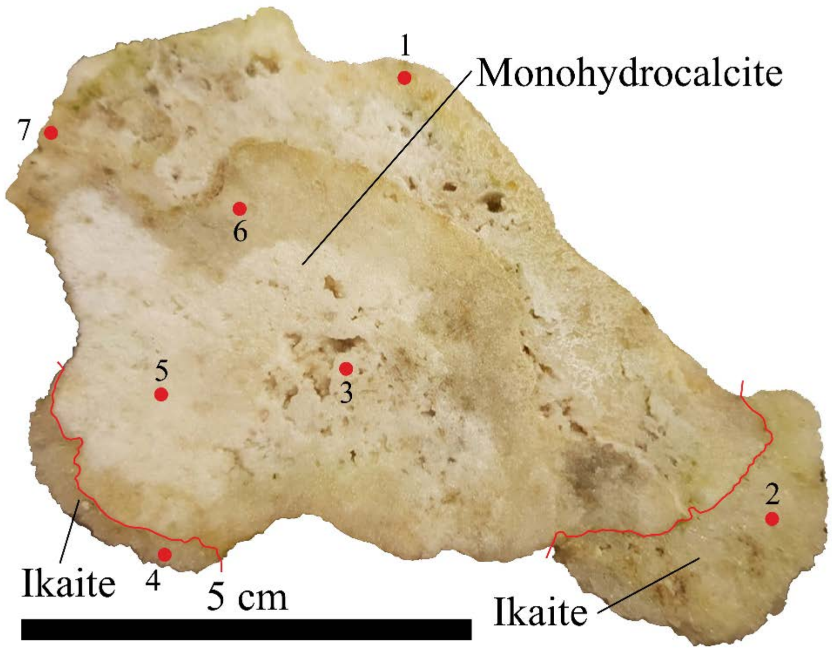


Figure 7. Photograph of the columnar slice of Column 1-2021 investigated with Raman at seven spots (red circles). Ikaite growth were found in the grey areas marked with red lines. The remaining spots were identified as monohydrocalcite.

4.3. CTD and Temperature (SCUBA and HOBO) Measurements

Figure 8a shows the compiled results of the CTD casts carried out in the inner part of Ikka Fjord, where the columns are found. The remaining casts were taken further out in the deeper parts of Ikka Fjord (<175 m) and into the much deeper Arsuk Fjord

(300–600 m depth) for comparison (Figures 1 and 8b). As the profiles in Figure 8a illustrate, the top brackish layer reached a temperature up to 14 °C and a salinity close to 0 PSU, i.e., almost pure freshwater. The column growth stops a few meters below sea surface depending on the tide with 2 m on average (Figure 3). Hence, the column growth zone ranges approximately from 2 m down to 22 m's water depth. In this columnar growth zone, the temperature ranges from 6–8 °C at the top and narrows into approximately 3 °C at the bottom (Figure 8a). The salinity data is more varied in the upper part of the water column but shows the same trend of narrowing into a single value of a salinity of approximately 33 PSU at the bottom close to the seabed (Figure 8a).

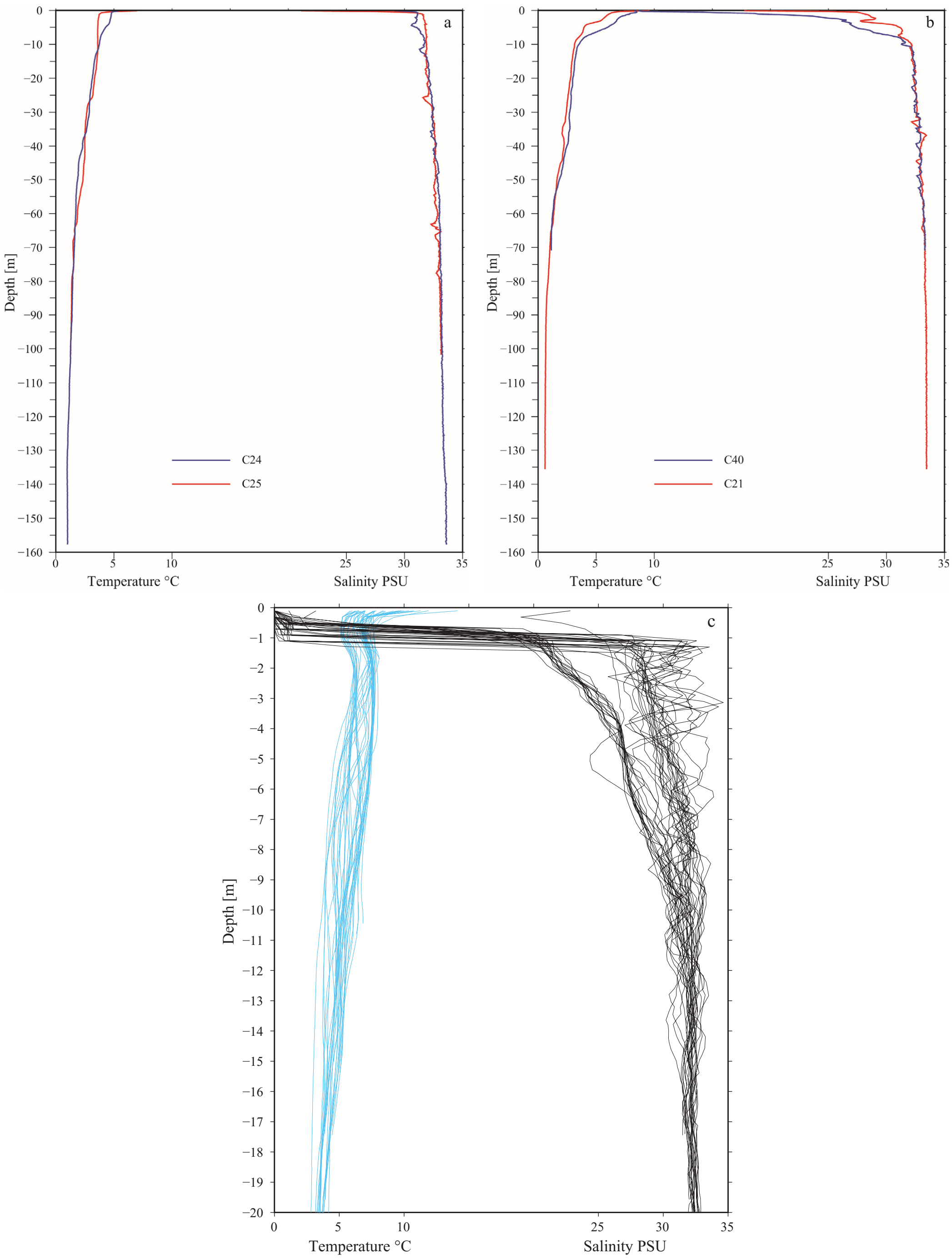


Figure 8. (**a**) CTD profiles (C24 and C25) from south of the Arsuk Island in Figure 1, (**b**) CTD profiles (C21 and C40) in outer Ikka Fjord in Figure 1, and (**c**) all CTD profiles in the inner part of Ikka Fjord with temperatures marked in blue and salinities in black.

The temperature results of the four HOBO dataloggers deployed in seawater are shown in Figure 9 and illustrate that the three shallowest (S3 at 12 m, S4 at 8.5 m, and S8 at 14 m water depth) all follow the same trend of temperature fluctuations from when they were deployed in end June 2021 to end August 2021. They vary between 3.8–6.3 °C, 4.2–8.2 °C, and 4.3–8.1 °C for S3, S4, and S8, respectively (Figure 9). In contrast, datalogger S7 deployed at 20.8 m water depth showed a slow but consistent increase in temperature of 3.3 to 4.1 °C during the 3-month summer period of 2021 (Figure 9 and Supplementary Material S2).

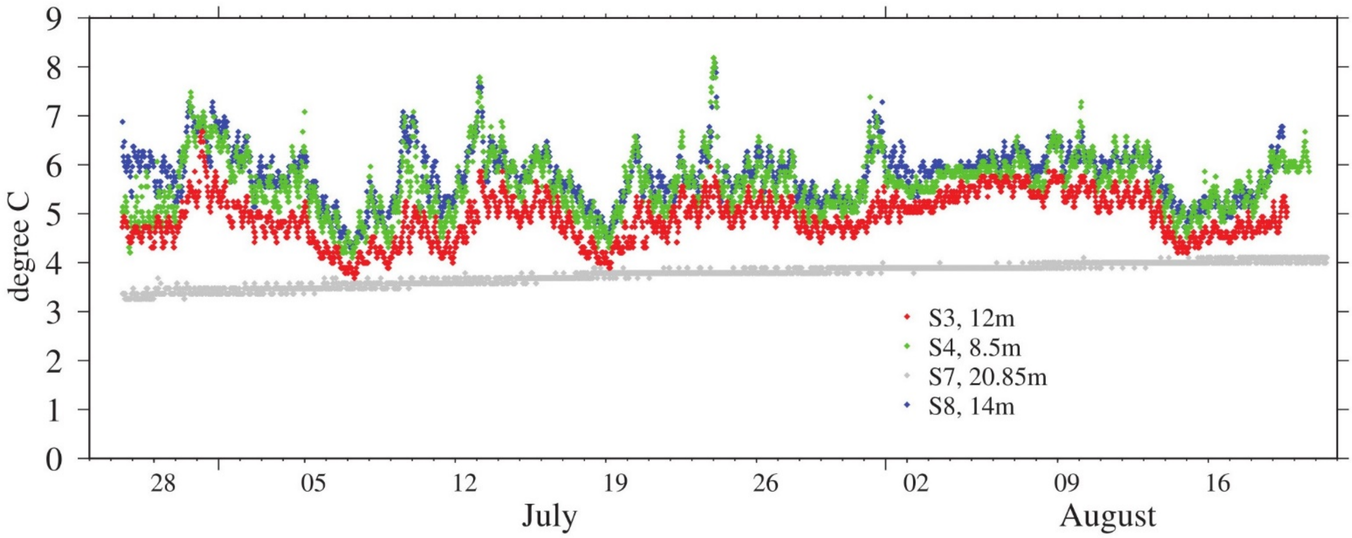


Figure 9. Compiled temperature profiles of the four HOBO dataloggers in summer of 2021.

4.4. Photo Comparison of Selected Columns from 1995–97 to Present Day

The Atoll and the Obelisk are two distinctive groups of columns that are easily recognized and easy to re-locate (Figure 2). The Atoll stands out as a massive almost eight-meter-wide structure, which divers can stand on at the lowest tides (20–30 cm below water surface). These columns were among those chosen for comparison of the visual changes that have happened to the columns over almost three decades from 1995–97 to 2021–22 (Figure 10a–d). The visual changes are both with respect to colour, the surface of the columns, and the biological life living on them. The seabed around the Atoll and the Obelisk is situated at around 10.5 m water deep, i.e., the columns are approximately eight meters tall. Both groups of columns are registered with GPS position, height, and their growth potential in Seaman et al. (2022) [11]. These two groups of columns are among the ones that have reached 100% of the growth potential, i.e., they cannot grow any taller [11]. What most of the columns of Ikka Fjord have in common is a change in colour from snowy white material to more yellowish, a more porous surface, and a lack of algae and macrofauna on the columns (Figure 10e,f and 3D photographs in Supplementary Material S3). In the nineties, the columns were teeming with biological life and had coral-reef appearances [1,32], whereas today, they appear ‘dead’. The Atoll shows signs of erosion on the top with structures standing out at the surface that have not been observed before (Figure 10a,b). In the nineties, the Atoll was covered in snowy white powder on the top that could be wafted up by hand and it supported a thriving community of blue mussels (*Mytilus edulis*) [32]. Sea urchins were plentiful in past years, grazing up and down the flanks of the columns [32], but they appear sparser in population by the summer of 2022. Furthermore, the columns look now to be devoid of the encrusting coralline algae, *Lithothamnion*, and *Clathromorphum*, and other algae growth (Figure 10a–d). Larger columns had filamentous algae growth, too, which is now largely gone. The top of the columns by summer 2022 were observed to be lacking the rosettes and crests at their tips (Figure 4a) because they are devoid of much of the sugary white crystal accumulations of fresh ikaite precipitation known from the nineties (Figure 10e). Instead, they are now made of solid-looking massive material (Figure 10f). New biological studies and the initiation of a monitoring programme are scheduled for summer 2023 to describe the macrofauna and flora of the columns and follow biological changes henceforth.

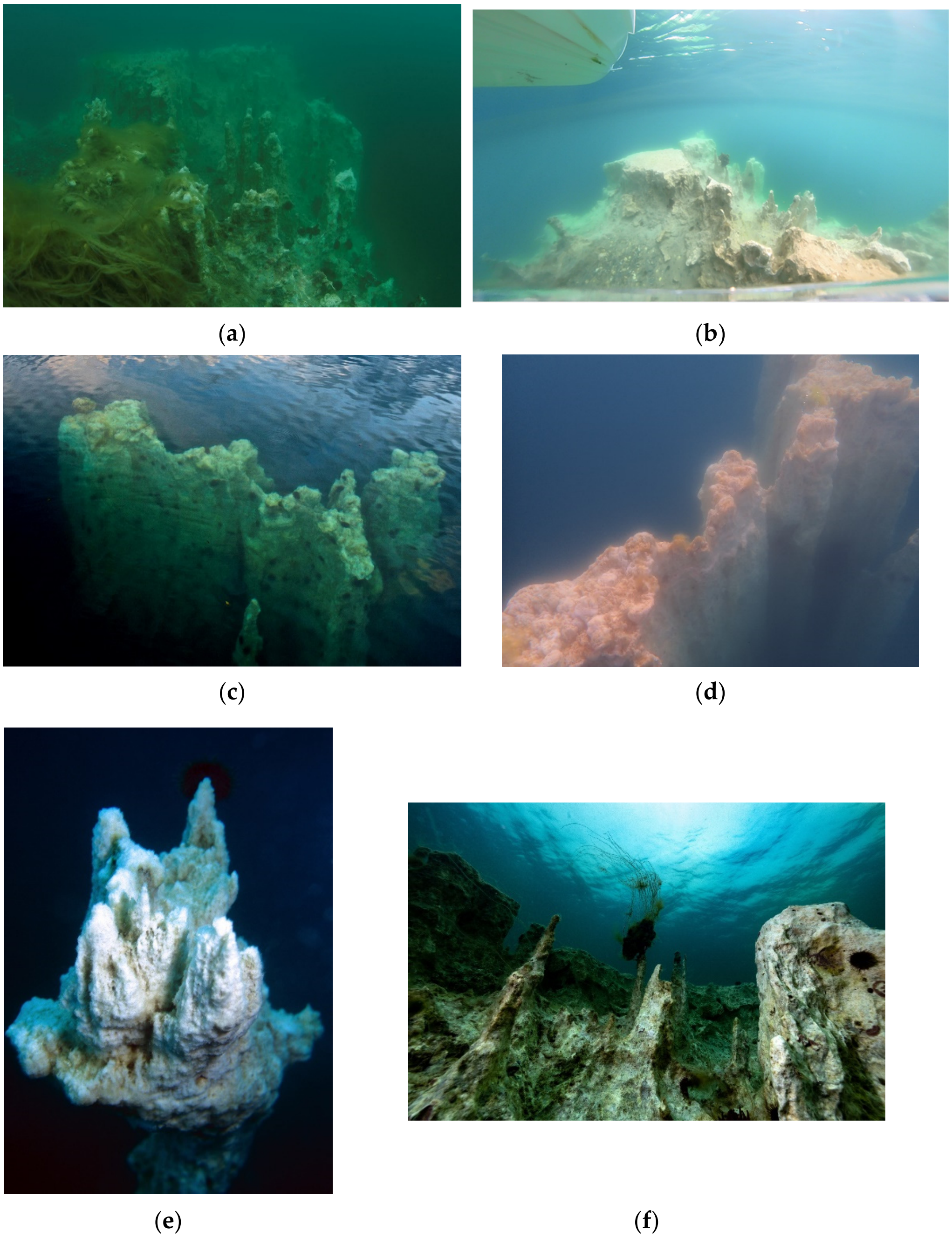


Figure 10. Comparison of the Atoll column in (**a**) summer of 1995 with (**b**) July 2022, (**c**) the Obelisk column row from the period 1995–97 compared to (**d**) the Obelisk in July 2022, (**e**) the tip of the columns as they were commonly observed in 1995–97 covered in fresh white ikaite powder, and (**f**) the side wall of the Atoll as it appeared in August 2021 yellowish and more porous surface. Photo credits: Richard Martin (**a**,**c**,**e**), Paul Seaman (**b**), Bengt Liljebladh (**d**), and Florian Huber (**f**).

5. Discussion

The first task was to verify if new mineral growth on the columns still consists of ikaite. Despite the summer of 2019 having the highest seawater temperatures ever recorded in Ikka Fjord since 1995, the results of this study indicate that ikaite is still precipitating as the primary mineral. This fits well with precipitation experiments of ikaite carried out in the laboratory. Several studies have reported ikaite forming at >6 °C e.g., [16,18,26,33–35] with Tollefsen et al. (2020) [26] reporting a hitherto highest temperature record of 35 °C. For many of these experiments, an inhibitor of calcite is included to stabilize ikaite precipitation at higher temperatures, e.g., orthophosphate [16,18,33] or magnesium [18,20]. Other factors favouring ikaite precipitation include a $CaCl_2/Na_2CO_3$ ratio ≈ 1 [34], possibly Mg^{2+}/Ca^{2+}ratios < 14 and a pH > 8.3 in solution [35], and a high citrate concentration [36]. Recent research found ikaite nucleation to be enhanced by the presence of mineral surfaces of quartz and mica [37]. Supersaturated solutions generally favour metastable phases like ikaite e.g., [4,18,34,35,38]. In Ikka Fjord, the Mg^{2+} ions of seawater act as an inhibitor of calcite and favour ikaite precipitation, whereas seawater $SO_4{}^{2-}$ ions were shown to have no effect [20]. It cannot be ruled out that the presence of orthophosphate in the column water and the bacterial biofilms observed enveloping ikaite crystals might also aid in its long-term stability in Ikka Fjord [6,17,19]. Nevertheless, clearly a threshold has been surpassed for the stability of ikaite in the columns of Ikka Fjord as seen from the mineral analytical results of XRD and Raman and visual inspections of the columns from year 2018 onwards. For the first time, actively growing columns have been observed to consist mainly of other minerals than ikaite, in this case, MHC with either minor aragonite and/or calcite. The order of alteration at present goes from ikaite to MHC, and from MHC to aragonite and/or calcite for the tufa columns of Ikka Fjord. We interpret these dehydration reactions going from highly hydrated ikaite ($CaCO_3{\cdot}6H_2O$) to less hydrated MHC ($CaCO_3{\cdot}H_2O$) to aragonite/calcite ($CaCO_3$) as a response to warming seawater. Whether aragonite in time will turn into the thermodynamically more stable calcite ($CaCO_3$) cannot be determined from our results. The columns have previously been described to contain minor calcium carbonate of biological origin as seen from ^{14}C-results [6]. Thus, whether the <4 wt% calcite observed in samples is a product of mineral alteration or of biological origin cannot be said, but the ≤20 wt% of aragonite is too large a proportion of the sample to be attributed to biology. In the past, the difference between the actively growing co-lumns made of ikaite compared to the broken-off pieces of columns composed of MHC, has been attributed to their connection or disconnection to the column water carrying the 'protective' orthophosphate of 9–25 ppm [6,7]. We have no reason to suspect the columns have less inflow of column water fed from meteoric water falling over the surrounding mountains. The multibeam survey of Seaman et al. (2022) [11] found 938 columns surpassing the approximately 650 columns mapped in 1995–96. Both instrumentation and resolution of the column mapping have benefitted from improved technology over three decades, but Seaman et al. (2022) [11] concluded the hydrological system feeding the submarine springs to run as effectively as in the nineties. If anything, the past years of Southwest Greenland, summers in particular, have been wetter and colder than on average [39,40] and hence, no shortage of meteoric water to supply the column water is expected. The hydrological profiles of Ikka Fjord and Arsuk Fjord of summer 2021 do not match the high seawater temperatures of 2019, and neither does the four HOBO dataloggers deployed from June to August 2021. There are shorter periods of >6 °C and mainly the upper parts of the columns are exposed to elevated temperatures of 6–8 °C, but not the whole seawater column as observed in 2019 [11]. At the bottom of the inner reaches of Ikka Fjord and at depth in the hydrological profiles of outer Ikka Fjord and Arsuk Fjord, low temperatures of 0–2 °C and salinities of 33–34 PSU were observed in 2021, equivalent to data in the past [9]. From our data there is no sign of a warming of seawater in the deeper currents in this area of Southwest Greenland. This leads us to conclude that other parameters are at play for controlling the seawater temperature in inner Ikka Fjord, where the columns are found. The inner fjord is relatively shallow, <30 m's depth, and water exchange with the coastal zone is restricted by the complicated topography with submarine sills and narrow channels. In addition, the strong stratification with freshwater from run-off on top limits the vertical diffusion and gives the fjord an estuarine character. The sills block icebergs from entering the inner part of the fjord, and strong meteorological forcing is required to exchange the basin water with coastal water. This makes the inner fjord more sensitive for other sources of heating, which needs to be explored further.

The slow mineral dehydration taking place in the seawater of Ikka Fjord fits well with laboratory data, where the temperature difference of precipitation and alteration, and the presence or absence of fluids are of importance e.g., [35]. The relatively incremental increase of temperature observed for Ikka Fjord, supports ikaite altering into MHC in a seawater environment. In contrast, when ikaite tufa samples are left above water and/or at ambient temperature, a direct change into calcite and a collapse of the column after several hours or days are observed [6,9]. The Mg^{2+} concentration of seawater inhibits both calcite and vaterite e.g., [41], but not aragonite e.g., [42] and can explain why aragonite is found as an alteration mineral in the columns. Monohydrocalcite is a metastable phase like ikaite and has been observed from experiments to be forming up to 100 °C [43,44]. At ambient temperature, it will either turn into calcite in Mg-free fluids over weeks or months, and into aragonite over >25 days in the presence of Mg-carrying fluids [33,45–48]. It is therefore not surprising to see aragonite forming and making up to 20 wt% of a column sample, although we assume the alteration from MHC to aragonite is going slower at the seawater temperatures of Ikka Fjord that from our observation has not surpassed 10 °C around the columns. It has been a matter of debate at which temperature ikaite alters into calcite, enforced by thermodynamics and of relevance for the paleoclimate conditions at which pseudomorphs after ikaite are formed e.g., [49]. From in situ temperature measurements of sediments hosting ikaite crystals, a temperature of 4 °C has been suggested [49], and references therein. Whether ikaite is now forming pseudomorphs in Ikka Fjord, made of MHC and/or aragonite and calcite in the altered columns has not been investigated. If with time the decomposition of ikaite takes place above 4 °C or at 6 °C, as observations suggests in Ikka Fjord, then this supports the observed mineral changes in the tufa columns as a response to a warming of seawater in Ikka Fjord. Our results suggest that the amount of energy added to the system by heat influences what alteration products are formed. Incremental increases in temperature lead to a slow dehydration reaction forming other metastable $CaCO_3$ phases instead of a direct alteration into calcite.

The Arctic Amplification is already having a marked effect on the Arctic region as documented in the recent study of Rantanen et al. (2022) [12], who found an average of four times faster warming of the Arctic than the rest of the globe for the period 1979–2021. As the tufa columns of Ikka Fjord are under protection by legislation of the Government of Greenland [13] and restrictions apply to sailing and diving among the columns, it is relevant to make predictions for the future of these unique columns. With the data at hand, we foresee a further alteration of ikaite into MHC as stated above, beyond the alteration that has already taken place unless cold seawater < 6 °C is continuously supplied. The mineral alteration means a decrease in molar volumes from ikaite of 113.55 cm^3/mol [50] to MHC of 48.70 cm^3/mol [51] or 16.23 cm^3/mol [52], while the aragonite-calcite transformation means an increase in molar volume from aragonite (34.05 cm^3/mol) to calcite (36.926 cm^3/mol) [53], but nevertheless a major volume reduction from the original ikaite. This loss of volume is likely the reason for the columns appearing fragile and easily broken, as was observed during the sampling in 2019. Therefore, utmost care should be taken when diving among the columns. An unguarded safety line can potentially cut several columns. New growth of ikaite will still be active on the columns at the same rate as in the past, supported by the data of Seaman et al. (2022) [11], but the presence of ikaite will be short lived if seawater temperatures go beyond 6 °C for longer time periods (weeks or months).

6. Conclusions

- New growth on the tufa columns of Ikka Fjord still consists of ikaite.

- However, older parts of actively growing columns now consist of monohydrocalcite and minor aragonite. Calcite only appears in trace amounts (<4 wt%). This suggests a slow dehydration of ikaite to monohydrocalcite, and from monohydrocalcite to aragonite in response to warming seawater > 6 °C, which is considered the long-term stability temperature threshold for ikaite in Ikka Fjord. The Mg^{2+} of seawater inhibits calcite and favours ikaite, monohydrocalcite, and aragonite.
- Elevated seawater temperatures > 6 °C of inner Ikka Fjord were found only for shorter time periods in the summer of 2021 and in the upper part of the water column surrounding the column garden. This contrasts with the warmer seawater temperatures of 6–9 °C for the whole water column measured in June and September 2019. An exchange of seawater with new cold seawater from the outer fjord, crossing all shallow submarine thresholds of the inner fjord, must have happened in between 2019 and 2021.
- The visual changes to columns compared to 1995–97 is striking and worrying. Columns are devoid of the fresh ikaite powder at their tips, and a colour change from white to yellow has taken place. Biological life on the surface of the columns is absent or diminished, and the columns have thereby lost their spectacular coral reef appearances of the nineties.
- We recommend a continuous monitoring of Ikka Fjord on maximum 5 years interval with respect to the mineralogy of the tufa columns and of the biological life inhabiting the columns. Monthly CTD measurements in inner and outer Ikka Fjord are recommended to monitor changes in seawater temperatures. Supplemented every five years by a new mapping survey of the number and distribution of tufa columns.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12111430/s1, S1: CTD profiles of Ikka Fjord and Arsuk Fjord in SW Greenland; S2: HOBO datalogger results; S3: 3D photographic imagery of tufa columns sampled in Ikka Fjord, 2019 and 2021; S4: XRDP diagrams of ikaite, monohydrocalcite, and mixed phases; S5: Raman data for ikaite, monohydrocalcite, aragonite, and calcite of columnar origin from Ikka Fjord, SW Greenland.

Author Contributions: Conceptualization, G.J.S., and P.S.; Methodology, G.J.S., T.B.-Z., M.P., B.L.; Validation, T.B.-Z., M.P., E.S., and B.L.; Formal analysis, G.J.S., P.S. and B.L.; Investigation, G.J.S., P.S., E.S., B.L., and R.G.; Resources, G.J.S., P.S., E.S., B.L., and R.G.; Data curation, T.B.-Z., and M.P.; Writing—original draft preparation, G.J.S.; Writing—review and editing, G.J.S., P.S., T.B.-Z., M.P., E.S., B.L., and R.G.; Visualization, E.S.; Supervision, G.J.S., and E.S.; Project administration, G.J.S.; Funding acquisition, G.J.S., E.S., and R.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Bolin Centre for Climate Research, grants 2019 and 2021, Carl Tryggers Stiftelse, grant number CTS 20:1579, Aase og Jørgen Münters Fond, grants 2019 and 112643 (2021), Aage V. Jensens Fonde, grant number 2020-0029, Eggertsjóður, grant 2018, University of Iceland's Research Fund, grants 2019 and 2020, and The Nordic Institute in Greenland (NAPA), grant number 22-11-0038.

Data Availability Statement: All data generated within this study are provided in Supplementary Materials.

Acknowledgments: We would like to acknowledge and thank the funding agencies that made this project possible, Jesper Sano Højdal, HydroCharting Aps for carrying out the CTD profiling on behalf of the IKKA project in 2021, Matthias Konrad-Schmolke and Carina Liebl at the University of Gothenburg for assisting with the Raman analysis and 3D scans of the columns, respectively, Maja Bar Rasmussen at the University of Copenhagen for assisting with the XRD analysis, and all IKKA colleagues over the years who have contributed with data to the project. Further, we would like to thank the Joint Arctic Command for their excellent logistical and diving support, as well as Blue Ice Explorer of Narsarsuaq, and Kunuk Albrechtsen and Jonathan Rasmussen of Arsuk in Greenland who have supplied the boats and skilled coxes required to access and work in Ikka Fjord. We would like to thank Uli Kunz and Florian Huber, SUBMARIS who aided with professional photographing and diving in 2021. This study was conducted under the Scientific Survey License numbers VU-00154 and SP-40 issued by the Mineral License and Safety Authority in Greenland, non-exclusive license numbers G19-037 and G21-044 for utilization of Greenland Genetic Resources and special permits from the Government of Greenland. We are grateful for the constructive comments provided by three anonymous reviewers, which improved the quality of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Buchardt, B.; Seaman, P.; Stockmann, G.; Vous, M.; Wilken, U.; Düwel, L.; Kristiansen, A.; Jenner, C.; Whiticar, M.J.; Kristensen, R.M.; et al. Submarine columns of ikaite tufa. *Nature* **1997**, *390*, 129–130. [CrossRef]
2. Pauly, H. Ikait, nyt mineral der danner skær. *Nat. Verden* **1963**, *41*, 12.
3. Pauly, H. "Ikaite", A New Mineral from Greenland. *Arctic* **1963**, *16*, 263–264. [CrossRef]
4. Johnston, J.; Merwin, H.E.; Williamson, E.D. The several forms of calcium carbonate. *Am. J. Sci.-Fourth Ser.* **1916**, *41*, 473–493. [CrossRef]
5. Stockmann, G.; Wilken, U. *Ikkasøjlerne—En Undersøisk Oase i Arktis*; Dansk Polarcenter: Copenhagen, Denmark, 2007; p. 86, ISBN 978-87-90369-04-0.
6. Buchardt, B.; Israelsson, C.; Seaman, P.; Stockmann, G. Ikaite tufa towers in Ikka Fjord, Southwest Greenland: Their formation by mixing of seawater and alkaline spring water. *J. Sed. Res.* **2001**, *71*, 176–189. [CrossRef]
7. Dahl, K.; Buchardt, B. Monohydrocalcite in the Arctic Ikka Fjord, SW Greenland: First Reported Marine Occurrence. *J. Sed. Res.* **2006**, *76*, 460–471. [CrossRef]
8. Seaman, P.; Buchardt, B. The Columns of Ikaite Tufa in Ikka Fjord; Monogr. *Greenland* **2006**, *44*, 39.
9. Hansen, M.O.; Buchardt, B.; Kühl, M.; Elberling, B. The fate of the submarine ikaite tufa columns in southwest Greenland under changing climate conditions. *J. Sed. Res.* **2011**, *81*, 553–561. [CrossRef]
10. Trampe, E.C.; Larsen, J.E.; Glaring, M.A.; Stougaard, P.; Kühl, M. In situ dynamics of O_2, pH, light, and photosynthesis in ikaite tufa columns (Ikka fjord, Greenland)—A unique microbial habitat. *Front. Microbiol.* **2016**, *7*, 722. [CrossRef]
11. Seaman, P.; Sturkell, E.; Gyllencreutz, R.; Stockmann, G.; Geirsson, H. New Multibeam Mapping of the unique *Ikaite* columns in Ikka Fjord, SW Greenland. *Mar. Geol.* **2022**, *444*, 106710. [CrossRef]
12. Rantanen, M.; Karpechko, A.Y.; Lipponen, A.; Nordling, K.; Hyvärinen, O.; Ruosteenoja, K.; Vihma, T.; Laaksonen, A. The Arctic has warmed nearly four times faster than the globe since 1979. *Commun. Earth Environ.* **2022**, *3*, 168. [CrossRef]
13. Government of Greenland. Selvstyrets Bekendtgørelse nr. 4, om Fredning af et Område ved Ivittuut og Kangilinnguit. Available online: http://lovgivning.gl/lov?rid=%7B80A814FF-16FE-42E1-BCF0-6F0E7ED70768%7D (accessed on 12 April 2010).
14. Marland, G. The stability of $CaCO_3·6H_2O$ (ikaite). *Geochim. Cosmochim. Acta* **1975**, *39*, 83–91. [CrossRef]
15. Plummer, L.N.; Busenberg, E. The solubilities of calcite, aragonite and vaterite in CO_2-H_2O solutions between 0 and 90 °C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O. *Geochim. Cosmochim. Acta* **1982**, *46*, 1011–1040. [CrossRef]
16. Bischoff, J.L.; Fitzpatrick, J.A.; Rosenbauer, R.J. The Solubility and Stabilization of Ikaite ($CaCO_3$•$6H_2O$) from 0° to 25 °C: Environmental and Paleoclimatic Implications for Thinolite Tufa. *J. Geol.* **1993**, *101*, 21–33. [CrossRef]
17. Trampe, E.C.; Richard, W.; Castenholz, J.; Larsen, E.; Michael Kühl, M. Phototrophic microbes form endolithic biofilms in ikaite tufa columns (SW Greenland). *Environ. Microbiol.* **2017**, *19*, 4754–4770. [CrossRef]
18. Stockmann, G.; Tollefsen, E.; Skelton, A.; Brüchert, V.; Balic-Zunic, T.; Langhof, J.; Skogby, H.; Karlsson, A. Control of a Calcite inhibitor (phosphate) and Temperature on Ikaite precipitation in Ikka Fjord, Southwest Greenland. *Appl. Geochem.* **2018**, *89*, 11–22. [CrossRef]
19. Stockmann, G.J.; Ranta, E.; Trampe, E.; Sturkell, E.; Seaman, P. Carbon mineral storage in seawater: *Ikaite* ($CaCO_3·6H_2O$) columns in Greenland. *Energy Procedia* **2018**, *146*, 59–67. [CrossRef]
20. Tollefsen, E.; Stockmann, G.; Skelton, A.; Mörth, C.-M.; Dupraz, D.; Sturkell, E. Chemical controls on ikaite formation. *Mineral. Mag.* **2018**, *82*, 1119–1129. [CrossRef]
21. Ranta, E.; Stockmann, G.; Wagner, T.; Fusswinkel, T.; Sturkell, E.; Tollefsen, E.; Skelton, A. Fluid-rock reactions in the 1.3 Ga siderite carbonatite of the Grønnedal-Íka alkaline complex, Southwest Greenland. *Contrib. Mineral. Petr.* **2018**, *173*, 78. [CrossRef]
22. Tollefsen, E.; Stockmann, G.; Skelton, A.; Lundqvist, L.; Sturkell, E. Secondary alteration of the Grønnedal-Ika igneous complex and the genesis of ikaite, $CaCO_3$•$6H_2O$, SW Greenland. *Chem. Geol.* **2019**, *510*, 18–30. [CrossRef]
23. Aðalsteinsdóttir, S.M. The Low-Temperature Weathering of the Grønnedal-Íka Carbonatite-Alkaline Silicate Igneous Complex in Southwest Greenland. Master's thesis, Faculty of Earth Sciences, University of Iceland, Reykjavík, Iceland, 2021; p. 82.
24. Seaman, P.G. The Development of Ikaite in a Fjord Environment with Special Reference to Ikka Fjord. Unpublished. Ph.D. Thesis, Imperial College of Science, Technology and Medicine, University of London, London, UK, 1998; p. 263.
25. Emeleus, C.H. The Grønnedal–Ika alkaline complex, South Greenland: Copenhagen. *Medd. Grønland* **1964**, *186*, 1–75.
26. Tollefsen, E.; Balic-Zunic, T.; Mörth, C.-M.; Brüchert, V.; Choo Lee, C.; Skelton, A. Ikaite nucleation at 35 °C challenges the use of glendonite as a paleotemperature indicator. *Sci. Rep.* **2020**, *10*, 8141. [CrossRef] [PubMed]
27. Rietveld, H. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **1969**, *2*, 65. [CrossRef]
28. Young, R.A. *The Rietveld Method*; Oxford Science Publications: Oxford, UK, 1993; p. 298.

29. Bruker-AXS. *TOPAS, Powder Diffraction Profile Refinement Program*; Bruker AXS GmbH: Karlsruhe, Germany, 2016.
30. FIZ. *Inorganic Crystal Structure Database*; Leibniz Institute for Information Infrastructure: Karlsruhe, Germany, 2020.
31. Sánchez-Pastor, N.; Oehlerich, M.; Astilleros, J.M.; Kaliwoda, M.; Mayr, C.C.; Fernández-Díaz, L.; Schmahl, W.W. Crystallization of ikaite and its pseudomorphic transformation into calcite: Raman spectroscopy evidence *Geochim. Cosmochim. Acta* **2016**, *175*, 271–281. [CrossRef]
32. Thorbjørn, L.; Petersen, G.H. The Epifauna on the Carbonate Reefs in the Arctic Ikka Fjord, SW Greenland. *Ophelia* **2003**, *57*, 177–202. [CrossRef]
33. Brooks, R.; Clark, L.M.; Thurston, E.F. Calcium carbonate and its hydrates. *Philos. Trans. R. Soc.* **1950**, *A243*, 145–167.
34. Rodríguez-Ruiz, I.; Veesler, S.; Gómez-Morales, J.; Delgado-López, J.-M.; Grauby, O.; Hammadi, Z.; Candoni, N.; García-Ruiz, J.M. Transient calcium carbonate hexahydrate (ikaite) nucleated and stabilized in confined nano- and picovolumes. *Cryst. Growth* **2014**, *14*, 792–802. [CrossRef]
35. Purgstaller, B.; Dietzel, M.; Baldermann, A.; Mavromatis, V. Control of temperature and aqueous Mg^{2+}/Ca^{2+} ratio on the (trans-) formation of ikaite. *Geochim. Cosmochim. Acta* **2017**, *217*, 128–143. [CrossRef]
36. Besselink, R.; Rodriguez-Blanco, J.D.; Stawski, T.M.; Benning, L.G.; Tobler, D.J. How short-lived Ikaite affects calcite crystallization. *Cryst. Growth Des.* **2017**, *17*, 6224–6230. [CrossRef]
37. Strohm, S.B.; Inckemann, S.E.; Gao, K.; Schweikert, M.; Lemloh, M.L.; Schmahl, W.W.; Jordan, G. On the nucleation of ikaite ($CaCO_3$x6H_2O)—A comparative study in the presence and absence of mineral surfaces. *Chem. Geol.* **2022**, *611*, 121089. [CrossRef]
38. Mangin, D.; Puel, F.; Veesler, S. Polymorphism in processes of crystallization in solution: A practical review. *Org. Process Res. Dev.* **2009**, *13*, 1241–1253. [CrossRef]
39. Danish Meteorological Institute. Weather Archive for Data from Qaqortoq, SW Greenland. Available online: https://www.dmi.dk/vejrarkiv/ (accessed on 8 September 2022).
40. National Snow & Ice Data Center. Available online: http://nsidc.org/greenland-today/ (accessed on 8 September 2022).
41. Nielsen, M.R.; Sand, K.K.; Rodriguez-Blanco, J.D.; Bovet, N.; Generosi, J.; Dalby, K.N.; Stipp, S.L. Inhibition of calcite growth: Combined effects of Mg^{2+} and ${SO_4}^{2-}$. *Cryst. Growth Des.* **2016**, *16*, 6199–6207. [CrossRef]
42. Bots, P.; Benning, L.G.; Rickaby, R.E.M.; Shaw, S. The role of SO_4 in the switch from calcite to aragonite seas. *Geology* **2011**, *39*, 331–334. [CrossRef]
43. Stoffers, P.; Fischbeck, R. Monohydrocalcite in the sediments of Lake Kivu (East Africa). *Sedimentology* **1974**, *21*, 163–170. [CrossRef]
44. Taylor, G.F. The occurrence of monohydrocalcite in two small lakes in the South-East of South Australia. *Am. Mineral.* **1975**, *60*, 690–697.
45. Kamiya, K.; Sakka, S.; Terada, K. Aragonite formation through precipitation of calcium carbonate monohydrate. *Mater. Res. Bull.* **1977**, *12*, 1095–1102. [CrossRef]
46. Munemoto, T.; Fukushi, K. Transformation kinetics of monohydrocalcite to aragonite in aqueous solutions. *J. Mineral. Petrol. Sci.* **2008**, *103*, 345–349. [CrossRef]
47. Fukushi, K.; Munemoto, T.; Sakai, M.; Yagi, S. Monohydrocalcite: A promising remediation material for hazardous anions. *Sci. Technol. Adv. Mater.* **2011**, *12*, 064702. [CrossRef]
48. Rodriguez-Blanco, J.D.; Shaw, S.; Bots, P.; Roncal-Herrero, T.; Benning, L.G. The role of Mg in the crystallization of monohydrocalcite. *Geochim. Cosmochim. Acta* **2014**, *127*, 204–220. [CrossRef]
49. Vickers, M.L.; Vickers, M.; Rickaby, R.E.M.; Wu, H.; Bernasconi, S.M.; Ullmann, C.V.; Bohrmann, G.; Spielhagen, R.F.; Kassens, H.; Schultz, B.P.; et al. The ikaite to calcite transformation: Implications for palaeoclimate studies. *Geochim. Cosmochim. Acta* **2022**, *334*, 201–216. [CrossRef]
50. Hesse, K.F.; Küppers, H.; Suess, E. Refinement of the structure of Ikaite, $CaCO_3 \cdot 6H_2O$. *Z. Krist.-Cryst. Mater.* **1983**, *163*, 227–231.
51. Hull, H.; Turnbull, A.G. A thermochemical study of monohydrocalcite. *Geochim. Cosmochim. Acta* **1973**, *37*, 685–694. [CrossRef]
52. Effenberger, H. Kristallstruktur und infrarot-absorptionsspektrum von synthetischem monohydrocalcit, $CaCO_3 \cdot H_2O$. *Monatsh. Fur Chem./Chem. Mon.* **1981**, *112*, 899–909. [CrossRef]
53. Perdikouri, C.; Kasioptas, A.; Putnis, C.V.; Putnis, A. The effect of fluid composition on the mechanism of the aragonite to calcite transition. *Mineral. Mag.* **2008**, *72*, 111–114. [CrossRef]