



doi:10.1016/S0016-7037(00)01304-2

Naturally precipitating vaterite ($\mu\text{-CaCO}_3$) spheres: Unusual carbonates formed in an extreme environment

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(Received June 24, 2002; accepted in revised form October 24, 2002)

Abstract—Vaterite, a rare hexagonal CaCO_3 polymorph, was identified in precipitates forming at a supraglacial sulfur spring, in Borup Fiord Pass, northern Ellesmere Island, Canadian High Arctic. Vaterite occurs in a precipitate mound along with calcite, gypsum, and native sulfur. The unusual conditions of the site, including an extremely cold climate, supersaturated alkaline waters, and the presence of gypsum, mimics conditions used to grow vaterite in laboratory experiments. Stable isotope data suggest that vaterite may preferentially form during colder periods of the year. Vaterite found at the site is characterized by 2- to 10- μm rounded to spherical shaped particles (comprising smaller 0.5- to 2- μm spheres) as both individuals and in chainlike structures. The spherical habit of vaterite resembles carbonate structures that have been interpreted to be organic; however, $\delta^{13}\text{C}$ values are indicative of an inorganic origin. The thick permafrost, and the extreme cold and dry environment make this site a good terrestrial analog for carbonate precipitates that might be expected at potential deposits associated with water discharge on other planetary bodies. Copyright © 2003 Elsevier Science Ltd

1. INTRODUCTION

McKay et al. (1996) sparked controversy on whether or not carbonate structures in the martian meteorite ALH84001 had an organic origin, with subsequent debate centering on whether or not inorganic processes could form carbonate globules at low temperatures (e.g., see discussion in Baker et al., 2000). Vecht and Ireland (2000) recently suggested that spherical carbonate structures found in the martian meteorite ALH84001 may have formed inorganically by carbonates pseudomorphing a precursor metastable vaterite phase (vaterite, a rare hexagonal CaCO_3 polymorph, typically grows with a spherical habit). The main constraint on their model is the rarity and thermodynamic instability of vaterite in natural environments. There is only one reported occurrence of vaterite precipitating spontaneously from natural waters (in Holkham Lake, UK; Rowlands and Webster, 1971). However, a reexamination of this site did not detect vaterite (Lucas and Andrews, 1996). It is not clear whether the original identification was mistaken or whether that vaterite was not present when the lake was resampled (Lucas and Andrews, 1996; Friedman, 1997).

Here, then, is presented a rare occurrence of vaterite precipitating from natural waters, from supraglacial sulfur springs in the Borup Fiord Pass area of northern Ellesmere Island, Nunavut, Canadian High Arctic (Figs. 1, 2). These results provide important information about environments in which vaterite may naturally occur and places constraints on the interpreted genesis of spherical carbonate structures. The extreme environment of this site provides a terrestrial analog for precipitates that may form at locations of water discharge on other ice-bearing planetary bodies (e.g., Mars, Europa).

2. VATERITE

Natural occurrences of vaterite are largely associated with organic tissue, gallstones, and urinary calculi (e.g., Prien and Frondel, 1947; Hall and Taylor, 1971; Lowenstam and Abbott, 1975; Rodgers, 1983) and have recently been reported in microbial biscuits (Giralt et al., 2001). Although vaterite was precipitated inorganically in the laboratory, it was originally thought not to occur as a naturally forming mineral (Ievins et al., 1955). However, rare occurrences have been reported in a contact metamorphic aureole in Ireland (McConnell, 1960), in zones of thermal metamorphism in Israel (Kolodny and Gross, 1974), in the Pesyanoe meteorite (DuFresne and Anders, 1962), and in carbonate concretions (Fong, 1981). Vaterite has also been found in drilling mud (Friedman et al., 1993; Friedman and Schultz, 1994). As mentioned above, there is only one previous report of vaterite precipitating from natural waters (Rowlands and Webster, 1971).

Vaterite is thought to be metastable under all known conditions and has a higher solubility than the other CaCO_3 polymorphs, calcite and aragonite (Fig. 3) (e.g., Plummer and Busenberg, 1982; Ogino et al., 1987). However, Albright (1971) suggested that vaterite is the most stable CaCO_3 phase at low temperatures ($<10^\circ\text{C}$ at 1 atm). Kralj et al. (1990) indicate that pure vaterite could only precipitate under a narrow range of initial conditions and within a pH range from 9.3 to 9.9. However, mixed calcite/vaterite was precipitated at slightly lower pH (8.5) in experiments by Vecht and Ireland (2000). Experiments by Flörke and Flörke (1961) also show that vaterite growth is favored by reaction of alkaline solutions with crystalline gypsum. Vaterite is highly unstable when exposed to water; it can recrystallize to calcite within 20 to 25 h at room temperature (Silk, 1970). At higher temperatures ($\sim 60^\circ\text{C}$), vaterite will transform to aragonite in 60 min (Ogino et al., 1987). As a result of these rapid reaction rates at low temperatures, vaterite was originally thought to have a very short

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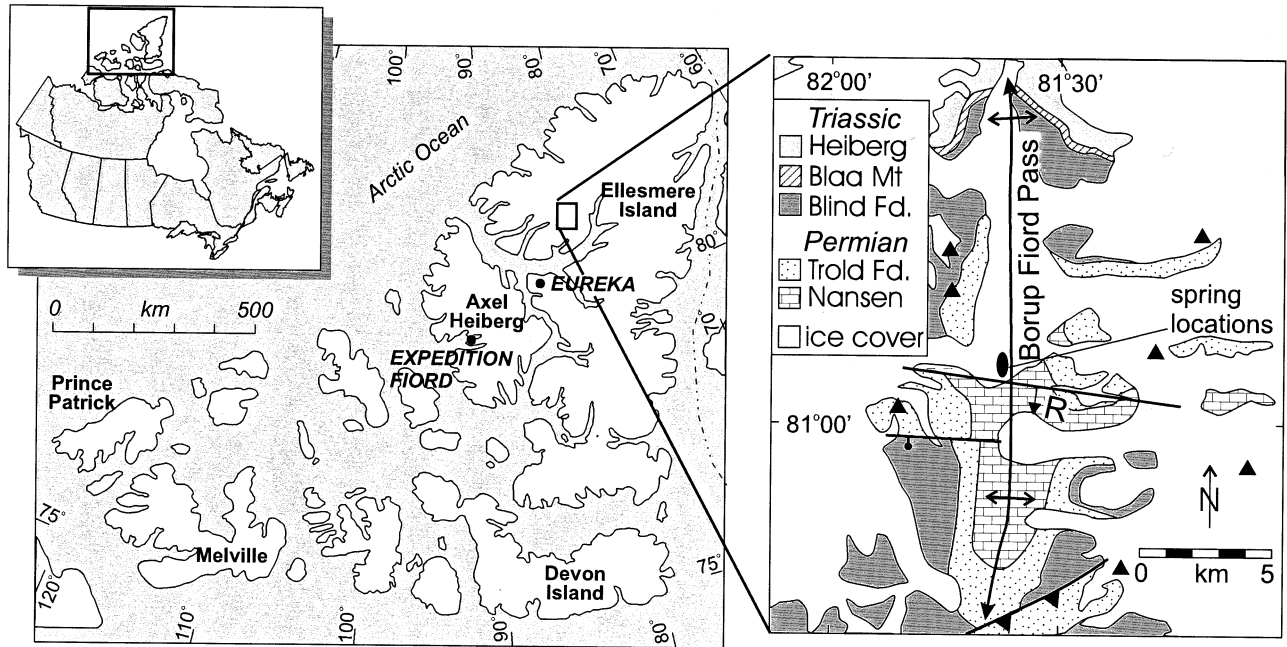


Fig. 1. Location map showing areas discussed in text as well as a generalized geology of the Borup Fiord Pass area.

lifespan. However, recent dating of natural occurrences suggests that vaterite may have greater longevity (Friedman et al., 1993; Friedman and Schultz, 1994).

Vaterite commonly precipitates in a spherical shape when grown in the laboratory from supersaturated solutions (e.g., Turnbull, 1973; Kralj, et al., 1990; Vecht and Ireland, 2000) and has also been reported to be in the form of spheres where it was formed in drilling muds from petroleum wells (Friedman et al., 1993; Friedman and Schultz, 1994). Vaterite spheres tend to be small, with diameters ranging from 0.05 to 5 μm (Kralj, et al., 1990; Vecht and Ireland, 2000).

3. SITE DESCRIPTION

3.1. Geology

Vaterite was identified in spring deposits located in a low valley informally named Borup Fiord Pass, northern Ellesmere Island, Nunavut, Canadian High Arctic (Figs. 1, 2). Bedrock in the region is dominated by Carboniferous to Triassic marine carbonates, evaporites, and clastics of the Sverdrup Basin (Thorsteinsson, 1974). The basin was deformed by evaporite diapirs (Balkwill, 1978), Cretaceous volcanism, diabase intrusions (Embry and Osadetz, 1988), and high-amplitude folds and thrust faults of the Eocene Eureka orogeny (Harrison et al., 1999). The valley floor of Borup Fiord Pass is largely underlain by a variety of Carboniferous to Upper Permian carbonates, clastics, and a volcanic unit lumped together into the Nansen and Troid Fiord formations (Thorsteinsson, 1974). Extensive glaciers occur in the high mountain ranges both to the west and east of Borup Fiord Pass, and flow downward and coalesce within the valley.

3.2. Climate

The climate at the Eureka meteorological station (140 km to the southwest) is characterized by polar desert conditions with a mean annual air temperature of -19.7°C (mean monthly temperatures range from -36.1°C in January to $+5.4^{\circ}\text{C}$ in July). Mean annual precipitation is less than 100 mm (Environment Canada, unpublished data). The region is characterized by up to 540 m of permafrost (Taylor and Judge, 1977).

3.3. Supraglacial Sulfur Springs

Vaterite deposits are associated with unusual supraglacial sulfur springs, interpreted by Grasby et al. (in press) to be related to dissolution of underlying evaporites of the Otto Fiord Formation. Ten sulfur springs and seeps were observed discharging from the surface of a $\sim 200\text{-m}$ -thick glacier. Most sites are easily spotted because of the bright yellow precipitates of native sulfur (Fig. 2a,b). Intermittent odors of H_2S are also common in the area. At the discharge sites, native sulfur is typically thinly dispersed over several square meters of the ice surface. At some localities, central mounds, composed of varying amounts of native sulfur, gypsum, calcite, and ice, stand up to 30 cm high (Fig. 2c, Table 1). Water temperatures of the spring discharge are low (1.0 to 2.3°C), although higher than surface melt water (typically around 0.2°C), and have pH values of 7.3 to 9.5. Total dissolved solids values range from 107 to 183 mg/L (Table 1).

4. MATERIALS AND METHODS

Precipitate samples were collected at seven discharge sites. At some locations, precipitates had obvious color differences, so multiple samples were collected. Given its rarity, vaterite was not expected at these



Fig. 2. Field photographs showing (a) water discharge from ice wall forming a large tufalike mound of native sulfur and gypsum, (b) seep along side of incised supraglacial meltwater channel depositing native sulfur, and (c) pipelike mound where vaterite was discovered (site E07) formed on top surface of ice sheet.

sites, so no special procedures to stabilize the samples were used. Water-saturated deposits (with a pastelike consistency) were collected and placed into sealed, sterile plastic bags. The samples were kept in the dark at 5° to 20°C (air temperature) for up to a month. After arrival in the laboratory, the precipitates were air dried in darkness at room temperature. Qualitative mineralogy of the samples was determined 2 months later by powder X-ray diffraction (XRD) using relative peak intensity on a Phillips 1700 XRD. Samples were rerun 4 months after. A second sample was collected a year later with similar methodology.

Water samples were passed through 0.45- μm filters and stored in the dark at 4°C in high-density polyethylene bottles until analyzed. Samples for cation analyses were acidified with ultrapure nitric acid to pH < 2. Unstable parameters (temperature, pH) were measured on site. Alkalinity was determined by an Orion 960 autotitrator. Major elements were determined by inductively coupled plasma–emission spectroscopy. Analytical error in concentration measurements was estimated to be less than 2%.

Samples were imaged by scanning electron microscopy (SEM) with a Phillips XL300 SEM with a LaB6 emitter. Semiquantitative elemental analysis was performed with a PGT digital energy-dispersive X-ray spectrometer. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for bulk carbonates were measured on CO_2 released by reacting CaCO_3 with phosphoric acid following the method of McCrea (1950). $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ was measured on CO_2 isotopically equilibrated with H_2O (Epstein and Mayeda, 1953), and δD was measured via H_2 produced by the Zn-reduction method of Coleman et al. (1982). Analytical errors for isotope data were estimated to be $\pm 0.2\%$ for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\pm 0.3\%$ for $\delta^{13}\text{C}$. Values are reported using the typical delta (δ) notation vs. Vienna Pee Dee Belemnite (v-PDB) for carbon and Vienna Standard Mean Ocean Water (v-SMOW) for oxygen and hydrogen.

The PHREEQC geochemical modeling program (Parkhurst, 1995)

was used for speciation and ion activity calculations based on the geochemical data for spring waters in Table 1. These results, in conjunction with temperature-dependent equilibrium constants (log K) from Plummer and Busenberg (1982), were used to calculate saturation indexes for calcite, aragonite, and vaterite.

5. RESULTS

XRD analyses indicate that the precipitates at the spring sites are dominated by gypsum, bassanite, native sulfur, and calcite (Table 2). Because bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) is simply a less hydrous form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), the two phases are referred to together as CaSO_4 minerals. The relative composition of the precipitates is highly variable, and any one phase can dominate the rest (e.g., CaSO_4 0 to 100%, native sulfur 0 to 99%, calcite 0 to 75%). Even at a single location, there is a high degree of variability in precipitate composition. Vaterite was detected at only one 30-cm-high precipitate mound (E07A, Table 2, Fig. 2c). This location is distinct by not having the yellow sulfur color that characterizes other deposits in the area (cf. Figs. 2b and 2c).

For most carbonate samples, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the precipitates show a fairly narrow range, +3.2 to +3.9‰, and 9.8 to 12.9‰, respectively (Table 2). Two samples, E07A and E09B, have distinctly higher $\delta^{13}\text{C}$ values (5.0 and 5.3‰) and lower $\delta^{18}\text{O}$ values (−6.7 and −0.8), respectively. E07A is the sample in which vaterite was identified.

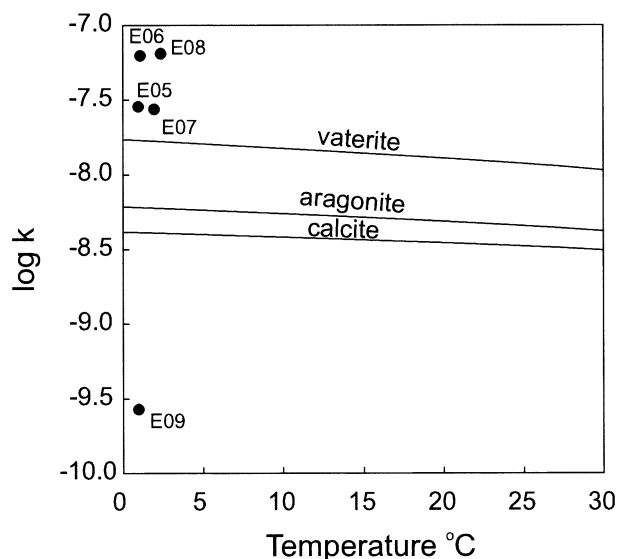


Fig. 3. Ion activity product of spring waters plotted with the phase boundaries for the CaCO_3 polymorphs calcite, aragonite, and vaterite between 0 and 30°C (after Plummer and Busenberg, 1982).

The calculated ion activity products for spring waters are plotted along with temperature-dependent stability fields for CaCO_3 minerals in Figure 3. With the exception of sample E09, the spring waters are supersaturated with respect to all three CaCO_3 polymorphs.

6. VATERITE IDENTIFICATION

Vaterite was identified from a sample collected in the year 2000 by means of powder XRD (Fig. 4a, Table 2). Previous reports indicate that vaterite is highly unstable and may alter to calcite, even in samples stored in the laboratory (e.g., Silk, 1970; Friedman, 1997). Therefore, the original sample was rerun after 4 months, and identical XRD patterns were obtained (Fig. 4b). This is consistent with evidence that suggests vaterite may be stable in some instances (Friedman and Schultz, 1994). An additional sample was collected from the same site in 2001. In this case, a technician inadvertently placed the sample in a drying oven at 60°C. This mistake was realized, and the sample was withdrawn within 15 min. Powder XRD of this sample also indicates the presence of vaterite, but at lower abundance than the year 2000 sample (3% as compared with 12%). Given the thermodynamic instability and rapid reaction rates of vaterite, the short time in the drying oven may account for the reduced vaterite content in the 2001 sample.

Precipitates from the mound where vaterite was identified have two dominant morphologies, well-defined euhedral vitreous crystals, and a fine-grained white powder (Fig. 5a). Energy-dispersive X-ray spectrometry analyses indicate that the large euhedral crystals have a CaSO_4 composition, representing the dominant gypsum/bassinite phase identified by XRD. In contrast, the fine white powdery substance has a CaCO_3 composition. SEM imaging of the white powder indicates two morphologies of CaCO_3 minerals. The dominant form was rodlike (Fig. 5b). However, secondary forms from 2 to 10 μm were rounded and ranged from flattened to spherical shapes (Figs. 5c,d). In some instances, several CaCO_3 spheres formed together, making a chainlike appearance (Fig. 5e). At higher magnification, the larger spheres were found to be comprised of smaller (0.5 to 2 μm) spherical carbonate structures. For other spring sites where vaterite was not detected by XRD, only rod-shaped CaCO_3 minerals were noted under SEM. However, subspherical sulfur particles were noted.

7. DISCUSSION

Given that the precipitates at Borup Fiord Pass are found as mounds forming around actively discharging water, they must be modern features. Thus, the spheroid CaCO_3 structures found in precipitates at site E07A are interpreted to be recently formed vaterite on the bases of the following: (1) the presence of characteristic XRD peaks for vaterite, (2) the fact that vaterite typically grows in spherical shapes in laboratory experiments, and (3) the observation that spherical CaCO_3 structures were only observed in samples where vaterite was detected. Although vaterite was identified in only one precipitate mound, its unstable nature makes it possible that it could have formed at other locations and was altered to calcite either before sampling or during sample transport.

Other than associations with organic tissue, vaterite formation is extremely rare in nature, with only one other reported case of the mineral precipitating spontaneously from natural waters (Rowlands and Webster, 1971). This being said, the unusual conditions of the Borup Fiord Pass site provide the ideal setting for vaterite growth. Precipitate mounds are forming in an extremely cold climate on glacial ice, consistent with the low-temperature stability field for vaterite predicted by Albright (1971). The discharge waters are alkaline and supersaturated with respect to vaterite, consistent with experimental conditions needed to grow vaterite in the laboratory (e.g., McConnell, 1960; Kralj et al., 1990). In addition, abundant CaSO_4 minerals are found in association with the precipitate mounds, consistent with experimental work showing preferential vaterite growth when alkaline fluids react with crystalline

Table 1. Chemical analyses of spring waters at Borup Fiord Pass. Calculated saturation index (SI) is shown for the three CaCO_3 polymorphs.

Sample	pH	T (°C)	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SO_4 (mg/L)	Cl (mg/L)	HCO_3 (mg/L)	SI calcite	SI aragonite	SI vaterite
E05	9.0	1.0	182	43	2.6	6.4	0.09	49.9	13.1	67.0	0.83	0.67	0.19
E06	9.5	1.1	153	34	1.4	3.5	0.26	27.8	7.2	79.0	1.17	1.01	0.53
E07	9.2	2.0	183	27	3.8	11.0	0.12	47.9	25.2	68.0	0.81	0.65	0.17
E08	9.4	2.3	174	38	1.5	3.3	0.33	31.4	7.4	92.0	1.19	1.03	0.55
E09	7.3	1.0	107	23	0.9	3.2	0.12	29.3	7.8	43.0	-1.12	-1.35	-1.83

Table 2. Analytical data for spring sites at Borup Fiord Pass. Mineralogy is based on semiquantitative assessment of relative peak intensity. Isotope data is for bulk carbonate precipitates and discharge water (H₂O). Multiple samples from the same discharge site are labeled A, B. n.d. = not detected; n.a. = not analyzed; tr. = trace amount.

Sample	XRD data						Carbonates		H ₂ O	
	Gypsum	Bassanite	Native sulfur	Calcite	Vaterite	Quartz	$\delta^{13}\text{C}_{\text{V-PDB}}$	$\delta^{18}\text{O}_{\text{V-SMOW}}$	$\delta^{18}\text{O}_{\text{V-SMOW}}$	$\delta\text{D}_{\text{V-SMOW}}$
E03	14	4	35	12	n.d.	35	n.a.	n.a.	-27.1	-197
E03A	1	n.d.	19	75	n.d.	5	3.2	11.5	n.a.	n.a.
E04	6	n.d.	48	46	n.d.	tr.	3.7	10.4	-26.7	-193
E05	n.d.	1	99	n.d.	n.d.	tr.	n.a.	n.a.	-25.7	-186
E06	2	n.d.	37	61	n.d.	n.d.	3.8	11.6	-27.0	-196
E07	n.d.	n.d.	43	57	n.d.	n.d.	3.9	12.5	-26.3	-187
E07A	3	29	4	52	12	n.d.	5.0	-6.7	n.a.	n.a.
E07B	n.d.	1	42	56	n.d.	n.d.	3.2	9.8	n.a.	n.a.
E08B	88	12	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	-27.3	-188
E09A	21	5	74	n.d.	n.d.	n.d.	3.7	12.9	-26.3	-189
E09B	28	13	n.d.	59	n.d.	n.d.	5.3	-0.8	n.a.	n.a.

gypsum (Flörke and Flörke, 1961). Experimental evidence also indicates that conditions favorable to vaterite formation can be produced in microenvironments during freezing of water (Fairchild et al., 1996; Killawee et al., 1998). Thus, it is the combination of these factors at this unusual spring site that forms conditions favorable to vaterite growth. However, the actual mechanism of formation of these precipitates is not yet clear; its study is hampered by the remote location and difficulty of winter access.

The $\delta^{18}\text{O}_{\text{carbonate}}$ values for the precipitates examined here (Fig. 6, Table 2 relative to v-SMOW) are extremely low for carbonate minerals. On the basis of data provided by O'Neil et

al. (1969), the $10^3\ln\alpha^{18}\text{O}_{\text{calcite-water}}$ value for the measured temperature of the spring discharge ($\sim 2^\circ\text{C}$) is $\sim 34\%$. Assuming equilibrium, this suggests that the carbonate minerals examined here precipitated from waters with $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of -21.1 to -24.2 (v-SMOW). This is close to the range measured for spring discharge waters of -25.7 to -27.3% (Table 2). However, for the two sites, E07A and E09B, calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ equilibrium values are much lower (-40.7 and -34.8% , respectively). These values are consistent with winter precipitation measured at Eureka (IAEA/WMO, 1998). Although Fairchild et al. (1996) show strong kinetic fractionation forming low $\delta^{18}\text{O}$ carbonates during freezing in closed systems, there was also a concurrent negative shift in $\delta^{13}\text{C}$ that is not observed in these samples (Fig. 6). Thus, the low $\delta^{18}\text{O}_{\text{carbonate}}$ values observed here might represent an equilibrium exchange, suggesting then that vaterite growth occurs preferentially during the winter months. This again is consistent with laboratory experiments that indicate vaterite growth and stability is favored by lower temperatures (Albright, 1971). It is interesting to compare the Borup Fiord site to saline springs at Colour Peak and Gypsum Hill, near Expedition Fiord on Axel Heiberg Island (230 km to the south-southwest; Fig. 1). Here, perennial saline springs are associated with gypsum/anhydrite diapires (Pollard et al., 1999). In this location, euhedral crystals are found that have a morphology similar to ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$); however, XRD analyses indicate that they are calcite. Given the thermodynamic instability of ikaite, Omelon et al. (2001) suggest that these samples altered to calcite during transport. In the field, ikaite morphology is described to be best developed early in the year (April) and by July, the crystals appear to disintegrate. Omelon et al. (2001) suggest that ikaite growth is seasonal and favored by colder winter temperatures.

The $\delta^{13}\text{C}$ values for precipitates at the Borup Fiord Pass sites range from 3.2 to 3.9‰. The two sites with anomalous low $\delta^{18}\text{O}$ values, including the site where vaterite was identified (E07A), have notably higher $\delta^{13}\text{C}$ values of 5.0 and 5.3‰ (Fig. 6, Table 2). As Grasby et al. (unpublished data) show evidence for active sulphate reducers in the spring waters, these high $\delta^{13}\text{C}$ values are unlikely to be related to methanogenesis (microbial methanogenesis, which can enrich ^{13}C in dissolved inorganic carbon, is not an important process when sulphate reducers are active; Whiticar, 1999). There is little information

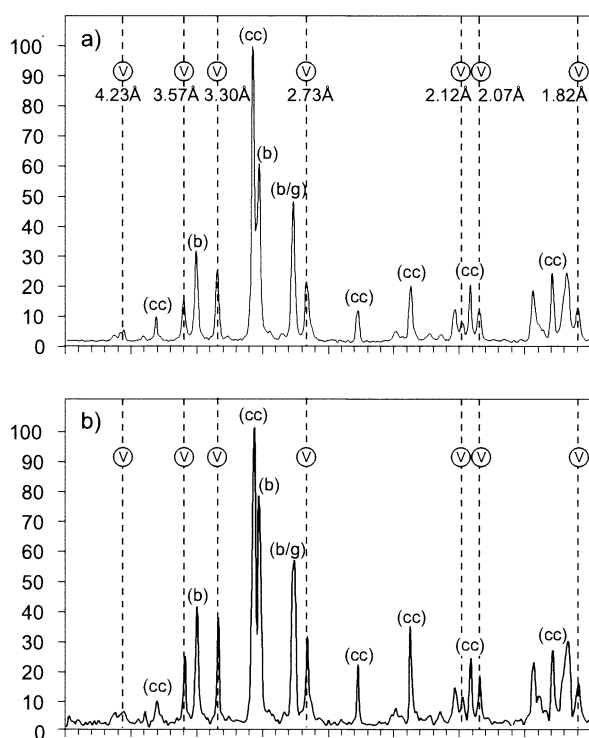


Fig. 4. XRD patterns showing positive vaterite identification for (a) initial run of sample E07A from year 2000 and (b) rerun of E07A 4 months later.

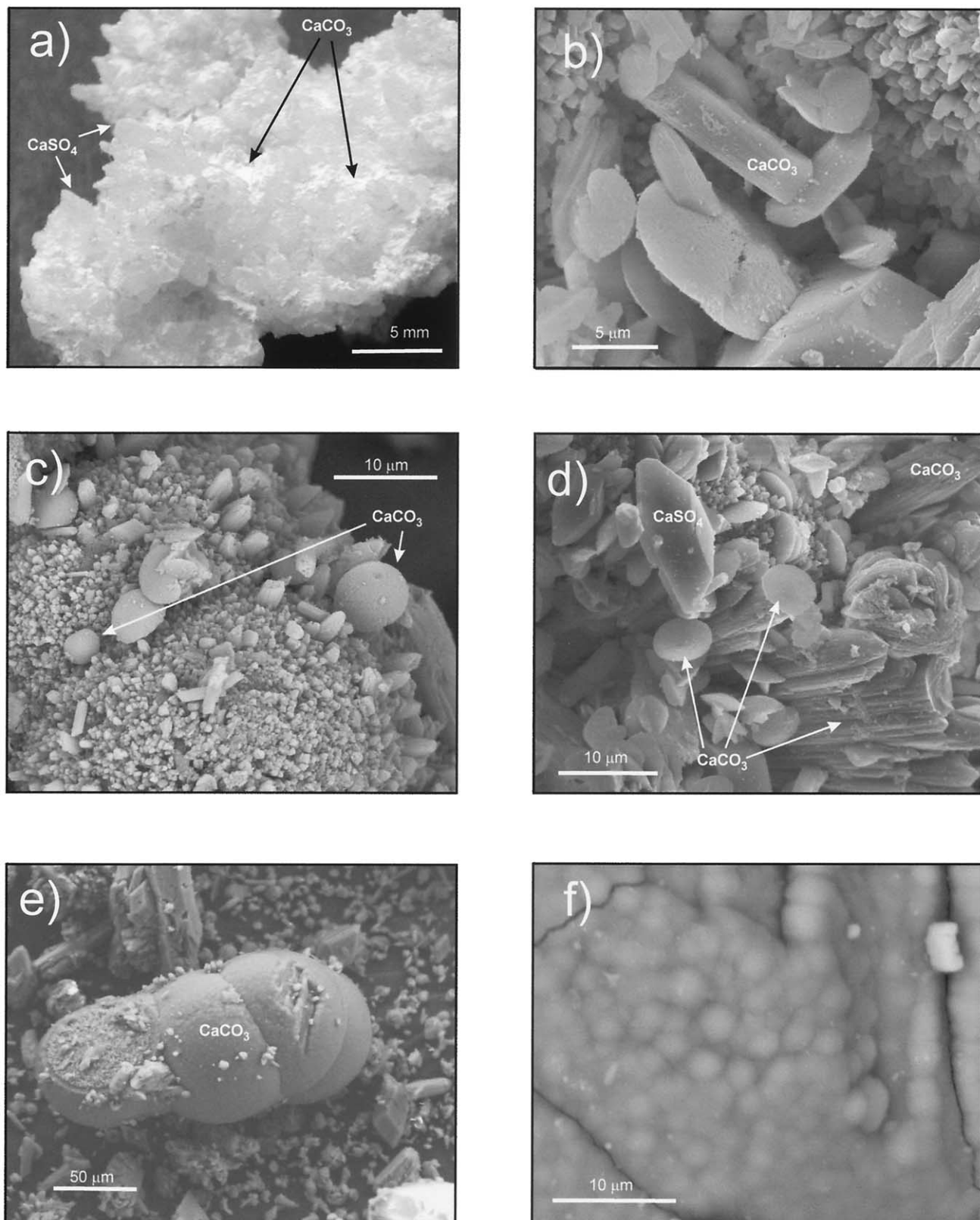


Fig. 5. (a) Photomicrographs of precipitates from site E07A showing euheedral gypsum crystals and fine grained carbonate material. SEM images showing variability of CaCO₃ structures, including (b) rodlike features, (c, d) flattened circular structures, and spheres, and (e) chainlike structures of spheres (f) Close-up of (e) showing micron-sized spheres that comprise the larger spherical structures.

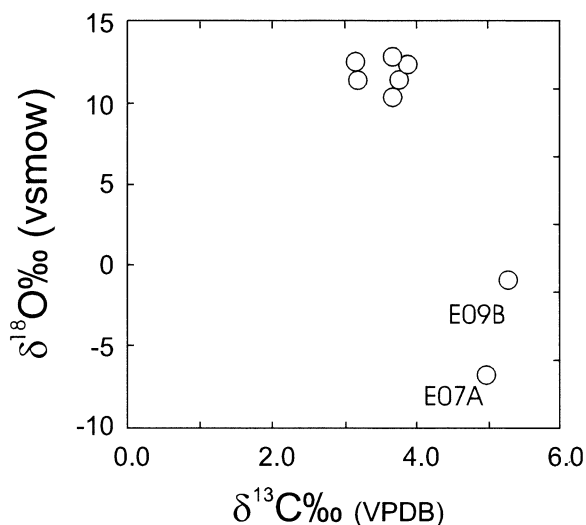


Fig. 6. Plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ values for bulk carbonates from precipitate mounds.

in the literature to indicate if there is a significant difference in fractionation factors for calcite and vaterite; however, it would likely be minor. Thus, the presence of vaterite alone would likely not be the cause of the higher bulk $\delta^{13}\text{C}$ values. The rapid freezing of bicarbonate groundwaters discharging into sub-0°C air temperatures has been shown to force growth of cryptocrystalline calcite enriched in ^{13}C by nonequilibrium reaction kinetics (Clark and Lauriol, 1992). So consistent with $\delta^{18}\text{O}$ data, $\delta^{13}\text{C}$ values for precipitate mounds E07A and E09B suggest these carbonates may have formed at lower temperatures than the other sites. What is interesting is that despite evidence for active biologic sulphate reduction as well as sulfur oxidation by bacteria in these spring systems (Grasby et al., in press), the $\delta^{13}\text{C}$ values of precipitates are typical of an inorganic source. Grasby et al. (2000) demonstrate that in carbonate-hosted sulfur springs, where active bacterial sulfate reduction can be demonstrated, the $\delta^{13}\text{C}$ values of dissolved inorganic carbon is consistently similar to the host rock. This suggests that the vast reservoir of inorganic carbon dissolved from the carbonate host rock overwhelms any signature of CO_2 produced by microbiologic activity. Similarly, dissolution of the carbonate dominated bedrock and till at the Borup Fiord Pass site may dominate the $\delta^{13}\text{C}$ signature of dissolved inorganic carbon in the discharge waters and subsequently in the precipitate deposits.

The spherical carbonates found at this site are formed by an amalgamation of smaller ovoid structures, consistent with vaterite grown in the laboratory by Vecht and Ireland (2000). These authors suggest that these smaller structures could be pseudomorphed to other carbonate phases, creating pseudobiogenic features similar to carbonate structures formed by nanobacteria (Folk, 1993). The discovery here of naturally occurring vaterite lends credence to this suggestion.

8. CONCLUSIONS

Vaterite, a rare hexagonal CaCO_3 polymorph, precipitates naturally as spheres 0.5 to 10 μm in diameter from supraglacial

sulfur springs in the Canadian high Arctic. Other than the previously discounted occurrence at Holkham Lake, UK (Rowlands and Webster, 1971; Lucas and Andrews, 1996), this is the only known occurrence of vaterite spontaneously precipitating from natural waters. The metastable existence of this calcite polymorph is likely favored by the extreme cold environment and high-pH waters.

The $\delta^{13}\text{C}$ value for the vaterite deposit studied here (+5.3‰) suggests that it has an inorganic origin, despite evidence for active microbial populations in the spring system. Given the thermodynamic instability of vaterite, it may rapidly alter to, and be pseudomorphed by, other carbonate phases forming pseudobiogenic structures as suggested by Vecht and Ireland (2000). Following Vecht and Ireland (2000), the inorganic precipitation of spherical vaterite places constraints on interpreted biologic origins of spherical carbonate structures in both terrestrial and extraterrestrial samples.

The Borup Fiord Pass site, along with Colour Peak and Gypsum Hill (Pollard et al., 1999; Omelon et al., 2001), are rare examples of groundwater discharge in extremely cold environments. In both cases, rare carbonate polymorphs that are not typically stable in more temperate climates are precipitating. Given recent evidence that liquid water has recently discharged on the surface of Mars (Malin and Edgett, 2000) and through the ice crust of Europa (Greeley et al., 2000), these high Arctic springs discharging through glacial ice and thick permafrost make them an excellent terrestrial analog for potential spring deposits associated with surface discharge of waters on other planetary bodies, and suggest that unusual carbonate minerals should be expected.

Acknowledgments— Supported by Natural Resources Canada's Polar Continental Shelf Project. This site was originally discovered and brought to the attention of the author by Benoit Beauchamp. Helpful reviews were provided by I. Fairchild, A. Vetch, and T. Ireland. Geological Survey of Canada contribution 2002143.

Associate editor: L. M. Walter

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