Vaterite after ikaite in carbonate sediment

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At the calcareous sinter dome of Shiowakka, Hokkaido, spherulitic vaterite was found in the carbonate sediments in early spring. The aggregates of ikaite formed in winter have changed to sandy carbonate sediments composed of calcite, vaterite and monohydrocalcite with an increase of temperature. The foamy aggregates and zonal structure in the spherules of vaterite indicate that the crystallization has been derived from the rapid decomposition of ikaite and subsequent growth in the spring water.

Keywords: Vaterite, Ikaite, Spherules, Foamy aggregate, X-ray powder diffraction, Optical properties, Shiowakka

I. Introduction

Vaterite is a trimorph with calcite and aragonite, and its occurrence is most rare among them. It is well known as artificial precipitation products in many previous works. Synthetic vaterite shows two forms as spherulitic aggregates and hexagonal plates (Gibson *et al.*, 1925). In nature, vaterite in the repair tissues of shells of certain gastropods was first reported by Mayer and Weineck (1932). The first observation in a geological environment was as an alteration product in hydrogel pseudomorphs after larnite, Ca_2SiO_4 from Ballycraigy, Northern Ireland (McConnell, 1960). It was found as fine fibrous and platy crystal. Albright (1971) had proposed that the stability field of vaterite being in low temperature, but the actual occurrence in a cold environment has been known from only Antarctica (Browne, 1973).

In mid-March, 1997 as the melting snow season, the first author has recognized vaterite

in sandy carbonate sediments wetted with a cold spring water of Shiowakka. In the calcareous precipitation at Shiowakka, calcite was predominant and occasionally encrusted by monohydrocalcite in summer season (Ito, 1993). In midwinter, the precipitation of calcite was not observed and only ikaite formed in the cold spring water at near freezing point (Ito, 1996). Although the conditions of high Mg/Ca and high $[\text{PO}_4]^{3-}$ contents in a water have been supposed to be favorable for the formation of monohydrocalcite from Lakes Fellmongery, South Australia (Taylor, 1975) and non-marine ikaite from Mono Lake, California (Bischoff *et al.*, 1993), both Mg/Ca and high $[\text{PO}_4]^{3-}$ contents of Shiowakka spring water are lower than those of waters.

II. Occurrence

Calcareous sinter-dome of Shiowakka precipitated from cold saline springs is located at Rawan, Ashoro-cho, Hokkaido, Japan. The chemical nature of this spring water is indicat-

Table 1. Chemical composition of Shiowakka spring water in winter, 12 Feb., 1998

Temp.* (°C)	pH	Ca (mg/l)	Mg (mg/l)	Cl (mg/l)	PO ₄ (mg/l)	HCO ₃ (mg/l)	NH ₄ (mg/l)
10.7	6.7	314	191	3910	1.15	5680	26.2

* : measured in a laboratory

Note. atmospheric temperature at the field was -3.6°C , the cold spring water temperature 8.7°C (at outlet) and 2.4°C (in 5 meters downstream contacted with ice).

Fig. 1. X-ray powder pattern of vaterite. (V, vaterite; c, calcite; m, monohydrocalcite.)

ed in Table 1. The presence of vaterite in sandy calcareous sediments was examined by X-ray diffractometer method (Fig. 1 and Table 2). The pattern includes that of calcite, but the unique diffractions of vaterite were confirmed by using a Gandolfi camera ($d=114.6\text{ mm}$) for handpicked four minute spherules. The sediments composed of calcite, vaterite and monohydrocalcite were formed by the decomposition of ikaite aggregates embedded in ice. The thickness of the sediments was around 7 mm. The loose appearance of sediments are clearly different from the incrustation of calcareous sinter formed in summer season. Thus, the grains of vaterite were concentrated by the

screening under 200 mesh and flotation in a heavy liquid of mixture of bromoform (gravity : 2.85) and acetone.

Under the microscope, vaterite is clear transparent foamy aggregates composed of irregular spherules (Fig. 2a), and is accompanied by rhombic and spherulitic calcite. Also, a few bipyramidal crystals of monohydrocalcite accompanied by calcite is observed. The diameter of vaterite spherules up to $50\text{ }\mu\text{m}$ is generally smaller than that of calcite. SEM observation reveals that some spherules consist of an eggshell-like crust (Fig. 3b), although no optical difference between an eggshell-like crust and a solid spherulitic crystal is recognized. The

Table 2. X-ray powder diffraction data of vaterite

This study			JCPDS Card No.33-268	
hkl	d obs.	I	d	I
004	4.242	16	4.226	25
110	3.581	54	3.573	60
112	3.299	99	3.294	100
114	2.735	100	2.720	90
211	2.313	11	2.318	5
205	2.286*		2.282	2
116	2.218	4	2.212	5
213			2.161	2
008	2.118	14	2.113	20
300	2.065	55	2.063	60
304	1.856	17	1.854	30
118	1.822	63	1.820	70
224,313	1.647	30	1.646	30

*: Overlapped diffraction of calcite
Cu/Ni rad. Diffractometer method (35kV, 20 mA,
Slit: 1°—0.15 mm—1°, Scan. speed: 1 deg./min.)

refractive indices of vaterite measured by immersion method are $N_{\min.}=1.548\pm0.002$, $N_{\max.}=1.648\pm0.002$, and the elongation of acicular crystal in radial aggregate is positive. But, the optic sign could not be decided due to minute crystal. The optical properties are useful for the identification of three components in the sediments. That is, monohydrocalcite has the lowest refractive indices among them, and moreover vaterite has smaller birefringence than calcite. The possibility of a plate-like crystal habit of vaterite from Ballycraigy was suggested by McConnell (1960) judging from the negative elongation. The radial aggregates in vaterite spherules (Fig. 2b), however, show positive elongation expecting the direction to be c-axis.

In summer season at Shiowakka, a small amount of vaterite is still stable in wet residual sediments. The temperature of surface of the residue increases up to 40°C in the sunshine but

that is always wet by spring water. The present vaterite is relatively stable, although Johnston *et al.* (1916) and McConnell (1960) reported that their synthesized equivalents of vaterite were unstable and rapidly transformed to calcite or aragonite in the presence of water at room temperature. The air-dried vaterite from Shiowakka has not changed over year and a half, and is still stable after a week even under the pure water at room temperature. The present experiments on the stability of vaterite by the treatment of heating in an electric furnace and X-ray powder diffraction confirmed that vaterite transformed to calcite around 400°C.

III. Formation of vaterite

Some previous studies on vaterite in geological environments show that the occurrences were related to the carbonation of the hydrogel (McConnell, 1960; Bentor *et al.*, 1963; Matsubara *et al.*, 1981), and these may be analogous to the vaterite formation in cements and mortars (Cole and Kroone, 1959). The occurrence of vaterite in aqueous environments is uniquely known from Holkham Lake, Norfolk (Rowland and Webster, 1971), but the physical and chemical condition on the formation has not been clear (Lucas and Andrews, 1996).

The present occurrence of vaterite does not correspond to the above mentioned case. Vaterite formation is closely related to the decomposition of ikaite which has formed in winter season. It was confirmed during the X-ray powder diffraction study for ikaite, that is, vaterite is formed in a short period from ikaite through the X-ray radiation (Ito, 1996). There are no reports on vaterite formed through decomposition of natural ikaite (Stein, C.L. and Smith, A.J., 1986; Council and Bennett, 1993). The reason was suggested that Mg ions interrupt the vaterite formation by Ito (1998).

On the other hand, the morphological fea-

Fig. 2. Photomicrographs of vaterite concentrated by heavy liquid. Vat, vaterite; Cal, calcite. Bars indicate 20 μm
 a) Foamy aggregates composed of spherulitic vaterite.
 b) Zoning with trace of crust in vaterite.
 c) Zonal arrangements of blackish impurities in vaterite.

tures of vaterite of Shiowakka (Fig. 2a, b) suggest that they have grown in a free space. The mode of occurrence, also, suggests vaterite to be precipitated with calcite in aqueous solution. The ambiguous zonal arrangements of blackish impurities in concordant with inner concentric circle structure in the spherulites (Fig. 2c) may indicate that vaterite took impurities during crystallization in spring water. Therefore, two steps of vaterite formation are considered. The first is the decomposition of ikaite and the second is the growing in solution. The nucleation of vaterite has probably occurred in crystal of ikaite and the growth of vaterite was also promoted by dissolution of ikaite. As the decomposition rate is controlled by the wetness of

ikaite crystal surface (Ito, 1996), the solution also may play an important role for growth of vaterite and calcite. It is also suggested that the higher initial concentration of Ca ion effects on the nucleation of vaterite among trimorphs in the synthesis of CaCO_3 by Baba *et al.* (1998).

The crystallization of vaterite might occur quickly by the very strong activation force for nucleation due to the spherulitic and foamy aggregates (Fig. 3a, b). It is assumed to be favorable for the formation of vaterite that the rapid decomposition of ikaite with an increase of temperature in the early spring season. These suggest that the crystallization of the orientated spherules and foamy aggregates begins along the outlines of ikaite crystals (Fig.

Fig. 3. Scanning electron micrographs of vaterite and calcite in carbonate sediments. Abbreviation is same as Fig. 2.

- Egg-shaped vaterite associated with calcite. Rhombic calcite is a pseudomorph after ikaite.
- Aggregates of vaterite and a hole (arrowed) on the eggshell-like crust.
- A row of vaterite spherules.
- Sporadic calcite pseudomorph after ikaite under the room condition.

3c). The spherulitic vaterite and calcite were formed distinctly after ikaite, and also vaterite formation was slightly earlier than calcite (Fig. 3a). The kinetics will determine which phase appears when the given driving force is appreciable for a number of possible transformation (Ptinis and McConnell, 1980). On the decomposition of ikaite, it is explained that apparently similar conditions did not always lead to the same quantity of products by the heterogeneous nucleation. Furthermore, the heterogeneity was distinctively indicated by the characteristic

zonal texture on a surface of calcite pseudomorph (Fig. 3d).

The eggshell-like crust suggests the effect of some substance like biofilms. Although vaterite is considered to be formed under the inorganic environment, the possibility of a biological activity concerned to the formation of vaterite at Shiowakka can not be eliminated.

On the other hand, no genetic relationship with vaterite and monohydrocalcite is observed. Monohydrocalcite was found as very minute euhedral crystal of about 10 μm on the

surface of both grains of vaterite and calcite. The change to monohydrocalcite from ikaite was impossible through grinding and boiling despite of easily case in vaterite (Ito, 1998). Therefore, monohydrocalcite might be precipitated in spring water by any other factor like as the activity of micro-organism (e.g. Taylor, 1975; Ito, 1993) than inorganic one in case of vaterite.

IV. Summary

The nucleation of vaterite at Shiowakka was derived from rapid decomposition of ikaite in a sunny day and subsequently the growth of spherulitic vaterite was accelerated in solution. The growth condition of the present vaterite in cold water in early spring season corresponds to the stability field at a low temperature determined by Albright (1971). The growth of vaterite spherulites, however, did not continued for a long time because of their very small diameter less than 50 μm .

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炭酸カルシウム堆積物中に産するイカアイト後のファテライト

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北海道, シオワッカの石灰華ドームにおいて, 冬に生じたイカアイトは春先の気温の上昇によって複数の炭酸塩鉱物の集合に変わる。それからファテライトがカルサイト, モノヒドロカルサイトと共に産することを初めて認めた。野外の産状からはファテライトの生成がイカアイトの分解に密接に関係していることが考えられた。

偏光顕微鏡と SEM による観察結果からは, イカアイトの急激な分解がファテライトの核形成の引き金となったと考えられる。結晶成長はイカアイトの溶解に伴ってその後も続くが, ファテライト球晶集合に見られる平面的な配列は初期の生成がイカアイト結晶に沿う形で進行したことを示す。SEM 像で確かめられたファテライトとカルサイトとの共生は, イカアイトの分解の際の不均一な核成長での生成を示唆する。他方, モノヒドロカルサイトの生成とイカアイトの分解の間には直接の成因関係は認められない。水質, 産状, 顕微鏡下の性質等を合わせ考えると, イカアイトの分解に伴う炭酸カルシウムに過飽和な条件下で起きた急激な晶出が, シオワッカにおけるファテライトの生成をもたらしたと言える。

Ashoro-cho 足寄町, Rawan 螺湾, Shiowakka シオワッカ