

Vaterite from Liawenee, Central Tasmania, Australia

By

Satoshi MATSUBARA, Akira KATO and Tokiko TIBA

Department of Geology, National Science Museum, Tokyo 160

The geological occurrence of vaterite ($\mu\text{-CaCO}_3$) is very rare and has been reported from Ballycraigy (McCONNELL, 1960), from the Pesyanoe meteorite (DUFRESNE & ANDERS, 1962), from Holkham Lake (ROWLANDS & WEBSTER, 1971), from Antarctica (BROWNE, 1973), and from Hatrurim (GROSS, 1977). Also it has been found in hard tissues of marine organisms (e. g. STOLKOVSKI, 1951; HALL & Taylor 1971; LOWENSTAM & ABBOTT, 1975) and in human calculi (e.g. GIBSON, 1974).

During the investigation of minerals in basaltic rocks from Tasmania, the authors recognized the occurrence of vaterite in a calcium aluminum silicate hydrogel forming spheroidal aggregate in amygdules of pillows of a basaltic rock exposed at Liawenee, near Great Lake. The present paper reports the occurrence and X-ray powder pattern, and strongly suggests that vaterite is favourably crystallized under the presence of low crystalline hydrous calc-silicate compounds.

The studied materials were collected by geological survey team from National Science Museum, Tokyo during the field trip on Tasmania in 1978.

Description

Occurrence: In the southwestern side of the Great Lake, midland of Tasmania, Cainozoic basaltic rocks are exposed as lava flows and unconformably overlies Jurassic dolerite (SUTHERLAND & HALE, 1970).

Vaterite was found as an amygdale fillings of tachylitic portion in basaltic pillows from the dump of Liawenee Canal. It occurs in white porcelain-like spheroidal aggregates up to 5 mm across associated with calcite, chabazite, thomsonite and philipsite (Fig. 1). Under the microscope vaterite occurs as very minute globules up to $20\ \mu$ across in an isotropic substance (Fig. 2 a, b), which is amorphous to X-ray. The vaterite grains, especially in outer crust of spheroidal aggregates, however, partly or completely have transformed to calcite. In the amorphous substance tacharanite also occurs as very minute crystal aggregates with a dendritic texture (Fig. 3).

X-ray powder study: The vaterite-bearing material was examined by the X-ray powder diffractometer. The observed reflections are for vaterite, calcite, tacharanite and an amorphous phase, which gives a very broad band around $\text{CuK}\alpha 2\theta = 25^\circ$. Along with calcite and tacharanite, only the strongest reflections ($d = 3.04\ \text{\AA}$ and $13.0\ \text{\AA}$, respectively) are observed. Fig. 4 is the trace of X-ray powder diffractometer in the

range of 20° to 51° (2θ in Cu/Ni radiation). The five reflection peaks corresponding to vaterite are clearly observed on the figure. The presence of an optically isotropic

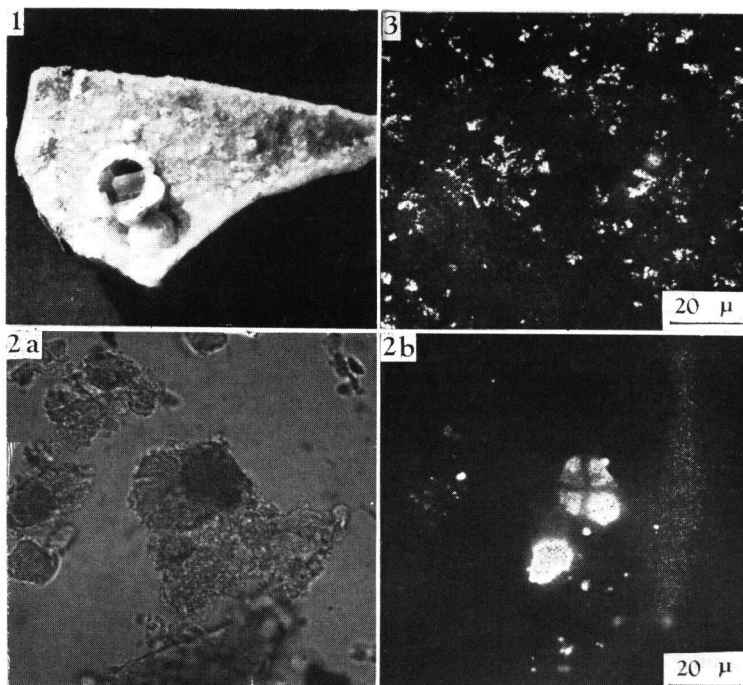


Fig. 1. Vaterite-bearing spheroidal aggregates on calcite and zeolites in amygdale of pillow basalt.

Fig. 2. Photomicrographs of vaterite-globules in an amorphous substance. (a) One polar and (b) crossed polars.

Fig. 3. Photomicrograph of tacharanite with a dendritic texture in an amorphous substance. Crossed polars.

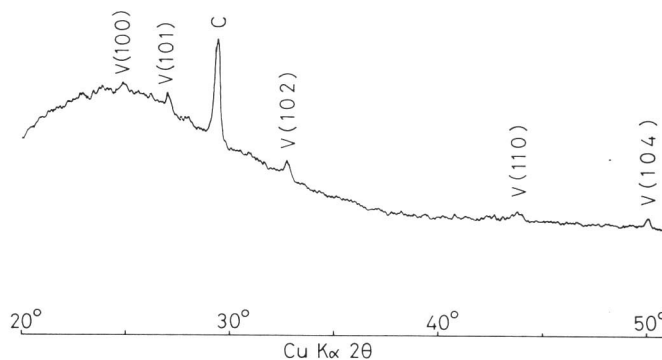


Fig. 4. X-ray powder diffractometer pattern of material including vaterite (V) and calcite (C).

substance is also shown by broad band around $2\theta=25^\circ$. The parameters of the vaterite pseudocell calculated after indexing by referring to JCPDS Card No. 24-30 are $a=4.126$ and $c=8.470$ Å, respectively. These values correspond to hexagonal unit cell parameters: $a=7.146$ ($=4.126 \times \sqrt{3}$) and $c=8.470$ Å.

Chemistry: On account of its very small grain size and the gel-like nature of material involving vaterite, the chemical study of bulk material was made by the wet chemical analysis except for H_2O and CO_2 (Table 1). The presence of the latter has been confirmed due to effervescence in dilute HCl.

Since none of the identified mineral phases in the material can take up such appreciable amount of Al_2O_3 as appeared in the chemical analysis, there is no doubt that this component is one of the essential constituent of the amorphous substance in co-existence with vaterite.

Table 1. Chemical analyses of tacharanite-bearing substance and tacharanite from Tasmania

	1	2	3	
SiO_2	43.65	3.96	46.5	1. Weight percent of tacharanite, calcite and vaterite-bearing amorphous substance from Liawenee (excluding H_2O and CO_2). 2. Atomic ratio for $Si+Al+Fe=5$. 3. Tacharanite from Gads Hill (SUTHERLAND, 1976).
Al_2O_3	9.04	0.97	5.9	
Fe_2O_3	1.06	0.07	0.36	
MnO	0.01	0	n.d	
MgO	tr	0	0.76	
CaO	31.08	3.02	27.0	
Na_2O	0.71	0.12	0.50	
K_2O	0.55	0.06	0.45	
H_2O^+			18.6	
Total	86.10		100.07	

This also leads to the suggestion that there is an upper limit in Al_2O_3 content in tacharanite and the phase in co-existence with this tacharanite will have a higher Al_2O_3 with a compositional gap between this phase and the tacharanite.

Consideration: Many experimental studies for equilibrium phase stability of $CaCO_3$ system indicate that vaterite is formed at low temperatures (e.g. ALBRIGHT, 1971). According to synthetic works by McCAULEY & ROY (1974), vaterite is not a real $CaCO_3$ but a slightly Ca-rich compound with small incorporations of (OH), HCO_3 or CO_2 (aq.). The geologically occurring vaterite, however, seems to have been formed within calcite stability field. It is suggested that the crystallization of vaterite is favoured by the presence of incompletely crystalline $Ca(OH)_2$ (McCONNELL, 1960) and tobermorite minerals (TAYLOR, 1961).

The occurrence of Liawenee vaterite suggests that it was formed as a metastable

crystal in gelatinous hydrous calcium aluminum silicate material. The dendritic tacharanite might have been developed after or during the solidification of gel.

Acknowledgements The authors express their sincere thanks to Dr. F. L. SUTHERLAND, The Australian Museum, for his guidance to the collecting site.

References

- ALBRIGHT, J. N., 1971. Vaterite stability. *Amer. Miner.*, **56**: 620–624.
- BROWNE, P. R. L., 1973. Secondary minerals from Dry Valley Drilling Project holes. *Antarctic Journ.*, **8**: 159–160.
- DUFRESNE, E. R. & F. ANDERS, 1962. On the retention of primordial noble gases in the Pesyanoe meteorite. *Geoch. Cosmoch. Acta*, **26**: 251–262.
- GIBSON, R. I., 1974. Descriptive human pathological mineralogy. *Amer. Miner.*, **59**: 1177–1182.
- GROSS, S., 1977. The mineralogy of the Hatrurim formation, Israel. *Geol. Surv. Israel, Bull.*, **70**: 1–80.
- HALL, A. & J. D. TAYLOR, 1971. The occurrence of vaterite in gastropod egg shells. *Miner. Mag.*, **38**: 521–522.
- LOWENSTAM, H. A. & D. P. ABBOTT, 1975. Vaterite; a mineralization product of the hard tissues of a marine organism (Ascidacea). *Science*, **188**: 363–365.
- MCCAULEY, J. W. & R. ROY, 1974. Controlled nucleation and crystal growth of various CaCO_3 phase by the silica gel technique. *Amer. Miner.*, **59**: 947–963.
- MCCONNEL, J. D. C., 1960. Vaterite from Ballycraigy, Larne, Northern Ireland. *Miner. Mag.*, **32**: 535–544.
- ROWLANDS, D. L. G. & R. K. WEBSTER, 1971. Precipitation of vaterite in lake water. *Nature (Phys. Sci.)*, **229**: 158.
- STOLKOVSKI, J., 1951. Essai sur le déterminisme des formes minéralogiques du calcaire chez les êtres vivants. *Inst. Oceanogr., Monaco, Ann.*, **26**: 1–113.
- SUTHERLAND, F. L., 1976. Tacharanite from Tasmania, Australia. *Min. Mag.*, **40**: 887–890.
- & G. E. A. HALE, 1970. Cainozoic volcanism in and around Great Lake, Central Tasmania. *Proc. Roy. Soc. Tasm.*, **104**: 17–32.
- TAYLOR H. F. W., 1961. The chemistry of cement hydration. “Progress in Ceramic Science” Vol. 1. 1–333 pp. Oxford, Pergamon Press.