

Brushite in the Remains of the Edo Period from Iwaki, Fukushima Prefecture, Japan

By

Satoshi MATSUBARA¹, Akira KATO¹ and Kousuke SEKIUCHI²

¹Department of Geology, National Science Museum,
3–23–1 Hyakunincho, Shinjuku-ku, Tokyo, 169

²Iwaki City Office, 15 Umemoto, Taira, Iwaki, Fukushima

Abstract Brushite is found as a rosette-like aggregate associated with vivianite on seeds or fragments of wood and animal bone in the remains of the Edo period from Shimoyunagaya, Iwaki City, Fukushima Prefecture. It is colorless to pale gray thin tabular crystal up to 10 mm in length. The representative chemical analysis by EDS is: CaO 31.83, P₂O₅ 40.26, total 72.09 wt.%. If the difference is H₂O, the empirical formula is Ca_{1.00}H_{1.00}PO₄·2.23H₂O on the basis of P=1. The unit cell parameters calculated by X-ray powder diffraction data are: $a=6.377(5)$, $b=15.214(5)$, $c=5.823(5)$ Å, $\beta=118.60(6)^\circ$. It is notable that the present brushite occurs in clayey soil including trash not being older than the eighteenth century.

Introduction

Brushite is a common mineral in small amounts in organic sediments (e.g. phosphorite and guano in cave), fossil bones (e.g. human skull) and cavities of phosphate pegmatite. Though the above mentioned occurrences in Japan were reported, they are powdery and minute needle-like crystals under 1 mm long (e.g. SAKAE & KIZAKI, 1972; MATSUBARA & KATO, 1980; MATSUBARA & TIBA, 1982).

During the excavation of the remains of the Yunagayatate (dwelling of the Yunagaya clan) by Iwaki Educational and Cultural Corporation, the third author recognized the occurrence of brushite in association with vivianite from clayey soil including trash at SK-30 pit. In this paper we report the peculiar mode of occurrence and the mineralogical properties.

Occurrence

The remains of the Yunagayatate is located at Joban-Shimoyunagaya Town, Iwaki City, about 4 km north of Izumi station of JR Joban Line (Fig. 1). Brushite and vivianite were only collected from SK-30 pit among 53 pits ranging from the eighth to eighteenth century. The SK-30 pit situated at near south-west margin of the surveyed area is approximately 50 cm in diameter and 150 cm in depth.

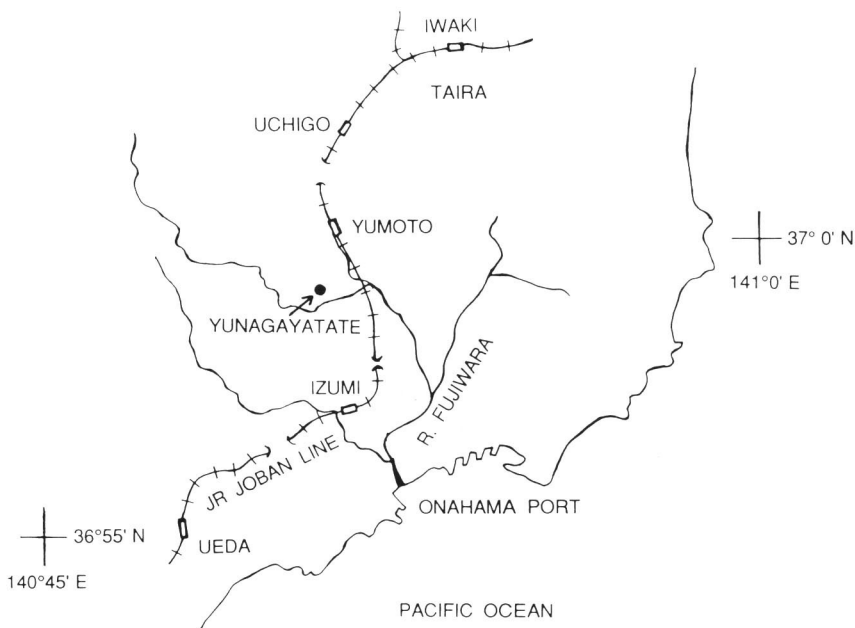


Fig. 1. The index map of the remain of Yunagayatate, Iwaki City, Fukushima Prefecture.

Phosphates are included in black soil layer which is about 30 cm thick and 100 cm below from the ground surface. The soil includes large quantity of water, consequently has strong clayey nature. From this soil were excavated many seeds, animal bones and hairs in association with old coins (Kan'ei-tsuho) and such fragments as wooden wares, knitted plants, tiles, papers, clothes and ceramics. The age of SK-30 pit is estimated as about eighteenth century from these remains by Iwaki Educational and Cultural Corporation (1995).

Brushite shows rosette-like aggregates and overgrowth on seeds or fragments of wood and bone after washing away black soil (Fig. 2). The crystal is thin tabular elongated [010], where well developed face with many striations is considered as $\{111\}$. The less developed face showing uneven or rough may be $\{\bar{1}03\}$. Rarely is observed slender $\{010\}$. It is colorless to pale gray. Crystals are reaching 10×7 mm in size and 2 mm thick. Perfect $\{010\}$ cleavage is observed. These habits and physical properties resemble those of gypsum. Vivianite grows sporadically on brushite crystals as minute crystal up to 0.5 mm in diameter. Also, it forms nodular aggregate consisting of tabular or granular crystals.

Optical Properties

It is colorless in thin section. The refractive indices are $\alpha = 1.538 \pm 0.002$ and

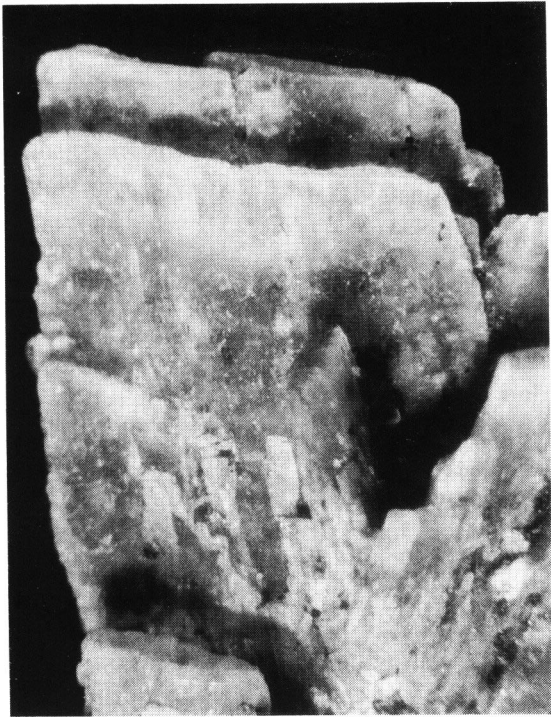


Fig. 2. Crystal group of brushite. Field view: approx. 9×7 mm.

Table 1. Optical properties for brushite.

	Dana II	Iwaki
Refractive Index		
α	1.539	1.538 ± 0.002
β	1.546	1.546 ± 0.002
γ	1.551	
2V		
sign	positive	positive
angle	86°	ca. 90°
Dispersion	$r>v$	$r>v$
Orientation	$X\wedge c -30^\circ$ $Z=b$	$X\wedge c$ ca. 25°

$\beta = 1.546\pm0.002$ measured by the immersion method. It is biaxial positive and 2V very large ($\sim 90^\circ$). The orientation $c\wedge X$ is approximately 25° . In Table 1, these properties are compared with those of brushite adopted by Dana's System of Mineralogy (PALACHE *et al.*, 1951).

Table 2. The X-ray powder data for brushite. 1, Synthetic brushite. $a = 6.363$, $b = 15.19$, $c = 5.815 \text{ \AA}$, $\beta = 118.48^\circ$. JCPDS 9-77; 2, Brushite from Iwaki, Fukushima Prefecture, Japan: $a = 6.377$, $b = 15.214$, $c = 5.823 \text{ \AA}$, $\beta = 118.60^\circ$. This study.

1		2				1		2			
d	I	d _{obs.}	d _{calc.}	I	h k l	d	I	d _{obs.}	d _{calc.}	I	h k l
7.57	100	7.63	7.61	100	0 2 0	2.252	2				2 4 0
4.93	2	4.94	4.94	<1	1 1 $\bar{1}$	2.172	20	2.174	2.174	10	1 5 1
4.24	100	4.243	4.243	40	0 2 1	2.148	16	2.150	2.152	6	2 4 $\bar{2}$
3.80	8	3.800	3.804	45	0 4 0	2.120	2	2.123	2.121	<1	0 4 2
3.75	<1				1 3 0	2.100	6	2.102	2.103	3	1 5 $\bar{2}$
3.63	2	3.636	3.637	<1	1 3 $\bar{1}$	2.084	10	2.087	2.088	2	3 1 $\bar{1}$
3.05	75	3.051	3.052	50	0 4 1	2.022	4	2.025	2.025	2	3 1 $\bar{2}$
			3.044		1 1 1				2.026		1 7 0
2.928	50	2.930	2.933	15	2 2 $\bar{1}$	2.001	10	2.004	2.006	6	1 7 $\bar{1}$
2.855	10	2.858	2.858	1	1 1 $\bar{2}$			1.999	2.000	5	2 2 1
2.797	2	2.800	2.799	<1	2 0 0	1.976	6	1.977	1.982	1	2 6 $\bar{1}$
2.670	4	2.670	2.674	3	1 5 0				1.976		1 1 2
2.648	4	2.647	2.649	3	1 3 1	1.943	2				3 3 $\bar{1}$
2.623	50	2.625	2.627	20	2 2 0	1.899	2	1.900	1.902	12	0 8 0
			2.629		1 5 $\bar{1}$	1.888	4				1 1 $\bar{3}$
2.603	30	2.606	2.609	8	2 0 $\bar{2}$	1.878	14	1.878	1.879	8	2 6 0
2.554	4	2.560	2.556	1	0 0 2	1.858	8	1.859	1.862	1	2 2 $\bar{3}$
2.532	2	2.533	2.536	5	0 6 0				1.855		1 3 2
2.520	4				1 3 $\bar{2}$	1.819	20	1.817	1.820	8	2 4 1
2.434	14	2.439	2.439	5	2 4 $\bar{1}$				1.819		2 6 $\bar{2}$
2.421	16	2.425	2.423	4	0 2 2	1.799	10	1.800	1.800	3	0 6 2
2.268	4	2.271	2.272	4	0 6 1	1.780	4	1.781	1.782	2	0 8 1

X-ray Powder Study

The X-ray powder data was obtained by the diffractometer using Cu/Ni radiation. The diffraction peaks corresponding to (010) were enhanced by preferred orientation due to perfect cleavage of {010}. In Table 2, the patterns of synthetic (JCPDS 9-77) and Iwaki materials are compared. The calculated cell parameters are; $a = 6.377(5)$, $b = 15.214(5)$, $c = 5.823(5) \text{ \AA}$, $\beta = 118.60(6)^\circ$.

Chemical Composition

The chemical analyses of the studied brushite were made by using Link Systems model QX2000 energy-dispersive spectrometer (EDS). Detected elements of higher atomic number than Na are P and Ca. Standard materials are wollastonite for Ca and GaP for P. Analytical procedure has been reported by YOKOYAMA *et al.* (1993). The representative chemical analysis is; CaO 31.83, P₂O₅ 40.26, total 72.09 wt.%. If H₂O is added as the difference, empirical formula

is $\text{Ca}_{1.00}\text{H}_{1.00}\text{PO}_4 \cdot 2.23\text{H}_2\text{O}$ on the basis of $\text{P} = 1$. If water of crystallization is taken as 2 in the above analysis, $\text{H}_2\text{O} = 25.57 \text{ wt.}\%$ is required, and then total is 97.66 wt.%. Analytical total except H_2O should be 73.82 wt.% calculated from ideal formula, $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$. All analyses, however, are about 2 wt.% lower than the expected total, because brushite was damaged by operating electron beam more than 30 seconds during measurement using a live-time of 60 seconds at 15 KV with 1 nA.

Discussion

Many examples of brushite formation from ancient human and animal bones have been reported. In Japan, needle-like crystals were found in inside of skull 1200 to 1300 years ago from the Nashinokizaka-No. 1 tomb at Zama, Kanagawa Prefecture (MATSUBARA & TIBA, 1982). However, no occurrence has been reported as the present case where large crystals of brushite grew in trash only 200 to 300 years ago. The possible source of phosphorous and calcium may be $[\text{CO}_3]^{2-}$ -bearing hydroxylapatite consisting of unidentified animal bones. Though the alteration of bones progresses under strong acid condition, brushite can not precipitate under such condition. Many products from wood considered as the source of acetic acid are excavated together with animal bones. These suggest that the present brushite has been formed by the chemical reaction between dilute acetic acid and $[\text{CO}_3]^{2-}$ -bearing hydroxylapatite under the ordinary temperature at about 100 cm underground (ca. $10\text{--}30^\circ\text{C}$), and large crystals, also, are able to grow during short time when the good conditions have been kept.

According to the definition of a mineral provided by the IMA Commission on New Minerals and Mineral Names (CNMMN), chemical compounds formed by the action of geological processes on anthropogenic substances cannot be considered as minerals (NICKEL, 1995). In the present case, brushite grows on such natural materials as seeds, woods and animal bones that have been accumulated by activities of people. However, their activities were not clearly for the purpose of creating minerals, namely, the present brushite can be accepted as a mineral.

Acknowledgements

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