Short Communications

Sassolite sublimated in a steam well at the Yunotani Geothermal Field, Aso Caldera, Kyushu. Sachihito TAGUCHI*, Paul P. PARMENTIER and Tatsuo YAMASAKI*,** **Research Institute of Industrial Science, Kyushu University 86, Fukuoka 812, Japan, and **Republic Geothermal, Inc., Santa Fe Springs, California 90670, USA.*

Introduction

Sassolite, H_3BO_3 , occurs locally in and around geothermal manifestations such as hot springs and fumaroles. The mineral was found for the first time in the solid state on the rim of the hot spring at Sasso, Italy (Palache, 1944). Smith (1958) also reported three occurrences of sassolite from the geothermal fields; Steamboat Springs, Nevada; The Geysers, California; and Norris Geyser Basin, Yellowstone Park, Wyoming. In Japan, it was found as sublimates around the fumaroles at Iwo-zima Island in Kyushu (Okano 1962), and at Showashinzan in Hokkaido (Mizutani, 1962).

The authors recognized sassolite as the sublimation product of a steam well in the vapor-dominated geothermal field of Yunotani in Aso Caldera, where this scale product caused a cessation of steam flow. The present report describes the occurrence and mineralogical data of the sassolite, and also discusses the conditions of its formation.

Mode of occurrence

The Yunotani geothermal field is situated in the well-known gigantic Aso Caldera, central Kyushu. Yamasaki *et al.* (1978) studied its geology and geochemistry, and recognized it as a vapor-dominated field. The well Yunotani No. 2 in which sassolite was formed is located about 300 meters north of mud ponds where the pH is as low as 2.7. The well discharged for the first few days a small amount of water together with steam, but finally dry steam was the only product from it. The HBO_2 content is 84.5 ppm in the initial water and ranges from 31.0 to 185.0 ppm in the condensed water (Yamasaki *et al.*, 1978 and Koga, personal communication).

The steam from the well gradually decreased in amount and became intermittent after 2 and a half years operation. Then, the well ejected debris, up

to 5 cm in diameter, of a white substance, which was later identified as sassolite. Sassolite also occurs at the surface pipeline joints and valves. Since sassolite samples at the surface show brownish staining probably due to impregnation of iron oxides, the white ejected samples used for this experiment.

The white sample has pearly luster, and shows a porous surface (Fig. 1). A very small amount of impurities such as mica-montmorillonite are included in it. The mineral appears as tabular crystals under the scanning electron microscope (Fig. 2).

Chemical and physical properties

In Table 1, the chemical composition of sassolite from Yunotani (Koga, unpublished data) is compared with that of other occurrences, and it can be seen that the Yunotani sample differs to some extent in its NH_4 content. The density of sassolite was measured in a pycnometer with toluene as the displace-

FIG. 1. Photograph of sassolite debris ejected from the Yunotani No. 2 well.

FIG. 2. Scanning electron micrograph of sassolite from the Yunotani No. 2 well. The white scale, below left, is equal to 10 micron.

TABLE 1. Chemical compositions of sassolite.

	Yunotani	Death Valley*	Iwo-zima Isl.**	Showashinzan***	Ideal
B ₂ O ₃ } H ₂ O }	98.22	57.19 42.81	54.11 41.85	} 99.1	56.39 43.61
SiO ₂	0.04		1.90		
P ₂ O ₅	0.009			0.1	
S			2.27		
SO ₄	0.20			0.5	
NH ₄	1.33			0.39	
F	0.05				
Cl	0.09		none	0.1	
Br	0.009				
Total	99.948	100.00	100.03	100.19	100.00

Analyst A. Koga, *Allen and Kramer (1957), **Okano (1962), ***Mizutani (1962)

ment liquid, to be 1.494 ± 0.009 . This is within the range of reported values, 1.48 ± 0.02 (Palache *et al.*, 1944). The indices of refraction are $\gamma = 1.468 \pm 0.004$, $\alpha = 1.347 \pm 0.004$. The α index was measured in a mixture of glycerin and water saturated with H₃BO₃. These values are considerably higher than those of previous workers (Table 2).

X-ray powder patterns were prepared for sassolite with nickel-filtered copper radiation, under the following experimental conditions: scanning speed 0.5°/min., accelerating voltage 40 kV, using current 20 mA, time constant 1 sec. The results are shown in Table 3 with other reported values for comparison. The cell dimensions were calculated using the computer program UNICS RSLC-3 (T. Sakurai) to be $a = 7.04 \text{ \AA}$, $b = 7.08 \text{ \AA}$, $c = 6.60 \text{ \AA}$, and $\alpha = 103.83^\circ$, $\beta = 101.07^\circ$, $\gamma = 60.08^\circ$.

Discussion

A phase diagram of H₂O-B₂O₃ system (Kracek *et al.*, 1938) is shown in Fig. 3, in which the pressure conditions of the well No. 2 at the well head and the measured maximum temperature are also shown. From the diagram it is obvious that sassolite is stable in the steam field, and that its stability limit gradually departs from the water saturation line with increasing temperature. The dotted area in Fig. 3 corresponds to the stability field of sassolite in the Yunotani well No. 2. It shows that sassolite probably sublimated in the well in place, with temperatures of 140 to 170°C and at pressures of 2.7 to 4.1 bars in a dry steam environment. The conditions of formation agree fairly well with the maximum measured temperature 172°C (Yamasaki *et al.*, 1978).

TABLE 2. Optical properties of sassolite.

	Yunotani	Italy ^{*1}	Kramer borate ^{*2} dist.	Death Valley ^{*3}	Iwo-zima Isl. ^{*4}	Boric acid ^{*5}
α	1.347 ± 0.004	1.340 ± 0.005	1.337 ± 0.005	1.340 ± 0.005	1.331 ± 0.003	1.337
β		1.456 ± 0.003		1.457 ± 0.003	1.448 ± 0.003	1.461
γ	1.468 ± 0.004	1.459 ± 0.003	1.454 ± 0.003	1.459 ± 0.003	1.453 ± 0.002	1.462
optic sign		Negative		Negative		
$2V_{\text{calc.}}$		17.0°		14.0°		

^{*1} Larsen (1921), ^{*2} Smith *et al.* (1958), ^{*3} Allen and Kramer (1957), ^{*4} Okano (1962), ^{*5} Kracek *et al.* (1938)

FIG. 3. Phase diagram of H₂O-B₂O₃ system showing stability field of sassolite (dotted area), the well head pressure ($P=2.7$ bars) and the measured maximum temperature ($T=172^\circ\text{C}$) of the Yunotani No. 2 well.

From the above observations it may be estimated that the sassolite in the Yunotani well No. 2 sublimated directly from the vapor and not through intermediate phases of HBO₂ I or HBO₂ II. Scale deposits of sassolite sublimates which reduce the discharge of steam from the well, as happened at Yunotani No. 2 well, can be easily removed by filling the well with water to dissolve the scale products. Moreover, sublimation of sassolite in a well could be avoided

TABLE 3. X-ray power diffraction data of sassolite from Yunotani, Aso.

Yunotani, Aso			(1)		(2)		(3)	
$d(\text{\AA})$	I/I_0	hkl	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0	$d(\text{\AA})$	I/I_0
14.4	<1	(Mi/Mo)						
9.1	<1	(Mi/Mo)						
6.04	4	100, 010	6.02	1	6.1	2	6.04	2
5.92	2	110	5.89	<1	5.9	1	5.91	<1
5.72	<1							
5.67	<1							
5.52	1							
4.97	<1	11 $\bar{1}$						
4.81	<1	01 $\bar{1}$?			4.8	<1		
4.62	1	10 $\bar{1}$	4.59	<1	4.60	<1	4.60	<1
4.21	1	101	4.20	<1	4.27	<1	4.21	<1
4.06	1	011?	4.04	<1	4.05	<1	4.06	<1
3.54	2	$\bar{1}$ 10?	3.52	<1	3.52	2	3.52	<1
3.38	2	zeol. ?						
3.183	100	002	3.18	10	3.19	10	3.18	10
3.023	1	1 $\bar{1}$ $\bar{1}$			3.04	<1	3.03	1
2.955	1	220	2.95	<1	2.97	1	2.95	<1
2.926	1	02 $\bar{1}$	2.92	<1	2.92	1	2.92	1
2.837	1	20 $\bar{1}$			2.85	1	2.84	<1
2.722	<1		2.71	<1	2.73	<1	2.72	<1
2.644	1	201?	2.64	<1	2.65	2	2.64	1
2.567	1	021	2.56	<1	2.57	1	2.56	<1
2.536	<1	22 $\bar{2}$					2.53	<1
2.502	<1				2.50	1	2.50	<1
2.371	<1							
2.307	<1	2 $\bar{1}$ 0, 20 $\bar{2}$			2.29	<1	2.30	<1
2.256	1	130, 31 $\bar{1}$			2.27	<1		
2.237	1	230	2.23	<1	2.23	1	2.23	<1
2.212	<1							
2.180	<1				2.17	<1		
2.107	<1				2.10	1	2.10	<1
2.096	1	1 $\bar{2}$ 1, 122, 23 $\bar{2}$			2.07	<1		
2.041	<1	311, 123			2.05	<1	2.04	<1
2.007	<1							
1.99	<1				1.992	<1		
1.948	<1		1.949	<1			1.949	<1
							1.905	<1
							1.888	<1
1.889	<1							
1.856	<1							
1.817	<1							
1.749	<1	42 $\bar{1}$						
1.693	<1	43 $\bar{1}$, 3 $\bar{1}$ 0			1.697	<1	1.692	<1
1.672	<1	$\bar{1}$ 31?			1.674	<1	1.670	<1
					1.654	<1		
					1.636	<1	1.642	<1
1.590	2		1.590	1	1.598	1	1.591	2

(1) Sassolite from Death Valley, California (Allen and Kramer, 1957)

(2) Sassolite from Kramer Borate District, California (Smith *et al.*, 1958)(3) Boric acid (H_3BO_3) (Allen and Kramer, 1957)

Mi/Mo=interstratified mica-montmorillonite, zeol.=zeolite

by setting the well head pressure higher than 4.1 bars.

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