MINERALOGICAL JOURNAL, VOL. 3, NOS. 5 & 6, PP. 296-305, AUG., 1962

TRIDYMITE CRYSTALS IN OPALINE SILICA FROM KUSATSU, GUMMA PREFECTURE

MITSUO SATO

Geological and Mineralogical Institute, Faculty of Science,
Tokyo University of Education

ABSTRACT

Tridymite occurs in the vicinity of Kusatsu Spa as extremely fine crystals in opaline silica which has replaced two pyroxene andesite. Specific gravity: 2.2±0.1, optical properties: $n_1 \geqq 1.478$, $n_2 \leqq 1.480$, $2V \cong 0$, elongation negative, showing straight but wavy extinction. Chemical composition: SiO_2 96.89, TiO_2 0.86, Al_2O_3 0.71, Fe_2O_3 tr., FeO none, MnO none, MgO none, CaO none, Na_2O 0.72, K_2O 0.16, $H_2O(+)$ 0.12, $H_2O(-)$ 0.08, P_2O_5 tr., total 99.54%. The d. t. a. curve shows two endothermic peaks, one at 128°C. and the other at 155°C.; they are attributed to the transition from the low to the middle form and from the middle to the high form respectively. Many sharp X-ray powder diffraction lines were confirmed, most of which have not been reported in previous papers. Under the microscope, noticeable texture of the silicified andesite was observed, suggesting that the tridymite has gradually crystallized out of opaline silica: some of its crystals are extremely small and appear to grade into opaline silica.

Introduction

Along the river Yugawa running through Kusatsu Spa, silicified rocks are distributed over considerable area. The writer discovered that some of them are largely composed of opaline silica and tridymite. Any report concerning such a mode of occurrence of tridymite has not yet been published*). The purpose of this paper is to pro-

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* Just after this paper had been completed, H. Minato reported the similar occurrence of tridymite associated with hydrated halloysite at the Jôshin Mine, Gumma Prefecture (Advances in Clay Science, 3, 264 (1961), in Japanese.)

vide the mineralogical data on the tridymite and some considerations of its origin.

Mode of occurrence

Kusatsu Spa, one of the famous hot springs in Japan, is located at the east foot of the Shirané Volcano. The Spa and its vicinities are covered with tuff breccia of andesite of the Shirané Volcano. Along the river Yugawa which runs from west to east across the Spa there are many hot springs and silicified rocks are distributed over considerable area (Fig. 1). Degree of silicification is at variance even within a single outcrop. It is impossible to confirm by the naked eye the texture of the original rock in intensely silicified area without observations under the microscope. The results of the macroscopic and microscopic observations of the specimens collected at Suzuran District are as follows:

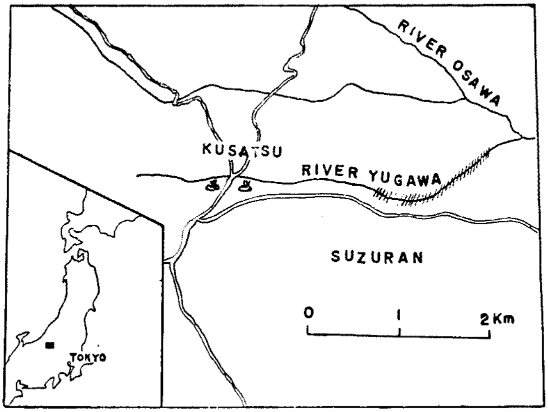
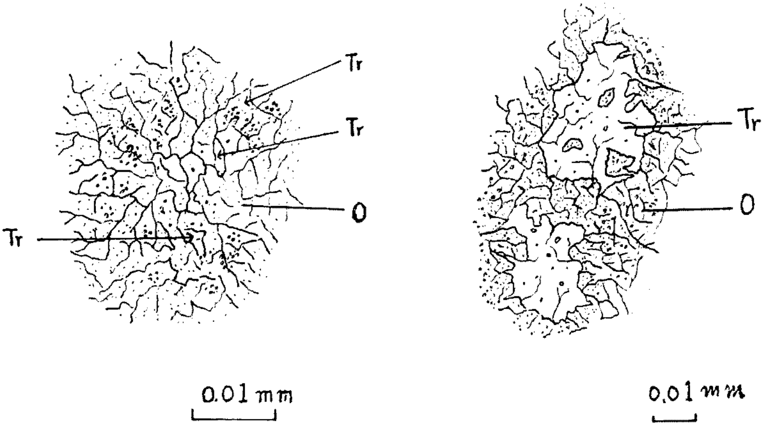


Fig. 1. Locality map.
Shaded area is the locality of tridymite.

The original fresh rock is two pyroxene andesite including a few corroded quartz grains as xenocrysts (Figs. 2A and 2a, Plate I). It is widely distributed over the highland around Kusatsu Spa. In partially silicified rocks, phenocrysts such as hypersthene and plagioclase have been partially silicified, whereas the groundmass has been completely altered (Figs. 2B and 2b, Plate I). In intensely silicified rocks, both phenocrysts and groundmass have been completely altered, and small wedge-shaped or acicular crystals of tridymite occur embedded in the silicified groundmass (Figs. 2C, 2c, 2D and 2d, Plate I). In addtion to tridymite, small amounts of the following minerals are found: augite relics, anatase (up to 0.4×0.4 mm.), barite and cristobalite.

Under the microscope with high magnification, the mode of occurrence of tridymite varies even within one thin slice. Extremely small crystals are distributed in opaline silica; it is worthy of notice that some of them appear to grade into opaline silica (Fig. 3).



a. Small crystals of tridymite.

b. Aggregates of tridymite crystals.

Fig. 3. Sketch shawing the mode of occurrence of tridymite (Tr) in opaline silica (O).

In places, aggregates of crystals are found surrounded by opaline silica. In this case, small cracks are frequently observed traversing the aggregates and extending into opaline silica (Fig. 3b).

In places, wedge-shaped crystals are found surrounded by opaline silica. Usually they are clear and transparent without crack, but

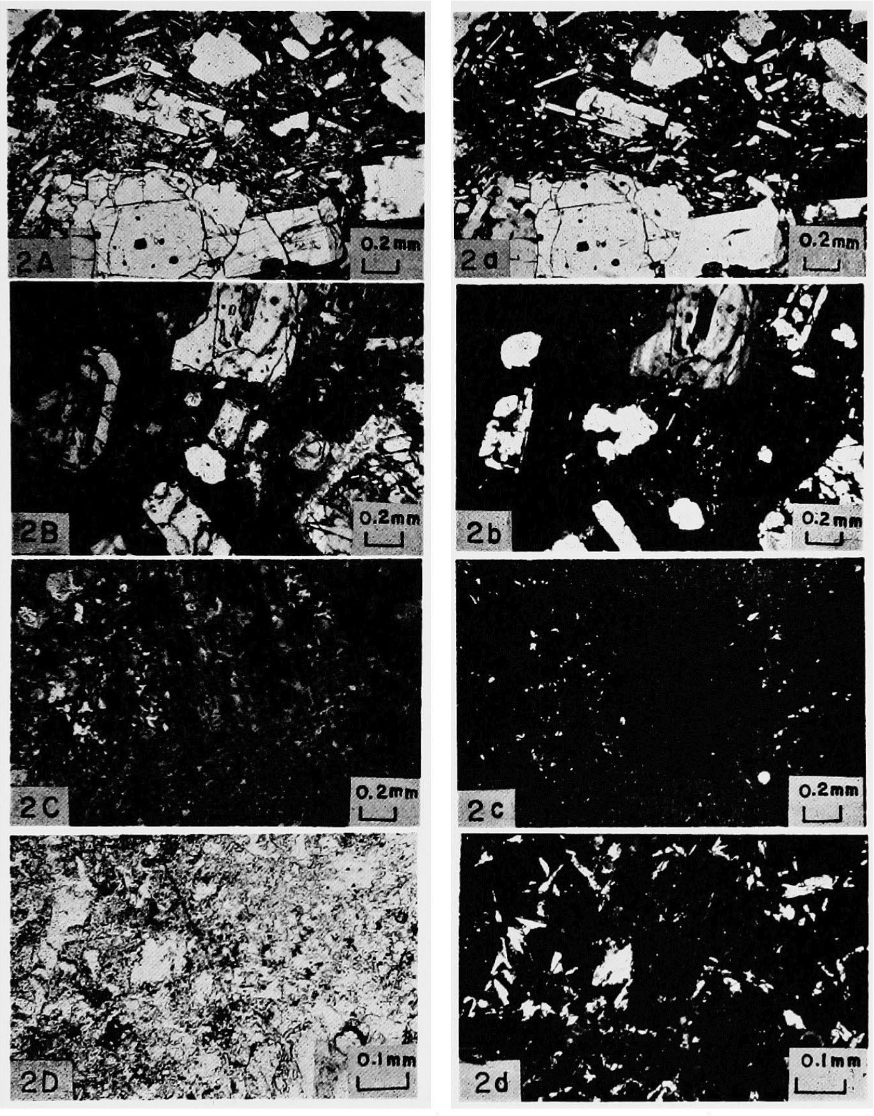


Fig. 2. Photomicrograph of the thin sections of
2A (open nicols) 2a (crossed nicols): fresh rock,
2B (,,) 2b (,,): partially silicified rock,
2C (,,) 2c (,,): intensely silicified rock,
2D (,,) 2d (,.): intensely silicified rock.
Dark part in 2b, 2c and 2d is opaline silica.
White accicular crystals in 2c and 2d are tridymite.

sometimes small cracks are observed developing from its margin into opaline silica (Fig. 4).

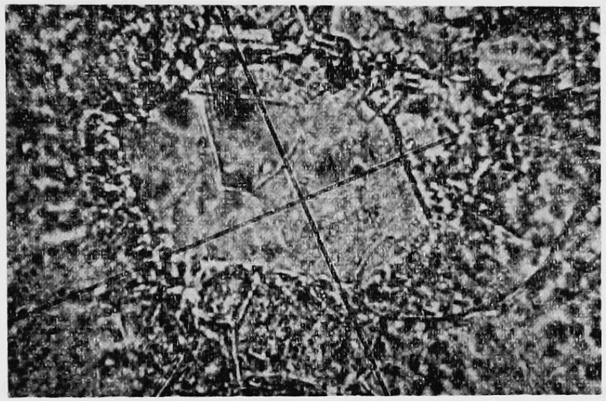


Fig. 4. Photomicrograph of a thin section showing the cracks developing from the margin of a tridymite crystal toward into opaline silica.

Furthermore, the following facts were noticed. Tridymite occurs only in the silicified groundmass. Some of the tridymite crystals include small particles of anatase, which is also distributed in both the silicified groundmass and phenocrysts.

Physical and chemical properties

A specimen of the intensely silicified rock was pulverized to fine grains. Opaline silica is easily dissolved in $HF \cdot NH_4F$ solution whereas tridymite is persistent against this treatment. So that, the grains were immersed into that solution for 4∼5 hours, washed with water and dried in room air. In the next step, Clerici's solution (specific gravity 2.4) was used and centrifugation was applied for the purpose of removing the minerals denser than tridymite from the obtained residue. Thus finally the writer could obtain a tridymite concentrate as free from impurities as possible.

The physical properties of the tridymite are as follows:

Specific gravity: 2.2±0.1 measured by a pycnometer.

Optical properties: $n_1 \geqq 1.478$, $n_2 \leqq 1.480$, $2V \cong 0$, elongation negative, straight but wavy extinction.

Differential thermal analysis curve is obtained as shown in Fig. 5.

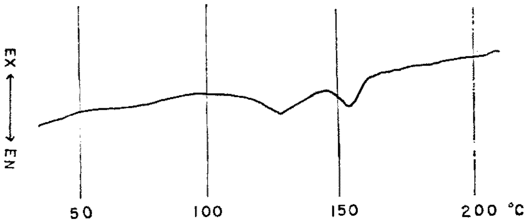


Fig. 5. The d. t. a. curve of tridymite from Kusatsu recorded by an automatic d. t. a. apparatus.

Operation conditions are as follows: thermocouple, chromel-alumel wires; sensitivity of amperes, $\pm 25\mu V$; heating rate, 2.5°C/min.; chart speed, 5 mm/min.; standard sample, alumina; heating in room air.

Two endothermic peaks are confirmed, one at 128°C. and the other at 155°C. It is considered that the former is due to the transition from the low to the middle form, and the latter from the middle to the high form.

The comparison of this with the data previously reported by some investigators is tabulated as Table 1.

Table 1. The inversion points of tridymite.

Source of tridymite	Inversion temp.		Authors
Synthetic: from quartz.	116°-119°C.	161°-166°C.	Fenner (1913)[5]
Natural: Plumas County, California.	127°	—	Lukesh and Buerger (1942)[12]
Natural: San Cristobal, Mexico.	121°	135°	Do.
Natural: from Krakatoa.	115°	150°	Barth and Kvalheim (1944)[3]
Natural: from Kusatsu.	128°	155°	M. Sato (1961)

The chemical compositions of the intensely silicified rock and the tridymite concentrate obtained from it are shown in Table 2.

Table 2. Chemical composition of the silicified rock and tridymite from Kusatsu.

	Silicified rock	Tridymite		Silicified rock	Tridymite
SiO_2	93.27%	96.89%	CaO	none	none
TiO_2	0.92	0.86	Na_2O	0.68	0.72
Al_2O_3	0.33	0.71	K_2O	0.21	0.16
Fe_2O_3	tr.	tr.	$H_2O(+)$	2.07	0.12
FeO	none	none	$H_2O(-)$	2.15	0.08
MnO	none	none	P_2O_5	0.03	tr.
MgO	0.02	none	Total	99.68%	99.54%

In Table 2, it is remarkable with the silicified rock that the Fe, Mg, Mn and Ca have been almost completely leached out, and with the tridymite that the contents of alkalies and titanium are about the same with the host rock while the amount of aluminium is rather high, although the tridymite concentrate is almost free from impurities except anatase.

X-ray powder diffraction data

The results are shown in Fig. 6 and Table 3. Diffraction angles were calibrated by using NaCl as internal standard. The writer could obtain a large number of weak reflections, which have not been reported in previous papers[1) 11)]. They were recognizable only when the divergence slit 2.5° was used (Fig. 6 C). The powder patterns correspond to the tridymite M[8)]. As to the crystallographic problems of tridymite, detailed discussions will be published in the near future.

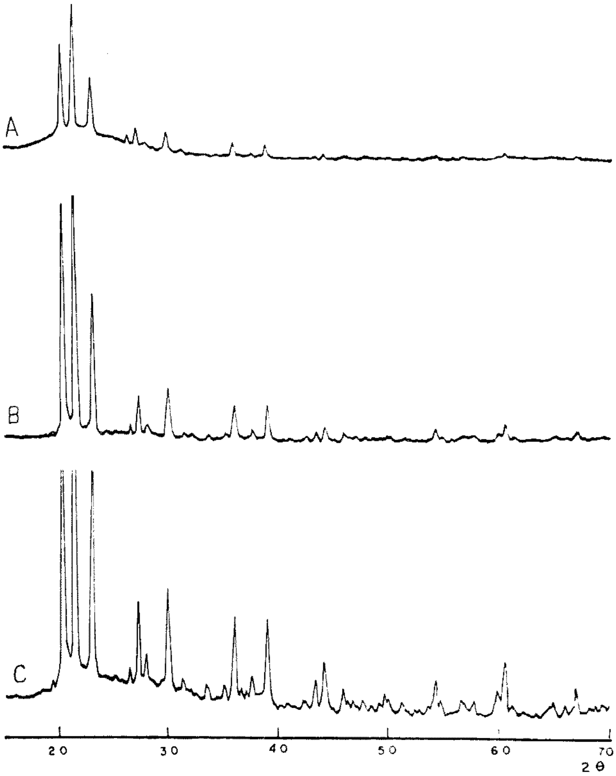


Fig. 6. X-ray powder patterns of tridymite from Kusatsu.

A: Silicified rock, divergence slit, 1°.
B: Tridymite concentration, div. slit, 1°.
C: Tridymite concentration, div. slit, 2.5°.

Operation conditions: Ni filtered copper radiation. 35 kV., 15 mA. Scanning speed, 2°/min.; scale factor, 32; multiplier, 1; time constant, 4; receiving slit, 0.4°.

Origin

The mode of occurrence of the tridymite observed under the microscope suggests that they have been formed as extremely fine particles in opaline silica. Although the aggregates of crystals are inferred to be the product of more advanced stage of crystallization,

Table 3. X-ray powder data for tridymite from Kusatsu. (Cu$K\alpha$ 1.5418Å.)

2θ	d(Å)	I	2θ	d(Å)	I
20.60°	4.311	67	46.41°	1.956	1
*20.86	4.258	3	*46.91	1.937	0.8
21.70	4.095	100	47.83	1.902	1
23.33	3.813	52	*48.61	1.873	0.3
*24.35	3.667	1	*49.36	1.846	1
*25.70	3.466	1	*49.81	1.830	1.5
27.48	3.246	15	*50.16	1.818	1.5
*27.80	3.209	0.3	51.36	1.779	1
*28.14	3.171	6	*51.83	1.764	0.5
*28.55	3.126	1.5	*52.43	1.745	1
*28.75	3.105	1	*52.83	1.733	1
*29.22	3.056	0.3	*53.68	1.707	1
*29.55	3.023	0.3	54.29	1.690	5
30.11	2.968	18	*54.82	1.674	1.5
31.48	2.842	2	56.72	1.623	1.5
*31.79	2.815	1	57.02	1.614	1.5
*32.21	2.779	0.8	57.77	1.596	2
*32.61	2.746	0.8	*58.32	1.582	0.5
33.64	2.664	2.4	*59.85	1.545	3
*34.51	2.599	0.8	*59.89	1.544	2.5
*35.28	2.544	3	60.53	1.530	6
36.14	2.485	13	61.30	1.512	1
*36.78	2.443	1	*63.43	1.466	0.6
*37.23	2.415	0.8	64.58	1.443	1.5
37.73	2.384	3.5	65.00	1.434	2
*38.41	2.344	0.8	*66.03	1.415	1.5
39.09	2.304	13	66.73	1.401	3
*40.34	2.235	0.5	66.98	1.397	1
*41.02	2.200	1	*67.13	1.394	0.5
*42.27	2.138	0.8	*67.75	1.383	0.5
*42.57	2.123	1	68.20	1.375	0.8
43.49	2.081	4	68.83	1.364	1
44.26	2.046	8	*69.43	1.354	0.8
*45.01	2.014	0.3	*69.68	1.349	0.8
45.95	1.975	3	*69.98	1.344	0.2

* Not reported in previous papers.

small cracks developing in opaline silica still remain in the aggregates. On the other hand, remarkable cracks developing from the margin of wedge-shaped crystals into opaline silica may be attributed to the crystallization force of tridymite.

Many reports have been published concerning dominant occurrence of cristobalite in association with opaline silica[14) 15) 16)], but none of dominant occurrence of tridymite in association with opaline silica as in the present case.

What is the basic factor in forming tridymite from opaline silica? Recent studies on tridymite[2) 4) 6) 7) 9) 10) 13)] have revealed that foreign ions such as alkalies and aluminium seem to be effective to promote the formation of tridymite, and they may even be taken into its crystal structure. As shown in Table 2, the tridymite concentrate of Kusatsu also contains aluminium and alkalies in appreciable amounts. Hence, the writer is inclined to consider that association of alkalies and aluminium in the opaline silica of Kusatsu was an effective factor for promotion of tridymite crystallization.

Acknowledgements

The writer wishes to express his sincere thanks to Prof. T. Sudo for his helpful guidance and suggestions. He also wishes to express his thanks to Dr. M. Tokunaga for his critical discussions and advice, and Dr. K. Oinuma, Dr. H. Hayashi and Dr. Y. Kato for their kind assistance during the investigation. Thanks are also due to A. Inami who kindly gave the specimen.

This study has been supported in part by a grant for the scientific research from the Ministry of Education.

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Manuscript received Aug. 8, 1961.