Direct Formation of Crystalline Silica from Acid Thermal Spring Water

Masami ICHIKUNI and Ryozo NAKAGAWA

Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received March 11, 1967)

Few examples of geyserite have been recorded from an acid-spring environment. The silica content of acid-spring waters being rather high as compared with that of alkaline-spring waters,[1] where siliceous precipitates are observed commonly, the reason for the rarity of geyserite in acid media must be sought elsewhere. Experimental studies on the polymerization of monomeric silica have shown that the rate of this reaction is extremely slow under acid conditions.[2] A slow rate of polymerization may result in the slow precipitation of silica, which favors the development of well-crystallized phases. Geyserites formed from neutral or alkaline spring waters are mostly X-ray amorphous because of their rapid rate of growth. Only aging for a long period of time can convert them in cryptocrystalline silica. The direct formation of low tridymite noted by Anderson[3] from Supan's acid spring, Lassen Volcanic National Park, is in good agreement with this line of thought.

The purpose of this paper is to report an interesting occurrence of geyserite at the Tamagawa Hot Springs, representative acid spring of Japan, and to discuss its genetic conditions with special emphasis on the direct formation of crystalline phases.

Samples

The samples used in this investigation were collected at the Tamagawa Hot Springs, Akita Prefecture. Table 1 shows the chemical composition of the spring water,[4] from which siliceous deposits are forming. The water issuing from the vents has a temperature of 97°C and a pH of 1.3, and contains a considerable amount of dissolved silica, which deposits gradually during the flowing of the spring water due to the decrease in silica solubility caused by the cooling of the water.

TABLE 1. CHEMICAL COMPOSITION OF THE SPRING WATER

Component	Content mg/*l*
Na^+	55
K^+	31
Ca^{2+}	99.2
Mg^{2+}	42.1
Fe^{2+}	62.4
Al^{3+}	118
F^-	70
Cl^-	2382
SO_4^{2-}	1128
H_2SiO_3	341
HBO_2	90
H_2S	1.6

TABLE 2. CHEMICAL COMPOSITION OF SILICEOUS DEPOSITS

Component %	TS-1	TS-2
SiO_2	82.83	86.03
TiO_2	0.45	0.12
Al_2O_3	0.56	0.28
Fe_2O_3	0.07	0.20
CaO	0.05	0.05
MgO	0.05	0.05
Na_2O	0.05	0.03
K_2O	0.04	0.04
$BaSO_4$	6.91	1.53
$PbSO_4$	0.32	0.11
$H_2O(-)$	4.55	5.14
$H_2O(+)$	4.90	6.47
total	100.68	99.95

Total Fe was calculated as Fe_2O_3.

Crystal siliceous deposits are found on the inner wall of a wooden sluice of spring water, at a distance of 150 to 300 m from the vents, where the water temperatures range from 70 to 90°C. As the deposits contain small amounts of rhombic sulfur and plumbian barite, these impurities were eliminated prior to the mineralogical investigation by X-ray diffraction. Sulfur was removed by shaking the finely-powdered samples with carbon disulfide for 20 min. The insoluble part of the samples was recovered, and thereafter placed in a hot 4% EDTA tetrasodium salt solution for 4 hr. This treatment was effective in dissolving barite without having any influence on the mineralogy of silica, but this caused an undesirable contamination with sodium. Consequently, chemical analysis was made on another portion of barite-containing

---

[1] T. Tarutani, *Onsen Kagaku (J. Balneol. Soc. Japan)*, **14**, 93 (1964).

[2] G. B. Alexander, *J. Am. Chem. Soc.*, **76**, 2094 (1954); G. Okamoto, T. Okura and K. Goto, *Geochim. Cosmochim. Acta*, **12**, 123 (1957); I. Iwasaki, T. Tarutani, T. Katsura and H. Arino, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 857 (1954).

[3] C. A. Anderson, *Am. Mineralogist*, **20**, 240 (1935).

[4] K. Noguchi, S. Ueno, M. Ichikuni and Y. Takahashi, "Geochemistry of the Tamagawa Hot Springs," Tokyo (1963), p. 94.

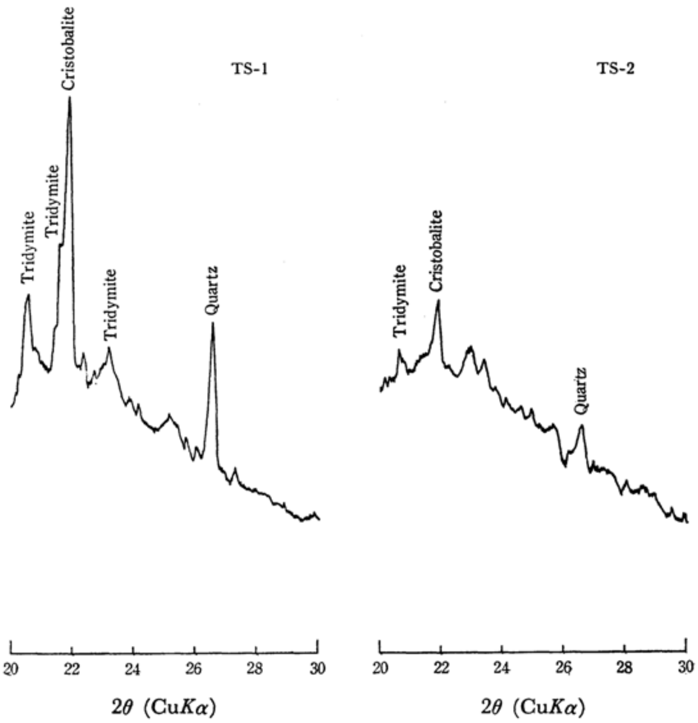

Fig. 1. X-ray diffraction patterns of samples TS-1 and TS-2.

samples. The results of chemical analysis are given in Table 2.

Results and Discussion

The X-ray diffraction patterns presented in Fig. 1 show a marked mineralogical difference between samples TS-1 and TS-2. Both samples were formed from the same spring water, differing only in temperature. The former, deposited at 90°C, contains some quartz, cristobalite, and tridymite, all in low forms, while the latter, formed at 80°C, is almost amorphous.

Noguchi *et al.*[4] reported a value of 260 ppm for the SiO_2 content of the spring water. In the light of recent solubility data,[5] this is too low to give birth to siliceous deposits while the water is still hot, and so it should be revised. The error in SiO_2 determination probably arose from neglecting the presence of a significant amount of fluoride in the water. Considering that no precipitation of silica is observed from the spring waters at temperatures above 90°C, a value of 400 ppm is recommended.

This assumed, the spring water may be slightly supersaturated with silica at 90°C. Thus, the sample TS-1 grew more slowly than the other one, TS-2, deposited at 80°C, where the degree of supersaturation is much enhanced.

Plumbian barite, depositing simultaneously with silica, provides a measure for estimating the rate of the growth of siliceous precipitates. A low ratio of silica to plumbian barite evidently reflects a slow rate of silica growth. It must be noted here that the weight per cent of precipitated silica in the samples is expressed as the sum of SiO_2 and H_2O contents. The ratio calculated from the data given in Table 1 are 12.76 for TS-1 and 59.54 for TS-2. Precipitated silica grew several ten times faster than plumbian barite. The average rate of growth of barite was estimated by Takano[6] at 0.05 mm/yr. Using this and the data on the densities of the two phases (2.2 g/cm^3 for precipitated silica and 4.5 g/cm^3 for plumbian barite), approximate rates of silica growth was calculated: 1.3 mm/yr for TS-1 and 6.0 mm/yr for TS-2.

In conclusion, the slow growth and high temperature favor the direct formation of crystalline silica, other factors being equal. However, strictly speaking, it is not clear whether the crystals are directly deposited from the solution or whether they are indirectly formed, for instance, through the conversion of amorphous silica. The conversion of this type generally requires considerable activation energy, which seems to be unavailable in the hot spring environment. In fact, gelatinous silica formed in the hot spring water remains amorphous even after standing for a long period of

---

[5] G. W. Morey, R. O. Fournier and J. J. Rowe, *J. Geophys. Res.*, **69**, 1995 (1964).

[6] B. Takano, private communication.

time.[7] The crystalline silica found in the sample TS-1 may, therefore, represent a direct product from the solution.

Some argument may arise as to the contamination of the siliceous precipitates with detrital crystalline siliceous matter originating from silicified rocks found nearby. However, the silicified rocks in this district are composed mainly of disordered low cristobalite (quartz, as well as tridymite, is a minor constituent, and is sometimes completely lacking), whereas the sample TS-1 contains quartz, cristobalite and tridymite, each in a comparable amount. This can be hardly expected unless quartz and tridymite grains are selectively adsorbed on the precipitates. Moreover, if the diffraction lines obtained on TS-1 are due to detrital components, why does the sample TS-2 not show the same lines? The sample TS-2 was found in the same sluice within 100 m from the point where the sample TS-1 occurred.

Thus, the crystalline phases detected in TS-1 may be concluded to be formed from dissolved silica in spring water. However, it must be stressed that the direct formation of quartz from an aqueous solution is said to be extremely rare in such cases, and that additional study will be necessary in order to confirm this important observation definitively.

We have no reliable information on the mechanism of the direct formation of crystalline silica from a solution. It is well known that, even in its stability range, tridymite cannot be formed from amorphous or other crystalline silica without the addition of a mineralizer, such as sodium tungstate, sodium carbonate, or water. This fact supports the view that some chemical components in spring water play an important role in the process of crystalline silica formation. Much experimental work remains to be done in order to explain fully this phenomenon.

It is worth noting that one of the chemical characteristics of silica precipitated from hot spring water is a low titanium oxide content, compared with that of residual silica, for example, the fumarolic alteration product of silicate rocks. Thus, the titanium oxide content may be useful in distinguishing between these two types of silica. This problem will be considered in a future paper.

After the present paper was submitted to this Bulletin, Harder and Flehmig[8] reported the synthesis of quartz from diluted solutions at a temperature of 20°C. It has been generally admitted that, at low temperatures, the formation of quartz from aqueous solutions is extremely rare, if not impossible, in a short time. This, however, has been shown to be a myth; our observations are amply supported by their experimental results.

The authors wish to express their appreciation to Professor Kimio Noguchi, Tokyo Metropolitan University, for his helpful criticism, and to Professor Shinichi Iwai and Dr. Joyo Ossaka, Tokyo Institute of Technology, for their many valuable suggestions. The financial support of the Matsunaga Science Foundation is also gratefully acknowledged.

---

[7] D. E. White, W. W. Brannock and K. J. Murata, *Geochim. Cosmochim. Acta,* **10**, 27 (1956).

[8] H. Harder and W. Flehmig, *Naturwissenschaften,* **54**, 140 (1967).