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THERMAL BEHAVIOR OF SiO_2-X AND ITS RELATION TO THE NATURAL SILICA MINERALS

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ABSTRACT

SiO_2-X, a silica polymorph known only since 1964, exhibits both ordered and disordered modifications. Two of the principal lattice spacings, 3.38 and 1.84 Å, are close to those of quartz, but its refractive index of 1.484 and its behavior on heating favor affinities with cristobalite. Its lattice spacing at 17.3–18.0 Å is unique among silica polymorphs. Possibilities for natural occurrences exist in near-surface deposits.

INTRODUCTION

The present study[1] of the system SiO_2-H_2O-$CaCO_3$ in the range 20–150°C, has the broad purpose of duplicating and understanding as far as possible the formation of chert in limestones. Acknowledgment is due to the Geology Department of Rice University for the use of a diffractometer with heating stage.

The phase SiO_2-X was first synthesized by Heydemann (1964) at 180°C, under conditions similar to those of the present study, and defined on the basis of its X-ray diffractogram (Table I) which does not correspond to any of the phases of silica listed by Sosman (1965) or by Eitel (1965). Following the recommendation of Sosman (1954) for synthetic polymorphs of silica, the designation "SiO_2-X" was chosen by Heydemann, and it should be retained until a natural occurrence is found. The present work confirms the results obtained by Heydemann, offers additional data and conclusions, and raises some questions. Other studies of silica in water have been conducted at temperatures above 240°C (Campbell & Fyfe, 1960; Fyfe and MacKay, 1962; Ernst & Blatt, 1964; Heald and Renton, 1966) and have yielded only quartz or disordered low cristobalite, as defined by Flörke (1955) and Eitel (1957). The above-mentioned workers found that at temperatures around 300°C, and under autogenous pressure, cristobalite is typically the first phase to crystallize, but at high values of temperature, pressure and pH, cristobalite is evanescent or non-existent, and only quartz is found.

METHODS

We initially determined that solutions of NaCl, $MgCl_2$ and NH_4OH did not produce any crystalline phases from silicic acid in runs up to 45 days at 150°C. We then tried a 2 percent KOH solution and were able to crystallize SiO_2-X from silicic acid and from modern sponge spicules (Table 2), although we obtained only cristobalite from Miocene diatomite and

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TABLE 1. X-RAY DIFFRACTION PATTERN OF SiO_2-X

d(Å)	Relative Intensity	*d*(Å) from Heydemann (1964)
18.0[1]	15	18.02
8.9	very weak ?	8.93
7.2	7	7.32
6.2	8	6.30
5.1	very weak ?	5.11
4.41	very weak ?	4.37
not detected		3.64
3.38	100	3.42
1.84	12	1.85

[1] Heating to 300° changes this to 17.3 Å.

TABLE 2. PHASES OF SILICA APPEARING ON X-RAY DIFFRACTOGRAMS

Reaction Time (days)	Specimen	SiO_2-X	Cristobalite	Quartz	Remarks
7	49	—	—	—	
7	51	—	—	—	Contained calcite
23	201	x	—	—	
30	SPS-1-9	*X*[1]	c	—	(Sponge spicules)
40	48	*X*	—	—	
40	50	x	c	—	Contained calcite
40	52	x	c	—	Contained calcite
41	203	*X*	c	—	Disordered SiO_2-X
41	205	*X*	c	—	
41	206	x	C	—	Disordered SiO_2-X
41	207	X	c	—	
41	208	x	C	—	Disordered SiO_2-X
41	210	x	c		
45	SPS-1-11	*X*	C	—	(Sponge spicules), disordered SiO_2-X
48	209	x	C	—	Disordered SiO_2-X
92	69	x	C	q	
92	70B	—	C	q	Contained calcite
92	71	x	C	q	Contained calcite
153	69A	x?	C	Q	7.2 Å peak of SiO_2-X survives
153	70A	—	C	q	Contained calcite

[1] Upper case letters indicate relatively larger amounts of the phase.

from wood-opal. The silicic acid used was Baker "reagent grade", analyzed as 76.3 percent SiO_2 and 23.7 percent volatiles (presumed H_2O), with particle size mainly below 50 microns although some are as large as 100 microns. Its refractive index is 1.420±0.004. About 2 percent of the grains appear brown in transmitted light, and these have a somewhat lower refractive index. The silicic acid is optically isotropic, and its diffractogram shows only a gentle swell in the 3 to 5 Å region, typical of amorphous silica. A series of 18 pyrex tubes, 9 mm outside diameter, 2.5 mm inside diameter and 20 cm long, were partially filled with silicic acid and a 2 percent aqueous solution of KOH. Powdered calcite was added to 6 of the tubes in order to evaluate its possible effect on crystallization of silica. Two additional tubes (SPS-1-9 and SPS-1-11) were prepared using spicules from a modern siliceous sponge (refractive index near 1.452) instead of silicic acid. Loaded tubes were frozen in liquid nitrogen to permit flame-sealing without loss of water. After heating for periods ranging from 7 to 153 days at 150±5°C, tubes were opened and the products examined with the petrographic microscope and the Norelco X-ray diffractometer, using CuKα radiation, with results which are summarized in Table 2. Because the ionization product of water at 150°C is $10^{-11.6}$ (Smith, 1963, p. 334), the solution is considered to have pH of 11.1 under the conditions of our experiments, although at room temperature it would be 13.5. In order to test the thermal stability of SiO_2-X above 150°C, X-ray diffraction studies at high temperature were made on the products of #205, #208, SPS-1-9, and SPS-1-11, using an R. L. Stone Co. heating stage and temperature control panel in conjunction with the Norelco diffractometer. Portions of the products of #205 and #208 were also heated for several days at 580° and 850°C and re-examined.

RESULTS

X-ray diffraction. SiO_2-X first appeared in #201 which reacted for 23 days, with a single prominent peak near 3.41 Å. Runs of 30 to 40 days duration developed the strongest and sharpest diffractograms of SiO_2-X, with the main peak at 3.38 Å and lesser peaks as shown in Table 1. In experiments of more than 30 days duration, disordered low-cristobalite also appeared, characterized by a rather broad peak centered on 4.07 Å with a shoulder near 4.31 Å. In still longer runs, SiO_2-X decreased in amount while low-cristobalite increased, and finally quartz peaks appeared without perceptible diminution in cristobalite. In the longest runs (153 days) only cristobalite and quartz remained, with a possible trace of SiO_2-X in #69A. The time of appearance and relative amount of each phase varied for unknown reasons, even between apparently duplicate runs. For this reason, and because of differences in amount of sample X-rayed, no quantitative estimates have been attempted in Table 2. However, the sequence of appearance—SiO_2-X, cristobalite, quartz—is invariable, suggesting that we are dealing with monotropic transformations tending towards the stable phase, quartz. Presence of calcite had no consistent detectable effect on the crystallization. The minor peaks of our SiO_2-X (Table 1) correspond closely with those of Heydemann, but they are weak, and not all are distinct on all diffractograms. The 18 Å peak is the most persistent; heating to 300°C consistently moves this peak to 17.3 Å. In five runs (203, 206, 208, 209, SPS-1-11) minor peaks are insignificant or absent, and in these diffractograms a nearly flat-topped main peak extends from 3.42 to 3.35 Å. We may call such material "disordered SiO_2-X."

Optical Properties. Under the microscope, SiO_2-X appears as rather uniform spherical aggregates of radial fibers up to 12 microns in diameter with very low birefringence and length-slow orientation. Some of these aggregates are free, while others have grown in clusters with mutual interference of their rims. No optical difference was noted between normal and "disordered" SiO_2-X. The mean refractive index of 1.484 ± .004 is somewhat higher than Heydemann's value of 1.47–1.48. It is difficult to determine accurately because of intimate mixture with optically isotropic material, which exhibits a range of refractive indices because of a variable content of cryptocrystalline cristobalite.

Thermal Studies. The object of thermal studies was to establish the behavior of SiO_2-X above 150°C, particularly to investigate the possibility that it might be a hydrate, and to look for possible potassium silicate phases. The products of runs 205 and 208 were heated for 6 days at 580°C and examined after cooling. The only significant changes were a sharpening of the principal peak of SiO_2-X at 3.38 Å, the shift of a minor peak from 18 Å to 17.3 Å, and a sharpening of the 4.07 Å peak of cristobalite. Other portions of #205 and #208, heated at 850° for 2 days and examined after cooling, had lost all their SiO_2-X and showed only low-cristobalite with some peaks of low-tridymite equivalent to "tridymite M" of Hill and Roy (1958). Raw silicic acid, subjected to identical heat treatment, developed no peaks at 580°C, and only peaks of disordered cristobalite at 850°C, in general agreement with the findings of Wahl *et al.*, (1961) and Verduch (1958).

Material from runs 205, 208, SPS-1-9 and SPS-1-11 was X-rayed during progressive heating on the Stone diffractometer heating stage, using two types of heating cycle.

1. Samples were heated to 920°C at a rate of 5–10°C per minute with hour-long interruptions for scanning the 3°–50° 2-theta region at 300°C and again at 550°C. At 300°C SiO_2-X showed only a very slight sharpening of the pattern, and a shift of the 18 Å peak to 17.3 Å. (In the case of "disordered" SiO_2-X, minor peaks did not materialize at any temperature, but the 3.42–3.35 Å flat-topped peak progressively narrowed to 3.38 Å, indicating improved structural order, and at the same time increased in height). At 550°C, SiO_2-X peaks were present but diminished, yet no increase in cristobalite was evident. On further heating through

700°C SiO_2-X was destroyed and high-cristobalite became well developed, increasing in quantity and quality up to the end of the run at 920°C.

2. Samples were heated steadily at 10–15°C per minute. SiO_2-X peaks remained strong up to 750°C, then fell off with increasing rapidity as high-cristobalite developed, the change being virtually complete by the time 850°C had been reached.

It is apparent that these reconstructive inversions do not take place at fixed temperatures. We are dealing with a monotropic change from one metastable phase to another metastable phase (at least below 873°C crostobalite is metastable), and the effect of increasing temperature is simply to increase the rate of inversion. Our results may be compared with those of Wahl *et al.*, (1961) who followed the inversion of various kinds of silica into cristobalite by similar heating techniques. They found that the rate of cristobalite formation became appreciable and increased rapidly in the general vicinity of 1000°C, but that those kinds of silica with less structural order (silica gel, etc.) began to transform at lower temperatures than did the more ordered kinds (chert and rock crystal).

Conclusions

In these experiments, crystalline phases formed much more slowly than in the experiments of Heydemann, who obtained SiO_2-X and cristobalite in 1 to 2 days at 180°C. Reasons for the difference in rate of formation are unknown, although the temperature difference of 30°C is undoubtedly a factor. The diffractograms of our products correspond closely with the data of Heydemann (Table 1), except that in our material the most prominent spacing (3.38 Å) is slightly narrower, suggesting a closer structural packing which would correlate with our slightly higher refractive index. Persistence of SiO_2-X diffraction peaks in samples heated for 6 days at 580°C shows that if there is any water involved it is quite firmly bonded. Differential thermal analysis is not helpful here in locating possible combined water, because the SiO_2-X cannot be physically separated from associated relics of hydrous silicic acid. The refractive index, which is close to that of cristobalite, remains our chief basis for asserting that SiO_2-X is not a hydrate. For reasons not yet understood, several of our runs yielded a disordered variety of SiO_2-X, with minor peaks obscure or absent. The two runs based on modern sponge spicules (SPS-1-9, SPS-1-11) behaved similarly to those based on silicic acid. The fact that our earlier work with Miocene diatomite had yielded only cristobalite suggests that simple aging produces a protostructure in silica which inhibits the formation of SiO_2-X. This clue is being pursued further.

Eitel (1957) has demonstrated the existence of sheets of silica tetrahedra in the silica minerals, and the main peak of SiO_2-X at 3.38 Å almost certainly corresponds to a spacing between these sheets. It is a little wider than the 101 of quartz but narrower than the 101 of low-cristobalite or the 001 of low-tridymite. The closeness of the 3.38 Å and 1.84 Å SiO_2-X peaks to major peaks of quartz is suggestive; on the other hand the low refractive index and the ready transformation to cristobalite suggest that the structure of SiO_2-X is related to that of cristobalite. The most unusual feature of SiO_2-X among silica polymorphs is the one abnormally wide spacing at 18.0 Å (17.3 Å after heating), for which we have no explanation, although we may note a near-correspondence to the 17.2 Å "b" axis of low-tridymite (Frondel, 1962, p. 264). Another minor peak, at 7.2 Å, is of particular interest because we have produced it in parallel experiments with wood-opal (disordered cristobalite), although no other peaks of SiO_2-X appeared in these experiments This 7.2 Å peak also persists in Sample 69A (Table 2) although cristobalite has virtually superseded SiO_2-X in this run, and the 3.38 Å main peak has practically disappeared. Two of the most important SiO_2-X peaks, those at 3.38 Å and 1.84 Å, correspond closely to two peaks which Endell (1948) found in his "Zwischenzustände" material, obtained by heating Kieselguhr (diatomite) to 1035°C and then cooling it. In material heated by Endell to 1100°C these spacings were not seen, and the pattern of low-cristobalite appeared instead. Unfortunately, powder diffractograms do not permit us to construct any crystallographic relations between these various minor peaks.

Granted that low-quartz is the stable phase of silica at 150°C, the preferred growth of SiO_2-X and low-cristobalite shows that they nucleate more readily than quartz. Appearance of metastable phases is understandable in terms of Ostwald's step rule, on the basis that the phase which represents the smaller decrease in entropy will be favored in nucleation (Lacmann, 1961). Further attempts to go directly from SiO_2-X to quartz in laboratory experiments would be instructive. We are now growing SiO_2-X from sponge spicules and other biogenous silicas in order to bring out possible differences in organization between "amorphous" silicas. Despite the unnaturally high pH required for catalysis in our laboratory experiments it seems possible that SiO_2-X could occur under certain conditions in nature, and mineralogists should be alert for it in young siliceous sediments and in weathered or hydrothermally altered tuffs. Perhaps the microspherules of tridymite[1] observed by Weir and Catt (1965, p. 102) in the English Chalk were originally SiO_2-X.

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[1] A sample of this material kindly furnished by A. Weir yielded an X-ray diffraction pattern identical with that of disordered low-cristobalite as cited by Flörke (1955).

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