THE CRYSTALLIZATION OF AMORPHOUS SILICA USING SALT CATALYSTS

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ABS TRACT

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by Paul D. Baranyai

It is known that the three common polymorphs of silica; quartz, tridymite, and cristobalite, crystallize within a large range of temperatures at atmospheric pressure. Each polymorph is stable within a certain range of temperatures. Tridymite and cristobalite are characteristic of high temperature environments.

An investigation of the various polymorphs was conducted using amorphous silica gel and various salts as catalysts to determine whether the two high temperature forms could be made to crystallize at temperatures below their respective thermal stability range. All work was carried out under one atmosphere of pressure at temperatures ranging \cdot from 600°C. to 900°C. Various concentrations of each salt were used. Each sample was heated for two hours.

There has been much work conducted at elevated temperatures and pressures for long durations of time. However, there has been little research conducted at the temperatures used in this study. Nor has there been much work dealing with the action of various salts toward the crystallization of amorphous silica gel.

The amorphous silica gel was prepared fresh from sodium silicate and hydrochloric acid. The gel was washed thoroughly with de-ionized water and was dehydrated at a low temperature. The powdered gel and salts were heated in covered platinum crucibles, and then x-ray powder photographs were taken of each sample. Each polymorph present was identified by the x-ray photographs. A spectrographic analysis was also made to determine whether any of the salts had entered into the atomic structure of the silica.

The results showed that at atmospheric pressure and at temperatures ranging from 600°C. to 900°C. the various polymorphs of silica can be crystallized by using various salts as catalysts. The polymorph which was formed predominately in all the sample sets was cristobalite - the highest-temperature polymorph. It was also found that sodium had entered into the structure of cristobalite. The open structure of cristobalite had been presumably stabilized by the sodium atoms.

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Paul D. Baranyai

A THESIS

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PURPOSE OF STUDY

This study was undertaken to investigate the crystallization of the polymorphs of silica from the amorphous state by the use of various salts. Varying concentrations of the following salts were mixed with the amorphous silica gel and heated at temperatures ranging from 600°C. to 900°C.: sodium chloride, calcium chloride, lithium chloride and potassium bromide. All of the heating was performed under one atmosphere of pressure. These four salts were chosen because they are common impurities which are found in the polymorphs of silica.

Although this study may not have direct geologic, implications, it is important to note that while the temperatures used in this study were below the stability range for tridymite and cristobalite, these were the resultant crystallization products.

Studies of the crystallization of silica gel using various catalysts are few at the temperatures used in this research.

INTRODUCTION

Silica, SiO₂, exists in a number of polymorphs which are stable at different temperatures and pressures. Among these polymorphs are quartz, which is stable at ordinary conditions, tridymite and the high temperature polymorph, cristobalite. Along with the above forms, three less common forms exist, which are metastable at ordinary conditions. These are keatite, coesite and stishovite.

The following table lists each polymorph and the thermal stability range at one atmosphere of pressure.

Table I

(Frondel, 1962, Page 1)

Name	<u>Thermal Stability Range-</u> one atmosphere in ^O C
α Quartz	Stable below 573
👂 Quartz	Stable 573-870
Tridymite	Stable 870-1470
४ tridymite	Below 117
<pre> tridymite </pre>	117-163
🗙 tridymite	16 3-1 570
Cristobalite	Stable 1470-1720
\varkappa cristobalite	Below 200
🖌 cristobalite	200-1720
Keatite	Metastable at ordinary conditions
Coesite	Metastable at ordinary conditions
Stishovite	Metastable at ordinary conditions

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Historically, quartz as a name was used first in the Middle Ages (Frondel, 1962) in Saxony for massive vein quartz. However, it was not until the 1850's that an adequate method of study was available.

Tridymite, the first polymorph of silica to be recognized in addition to quartz was described by von Roth in 1868, and he described cristobalite in 1884. Since the first acknowledgment of these polymorphs of silica, other individual polymorphs closely related in crystal structure have been identified. Merion in 1884 was the first to observe the high and low forms of tridymite. In 1890, Mallard described the high and low forms of cristobalite. Fenner, who in the early 1900's investigated the stability relations of these polymorphs, was the first to define the existence of middle tridymite. It was not until much later that additional polymorphs of silica were synthesized in the laboratory. The first of these was Coesite, synthesized in 1953 by L. Coes. Coesite was obtained originally in the temperature range between 500-800°C and at 35,000 atmospheres for periods of about fifteen hours. P. P. Keat synthesized Keatite in 1954. Keatite was obtained over a range of temperatures from 380-585°C and 5,000-18,000 p.s.i. Then in 1961 Stishov and Popova synthesized Stishovite. Stishovite was first synthesized at temperatures between 1200-1400°C and a pressure reported to be about 160 kilobars. Since the initial syntheses of these polymorphs, two have been identified in nature. Coesite was found in nature at Meteor Crater, Arizona. It occurs abundantly in sheared and compressed areas of sandstone as a fine grained nearly istropic matrix in which the fractured quartz are embedded. Stishovite has also been found in association with coesite

and silica glass at Meteor Crater, Arizona, and in other areas.

The phase relationship between the three common polymorphs is given in Figure 1.





(Frondel, 1962, page 5)

 \propto quartz is stable under atmospheric pressure at temperatures up to about 573°C. At this temperature it undergoes a reversible rapid inversion (displacive) to β quartz.

Closely related in structure to \propto quartz, β quartz is stable at atmospheric pressure at temperatures from 573°C up to 870°C. Over 870°C and up to 1470°C the stable polymorph at atmospheric pressure is tridymite. The type of inversion between β quartz and tridymite at 870°C is of the sluggish (reconstructive) type. β cristobalite is the stable polymorph of silica at atmospheric pressure at temperatures from 1470°C to its melting point 1723°C.

The differences in free energy between the three polymorphs is small and the stability relations apparently can be altered by the entrance of H_2^0 or of cations into interstital positions. The metastable formation of the relatively open, highly symmetric structure of cristobalite apparently is favored in this way over tridymite and quartz.

STRUCTURE OF THE POLYMORPHS

(Frondel, 1962)

Table II

Quartz-Hexagonal (lattice dimension) $A_0=4.90290 \pm 0.0003 kx$ $C_0=5.39365 \pm 0.0003 kx$ Temperature $18^{\circ}C$ $A^{\circ}=kx$ (1.00202)

 α tridymite-Hexagonal

$$A_{o} = 5.04 A^{o}$$

 $C_{o} = 8.24 A^{o}$

β cristobalite-Isometric

A_o=7.1285A^o

Temperature 250°C

REVIEW OF EARLY LITERATURE

Much work has been conducted on the presence of silica in fresh water, sea water and also silica in hot-spring waters. K. B. Krauskopf (1956) reviews the early literature on low temperature dissolution and precipitation of silica, and comes to some conclusions on the solubility and precipitation of silica in different geologic environments.

- The solubility of amorphous silica is little affected by changes of pH in the range of 0-9, but increases rapidly as the pH rises above 9. In other words, silica is no more soluble in very dilute alkali than in acid, contrary to a common geologic assumption.
- 2) Silica is added to natural waters by, a. volcanoes and springs associated with volcanic activity and by b. dissolution of silica and silicates during weathering. Probably most of the silica from weathering is in true solution. Volcanic and hot springs silica may be initially in true solution, but if the concentration is high, it will partly change to the collodial form as the solutions cool.

However, his work makes no mention of the polymorphs of silica. Whether or not these were formed during dissolution of the silica is not known. White, Brannock and Murata (1956) noted the presence of cristobalite (opal) precipitated in hot-spring waters at Steamboat Spring, Nevada. They make this statement.

> The relations of amorphous opal, of opal with an x-ray pattern of cristobalite and of true cristobalite are not known. (White, 1956)

Tridymite was found by Anderson forming in lavas that were being altered by sulphuric acid at temperatures close to 90°C.

White made this closing observation:

The origin of cristobalite and tridymite in hot-springs is not clear. The minerals have formed metastably at temperatures far below equilibrium temperatures and in contact with waters that were strongly supersaturated in silica with respect to the stable mineral quartz. (White, 1956)

Carr and Fyfe attempted crystallization of amorphous silica at pressures ranging from 15,000 p.s.i. to 59,000 p.s.i. The temperatures varied from 325°C to 448°C. The time varied from six hours at 59,000 p.s.i. to 840 hours at 15,000 p.s.i. Table III gives a partial list of their results.

t (hours)	Products
9	Quartz
9	Poor Cristobalite
9	Poor Cristobalite
12	Keatite+Quartz
15	Keatite+Quartz
96	Quartz
120	Quartz
576	Cristobalite
	t (hours) 9 9 9 12 15 96 120 576

Table III

It should be noted that tridymite was not formed in any of their experiments in sufficient quantity to appear on x-ray photographs.

J. F. Corwin (1953) and others conducted a study of the effects of flouride and alkali on the transformation of amorphous silica to cristobalite or quartz. When silica glass was heated with water or aqueous solution at 400°C and 340 atmospheres, quartz was formed when flouride or strong alkali was present. However, in acidic or neutral solutions, even when sodium or potassium chlorides were present, only cristobalite was formed. It was the authors belief that quartz was formed only from the ions of orthosilicic acid. Such ions are present in solution above pH 10-12. The less ionic forms, or molecular orthosilicic acid, lead to the formation of alpha cristobalite.

A. G. Verduch carried out experiments at temperatures ranging from 945-1085^oC. Figure 2 shows isothermal rate curves of the transformation of amorphous silica to cristobalite.

Figure 2



W. G. Hill and Rustum Roy performed experiments in an attempt to determine the q- β inversion in cristobalite. It was found that the inversion was variable and depended on the structure of the starting material and on the temperature and length of heat-treatment. The temperatures involved were in the 1500°C to 1600°C range. The duration of these experiments ranged from $\frac{1}{2}$ hour to 76 hours. Only the silica gel was heated.

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There were no fluxing agents used. The resulting x-ray patterns showed, in the case of the heated silica gel, only cristobalite.

Although there has been much work carried on with silica gel, to the author's knowledge little work has been done at the temperatures used in this work. Nor, has there been much work dealing with the action of various salts toward the crystallization of silica gel.

EXPERIMENTAL PROCEDURE

Many commercial brands of silica gel are available; for example, "Celite"-John-Mansville Company, "Hi-Sil"-Pittsburg Plate Glass, Estersil-Product Information Bulletin, E. I. duPont de Nemours and Company, Fine Silica Gels-Davison Chemical Corporation Product Bulletin (Iler, R. K.). However, the silica gel used in this work was prepared by the author. By doing this, a truly amorphous gel was obtained, as was shown by the absence of lines in an x-ray powder photograph taken of the gel. The commercial brands may or may not be truly amorphous as shown by Table IV.

Table IV

"Celite" - 89.7% SiO₂, 3.7% Al₂O₂ Ignition loss 3.7% "Hi-Sil" - 86.5% SiO₂, 3.0% CaO Ignition loss 14.0% Estersil - 85-90% SiO₂

Fine silica gels - 99% minimum SiO₂

The gel was prepared by mixing a solution of Na_2SiO_3 and hydrochloric acid. The sodium silicate solution was prepared from the crystal form obtained from the General Chemical Division of the Allied Chemical and Dye Corporation. The maximum limits of contained impurities were as follows: Chloride (Cl)-0.005%, sulfate (So_4) -0.01%, heavy metals (as Pb)-0.001% and iron (Fe)-0.005%. The solution was prepared to give a density of 1.15 grams/cc. The concentrated hydrochloric acid was prepared to obtain a 6N solution. According to Babor and Lehrman, (1957), the acid should be added to the sodium silicate, solution. However, when 100ml of acid was poured into 100ml of sodium silicate, accompanied by continuous stirring, a firm gel did not develop.

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After 24 hours, the gel was still not firm, so 10ml of sodium silicate was poured into 10ml of 6N HCL. As the Na_2SiO_3 was poured into the acid, the mixture was continuously stirred. In about 5 minutes the solution had set to a firm gel, according to this idealized reaction, $\text{Na}_2\text{SiO}_3 + 2\text{HCl} --- \text{H}_2\text{SiO}_3 + 2\text{NaCL}$. It was decided to make small batches of gel (50 ml - total) rather than one large batch. The reason for this was ease of preparation and more thorough washing. One liter of Na_2SiO_3 was prepared and filtered free of any precipitated silica before each batch was prepared.

When the gel set, they were cut in half and washed with de-ionized water. Distilled water was used by Zielke (1950), but as a spectographic analysis was to be made, the de-ionized water would afford the greater purity. The gels were washed until they were free of the Clas was shown by the absence of a precipitate with silver nitrate. They were then placed in changes of de-ionized water for three days. The water was frequently changed during this time. It was shown in Smits thesis (1926) that sodium chloride in solution acts to increase the solubility of gelatinous silica. Periodic checks were made with the silver nitrate and were, in all cases, negative, which was shown by the lack of a percipitate. At the end of this period, the gels were allowed to dry at room temperature for 24 hours. Finally, the gels were dehydrated in the electric furnace for four hours at 360°C. A sample of this powder was prepared, in a manner to be discussed later, for x-ray diffraction analysis. This sample was shown to be amorphous by an absence of lines and the presence of a diffuse halo.

Silica gel was then prepared for heating with the four salts, sodium chloride, calcium chloride, lithium chloride and potassium bromide.

Extreme care was taken in assuring as complete a mixture as possible between the silica and the salts. Each sample of gel and salt were ground together for one half hour. In all, eight sets were made - four sets at a 2% concentration of each salt, and four sets at a 5% concentration of each salt.

Because the furnace used could not be controlled more accurately than $\pm 10^{\circ}$ C., the temperature interval used throughout the heating was 60° C. The initial temperature was 600° C and rose in five increments of 60° C each to 900° C., the maximum temperature reached in all cases. The mixtures of silica and salt were heated in covered platinum crucibles. Platinum was used because of its inactivity toward the salts and its high melting point, 1769.3° C.

Zielke (1950) stated that upon washing his heated samples, very little, if any, salt remained. He concluded that much of the salt must have escaped during the heating period. Because of this, he heated his sample of $CaCl_2 + SiO_2$ in a closed copper tube. It should be pointed out that the author found that it was necessary to wash his heated samples three and four times before the salt was completely washed away. Because of this, it was decided that no special heating receptacle was necessary and that the covered platinum crucibles would be sufficient for this work.

A ninth set was made containing a 2% concentration of each of the four salts and these were heated at 100° C intervals.

Each sample within the nine sets were heated for two hour durations. At the end of heating each set, the samples were washed with deionized water until free from the salt.

Each sample was weighed before heating and after heating. The loss of weight, as shown in Table V can be attributed to loss of H_20 and a small loss of the salt.

	<u>Sample</u>	Temp	erature oc	<u>Weight</u> <u>before</u> heating (gms)	<u>Weight</u> <u>after</u> heating (gms)	<u>%</u> Loss
1)	2%KBr	a.	600	0.3437	0.3408	8.5
		Ъ.	660	0.3383	0.3346	11.0
		с.	770	0.3384	0.3347	11.0
		d.	780	0.3377	0.3334	12.6
		e.	840	0.3385	0.3336	13.1
		f.	900	0.4650	0.3601	13.3
2)	2%LiC1	a.	600	0.3392	0.3110	8.4
•		Ъ.	660	0.3412	0.3040	10.9
		с.	720	0.3396	0.3026	10.9
		d.	78 0	0.4462	0.2934	12.8
		e.	840	0.3317	0.2851	14.1
		f.	900	0.3899	0.3370	13.6
3)	2%NaC1	a.	600	0.3387	0.3109	8 .3
		Ъ.	660	0.3414	0.3185	6.7
		с.	720	0.3386	0.3116	8.0
		d.	780	0.3402	0.3023	11.1
		e.	840	0.3353	0.2944	12.2
		f.	900	0.3850	0.3352	12.4
4)	2%CaC1	a.	600	0.3395	0.3143	7.5
-		Ъ.	660	0.3374	0.3087	9.5
		с.	720	0.3414	0.3061	10.3
		d.	780	0.3437	0.3086	10.3
		e.	840	0.3383	0.3007	11.1
		f.	900	0.3786	0.3341	11.8

Table V

	<u>Sample</u>	Temp	erature ^o C	<u>Weight</u> <u>before</u> heating (gms)	<u>Weight</u> <u>after</u> heating (gms)	<u>%</u> Loss
5)	5%KBr	a.	600	0.3600	0.3476	3.5
		b.	660	0.3548	0.3310	6.8
		с.	720	0.3504	0.3056	12.8
		d.	780	0.3546	0.3030	14.6
		e.	840	0.3580	0.3080	14.0
		f.	900	0.3610	0.3100	14.2
6)	5%LiC1	a.	600	0.3496	0.3115	10.1
		Ъ.	660	0.3506	0.3114	11.2
		с.	720	0.3492	0.3030	13.3
		d.	780	0.3514	0.2966	15.6
		e.	840	0.3498	0.2954	15.4
		f.	900	0.3887	0.3275	15.7
7)	5%NaC1	a.	600	0.3647	0.3401	6.8
		Ъ.	660	0.3627	0.3357	8.5
		с.	720	0.4678	0.3320	9.8
		d.	780	0.3650	0.3114	14.7
		e.	840	0.3670	0.2976	19.1
		f.	900	0.4432	0.3762	14.9
8)	5%CaCl,	a.	600	0.3656	0.3524	8.7
	2	b.	660	0.3577	0.3544	9.1
		с.	720	0.3606	0.3574	8.9
		d.	780	0.3628	0.3583	12.3
		e.	840	0.3633	0.3585	13.1
		f.	900	0.5244	0.5182	11.9

Table V (con't.)

As each set was completed, samples were prepared for analysis using x-ray powder methods. The samples were ground to a uniform size--approximately 200 to 300 mesh.

There are essentially three methods of preparing a powder mount. (Azaroff, 1958)

- By fashioning the sample itself into a suitable shape,
- 2. By coating the outside of a thin fiber with the specimen powder,
- 3. By placing the powder inside a capillary holder.

Of the three methods, the first one was used in preparing the specimens for this work. It was the most suitable, because it introduced no material other than the sample in the path of the x-ray beam. The use of a clear nail polish was necessary to act as a suitable binder for the powder. A few milligrams of the powder were mixed with the polish until a homogenous paste was obtained. A uniformly shaped rod was formed by rolling the sample between two pieces of ground glass. The thickness of the rod was approximately 0.5 mm. and 10mm. in length.

A Debye-Scherrer type camera was used to make the x-ray photographs. The film was mounted according to the Straumanis-Ievins method. The diameter of the camera used was 114.6 mm. For this diameter, the conversion factor from millimeters distance on the film to angle of arc is 1° per mm. The film used was the NO-SCREEN MEDICAL x-ray SAFETY film. The width of the film is 1 3/8 inches. The development of film followed a set procedure: a period of 4 minutes in the developer, 30 seconds in the stop and 10 minutes in the fixer at 70° C. An exposure time of 5.2 hours was found to give the best picture.

The target element used was copper. Copper produces $K \propto$ radiation of 1.5418 ($K \propto = 1/3$ ($K \propto _2 + 2K \propto _1$)). The $K \propto _2$ has a wave length of 1.54050. The K β radiation is quite short, being only 1.39217. The filter element used was nickel.

As can be seen from Figure 3, K α' and K α' have wave 1 2 lengths which are quite close.



(Azaroff, 1958, p. 33)

Because of this it is customary to group these together and to assign to the combination a wave length which is the intensity-weighted mean of the two wave lengths. Namely $K \propto = 1/3$ $(K \propto 2 + 2K \propto 1)$. The nickel filter was used to absorb the $K \not\beta$ radiation.

X-RAY DIFFRACTION THEORY

In the crystalline state, the atoms are arranged in patterns which are characterized by periodic repetition in three directions. A consideration of repetition in two directions will enhance the understanding of 3 dimensional repetition. First, consider a single geometric point (A). This point can be translated in two directions, say t_1 and t_2 (Figure 4). Continued translation of this point (Figure 4) generates an infinite collection of points.

Figure 4

Ъ a

This collection of geometrical points produce what is called a lattice net. If the pattern is repeated in three directions, a space lattice is generated. In a crystal, where the pattern is a group of atoms not points, the repetition defined by the three conjugate translations is called a crystal structure. The periodic repetition of this pattern in three directions produces an identical atom at each point of the lattice. This simple pattern can be termed a lattice array of atoms. A single crystal can be regarded as several lattice arrays of atoms.

The lattice array of atoms can be regarded as an infinite stack of parallel, equally spaced planes. Figure 5 shows that the path length from the incoming wave front, to the plane, and to the scattered wave front is longer in the case of the lower plane.

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(Azaroff, 1958, p. 8)

The greater path difference, \bigtriangleup , is equal to ABC.

 $\triangle = ABC$ = 2AB (AB = BC...ABC = 2AB) AB = d_{hk1} Sin θ The total path difference is $\triangle = 2AB$

= $2d_{hk1}$ Sin θ

If both of these planes are to scatter in phase, the path difference, \triangle , must be an integral number of wave lengths. That is, $n\lambda$, where n is an integer. Therefore, the conditions for scattering-in-phase is

n**λ=** ∆

= $2d_{hk1}$ Sin θ

This condition for scattering-in-phase is known as Bragg's law. The positions of x-ray reflections on the film depend on the shape and type of the crystal unit cell and the relative intensities of these reflections depend on the arrangement of the atoms with the cell.

The principles involved in the production of a powder diagram can be shown in the simplified arrangement shown in Figure 6.





(Azaroff, 1958, p.13)

By using a cylindrical type of film arrangement, a much greater range of 2θ can be recorded. As shown in Figure 7, the distance S between similar arcs corresponds to 4θ .

Figure 7



(Azaroff, 1958, page 25)

 $S = R \cdot 4\theta$ or $\theta = S/4R$ $4\theta = S/R$ $\theta = (1/4R)S$ radians $\theta = (180/\tau\tau \cdot kR)S$; (R = 180/ $\tau\tau$ mm. in radians) $\theta = (180/\tau\tau \cdot kr)S = s/4$ degrees
Once the arc length S is determined, Sin θ can immediately be found, and from this, d, can be found by a simple calculation. When the d spacings have been calculated from several lines on the powder film, the lines are arranged according to their relative intensities. Once this is done, the INDEX TO THE POWDER DATA FILE (ASTM) can be used to identify the mineral. In the case of this paper, it was used as a means of identifying the various polymorphs of silica.

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<u>Table VI</u>

X-RAY DATA

		most inter	nse lines
QUARTZ			
X	3.34	4.26	1.82
ß	3.42	1.85	1.57
CRISTOBALII	E		
æ	4.04	2.49	2.85
ß	4.15	2.53	1.64
TRIDYMITE -	a (exper	IMENTAL D-S	SPACINGS)
	4.30	4.08	3.81
	4.30	3.81	4.08
	4.39	4.12	3.73
KEATITE			
	3.42	3.33	3.11
COES ITE			
	3.099	2.722	2.705
STISHOVITE			
	2.959	1.530	1.981
SILICON			
	3.14	1.92	1.64

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INTERPRETATION OF X-RAY POWDER PHOTOGRAPHS

a) <u>600</u>°C

The most intense line on the photograph is that of alpha tridymite. In all, two lines of alpha tridymite are present, 4.29 and 3.82. Along with this, alpha cristobalite is also present. The lines measured show the most intense line of cristobalite, 4.04, and the second most intense line of cristobalite, 2.45.

The amorphous silica is present also as is indicated by a wide diffuse halo.

Ъ) <u>660⁰</u>С

Two lines are evident at this temperature. These lines are found to be that of alpha cristobalite. Amorphous silica is also present.

c) 720⁰C

The three most intense lines of alpha cristobalite are present at this temperature. Along with this polymorph, there appears another line which coincides with a line for keatite (?). A wide diffuse halo is again present showing the presence of amorphous silica.

d) 780^oC

Only one line can be measured on this photograph. This line is the most intense line of alpha cristobalite. Again amorphous silica was detected. No other polymorph is present.

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 $\mathbf{u}_{\mathbf{i}} = \mathbf{u}_{\mathbf{i}} + \mathbf{u}_{\mathbf{i}} +$

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e) <u>840</u>°C

All three lines of alpha cristobalite are present along with the halo for amorphous silica.

f) <u>900</u>°C

Alpha tridymite is present with alpha cristobalite. Amorphous silica is also present. <u>Set 2</u> Si0₂ + 2%LiC1

a) 600⁰C

One line is present and is the strongest line of alpha cristobalite. A strong halo of amorphous silica is also present.

b) 660⁰С

Alpha quartz is present in this sample as all three lines are present. Amorphous silica is again present. No other polymorph is indicated.

c) 720[°]C

Alpha quartz is again present. There is no evidence of either cristobalite or tridymite. Amorphous silica is present.

d) <u>780</u>°C

In this film, the two strongest lines of alpha cristobalite are present. With the exception of amorphous silica, there is no other polymorph or silica present.

e) <u>840</u>°C

For the first time, Beta cristobalite is present. Two of the three most intense lines of beta cristobalite are present. Amorphous silica is also present.

f) 900^oC

The last sample of 900°C shows all three lines for alpha tridymite to be present. Amorphous silica is also evident.

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 $\underbrace{\text{Set } \underline{3}}_{2} \quad \underbrace{\text{Si0}}_{2} + 2\% \text{NaCl}$

a) <u>600</u>°C

This sample has no sign of any of the three polymorphs of silica. Only a strong diffuse halo is present, indicating an amorphous substance.

b) <u>660</u>°С

Two lines are present. These are the two most intense lines of alpha cristobalite. Amorphous silica is also present.

c) <u>720</u>°C

Four line determinations are made of this sample. It was found that the three most intense lines for alpha cristobalite are present. Also, the line for keatite is evident d= 3.13. (?) The diffuse halo for amorphous silica is present.

d) 780⁰C

Three lines were measured. Two lines belong to the alpha cristobalite polymorph of silica. The third line appears again to belong to the polymorph keatite d= 3.33 (?). Amorphous silica is again present. The 3.33 may also be that of alpha quartz.

e) <u>840</u>°C

Two lines of alpha cristobalite are present being the two most intense. Also, the most intense line of alpha tridymite is present. Amorphous silica is also present.

f) <u>900</u>°C

A total of four lines were measured. The d spacings for alpha tridymite are present in three lines. The d spacing

of alpha cristobalite is present in the fourth line. Amorphous silica is once again present.

$$\frac{\text{Set } 4}{\text{a}} \quad \begin{array}{l} \text{Si0} + 2\% \text{CaCl} \\ 2 \end{array} \\ \begin{array}{c} 2 \end{array} \\ 2 \end{array}$$

There is no crystallinity present in this sample. The amorphous silica halo is again present.

b) <u>660</u>°C

One line is present and it is determined that it is that of alpha cristobalite. Also, the amorphous silica is present.

c) <u>720</u>°C

Three lines of alpha cristobalite are present. The line for keatite is again present along with the halo of amorphous silica.

d) 780⁰C

Alpha cristobalite is present in the sample. The three most intense lines are present. Another line measured appears to belong to the most intense line of coesite (???). Here again, amorphous silica is present as the diffuse halo.

e) <u>840</u>°C

After measuring the three most intense lines on the powder photograph, it is determined that alpha cristobalite is present. Two other lines are measured and one appears to be the polymorph keatite (?). The halo is present indicating the presence of amorphous silica.

f) 900^oC

Three strong lines of alpha cristobalite were measured. Again keatite appears (?) to be present. Amorphous silica is still present in the sample.

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a) 600⁰C

Two lines were measured and the calculation of the dspacings show the alpha cristobalite polymorph to be present. Amorphous silica is also present.

b) 660^оС

Alpha cristobalite is also present in this sample. No other polymorphs are present. Amorphous silica is present.

c) 720°C

The three most intense lines of alpha cristobalite are present. Also, there appears again the line for the polymorph keatite (?). The presence of amorphous silica is again noted.

d) <u>780</u>°C

The only polymorph present in this sample is alpha cristobalite. Amorphous silica is again present.

e) <u>840</u>°C

Although the most intense line of alpha cristobalite is present, alpha tridymite seems to be more evident in this sample. The halo of amorphous silica is also present.

f) <u>900</u>°C

Again the most intense line of alpha cristobalite is present. Alpha tridymite is again more evident. Amorphous silica is again present.

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<u>Set 6</u> Si0₂ + 5%LiC1

a) 600⁰C

The three most intense lines of alpha quartz are determined from the d-spacings. No other polymorph of silica is present. The amorphous silica is again present.

b) 660⁰C

Alpha quartz is again the only polymorph of silica present. The diffuse halo for silica is present.

c) 720^oC

Amorphous silica is present. The only polymorph of silica is again alpha quartz.

d) 780^oC

Two polymorphs exist in this sample along with the amorphous silica. One is alpha quartz, while the other is alpha tridymite. No cristobalite is present.

e) <u>840</u>°C

The most intense lines of alpha cristobalite are present. One line of quartz is also present. Amorphous silica is again present.

f) 900⁰C

Alpha cristobalite is determined by calculating three lines. These are the three most intense lines on the powder photograph. Again amorphous silica is present. Along with the amorphous silica and alpha cristobalite, a line of keatite (?) is again found.

<u>Set</u> 7 Si0₂ + 5%NaCl

a) <u>600</u>°C

Only alpha cristobalite is found in this sample. The two most intense lines are present. Again amorphous silica is found to be present.

b) <u>660</u>°C

One line of keatite (?) is again found. Amorphous silica is present. The three most intense lines of alpha cristobalite are also present in this sample.

c) <u>720</u>°C

The diffuse halo of amorphous silica is again noted. Calculations of the three most intense lines on the film show alpha cristobalite to be present again. Also, the one line for keatite (?) is present.

d) <u>780</u>°C

Alpha cristobalite is present in this sample. Amorphous silica is shown again by the diffuse halo. The most intense line of alpha tridymite is also present. Again one line of the polymorph keatite is present.

e) 840°C

Two polymorphs of silica are present in this sample along with amorphous silica. Both alpha cristobalite and alpha tridymite are present.

f) <u>900</u>°C

Again the amorphous silica is present. Alpha tridymite is represented by its three most intense lines. Alpha cristobalite is present also in this sample. <u>Set 8</u> Si0, + 5%CaCl₂

a) 600°C

Only amorphous silica is present in this sample.

b) 660^oC

No polymorphs of silica are found in this sample. Only the amorphous silica exists.

c) <u>720^oC</u>

Amorphous silica is in this sample also. The three most intense lines of alpha cristobalite are found to be present. There also is a slight line which is interpreted to be that of alpha quartz.

d) 780^oC

Alpha cristobalite is again present. It is determined from its three most intense lines which are present. Again, there is the presence of amorphous silica. One line of keatite (?) is also present.

e) 840^oC

The polymorph keatite (?) again is represented by one line along with the diffuse halo for amorphous silica. Three intense lines for alpha cristobalite are found to be present.

f) 900⁰C

This sample also contains alpha cristobalite represented by its three most intense lines. Keatite (?) and amorphous silica are also present.

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 $\frac{\text{Set 9}}{2} \quad \text{Si0}_{2} + 2\% \text{ (CaCl}_{2} + \text{NaCl} + \text{LiCl} + \text{KBr})$

a) <u>600</u>°C

Alpha cristobalite is present. Amorphous silica is also present. One list of quartz is observed. Also, there appears to be a line for keatite (?).

b) 700⁰С

Amorphous silica is again present. One line of quartz is present. There are three distinct lines of alpha cristobalite present.

c) 800^oC

Two intense lines of alpha cristobalite are present along with the amorphous silica. Also, three lines of alpha tridymite are present.

d) 900^oC

Alpha tridymite is indicated by three strong lines. Alpha cristobalite is also represented. The diffuse halo of the amorphous silica is also present.

<u>Table VII</u>

°c	Set	I	II	III	IV
	600		∝ CRISTOBALITE	AMORPHOUS	AMORPHOUS
	660	∝ cristobalite	X QUARTZ	QCRISTOBALITE	QCRISTOBALITE
	720	CRISTOBALITE and ?KEATITE	QQUARTZ	CCRISTOBALITE and ?KEATITE	CRISTOBALITE and ?KEATITE
	780	∝ CRISTOBALITE	CRISTOBALITE	CRISTOBALITE and KEATITE or QUARTZ	CRISTOBALITE and ?COESITE
	840	Q CRISTOBALITE	¢CRISTOBALITE	X CRISTOBALITE and X TRIDYMITE	CCRISTOBALITE and ?KEATITE

		🗙 TRIDYMITE		X TRIDYMITE	CRISTOBALITE
	900	and	TRIDYMITE	and	and
•	C	CRISTOBALITE		CRISTOBALITE	?KEATITE

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	<u>Table VII</u> (con't.)									
C	Se C	t V	VI	VII	VIII					
	600	∝ CRISTOBALITE	QUARTZ	≪CRISTOBALITE	AMORPHOUS					
	660	CRISTOBALITE	QUARTZ	CRISTOBALITE and ?KEATITE	AMORP HOUS					
	720	CCRISTOBALITE and ?KEATITE	QUARTZ	CCRISTOBALITE and ?KEATITE	CCRISTOBALITE and QQUARTZ					
	780	≪ CRISTOBALITE	Q QUARTZ and X TRIDYMITE	CCRISTOBALITE and CTRIDYMITE ?KEATITE	CRISTOBALITE and ?KEATITE					
	840	X TRIDYMITE and XCRISTOBALITE	CRISTOBALITE and CQUARTZ	CRISTOBALITE and CTRIDYMITE	CCRISTOBALITE and ?KEATITE					
	900	X TRIDYMITE and X CRISTOBALITE	CRISTOBALITE and ?KEATITE	X TRIDYMITE and XCRISTOBALITE	CRISTOBALITE and ?KEATITE					

Table VII (con't.)

Set

°C

	CRISTOBALITE
	and
600	🗙 QUARTZ
	and
	?KEATITE

IX

660

700 720 CRISTOBALITE and C QUARTZ

800 780 X TRIDYMITE and X CRISTOBALITE

840

900 and CRISTOBALITE The temperatures involved in this research were within the stability range for \bowtie quartz 573-870°C with the exception of the 900°C temperature. This temperature was within the stability range for tridymite (870-1470°C).

The significance of the temperature range used becomes evident upon examination of Table VII. For the intervals from 600-840°C, cristobalite is the prominent polymorph of silica present. Again, quartz is stable in this range of temperatures. Therefore, this suggests that cristobalite formed directly upon heating with the catalysts. This is true, because quartz, being the stable polymorph, could not invert to cristobalite at these temperatures.

According to Robert B. Sosman (1927), there are six possible permutations: 1) quartz to tridymite, 2) quartz to cristobalite, 3) cristobalite to tridymite, 4) cristobalite to quartz, 5) tridymite to cristobalite, 6) tridymite to quartz.

Refering to Table VIII, we can see that the three polymorphs of silica can each undergo three transformations at varying temperatures. These transformations (inversions) are of the reconstructive type.

Table VIII

Temperature Range	Quartz	<u>Tridymite</u>	<u>Cristobalite</u>
Below 870 ⁰ C	No change	To cristo- balite	To tridymite
		To quartz	To quartz

Table	VIII	(con'	't.)
		•	

Temperature Range	Quartz	<u>Tridymit</u> e	<u>Cristobalite</u>
87 0-14 70 ⁰ C	To cristo- balite To tridymit	No change e	To tridymite
1470 ⁰ C to melting	To cristo- balite	To cristo- balite	No change

Three principles which should be kept in mind when studying the transformations of silica are:

- Under conditions of constant and uniform temperatures and pressure, a stable form will show no tendency to change into an unstable form.
- 2) Under conditions of constant temperatures and pressure, an unstable form may change either to the form stable or into some other unstable form.
- 3) Under conditions where the temperatures are not constant or uniform, or are not uniform over all parts of the material under observation, almost any form or combinations of forms, stable or unstable, may be found.

Considering the sets with a 2% concentration (I-IV), crystallization occurred in only set I and II at 600°C. The melting points of the salts used were low enough to fall in this temperature. While those salts used in sets III and IV had higher melting points than 600°C. However, this trend does not follow through. At 660°C crystallization was evident. Although not strongly evident, as only one line was present in III, IV at the 660°C temperature. By 720°C, the crystallization was strongly present in each set. Cristobalite is the dominant

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polymorph of silica up to and including 840°C. At 900°C the dominant polymorph is tridymite. However, some cristobalite is again present. Tridymite could not invert to cristobalite for it is stable at this temperature. Therefore, either tridymite formed directly with cristobalite or most of the cristobalite inverted to tridymite. The latter does not seem probable, in as much as the change from one polymorphic form to another is extremely slow and sluggish. This is shown by the existence of tridymite and cristobalite at ordinary temperature. (Mason, 1952)

In sets V-VIII, cristobalite is the dominant polymorph up to and including the 720°C temperature. The amount of crystallization, however, has increased at the lower temperature, with the exception of set VIII, as is indicated by an increase in the number of lines present. At the temperature of 780° C, both cristobalite and tridymite are present. Neither of these are the stable polymorph at this temperature. In set VI quartz is present with tridymite. Here the tridymite may have formed first and inverted to quartz, or both quartz and the unstable polymorph tridymite formed together. In set VII, both unstable polymorphs of silica are present, cristobalite being the more abundant. Again, either these polymorphs formed separately, or cristobalite formed and some inverted to tridymite (the temperature involved being more conducive to an inversion from cristobalite to tridymite.) However, as stated previously, this does not seem to be the case. Set VIII appears to consist of the polymorph cristobalite. Only the polymorph keatite (?) appears to be present with cristobalite. •

The presence of keatite was determined from one line measurement (d=3.13) and should not be considered an accurate identification. (Although the d- spacing 3.13 is evident in many samples.)

Set IX is found to contain cristobalite and some quartz up to and including 700° C. In the temperature from $800-900^{\circ}$ C, tridymite is the abundant polymorph with some cristobalite. At 800° C both are unstable and they may form separately or cristobalite may invert to tridymite. At 900° C tridymite is the stable polymorph and would not invert to cristobalite. Therefore, cristobalite must have formed independently and may have inverted in part to tridymite. Again, the assumption that both polymorphs formed separately may be more valid.

In all sets, it was noted, that amorphous silica exists.

While weighing the samples after they had been heated, it was noticed that the higher temperature samples appeared to be more heavy than the samples at lower temperatures. With this in mind, it was decided to run a volume to weight analysis for two samples in each set. These samples were 600°C and 900°C. Each sample was ground in an agate mortar to a uniform size of approximately 200 -300 mesh. An equal volume of each sample was taken. The volume was calculated to be 0.2000 cc. Table IX gives the difference in weight of each set.

<u>Sample</u>	<u>600⁰C weight (gms)</u>	<u>900⁰C weight</u> (gms)	<u>weight</u> <u>increase</u> (gms)
1	0.0152	0.0627	0.0475
2	0.0131	0.0720	0.0589
3	0.0142	0.0648	0.0506
4	0.0160	0.0478	0.0318
5	0.0146	0.0703	0.0557
6	0.0150	0.0597	0.0447
7	0.0288	0.0740	0.0452
8	0.0124	0.0347	0.0223

Table IX

In each case, the 900°C sample was more dense than the 600° C sample. This would be consistent with the increase in crystallinity from $600-900^{\circ}$ C, that was found in each set. The atoms became more closely packed as the temperature increased giving rise to observed increase in density.

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SPECTROGRAPHIC ANALYS IS

Prior to the preparation of the samples for x-ray analyses, it was noted that the samples were washed free from the salts. It was decided to do a qualitative analyses of the samples to determine whether the salts had entered into the structure of the polymorphs. The samples were again washed with de-ionized water to assure complete removal of the salts. A test for the salts after the first washing showed the absence of any salts in the samples. The samples were washed twice more and then allowed to dry at room temperature for a 24 hour period.

Each sample was weighed and ground in an agate mortar to a size of approximately 150-200 mesh. To each sample an equal amount of spectrographic graphite was added. This mixture was then stirred together in a glass vile and shaken together for five minutes, to assure a uniform mixture.

Spectrographic carbon electrodes were used. A $\frac{1}{4}$ inch outside diameter rod was used and a shallow cavity approximately 0.3mm. deep was drilled into the rod. The samples were placed in the holder and packed tightly by pressing the sample into the holder.

The author desired to identify only one element in each sample. It was therefore decided to record the spectra of each of the salts being sought. This would provide a rapid means of identifying the salts if they were present in the sample. Also, mixtures of the salts and silica gel were prepared as above and the spectra of these were also recorded.
PROCEDURE

Before each salt was run, iron electrodes were used in the desired wave length of each salt to produce an iron spectra for purpose of orientation on the plate. Each salt was then run three times for varying exposure times and per cent transmission. Table X shows the wave lengths used along with times and per cent transmission.

Table	X
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Sam	<u>ple</u>	Wave length (A ⁰)	% Transmission	<u>Time</u> in seconds
1.	Fe	4200-5200	80	5
2.	CaC1 ₂	4200-5200	80	20
3.	CaCl ₂	4200-5200	90	20
4.	CaC12	4200-5200	100	20
5.	Fe	5700-6600	80	5
6.	NaC1	5700-6600	80	20
7.	NaC1	5700-6600	90	20
8.	NaC1	5700-6600	100	15
9.	Fe	6700-7600	80	5
10.	LiC1	6700-7600	80	20
11.	LiC1	6700-7600	90	20
12.	LiC1	6700-7600	100	15
13.	Fe	7600-8400	80	5
14.	KBr	7600-8400	80	20
15,	KBr	7600-8400	90	20
16.	KBr	7600-8400	100	15

Eastman Kodak Spectrum Analysis Film #1 was used for recording the spectrum. It was developed in D-19 developer, at 70° F. for $2\frac{1}{2}$ minutes, stopped for 30 seconds and fixed for 8 minutes, washed and dried.

The samples were arced under the following conditions.

Excitation:	Low voltage continuous
Voltage:	250 volts
Current:	10 amps
Resistance:	0
Inductance:	50
Capacitance:	20 mfds.
Time:	20 seconds
Transmission:	80%
Slit width:	20

Each sample was run at the wave length of the salt sought after. Each sample showed the distinct lines for Silicon and Carbon. Table XI gives the results for each set.

Table XI

<u>Set</u>	Analysis
I	No potassium could be found in any of the six samples.
11	There appears to be a very slight trace of lithium present. (?)
III	A trace of sodium appears in all samples.
IV	No trace of calcium present.
v	No trace of potassium is present.
VI	There might be a slight trace of lithium here. (?)
VII	A trace of sodium is present.
VIII	No calcium is present.

The result of the spectrochemical analysis appears to be consistent with a remark made by Brian Mason, (1952).

> Cristobalite has been found with a considerable amount of sodium in interstitial solid solution, and the sodium atoms presumably stabilize the open structure of this mineral.

CONCLUS ION

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The immediate conclusion which was reached from this study was that the introduction of various salts promoted the crystallization of the amorphorous silica gel. This was demonstrated by the fact that the silica gel when heated alone did not crystallize at a temperature of 900° C. It was noted that crystallization of the silica gel took place at or above the melting points of the salts used.

The high-temperature polymorph of silica, cristobalite, appears to be the dominant crystallization product at nearly all temperatures below 900°C. At 900°C. some of the cristobalite, which crystallized first, has inverted to tridymite.

It appears that crystallization will occur at temperatures slightly above the melting point of the salts involved. It is conceivable, therefore, that either of the high-temperature polymorphs of silica could be formed in nature at temperatures far lower than here-to-fore expected. Perhaps the use of tridymite or cristobalite as geologic thermometers is not wise.

The crystallization obtained in this research was conducted in a dry state. Very little water was available to enter into the crystallization. In nature, however, there is an abundance of water which would tend to lower the temperature at which these polymorphs might crystallize. Concentrations of the salts may also be greater in nature than those used in this research.

The samples were heated for a relatively short duration of time (two hours). It is logical therefore to assume that at longer periods of exposure to temperatures below 600^oC., crystallization of either tridymite of cristobalite would occur.

It was seen in the spectrographic analysis of the samples that sodium was found to be present at all six temperature ranges in the polymorph cristobalite. This is consistent with what is found in nature. It appears that the sodium atoms stabilize the open structure of cristobalite and considerable amounts of sodium have been found in interstitial solid solution with cristobalite.

SUGGESTIONS FOR FUTURE STUDY

In the situation where both tridymite and cristobalite exist together, either tridymite formed directly with cristobalite or some of the cristobalite inverted to tridymite. The change from one polymorphic form to another is rather slow and sluggish. In any future research of this nature, the samples should be heated for longer durations.

It is also suggested that greater concentrations of the various salts be used. Concentrations of at least 10% should be tried. The various salts should be mixed with each other.

In as much as this research was conducted in a dry state, perhaps by heating the silica and salts in an atmosphere containing water vapor the temperatures used in this research could be lowered.

Also, an attempt should be made to heat the samples under two or three atmospheres of pressure.

By the use of a differential thermal analysis (D.T.A.) apparatus, the various inversion points could be recorded. Also, by using this apparatus, various pressures, temperatures and atmospheres could be obtained.

If the temperature increment could be controlled more precisely, then smaller increments should be used in the 600° C to 900° C range. This would be the advantage of the D.T.A. apparatus. A constant record of temperatures would be available and more discrete sampling could be had.

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