On the Rate of the Sluggish Inversion of Silica Stone
Kinetics of the Polymorphous Transition of Silica

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Introduction

Quite a few qualitative investigations have been reported on the sluggish inversion of silica stone. However, only few publications on the rate of conversion* have appeared.

Mellor and Campbell[1] have studied the speed of conversion of quartz into cristobalite by making 15 successive burns in a china biscuit kiln to cone 10, and measuring the density of the product after each burn. The authors proposed the following experimental formula,

$$x = e^{-kn} \tag{1}$$

where x is the fraction which remains unchanged at the number of burns n, and k is a constant.

Nakai and Fukami[2] had determined precisely the density of the Merk's silica stone powder after firing several hours in an electric furnace. As a result, they proposed the following experimental formula,

$$1 - x = k \log t \tag{2}$$

where t is the time required for firing. This formula, however, is not in good agreement with the experimental data.

Avgustinik and Kurdevanidge[3] determined the rate of conversion of α-quartz into metastable α-cristobalite at 1200°, 1300°, 1400° and 1500°C±15°C through pycnometric determinations of the density after 0.5, 1, 3 and 6 hrs. heating at the given temperatures. Assuming a unimolecular, a bimolecular, or the Jander rate equation, and by application of the Arrhenius' equation, linearity between $\log k$ and $1/T$ (T is a firing temperature in °K) is fulfilled only for the bimolecular reaction. Thereby the following experimental formula was proposed.

$$k = e^{(a/\delta^{0.064} - b \times 10^4/T)} \tag{3}$$

where δ is the diameter of the grain, and a and b are constants.

Segawa[4] measured the linear expansion of silica stone rod by heating it at a uniform

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* In this report, the word "conversion" means the sluggish inversion of α-quartz to α-cristobalite.

[1] J. W. Mellor and A. J. Campbell, *Trans. Engl. Ceram. Soc.*, **15**, 77 (1915).

[2] T. Nakai and Y. Fukami, *J. Soc, Chem. Ind., Japan*, **38**, Supple. binding, 340 (1935).

[3] A. I. Avgustinik and O. K. Kurdevanidge, *J. Appl. Chem.* (*U.S.S.R.*), **19**, 1189 (1946).

[4] K. Segawa, *Tech, Rep. Yawata Iron Works*, **26**, 1 (1951).

rate of temperature rise. Assuming that the reaction is of the primary nature, he showed the linearity between $\log k$ and $1/T$.

According to the results of Mellor and Campbell, Nakai and Fukami, and Segawa, the conversion of α-quartz to α-cristobalite have the nature of primary reaction. On the contrary, Avgustinik and Kurdevanidge claimed that it is of the secondary nature. In order to clarify the contrariety between these two hypotheses, the following experiments are carried out using many sorts of silica stone of different geological origin.

TABLE I

SILICA STONE SAMPLES

Silica stones	Type of occurence	Locality		Size of single crystals
A	Radiolarian chert	Kuroda,	Japan	0.2 mm-submicroscopic, mostly 0.005 mm
B	Chert	Tamba,	〃	0.2 mm-submicroscopic,
C	Recrystallized chert	〃	〃	0.02-0.002 mm, mostly 0.01 mm
D	Vein quartz with chert	Youra,	〃	2.5 mm-submicroscopic
E	Vein quartz	Tamba,	〃	1.0–0.05 mm, mostly 0.5 mm
F	Pegmatite quartz	Fukushima,	〃	1.0–0.01 mm
G	Rock crystal	Yamanashi,	〃	Single crystal

TABLE II

CHEMICAL ANALYSIS OF SILICA STONES

	A	B	C	D	E	F
SiO_2	94.12	95.68	97.23	98.35	99.13	99.72
Al_2O_3	1.87	2.87	0.20	0.52	0.01	0.00
Fe_2O_3	1.89		2.17	0.43	0.63	0.14
CaO	0.25	0.81	0.09	0.05	0.09	0.10
MgO	0.66	0.24	0.03	0.28	0.01	0.00
MnO	0.24	—	—	—	—	—
Alkalis	—	—	0.18	—	0.11	—
Ig. loss	0.77	0.19	0.09	0.35	0.10	0.00
Total	99.80	99.79	99.99	99.98	100.08	99.96

Experimental

Several silica stones of different geological origins were adopted as samples (Table I, II). And experimental results were shown in Table III.

TABLE III

(1) Silica stone sample	Firing atmosphere	(2) Firing temp. (°C)	(3) Hours heated (hr.)	(4) Apparent density after firing	(5) Residual quartz (%)	(6) Rate constant k_1	(7) Half life time (hr.)	(8) Energy of activation (kcal.)	(9) Frequency coeff. (sec^{-1})	d_0	d_α	d_β
B	in air	1203	2	2.658	96	0.0201	34	81	6.3×10^6	2.689	2.673	2.339
		1300	2	2.598	80	0.113	6.1					
		1431	2	2.394	19	0.838	0.8					
		1540	2	2.338	0	—	—					
		1540	4	2.339	0	—	—					
C	in air	1311	3	2.628	96	0.012	57	120	2.2×10^{11}	2.659	2.641	2.320
		1395	3	2.510	62	0.158	4.4					
		1450	3	2.363	15	0.633	1.1					
		1550	1	2.319	0	—	—					
		1550	4	2.321	0	—	—					
D	in air	1400	3	2.545	75	0.0953	7.3	123	1.05×10^{15}	2.666	2.638	2.300
		1449	$3\frac{8}{60}$	2.434	43	0.270	2.6					
		1498	3	2.333	11	0.734	0.94					
		1530	1	2.302	0	—	—					
		1530	4	2.298	0	—	—					
E	in air	1240	$3\frac{5}{60}$	2.615	98	0.00722	96	145	2.1×10^{15}	2.642	2.624	2.289
		1277	3	2.599	94	0.0224	31					
		1411	3	2.334	4	0.630	1.1					
		1537	1	2.288	0	—	—					
		1537	4	2.290	0	—	—					

(1) Silica stone sample	Firing atmosphere	**(2)** Firing temp. (°C)	**(3)** Hours heated (hr.)	**(4)** Apparent density after firing	**(5)** Residual quartz (%)	**(6)** Rete constant k_1	**(7)** Half life time (hr.)	**(8)** Energy of activation (kcal.)	**(9)** Frequency coeff. (sec^{-1})	d_0	d_α	d_β
F	in air	1448	$5\frac{1}{2}$	2.609	92	0.0159	44	205	6.03×10^{20}	2.652	2.635	2.322
		1498	3	2.559	78	0.084	8.2					
		1520	3	2.498	60	0.171	4.1					
		1538	3	2.443	42	0.292	2.4					
		1650	1	2.320	0	—	—					
		1650	4	2.324	0	—	—					
B	in reducing atmosphere (0.2 atm. press. CO & 0.8 atm. press. N_2)	1201	2	2.635	90	0.0534	13	68	1.8×10^{5}	2.690	2.673	2.340
		1300	2	2.531	61	0.251	2.8					
		1350	2	2.455	38	0.489	1.4					
		1431	2	2.358	6.2	1.38	0.5					
		1600	1	2.338	0	—	—					
		1600	4	2.341	0	—	—					
D	in water vapor	1298	3	2.604	91	0.0310	22	96.2	0.79×10^{12}	2.666	2.638	2.299
		1350	3	2.562	81	0.0752	9.2					
		1400	3	2.449	47	0.248	2.8					
		1451	$3\frac{8}{60}$	2.356	19	0.538	1.3					
		1500	$3\frac{2}{60}$	2.314	4.7	1.006	0.69					
		1540	1	2.297	0	—	—					
		1540	4	2.301	0	—	—					

The sample stones (**1**) were fired at the given temperatres (**2**) during given hours (**3**). The fluctuation of the furnace temperature was ±5°C. Platinum boat was used when the stone was fired in air or in steam. When the stone was fired in the reducing atmosphere, samples were enclosed in a carbon capsule, and fired in the furnace tube which was packed with carbon granules. The density of the fired samples was determined by a pycnometer at 25±0.02°C (**4**). The experimental error in density determinations was 0.002 (0.1%). The difference between the apparent density and the true density was less than 0.01. The amount of the residual quartz (**5**) after firing was calculated from,

$$x = \frac{d_\alpha}{d_\alpha - d_\beta}\left(1 - \frac{d_\beta}{d}\right)\times 100 \tag{4}$$

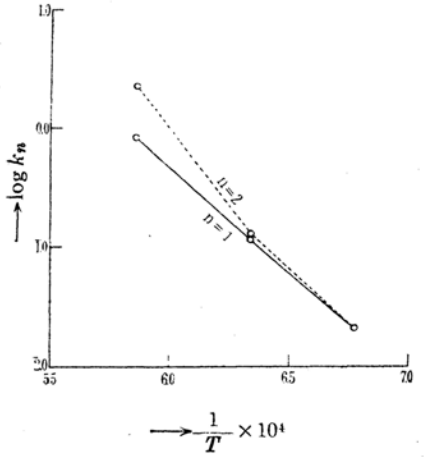

Fig. 1. Chert fired in air (Sample B).

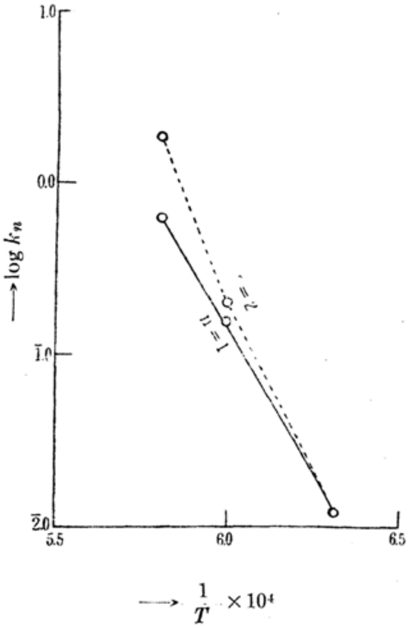

Fig. 2. Recrystallized chert fired in air (Sample C).

where d_α is the density when no quartz is converted (corrected as related later), d_β is the density when all quartz is converted, and d is the density at any time of firing. As is shown in the Figures 1, 2, 3, 4 and 5 linearity between $\log k$ and $1/T$ is satisfied only for the primary reaction for all sorts of silica stone. Differential rate equations of the higher order, namely those of the third and 4th order etc., were calculated, but a larger deviation from the straight line was found to occur. Accordingly, the half life time (**7**), the energy of activation (**8**) and the frequency coefficient (**9**) were calculated only from the rate constants of the primary reaction (k_1).

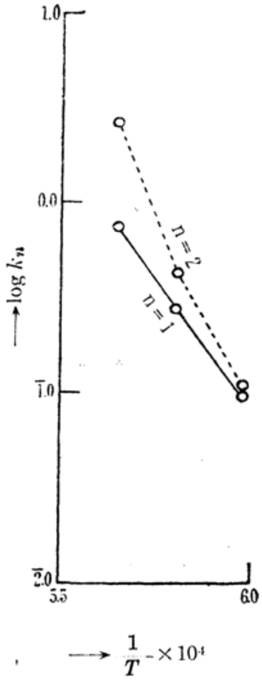

Fig. 3. Vein quartz with chert fired in air (Sample D).

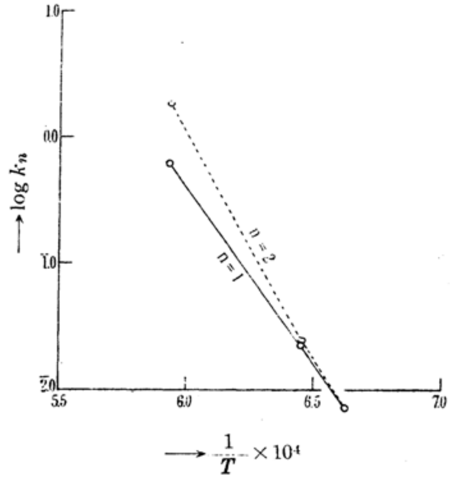

Fig. 4. Vein quartz fired in air (Sample E).

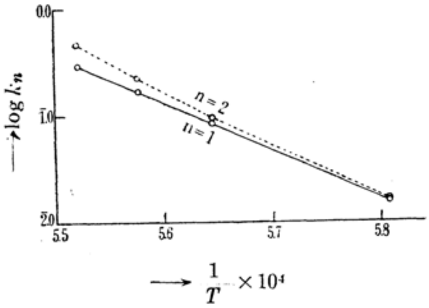

Fig. 5. Pegmatite quartz fired in air (Sample F).

Discussion

What is noteworthy is the contrast between vein quartz (Sample E) and recrystallized chert (Sample C). Vein quartz includes far less impurities, and its crystals are developed to such an extent as about one hundred times larger in diameter than those of recrystallized chert. Therefore, though intuitively the rate constant of vein quartz may seem smaller than that of the recrystallized chert, the experimental results indicate that the former is about three fold of the latter. Therefore, vein quartz is proved to be excellent as a refractory material; because of its extremely high rate of conversion notwithstanding its chemically high purity.

The rate of the chemical reaction of silicates is affected by reducing firing[5,6,7,8]. The conversion rate of silica stone was

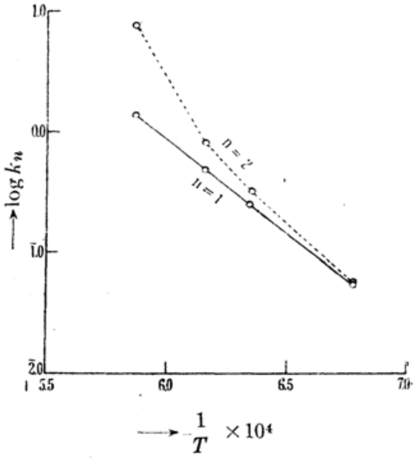

Fig. 6. Chart fired in reducing atmosphere (Sample B).

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5) F. Thomas, *Chem. Ztg.*, **36**, 25 (1912).
6) S. Kondo, *J. Japan Cer. Ass.*, **29**, 367 (1918).
7) A. E. Vickers and L. S. Theobald, *Trans. Cer. Soc.*, (*Engl.*), **24**, 86, 98 (1924-5).
8) A. E. Badger, *J. Am. Cer. Soc.*, **16**, 107 (1933).

determined in reducing atomospher also. Linearity between log k and $1/T$ existed only for the primary reaction (Fig. 6). The rate was compared with that in air (Fig. 7.). In reducing atmosphere, the rate constant had always higher value than that in air (oxidizing). The difference is decreased as the temperature rises, and at about 1730°C, diminishes to zero.

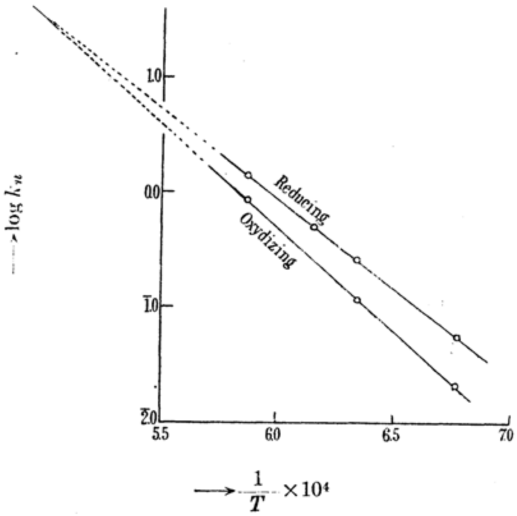

Fig. 7. Rate of conversion of chert in reducing firing compared with that in oxidizing firing (Sample B).

The reaction rate of silicates is considerably accelerated by the presence of water vapor⁹⁾. It was attempted to find the rate constant of the conversion of silica stone in water vapor. Linearity between log k and $1/T$ is satisfied also for the primary reaction in the presence of water vapor of one atmospheric pressure. The rate of the conversion in water vapor of one atmospheric pressure was compared with that in air which contains water vapor of about ten mm Hg (Fig. 8). In steam, the rate constant had higher value than that in air. The difference is decreased as the temperature rises, and at about 1600°C, diminishes to zero.

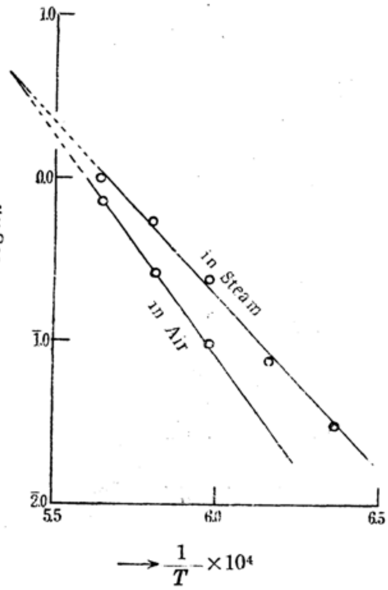

Fig. 8. Comparison of conversion rate of silica stone in steam with that in air (Sample D).

From the density determinations by Nakai and Fukami²⁾, the rate constants k were calculated using a primary (k_1) or secondary (k_2) rate equation, whereby the uniformity of the rate constants could be obtained only when the primary rate equation was adopted (Table IV). Jander's rate constant k_J was also calculated using his well-known equation,

$$(1-\sqrt[3]{x})^2 = k_J t \tag{5}$$

and tabulated in Table IV. The deviation of k_J was large at the early stage of the reaction. According to his diffusion theory, closer agreement between his equation and experimental results is to be expected in the earlier period of the reaction. On the contrary, however, greater deviations have appeared in an earlier period of the reaction. This proves that his theory is not applicable to the conversion of silica stone.

TABLE IV

FIRING AT A CONSTANT TEMPERATURE

(1400°C ± 10)

Hours heated	Density²⁾	k_1	k_2	k_J
0	2.648	—	—	—
5	2.553	0.063	0.073	0.0020
10	2.483	0.065	0.092	0.0038
15	2.415	0.079	0.149	0.0067
20	2.388	0.076	0.18	0.0075
30	2.368	0.064	0.19	0.0066
40	2.354	0.056	0.21	0.0064
50	2.340	0.057	0.33	0.0069
60	2.332	0.062	0.67	0.0072
70	2.327	0.059	0.87	0.0066
80	2.322	—	—	—

Grain size.—Influence of grain size on the reaction rate must be considered when solid reaction is treated. The writer obtained the following results. As a sample, the author used grains of vein quartz washed by concentrated hydrochloric acid and water repeat-

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9) R. Smoluchowski, "Phase Transformations in Solids", John Willy & Sons, Inc., New York, 1951, p264, 267, 276.

edly. Coarse grains were mixed with fine grains of the same quantity, put in a platinum boat, and the mixture was fired twice in the furnace. After cooling down, the grains were separated from each other, and densities were determined (Table V). For particles of diameter between 9 and 0.4 mm., decrease of density was equal within the experimental error; accordingly, the rate of conversion is uniform. Particles of these sizes were used all through our experiments.

TABLE V
INFLUENCE OF GRAIN SIZE ON THE RATE OF THE CONVERSION

	Coarse grains	Fine Grains
Diameter (mm.)	9–7	1–0.4
Apparent density (unfired)	2.640	2.642
Apparent density (fired once)	2.608	2.608
Apparent density (fired twice)	2.572	2.571

Jander's relation[10)]

$$k \backsim 1/\delta^2 \qquad (6)$$

was not applicable to the conversion of silica stone.

For the rate of the conversion of silica stone (polycrystal aggregates), the following five factors are significant.

1. Area of the macroscopic surface of grains.
2. Distribution of imperfections in crystals.
3. Degree of solid solution.
4. Liquid and gaseous inclusions.
5. Area and condition of boundary surface between single crystals.

(A) When the factor 1. is the rate-determining step, Jander's relation (5) is applicable. For example, when fine powder of very pure, perfect, single crystals is used as a sample, or when very effective liquid mineralizer is used, this is perhaps true.

(B) When the factors 2., 3., and 4. were the rate-determining steps, the rate of conversion would have nothing to do with grain size.

(C) When the factor 5. is the rate-determining one,

(C_1) if the grain is polycrystalline, the rate of conversion follows (B),

(C_2) if the grain is a single crystal, the rate of conversion follows (A).

Silica stones as raw materials for fire bricks, the writer supposes, belong to group (B) or (C_1).

Irreversible Expansion of Aggregates.—Silica stone is an aggregate made up of anisotropic quartz crystals. Therefore, correction must be made on the irreversible thermal expansion of aggregates[11),12)] when we wish to determine the quantity of residual quartz by the apparent density determinations. As is shown in Fig. 9[13)] above 800°C, the value of axial ratio is kept almost constant. On the other hand, it is hardly possible for the sluggish inversion of silica stone without mineralizer to proceed below 1100°C. Therefore, when fired within the temperature interval of 800—1100°C, they show the diminution of density (Δd), in spite of the fact that no sluggish inversion occurred.

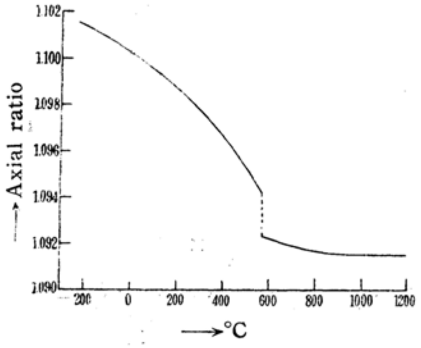


Fig. 9. The thermal variation of the axial ratio of quartz after Sosman[13)].

Now Δd was determined experimentally, and it was found that silica stone always shows about the same degree of density diminution (0.60–0.64%) when fired in the temperature interval mentioned above, regardless of its mode of occurrence and origin. Assuming that the orientation of each crystal is completely random, this density diminution is calculated to be 0.75% from the data[13)] of the axial ratio. Therefore, experimental data and calculated value are in good agreement. From this Δd, d_α was calculated by the following formula,

$$d_\alpha = d_0 - \Delta d \qquad (7)$$

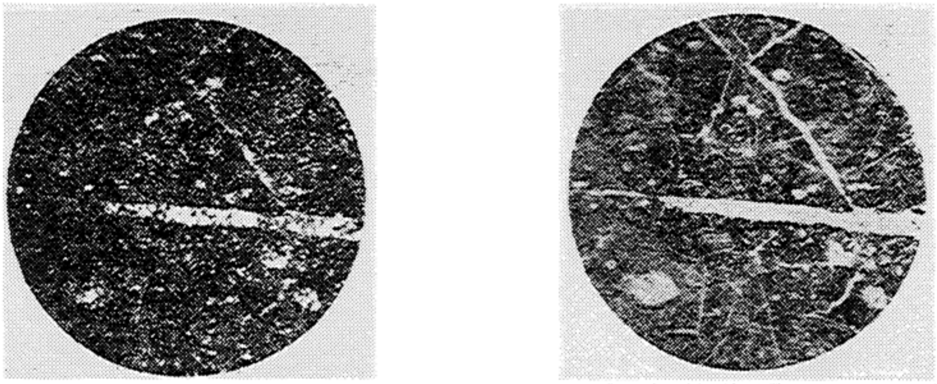
in which, d_0 is the density of the unfired sample.

[10)] W. Jander, *Z. anorg. allg. Chem.*, **163**, 1 (1927).

[11)] J. B. Austin, *J. Am. Cer. Soc.*, **35**, 243 (1952).

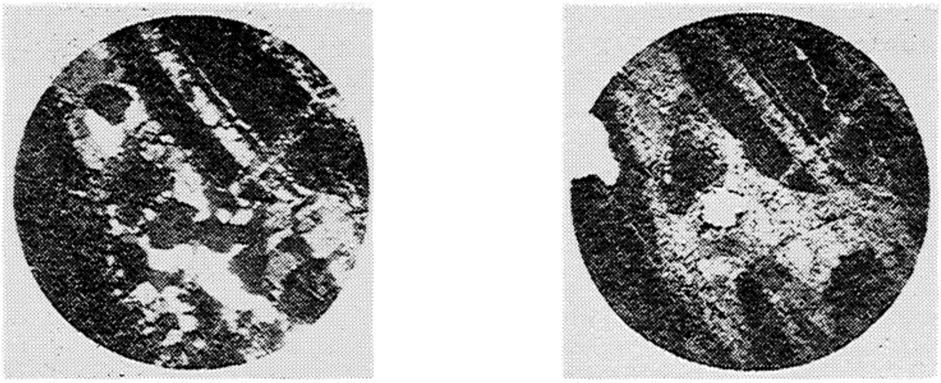
[12)] R. B. Sosman, "The Properties of Silica", The Chemical Catalog Company, New York, 1927, p. 388.

[13)] ibid., p. 375.



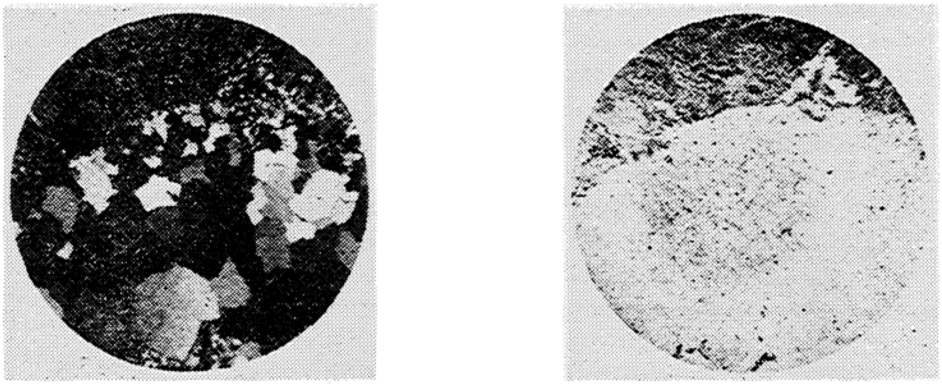
(Crossed nicol.) (Opened nicol.)

Fig. 10. Photomicrographs of radiolarian chert. (×40, Sample A; Kuroda, Japan.) Elliptical spots of various sizes is the pseudomorphs of Radiolaria by substitution.



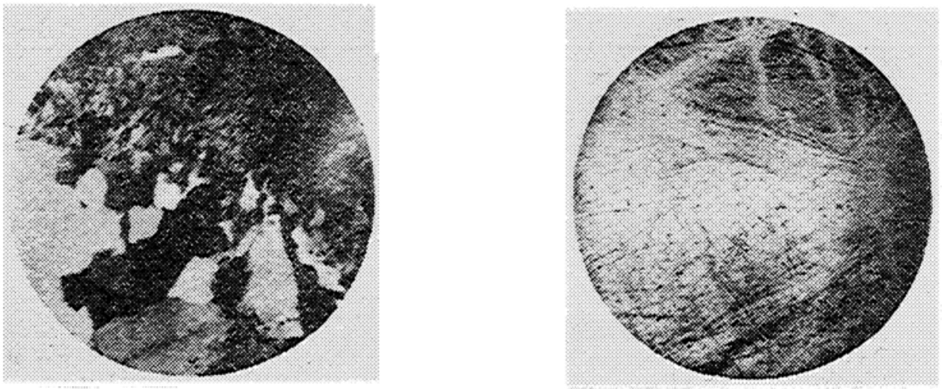
(Crossed nicol.) (Opened nicol.)

Fig. 11. Photomicrographs of chert. (×50, Sample B; Tamba, Japan.)



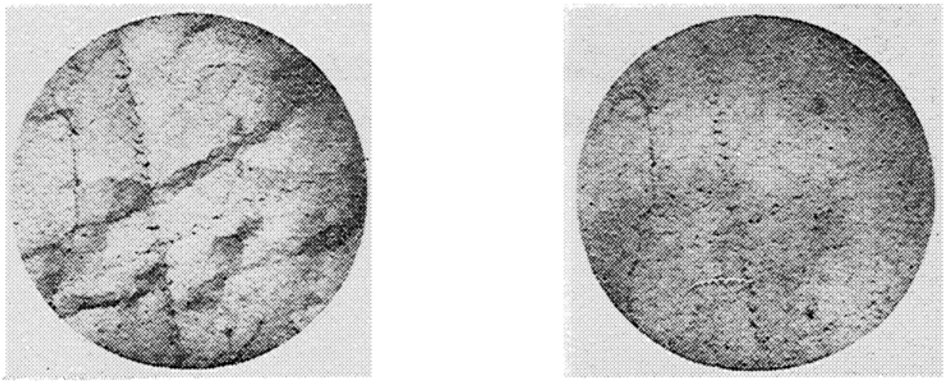
(Crossed nicol.) (Opened nicol.)

Fig. 12. Photomicrographs of recrystallized chert with vein quartz. (×40, Tamba, Japan.) Upper part of the photographs show recrystallized chert (Sample C), and lower part of the photographs show vein quartz (Sample E).



(Crossed nicol.) (Opened nicol.)

Fig. 13. Photomicrographs of vein quartz with chalcedonic chert. (×40, Sample D; Youra, Japan.)
Upper part of the photographs is chalcedonic chert, and lower part is vein quartz.



(Crossed nicol.) (Opened nicol.)

Fig. 14. Photomicrographs of pegmatite quartz. (×40, Sample F; Fukushima, Japan.)
The photograph by crossed nicol reveals mosaic structures.

Summary

(1) It was found that the soluggish inversion of silica stones of different geological origins, from quartz to cristobalite, was the primary reaction when fired in air, in steam or in reducing atmosphere of carbon monoxide.

(2) Effect of firing atmosphere on the conversion rate of silica stone was investigated.

(3) Influence of grain size on the rate of conversion was investigated, and it was found that Jander's, relation $k \backsim 1/\delta^2$ was not applicable to the conversion of silica stone.

(4) Irreversible thermal dilatation of anisotropic aggregates was examined, and the necessary correction to determine the conversion rate by determination of the density was devised.

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