Relations between the Substructure and the Rate of the Sluggish Inversion of Quartz Rock

By Taneki TOKUDA

(Received March 31, 1958)

Rate of the Sluggish Inversion from Quartz to Cristobalite. — We have confirmed the fact that all of these quartz specimens were slowly converted into cristobalite when heated at 1000~1600°C in air, carbon monoxide, or steam. Tridymite has never been detected by X-ray diffraction. The rate of the sluggish inversion from quartz to cristobalite was calculated from density measurement using the following formula,

$$X=D_2(D_1-D)/D(D_1-D_2)$$

where X is the fraction converted, D is the apparent density at a given time of firing, D_1 is the apparent density of quartz aggregates, D_2 is the apparent density of cristobalite aggregates (D_1 and D_2 was corrected for irreversible expansion of polycrystal aggregates[1]). It was found that this sluggish inversion is a reaction of the first order although the rates are found to be different for air, steam, or for such a reducing atmosphere as carbon monoxide. The results obtained when heated in air are shown in Fig. 1. Chemical analysis of the quartz rock specimens is shown in Table I.

These specimens are divided into three classes as can be seen in this figure ; a) pegmatite quartz, b) recrystallized cherty part or interstitial quartz veinlet part in

TABLE I

CHEMICAL ANALYSIS OF QUARTZ SPECIMENS

Sample No.	3	5	6	9	10	12
Classification	Unmetamorphosed (Radiolarian) red chert	Slightly metamorphosed red chert	Recrystallized part in red-white silica stone	Vein quartz in red-white silica stone	Vien quartz in green-white silica stone	Pegmatite quartz
Locality	Kuroda	Tamba	Tamba	Tamba	Wakasa	Hongū
SiO_2	94.12	95.68	97.23	99.13	99.40	99.72
Al_2O_3	1.87	2.87 (Al₂O₃ + total iron)	0.20	0.01	0.12	0.00
Total iron as Fe_2O_3	1.89		2.12	0.63	0.15	0.14
CaO	0.25	0.81	0.09	0.09	trace	0.10
MgO	0.66	0.24	0.03	0.01	—	0.00
MnO	0.24	—	—	—	—	—
Alkalis	—	—	0.18	0.11	0.10	—
Ig. loss	0.77	0.19	0.09	0.10	0.05	0.00
Total	99.80	99.79	99.99	100.08	99.82	99.96

1) T. Tokuda, This Bulletin, 28, 435 (1955).

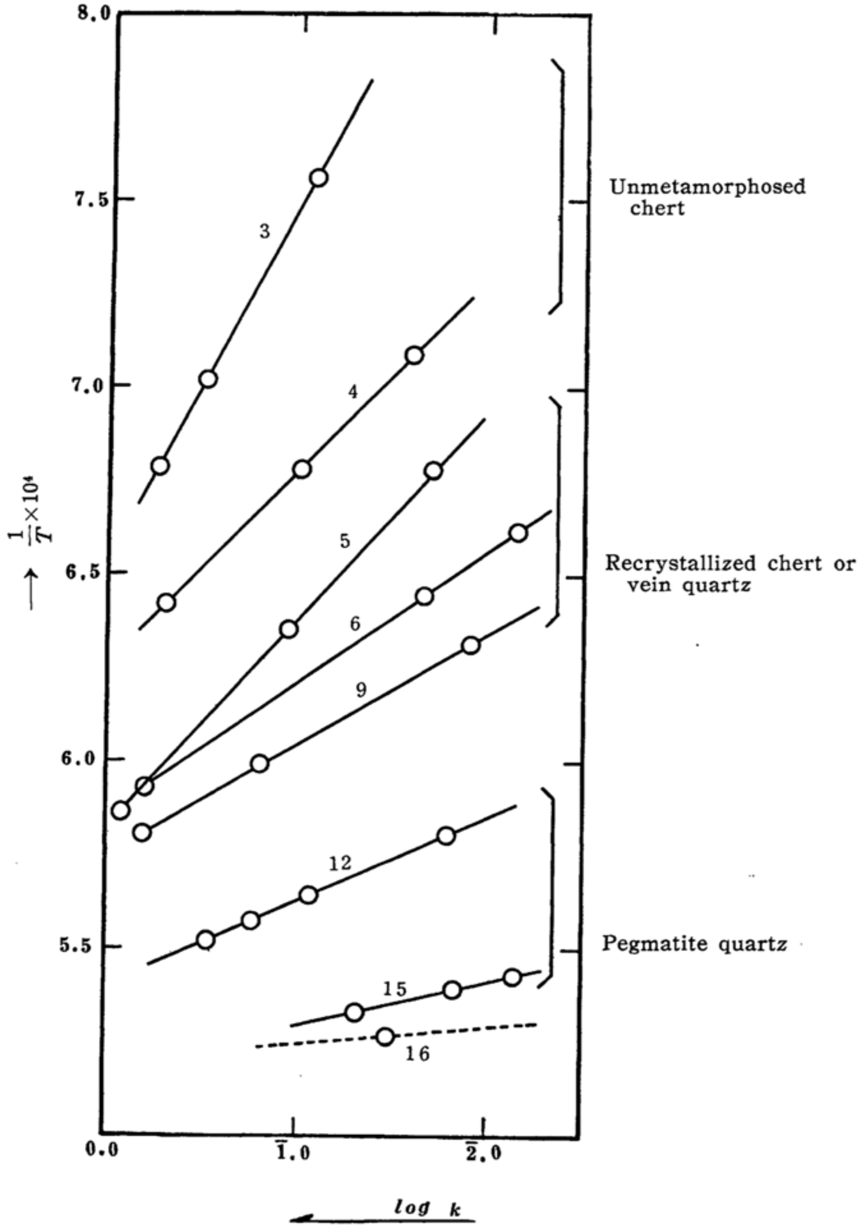

Fig. 1. The rate of the sluggish inversion of several specimens of natural quartz in Japan from quartz to cristobalite (This inversion was a reaction of first order, and k(hr.$^{-1}$) is a rate constant) when heated at a constant temperature (T°K) in an electric furnace. The heating atmosphere was the air. Numbers (1—14) on lines indicate the sample numbers in Table III.

silica stone and c) unmetamorphosed or slightly metamorphosed chert. Quartz occurring as veinlets in the green-white silica stone or red-white silica stone belongs to the same group as recrystallized chert, but not to the pegmatite quartz group.

Variation of Line Breadths.—In order to compare the imperfection of quartz crystals of contrasted geologic origin, the width at half maximum of lines $(234)\alpha_1$, and $(240)\alpha_1$ was determined by means of "Norelco" X-ray diffractometer. Filtered copper K-rays were used with the X-ray tube running at 35 kV., 10 mA. The scanning speed of the GM-counter was 1/8° per minute. Operation condition of the rate meter was, scale factor 4, multiplier 1, and time constant 16 sec. Divergence and scatter slits were 4°, and receiving slit was 0.006 (inches).

TABLE II

GRAIN SIZE OF QUARTZ SPECIMENS VS. INTENSITY AND WIDTH AT HALF MAXIMUM

	Intensity (cps)	width at half maximum (Degree)
<400 mesh	75.0	0.505
<200 mesh	75.6	0.500

Grain size effect was checked with vein quartz specimens (Table II). As shown in the table, the difference of line breadth and intensity obtained from two specimens, the one ground to pass a 200-mesh, screen and the other ground to pass a 400-mesh, was smaller than 1%. Therefore, in the following, all the measurements were made with samples which were ground to pass a 200-mesh screen. The results obtained for $(234)\alpha_1$ are shown in Table III. Those specimens of quartz which contain more impurities and smaller activation energy of sluggish inversion, have larger line breadth.

Lattice Spacing Variation.— Variation of the spacings of quartz specimens has been measured in the back reflection region. Relative values of the spacings (234) and (240) have been determined by mixing silicon powder with the quartz specimens, and measuring the relative positions of the $(642)\beta_1$ reflection of the silicon and the $(240)\alpha_1$ reflection of quartz. The 2θ value of the $(642)\beta_1$ reflection was taken as 147.152° (at 20°C). Results obtained are shown in Table III. As is shown in this table, those quartz specimens which contain more impurities and smaller activation energy of the sluggish inversion, have larger spacings.

These results, obtained by the measurement of variation of line breadth and lattice spacings, suggest that the impurities might be included in the quartz matrix forming a solid solution. Lattice distortion due to the formation of solid solution would be one of the causes which lower the activation energy of the sluggish inversion.

Conclusion

1) The sluggish inversion of quartz rock of different origins, from quartz to cristobalite, was the primary reaction

TABLE III

WIDTH AT HALF MAXIMUM AND SPACING OF $(234)\alpha_1$ (AT 20°C) VS. ACTIVATION ENERGY OF SLUGGISH INVERSION FROM QUARTZ TO CRISTOBALITE ($CuK_{\alpha_1}=1.540501$ Å)

No.	Classification of quartz specimens	Locality	Silica content (%)	Line breadth (Degree)	D (Å)	Diffraction angle (2θ) (Degree)	Spacings (Å)	Energy of activation (kcal.)
1	Siliceous shale	Kamiiso, Japan	—	1.5	230	153.16	0.792	—
2	Hot spring product	Onikōbe, 〃	—	0.8	620	153.17	0.792	—
3	Unmetamorphosed (Radiolarian) red chert	Kuroda, 〃	94.12	0.8	620	153.53	0.79125	48
4	Unmetamorphosed (Radiolarian) grey chert	Kyōto 〃	94.42	0.700	760	153.54	0.79124	88
5	Slightly metamorphosed red chert	Tamba, 〃	95.68	0.650	910	153.55	0.79123	81
6	Recrystallized red chert (Chert part of a breccia)	〃 〃	97.23	0.530	1220	153.57	0.79120	120
7	Recrystallized white chert and vein (A breccia)	Ofuku, 〃	—	0.525	1250	—	—	—
8	Quartzite	Hwang He Do, Korea	—	0.515	1290	153.57	0.79120	—
9	Vein quartz (Vein part of a breccia)	Tamba, Japan	99.13	0.500	1340	153.57	0.79120	145
10	Vein quartz (Vein part of a breccia)	Wakasa, 〃	—	0.455	1670	—	—	—
11	Quartzite	Okuyama, 〃	—	0.447_5	1730	—	—	—
12	Pegmatite quartz	Hongū, 〃	99.72	0.427_5	1930	153.58	0.79119	205
13	Quartzite	Yakeyama, 〃	—	0.412_5	2110	—	—	—
14	〃	Yagen, 〃	—	0.410	2140	—	—	—
15	Pegmatite quartz	Kawamata, 〃	99.75	0.305	6230	—	—	380
16	Rock crystal	Brazil	99.95	0.250	Standard	153.59	0.79117	very large

when fired in air, in steam, or in reducing atmosphere of carbon monoxide.

2) Those specimens of quartz rock which contain more impurities and smaller activation energy of the sluggish inversion, have larger spacings and larger line breadth.

3) The lattice distortion caused by the formation of solid solution would be one of the causes which lower the activation energy of the sluggish inversion.

Institute of Scientific and Industrial Research, Osaka University, Sakai Osaka