

Atomic Weight of Oxygen in Quartz of Contrasted Geologic Origin

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(Received July 26, 1955)

It is obvious that the study of the oxygen isotope abundances in silicate rocks, which form about 99% of the outer shell of the earth, may yield valuable information on the origin of the rocks. Therefore, the atomic weight of oxygen combined in silicate minerals and in silica stones of contrasted geological origin was investigated. And some new knowledge on silica stones in Japan has been obtained.

Experimental

Some reactions have been known for decomposition of silicate minerals and rocks:

- (a) $\text{SiO}_2 + 2\text{C} + 2\text{Cl}_2 \xrightarrow{>1200^\circ\text{C}} \text{SiCl}_4 + 2\text{CO}^{(1)}$
 (b) $\text{SiO}_2 + 2\text{CCl}_4 \xrightarrow{1000^\circ\text{C}} \text{SiCl}_4 + 2\text{CO} + 2\text{Cl}_2^{2,3,4,5)}$
 (c) $\text{SiO}_2 + 2\text{C} \xrightarrow{2000^\circ\text{C}} \text{Si} + 2\text{CO}^{6,7)}$

- (d) $\text{SiO}_2 + 4\text{M}^+ \rightarrow \text{Si} + 2\text{M}^+_2\text{O} \xrightarrow[300\sim 310^\circ\text{C}]{\text{Cl}_2} \text{SiCl}_4^{\wedge}$
 $+ 2\text{M}_2\text{O} \xrightarrow[400\sim 500^\circ\text{C}]{\text{HCl}} 2\text{M}^+_2\text{Cl}_2 + 2\text{H}_2\text{O}^{8,9)}$
 (e) $\text{SiO}_2 + 4\text{KHF}_2 \xrightarrow{230^\circ\text{C}} \text{K}_2\text{SiF}_6 + 2\text{KF} + 2\text{H}_2\text{O}^{8,10)}$
 (f) $3\text{M}^{++}_2\text{SiO}_4 + 8\text{ClF}_3 \xrightarrow[430^\circ\text{C}]{\text{Pt, HF}} 6\text{M}^{++}\text{F}_2 + 3\text{SiF}_4$
 $+ 4\text{Cl}_2 + 6\text{O}_2^{11,12)}$
 (g) $\text{M}^{++}_2\text{SiO}_4 + 4\text{F}_2 \xrightarrow[420^\circ\text{C}]{\text{HF}} 2\text{M}^{++}\text{F}_2\text{SiF}_4 + 2\text{O}_2^{12)}$

The reaction (e) was used for this investigation. The obtained water and also standard water (tap water of Osaka city¹³⁾) were decomposed electrolytically, and the obtained oxygen was recombined respectively with the hydrogen gas in the same bomb. And the density difference between these two kinds of water was determined by the froat method.

The obtained results are shown in the Table I.

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TABLE I
THE DENSITY DIFFERENCES BETWEEN THE OXYGEN IN ROCK SAMPLES AND THAT IN
STANDARD WATER DETERMINED IN THE FORM OF WATER

No.	Rocks and Minerals	Excess Density of Water (γ)	Locality
<i>Sedimentary rocks</i>			
1	Quartz schist	5.8	Mikawa (Okuyama), Japan
2	"	4.4	" (Yagen), "
3	Vein quartz (Sedimentary?)	4.1	Wakasa, "
4	" (")	3.8	Tamba, "
5	Recrystallized chert	4.7	" "
6	"	3.8	" "
7	Radiolarian chert	3.0	Kuroda, Shiga, "
8	Diatomite	3.4	(Commercial) "
9	"	5.0	" "
<i>Igneous minerals</i>			
10	Microcline	2.0	Yamanashi, "
11	Augite	1.5	Fukushima, "
12	Tourmaline	2.0	Hyōgo, "
<i>Sedimentary rocks</i>			
13	Cheshire orthoquartzite	3.4	Vermont
14	Arkose	3.2	Connecticut
15	Dover flint	6.1	England
16	Moquoketa shale	4.3	Iowa
<i>Igneous rocks</i>			
17	Gneissic granite	2.8	South Dakota
18	Greenland basalt	1.8	
19	Basalt	2.4	Columbia River, Oregon
20	Lavas	2.7	Paricutin

(No. 1~No. 12). Those by P. Baertschi¹⁴⁾ obtained using the massspectrometer are also shown in the same Table (No. 13~No. 20). Excess density of oxygen in these silica stones, namely Mikawa quartz schist, chert, vein quartz, and diatomite was $+3.0 \sim +5.8\gamma$, and that in the igneous minerals, namely microcline, augite and tourmaline was $+1.5 \sim +2.0\gamma$. According to P. Baertschi, excess density of oxygen in sedimentary rocks was $+3.2 \sim +6.1\gamma$, and that in igneous rocks is $+1.8 \sim +2.8\gamma$. Therefore, the results of the author by the froat method is in good agreement with those of P. Baertschi by the massspectrometer, in spite of the fact that chemical procedure of decomposition of rocks and method of determination of oxygen abundance ratio of the present author is based on an entirely different principle from that of P. Baertschi.

Discussion

It has been known that chert and diatomite are sedimentary rocks. Therefore, the obtained value; $+5.0 \sim +3.0\gamma$, is recognizable. From the results on Mikawa quartz schists; $+5.8 \sim +4.4\gamma$, It is recognized that Mikawa silica stone is a metamorphic rock of sedimentary origin. And the stone has been grown, may be, from chert¹⁵⁾. It is noteworthy that the vein quartz in the Tamba

silica stone and in the Wakasa silica stone has the value, $+4.1 \sim +3.8\gamma$, as high as the recrystallized chert, $+4.7 \sim +3.8\gamma$. They clearly, belong to a group of sedimentary rock, and not to that of igneous one. Accordingly, these kinds of vein quartz are presumed

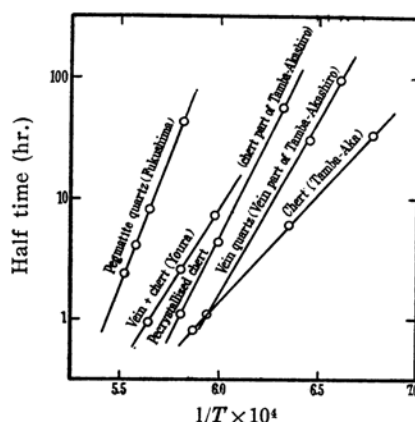


Fig. 1. Half time (hr.) of sluggish inversion from quartz to cristobalite (This inversion is a reaction of first order) when heated at a constant temperature ($T^{\circ}\text{K}$) in an electric furnace. The firing atmosphere is air.

14) P. Baertschi, *Nature*, **166**, 112 (1950).

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not to be igneous rock, but to be segregation product^{16,17,18}.

According to the experimental results of the author¹⁹, sluggish inversion of silica stone from quartz to cristobalite is a reaction of first order. Half times of silica stones are compared with each other in the Fig. 1. As is shown in the Figure, half time of vein quartz is closer to that of chert than to that of pegmatite quartz, in spite of the fact that its chemical composition, density (Table II, Fig. 2), and degree of crystal growth (Fig. 3) are closer to that of pegmatite than to that of chert.

According to O. F. Tuttle²⁰ and M. L. Keith²¹, vein quartz is presumed to be grown at far lower temperature than the quartz in igneous rocks such as pegmatite, granite, and rhyolite; namely at a similar temperature to that of the cryptocrystalline quartz, found in limestone. This result does not contradict our results. According to Keith, Davis, Tuve, and Dork^{7,22}, the samples of quartz known to have been formed at low temperature have higher content of O¹⁸ than do the samples that have been formed at high tem-

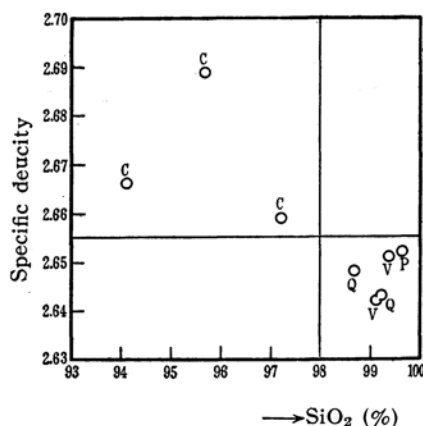


Fig. 2. Relation between specific density and silica content of silica stone.

C: Chert

Q: Quartzite

V: Vein quartz P: Pegmatite quartz

peratures. The atomic weight of oxygen in silicate minerals and rocks is useful for the investigation of their geological origin, and will be used as a geological thermometer²³.

TABLE II
CHEMICAL ANALYSIS AND SPECIFIC DENSITY OF SILICA STONE

Classification	Pegma- tite quartz	Vein quartz	Vein quartz	Quartz- ite	Quartz- ite	Vein and chert	Recrys- tallized chert	Chert	Radio- larian chert
Common name	Fuku- shima silica stone	Vein part of Wakasa- Aoshiro silica stone	Vein part of Tamba- Akashiro silica stone	Mikawa silica stone (Yagen)	Mikawa silica stone (Oku- yama)	Youra silica stone	Chert part of Tamba- Akashiro silica stone	Tamba- Aka silica stone	Kuroda silica stone
SiO ₂	99.72	99.40	99.13	99.25	98.69	98.35	97.23	95.68	94.12
Al ₂ O ₃	0.00	0.12	0.01	tr.	0.38	0.52	0.20	} 2.87	1.87
Fe ₂ O ₃	0.14	0.15	0.63	0.09	0.20	0.43	2.12		1.89
CaO	0.10	tr.	0.09	—	0.07	0.05	0.09	0.81	0.25
MgO	0.00	—	0.01	0.07	0.29	0.28	0.03	0.24	0.66
MnO	—	—	—	0.65	—	—	—	—	0.24
Alkalis	—	0.10	0.11	—	0.17	—	0.18	—	—
Ig. loss	0.00	0.05	0.10	0.24	0.10	0.35	0.09	0.19	0.77
Total	99.96	99.82	100.08	100.68	99.95	99.98	99.99	99.79	99.80
Specific density	2.652	2.651	2.642	2.643	2.648	2.666	2.659	2.689	2.667

16) S. Iwao, T. Anzai and T. Okabe, *Bull. Geol. Survey Japan*, 2, 10 (1951).

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19) T. Tokuda, *This Bulletin*, 28, 435 (1955).

20) O. F. Tuttle, *Am. Min.*, 34, 723 (1949).

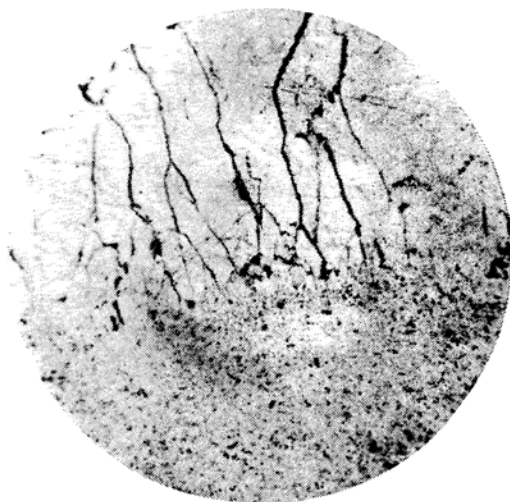
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22) M. L. Keith, M. A. Tuve, G. L. Davis and J. B. Doak, *Carnegie Institution of Washington Year Book*, No. 49, 36 (1950).

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(Crossed nicol.)



(Opened nicol.)

Fig. 3. Photomicrographs of vein quartz with recrystallized chert. ($\times 40$, Wakasa silica stone, Japan) Upper part of the photographs show vein quartz, and lower part show recrystallized chert.

Grateful acknowledgement is made to Prof. T. Ao of Osaka University and Prof. S. Matsushita of Kyoto University, for their guidance, and to Master K. Kurita for his cooperation. Thanks are also due to the

Education Ministry for a Scientific Research Grant.

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