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A Note on Visco-elastic Behavior of Obsidian

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Abstract

Visco-elastic properties of obsidian which is considered to represent original magma were experimentally investigated by the statical method.

Results obtained are summarized as follows:

1. Viscosity shows the characteristic of glassy materials; it decreases sharply at about 750°C. Various heating rates do not effect it. Under constant temperature i. e. 850°C, it is constant with time. There is no difference between the values of a heating process and a cooling one.

2. Young's modulus hardly decreases with temperature up to above 700°C but then it begins to decrease significantly from above 750°C.

Considering these results, the writer proposes to discuss some properties of obsidian. Furthermore, obsidian heated at 800°C and 1000°C for a few hours was analyzed with X-ray diffraction.

1. Introduction

When cooled under such a condition that liquid does not crystallize, this liquid gradually stiffens down to the room temperature it forms glass. Then natural glasses such as obsidian and pitchstone are considered as the products under the above-stated condition in an original magma. Thus one can expect that they are the products by quenching of magma which existed at elevated temperatures and high pressure. So the studies of their physico-chemical properties are very interesting and important owing its contributions to understanding the volcanic activities.

In his previous paper¹⁾, the writer discussed the viscous behavior of the new lava from Syowa-Sinzan (or Showa shinzan) at high temperatures. The new lava showed almost the same results as the 1950 Oshima lava²⁾. Under the increasing temperature at the various rates, viscosity depends not only upon T , but also upon dT/dt . Experiments under constant temperature showed that viscosity increases with time and approached an asymptotic value. To account for these results the writer suggested that the crystallization may occur in the unstable part of the groundmass of rocks.

In the present paper, the writer reports the results of measurement of the viscosity and Young's modulus of obsidian as a typical unstable part of rocks and the temperature condition under which obsidian may crystallize

at the highest of velocity of crystallization. Furthermore, the writer heated obsidian under that condition for a few hours and obtained some changes on X-ray diffraction chart.

2. Method

The method of experiment is the same as that stated in the previous paper¹⁾. Temperature is raised at a constant and definite rate and the load is applied from long before the commencement until the end of heating, to obviate any effects of the thermal history of the specimen.

Thus viscosity is derived from the following equation :

$$\eta = \tau E_U / 3 = (1/3) \{ (Wl^3 g / 4 bd^3) + (5wl^3 g / 32 bd^3) \} (dt/dX)$$

where all notations are the same as listed in the previous paper.

Unrelaxed Young's modulus (E_U) can be obtained from the weight of a load and the instantaneous part of deformation when a load is applied.

3. Specimens

a) Shirataki Obsidian³⁾.

This specimen is a typical natural glass, collected by Dr. T. Ishikawa from Shirataki, Hokkaido. There are specimens of Shirataki obsidian in which many little white spherulites are scattered. In the present experiments the writer tested obsidian which does not contain them at all. O. Tsunaka⁴⁾ has already explained its geological occurrences. Phenocrysts of plagioclases and magnetite are scattered in the groundmass of colourless glass.

Table 1. Chemical Composition of Specimens (%)

Specimen	Shirataki Obsidian	Wadatōge Obsidian
SiO ₂	74.41	76.24
Al ₂ O ₃	13.33	12.56
Fe ₂ O ₃	0.08	0.68
FeO	0.86	0.58
MgO	0.43	0.23
CaO	1.90	0.96
Na ₂ O	2.99	2.84
K ₂ O	4.30	4.20
H ₂ O ₊	0.23	0.69
H ₂ O ₋	0.29	0.17
TiO ₂	0.05	0.38
P ₂ O ₅	0.23	0.25
MnO	0.05	0.05
Total	99.15	99.83
Analyst	T. KUSHIDA	Y. KAWANO

b) Wadatôge Obsidian³⁾.

Collected by Dr. Y. Kawano from Wadatôge, Nagano Pref., phenocrysts of plagioclase, biotite and augite are scattered sparsely in the groundmass of colourless glass. There are two kinds of Wadatôge obsidian one of which forms bubbles (10–300 μ in diameter) by heat treatment at about 1000°C for 10 minutes and the other forms bubbles (100 μ in diameter) at about 800°C for 10 minutes. In the present experiment the writer tested the former to obviate any effects of bubbles.

Chemical composition of these obsidians are cited in Table 1.

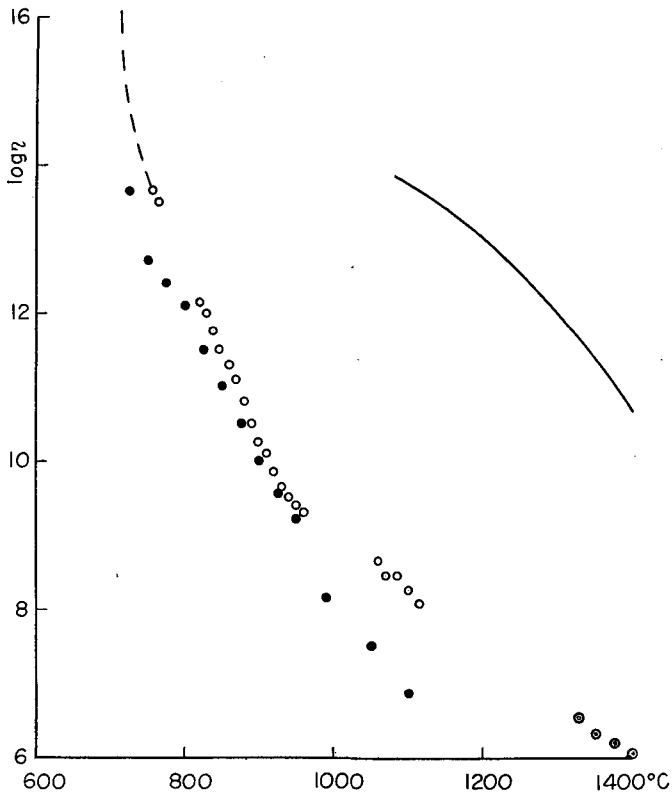


Fig. 1. Viscosity-temperature curve of Obsidian and some silicates. (in Poises).

Open circles ; Shirataki Obsidian

Closed circles ; Wadatôge Obsidian

Solid line ; Silica glass (Volarovich and Leontieva)

Double circles ; Oki Obsidian (Kani)

4. Results

I. Viscosity

a) Results obtained at the heating rate 600°C/hour are graphically represented in Fig. 1 where temperature (T) is plotted along the abscissae, while the logarithm of viscosity ($\log \eta$) along the ordinate.

The viscosity of Shirataki obsidian may be considered to be the same as that of Wakatōge, their viscosity decrease by one order of magnitude with the increase of 50°C in temperature.

Supposing that $\log \eta$ - T relations are linear at the temperature range between 800° and 950°C, one obtains the empirical formulae expressing the two curves in Fig. 1 are as follows

$$\log \eta = -1.9 \times 10^{-2} T + 27 \text{ (Wadatōge)}$$

$$\log \eta = -1.9 \times 10^{-2} T + 28 \text{ (Shirataki)}$$

As obsidian vesicates the volatile materials, so the viscosity at temperatures higher than 1000°C does not show the viscosity of its substantial part.

In the figure are to be found the viscosity-temperature curves of several silicates, according to other workers' measurements for comparison. The viscosity at temperatures higher than 1300°C are measured by K. Kani⁵⁾; the extremely viscous melts of silica glass are measured by M.P. Volarovich

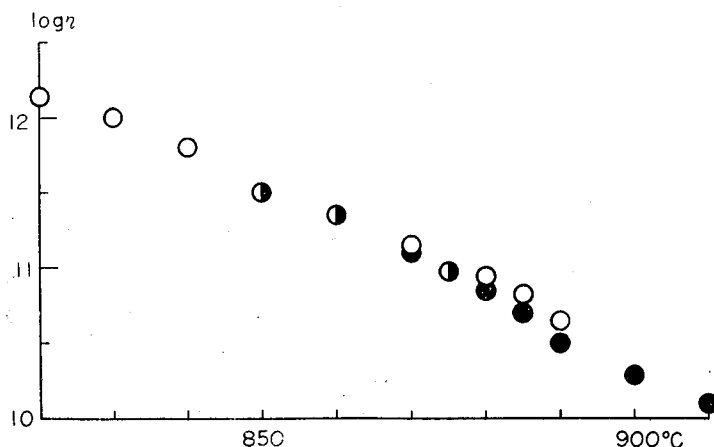


Fig. 2. Viscosity versus temperature with various heating rates for obsidian.
 Open circles ; 100°C/hour
 Closed circles ; 600°C/hour.

and A. A. Leontieva⁵⁾ who used the fiber-elongation method with micrometric measurements under load, at temperature up to 1450°C.

b) The results obtained at the heating rates of 600°C/h and 100°C/h are shown in Fig. 2. There is no difference in viscosity at the temperatures range between 800° and 900°C, as Oshima lava and Syowa-Sinzan lava.

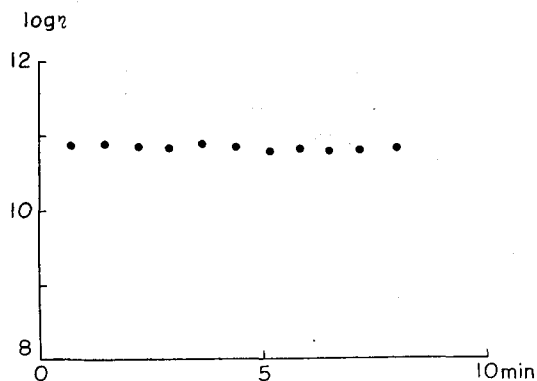


Fig. 3. Viscosity-time curves for obsidian at constant high temperature (850°C)

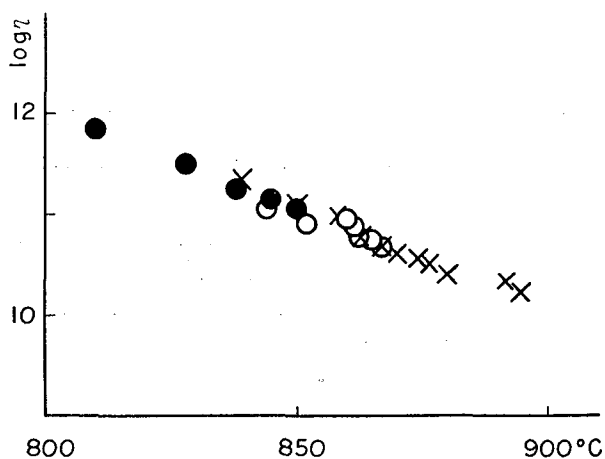


Fig. 4. Variation of viscosity coefficient with temperature of obsidian.

Open circles ; heating stage 1st run up to 870°C
 Closed circles ; cooling stage
 Cross ; heating stage 2nd run up to 900°C.

c) The results of experiments under constant temperature, viz., 850°C reached by rapid heating, showed that viscosity is constant with time. (Fig. 3).

d) There is no difference between the values of a heating process and a cooling one at the temperature range between 800° and 900°C. (Fig. 4). As the measurement of viscosity at high temperatures is accompanied by a large deformation in specimen, so measurement is confined within the narrow temperature range 100°C at 800°C with only one specimen.

II. Young's modulus

Young's modulus for the instantaneous part of deformation hardly decreases with the rise of temperature up to above 700°C and then it begins to decrease significantly from above 750°C. (Fig. 5).

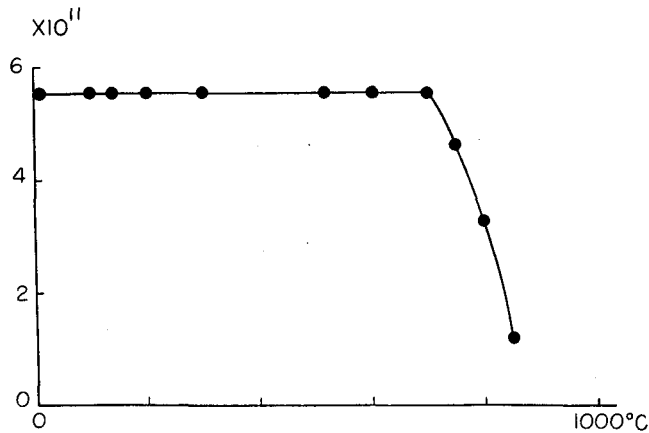
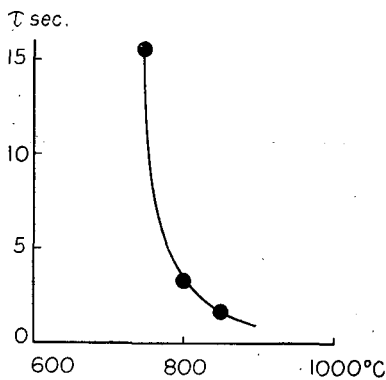


Fig. 5. Variation of Young's modulus of obsidian.



Variation of relaxation times with temperature calculated from viscosity and Young's modulus is shown in Fig. 6.

Fig. 6. Variation of relaxation times with temperature.

5. Discussions

Temperature changes in viscosity of obsidians shown in Fig. 1 may be characteristic of glassy materials. That is, there is no sharp melting point as there is with a crystal. Silicons and oxygens in obsidian are not arranged as they are in quartz and the molecules can be jointed in a quite irregular structure by only slight distortions of the bond angles of the oxygens. Some of the bonds in the glass are under more strained state than others and are fairly easy to break. Thus as the temperature raised, some bonds will break, the molecules may join again in a different arrangement resulting in permanent distortion of the material. It is in this way that glass flows at high temperatures.

As the actual obsidians generally contain Na_2O , or other constituents which weaken or strengthen the bond, their viscosities are different from a silica glass composed of pure SiO_2 .

Such glassy or vitreous states are produced when a liquid is cooled rapidly to its melting point. However, it must be noted that volatile materials begin to vesicate as bubbles when obsidian is heated up to high temperatures and ordinary pressure. Recently in order to make clear the mechanism of pumice formation Shimozuru et al.,⁷⁾ Sakuma and Murase⁸⁾ discussed the above processes. Therefore, the formation of obsidian must require the condition of a cooling under high pressure as well as rapidity.

Consideration of activation energy furnishes a key to bring about the substantial structure of glass connected with the phenomena of viscosity, electric conductivity, elastic after-effects and so on. It can be determined generally by using an Arrhenius equation :

$$\ln k = \ln A - E/RT$$

where k : velocity constant in chemical reaction
 A : frequency factor
 R : gas constant
 E : activation energy
 T : temperature.

This equation holds accurately for the non-association substances of a non-polar type or the substances whose degree of association is not dependent on temperature.

If the substances possess dielectric polarization and their coordination numbers and structures depend on temperature, $\ln \eta^{-1}/T$ relation is not

generally linear and also does not hold in broad temperature range of glass which is complex in its constitution. In the present experiment, however, the writer supposes that A and E depend on temperature; he utilizes the concept of activation energy and compares the activation energy of obsidian with that of Syowa-Sinzan new lava obtained from previously reported experiment. The results are shown in Fig. 7 where dotted lines indicate the ideal energy curves of obsidian and Syowa-Sinzan new lava according to the Preston et al while the absolute values have not the physical meaning.

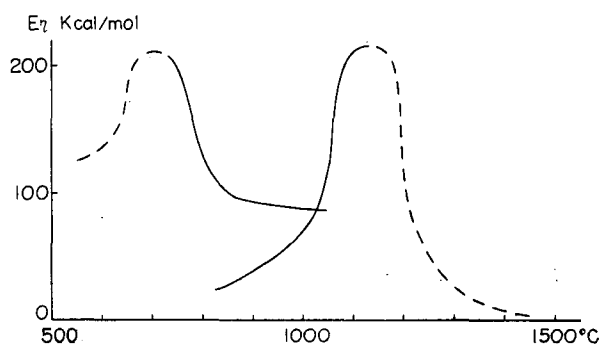


Fig. 7. Variation of activation energy with temperature.
Left side; Obsidian
Right side; Syowa-Sinzan new lava.

The ideal energy of glass is zero at $T^{\circ}K$ and a certain constant value between room temperature and about $200^{\circ}C$; it takes maximum value at softening temperature range and becomes a certain constant value above a liquid phase again.

Kê⁹⁾ mentioned that the grain boundaries in polycrystalline metals, where many disordered groups aggregate, behave in a viscous manner; then he proceeded to investigate the coefficient of viscosity and its temperature variation of polycrystalline metals. It may be expected that similar mechanism may operate in rocks such as Syowa-Sinzan new lava which have a glassy part in the groundmass.

Although it seems to be true that the activation energy for slip is comparable with that of grain boundary viscosity, there is not as yet sufficient evidence to enable one to say that the processes have the same origin. Then, by using only the activation energy of flow, one cannot solve the

problem of what part of the rock deforms instantaneously and what part behaves anelastically.

Some words should be added here about reasons for the increase in viscosity of Syowa-Sinzan new lava with time at constant temperature. In the previous paper, the writer suggested that unstable parts in groundmass of the rocks might crystallize when they were heated in laboratory. The present experiment shows that viscosity is constant with time and thermal hysteresis has no effect on it at above 800°C . This is shown in Figs. 2, 3, and 4. Young's modulus, however, decreases sharply at about 700°C . (Fig. 5). This means the state of obsidian changes at such temperature. Accordingly, one must discuss viscosity at about 700°C , and in fact, Syowa-Sinzan new lava shows the viscosity-time relation at above 10^{13} poises as shown in previous paper, but the present method of viscosity measurement is inapplicable to more than 10^{15} poises with good accuracy. Other method, therefore, are required to conquer this difficulty.

Considering that the upper limit of this method is 10^{15} poises, however, viscosity of obsidian must rise sharply as shown in Fig. 1 by a dotted line.

6. Concluding remarks

In this paper, the writer discussed the visco-elastic behavior of obsidian at high temperatures. The conclusions must be important to an understanding of volcanic phenomena and to glass manufacture.

Also the writer made mention of the essential considerations in the

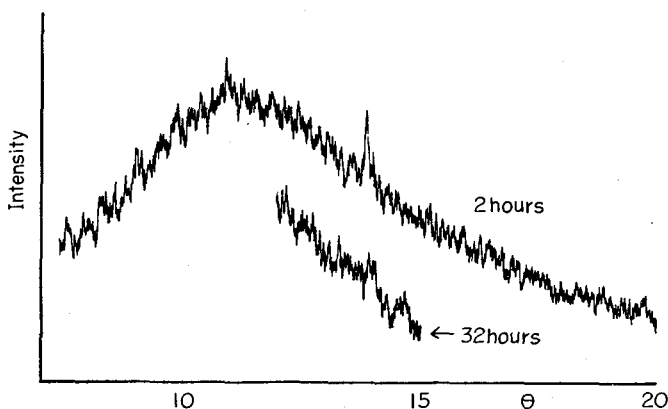


Fig. 8. X-ray diffraction patterns of obsidian heated at 1000°C for two hours and thirty two hours.

viscosity of rocks, let him add a few more words in conclusion further. Though physico-chemical properties of obsidian may be not the same as those of glass in groundmass or rocks, he tested whether obsidian crystallizes or not within a short time as a result of heating at high temperatures.

It seems plausible that the velocity of crystallization is most fast within the temperature range where some properties of obsidian change abruptly. Then the writer heated obsidian in a platinum crucible for a few hours at 800°C and 1000°C and obtained X-ray diffraction pattern with "Norelco" X-ray spectrometer. The pattern of heat treatment (for two hours at 1000°C) is shown in Fig. 8 where the abscissae is the intensity of diffraction, while the ordinate is the angle 2θ which the diffracted beam makes with the incident one. The pattern in Fig. 8 indicates that obsidian is glassy as previously stated. From this pattern one sees there is a peak at $\theta=14^\circ$ which corresponds to the maximum intensity of a plagioclase.

The intensity is given by the Debye equation

$$I = \sum_m \sum_n f_m f_n (\sin sr_{mn}/sr_{mn})$$

where $s=4 \sin \theta/\lambda$, r_{mn} denotes the distance from atom m to atom n , and f_m, f_n the scattering factors for atoms m and n , and the wave length of X-ray (λ) which is here taken as 1.54 Å.

Considering these relations, the changes of the intensity of the peak at $\theta=14^\circ$ may mean that the quantity of plagioclase changes with duration of heat treatment. In the present experiment the writer could not gain the changes which have a physical meaning. However, it seems that the more the specimens are heated, the more the peak lost its sharpness. The diffraction pattern of obsidian after 32 hours heat treatment is illustrated in Fig. 8 too. Although systematic investigations are necessary in order to discuss the effect of a heat treatment further, one may expect that viscosity-time relation in ordinary igneous rock such as Syowa-Sinzan and Oshima lavas depends on the crystallographical changes of unstable parts in the groundmass of the rocks.

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