EFFECTS OF WATER ON THE GLASS TRANSFORMATION TEMPERATURE OF RHYOLITIC ROCK MELT

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The glass transformation temperature (T_g) of rhyolitic rock melt was considerably influenced by the content of water in the melt. T_g determined by means of the differential thermal analysis-thermogravimetric analysis under various experimental conditions ranged from 490° to 760°C, and decreased linearly with increasing water content in the melt at T_g . The experimental equation for the relation was $T_g = 778 - 223 W_{H_2O}$. The decrease of T_g with the increase of water may be explained by a decrease of the degree of polymerization of silicate anions in the rock melt as was analogized from the case of organic polymer solution.

In the experiments under the same conditions (sample grain size, heating rate), a strong correlation was observed between T_g and water released between T_g and 950°C. On the other hand, it was difficult to find a certain relationship between T_g and water released at above 950°C. These results can be explained in terms of the difference of the force constant of OH bonding of water. The water which had a smaller force constant dissociated from the melt structure at lower temperature, moved freely among the melt structure and destroyed Si-O-Si bonds by the collision with the bonds. Thus the water had a direct effect upon T_g .

INTRODUCTION

A basic study on the glass transformation temperature (T_g) of the rock melt (the silicate melt having a composition corresponding to that of a igneous rock) is very important to understand the physical properties and the structure of a magma, and the genesis of a glassy rock.

Generally, a material which is changed into the "amorphous solid" state has two distinct characteristic temperatures. One is the melting temperature (T_m) or liquidus temperature (T_l), and the other is T_g . T_m (or T_l) is a "first-order transition" temperature, whereas T_g at which the material transforms from the super-cooled liquid state to the glassy state is considered to be a "second

-order transition" temperature (Boyer and Spencer, 1944; Spencer and Boyer, 1946; Carmichael *et al.*, 1974).

The glass transformation temperature is very important to gain a better understanding of not only the physical properties such as viscosity (Narayanswamy, 1971; Carmichael *et al.*, 1974), heat capacity, thermal conductivity and melting temperature of a melt (Sakka and Mackenzie, 1971), but also the movements and the polymerization degree of the segments in the melt (Fox and Flory, 1950; Gordon, 1963).

Few reports on T_g of a rock melt have been published to date. Shaw (1968) found an indication of T_g for a rhyolitic obsidian at about 700°C by the change in the slope of

the diffusion coefficient for water. Taniguchi (1974) reported that T_g for a rhyolitic obsidian was about 670°C by means of the differential thermal analysis. Bacon (1977) reported that T_g for a rhyolitic glass determined on the basis of the mean specific heat measurement was about 790°C. These three values are not consistent with each other. The different method used for the determination and the different water content in the sample might cause the discrepancy.

The purpose of this study is to determine T_g of rhyolitic rock melts of various water contents and to consider the effect of water on the melt structure on the basis of the relationship between T_g and the water content.

SAMPLES

The volcanic glasses separated from obsidians were used in the experiments. The chemical compositions of the volcanic glasses and the obsidians have been already reported by Kawano (1929) and Taniguchi (1974). The contents of SiO_2 and water of the samples are shown in Table 1. Though some values of SiO_2 content in this table are

Table 1. The explanations of the samples used in the present experiments.

Sample No.	Locality	SiO_2^* (wt. %)	$\text{H}_2\text{O}(+)$ (wt. %)	Reference
1	Himeshima	76.2**	0.36***	Kawano(1929)
2	Shirataki	75.4**	0.96***	Kawano(1929)
3	Tokachi	76.0	0.63	Taniguchi(1974)
4	Kawasaki	76.1	1.12	Taniguchi(1974)
5	Koshigatake	75.3**	0.79***	Kawano(1929)
6	Kozushima	76.4	0.39	Taniguchi(1974)
7	Wadatoge	77.0**	1.14***	Kawano(1929)

* The silica content on the anhydrous basis.

** The silica content of bulk rock (obsidian).

*** Water content determined in the present experiment.

the bulk rock composition, they are regarded to be nearly equal to the SiO_2 content of glass, since the total amount of crystals in those obsidians are less than 1 vol. %. The SiO_2 content ranges from 75.3 to 77.0 wt. % and the average is 76.1 wt. %. These values indicate that the samples can be regarded as almost identical with each other in the accuracy required for the later discussions. Since the water contents are very important in the later discussion, those of some samples (sample nos. 1, 2, 5, 7) has been reanalysed in the present experiments.

TGA-DTA ANALYSIS

Thermogravimetric analysis (TGA) – differential thermal analysis (DTA) curves were determined by means of a TGA-DTA system of Rigaku Denki (high temperature type) in air with $\alpha\text{-Al}_2\text{O}_3$ as standard material.

Figure 1 shows TGA-DTA curves of the sample of Kozu-shima as an example. Figure 2 is generalized TGA-DTA curves of rhyolitic rock melts. Generally, two types of losses in weight appeared on the TGA curve. The first weight loss appeared in a region of 100°–300°C, and the second in a region of 400°–1100°C. However, some samples gave the TGA curves that kept the weight constant at the temperature range between 900°C and 1000°C.

All DTA curves showed an endothermic peak at a temperature between 450°C and 800°C, and an exothermic peak at about 1200°C. Some DTA curves showed not only the two peaks mentioned above but a weak endothermic peak ranging from 100° to 200° C, and the starting temperature of this peak agreed with that of the first weight loss on the TGA curve. Taniguchi (1972) demonstrated on the basis of the infra-red

Fig. 1. Example of TGA-DTA curves of the rhyolitic rock melt from Kozushima. P_{gt} =glass transformation point. T_g =glass transformation temperature.

Fig. 2. Generalized figure showing TGA-DTA curves of rhyolitic rock melt.

spectral data that the amount of water in volcanic glasses decreased rapidly by heating at 120°C. Consequently, the phenomena which were seen over a temperature range from 100° to 300°C on TGA-DTA curves were due to the evaporation of adsorptive water in the sample. The exothermic peak mentioned above was due to the nucleation of cristobalite.

Tool and Eichlin (1931), Kühne and Skatulla (1959) and Yamamoto *et al.* (1964)

reported that the DTA curve of glass showed an endothermic peak due to the glass transformation. According to their studies, T_g is the starting temperature of the endothermic peak. In the present experiments, the endothermic peak appeared at temperature between 450°C and 800°C is not directly related to the weight loss. In the samples heated up to a temperature between the endothermic peak and the exothermic peak the nucleation of crystal was not observed. The scanning electron microscopical observation ($\times 10,000$) showed that the sample quenched from the temperature of $T_g + 30^\circ\text{C}$ had not any texture which indicated the vesiculation in the sample. By this fact, it was estimated that the peak was not concerned in the separation of vapour phase in the melt. These facts support the conclusion that the endothermic peak which appeared at temperature between 450°C and 800°C was due to the glass transformation.

The weight loss which began at above 400°C was due to the release of constitution

Table 2. T_g and the various water contents determined on the basis of the TGA-DTA curves.

Sample No.	Experimental Condition*	T_g ($^{\circ}\text{C}$)	$\text{H}_2\text{O}(T_g\sim)^{**}$ (wt. %)	$\text{H}_2\text{O}(T_g\sim 950)^{***}$ (wt. %)	$\text{H}_2\text{O}(950\sim)^{****}$ (wt. %)
1	A	694	0.36	0.07	0.29
	B	685	0.32	0.14	0.18
	C	702	0.32	0.12	0.20
	D	680	0.27	0.11	0.16
	E	712	0.22	0.06	0.16
2	A	567	0.93	0.43	0.50
	B	557	0.90	0.48	0.42
	C	538	0.77	0.47	0.30
	D	557	0.82	0.51	0.31
	E	576	0.90	0.40	0.50
3	A	741	0.45	0.01	0.44
	B	746	0.45	0.00	0.45
	C	754	0.45	0.00	0.45
	D	698	0.45	0.07	0.38
	E	723	0.42	0.04	0.38
4	A	580	0.99	0.55	0.44
	B	545	0.99	0.60	0.39
	C	494	0.96	0.65	0.31
	D	551	1.03	0.64	0.39
	E	561	1.04	0.52	0.52
5	A	626	0.76	0.23	0.53
	B	632	0.68	0.27	0.41
	C	658	0.55	0.22	0.33
	D	594	0.72	0.36	0.36
	E	616	0.76	0.22	0.54
6	A	666	0.39	0.07	0.32
	B	672	0.35	0.13	0.22
	C	703	0.33	0.14	0.19
	D	665	0.39	0.16	0.23
	E	683	0.39	0.09	0.30
7	A	573	1.06	0.50	0.56
	B	568	0.96	0.54	0.42
	C	592	0.73	0.41	0.32
	D	546	1.03	0.63	0.40
	E	580	1.08	0.45	0.63

* A=(sample grain size: 48–100 mesh, heating rate: $10^{\circ}\text{C}/\text{min}$), B=(100–150, 10), C=(150–200, 10), D=(48–100, 5), E=(48–100, 20).

** Total water remained at T_g .

*** Water released between T_g and 950°C .

**** Water released at above 950°C .

water judging from the infra-red spectral data by Taniguchi (1972).

In some samples the slopes of the weight losses became steeper at T_g . This fact may be interpreted as follows. The silicate anions in the rock melt begin to dissociate, rotate and translate at T_g during heating, and concomitantly the structure of the melt begins to become loose. These effects promote the dissociation of the constitution water and its easy movement at above T_g . This behavior is in harmony with the idea that the effect of water below T_g is not significant, but an increase in the thermal expansion with addition of water at above T_g is pronounced (Maklad and

Kreidl, 1971).

The increase in weight by the oxidation of ferrous iron in the sample, which were used for the measurements of TGA-DTA curves, were estimated to be less than 0.05 wt. % on the basis of the results of chemical analysis. Since the increase was very small comparing with the weight loss on the TGA curve, the amount of weight loss on the TGA curve is fairly a good approximation of the amount of constitution water released. Then, we can calculate directly the amount of water released at an arbitrary temperature by use of the TGA curve.

The experimental results are sum-

marized in Table 2. The amount of water remained in the sample at T_g was calculated from the chemical composition and the TGA curve.

DISCUSSION

Effect of water on T_g

Structural formulas of water in a glass, which were mainly identified in artificial simple glasses on the basis of infra-red spectral data (Scholze, 1959; Adams, 1961), are illustrated below.

- (1) $\equiv \text{Si-OH}$ free OH
- (2) $\equiv \text{Si-OH}\cdots\text{O} < \text{hydrogen-bonded OH}$
with bridging oxygen
- (3) $\equiv \text{Si-OH}\cdots\text{O} - \text{hydrogen-bonded OH}$
with non-bridging oxygen

Water contained in the volcanic glasses of obsidians are mainly free OH (Taniguchi, 1972). Several authors (Scholze, 1959; Walsh *et al.*, 1956; Burnham and Davies, 1974) demonstrated that the water dissolved in the silicate melts was linearly proportional to the square root of the partial pressure of water, $(P_{\text{H}_2\text{O}})^{1/2}$. Their experimental results indicate the presence of the following reaction between a water molecule and a network structure of the rock melt,

This reaction means that an oxo-bridge is destroyed by a water molecule, and the average degree of polymerization (DP) of silicate anions in the rock melt decreases with increase of water. The degree of polymerization of molecules in an organic polymer solution is inversely proportional to the number of the broken bonds (Gordon, 1963). When compared with this fact, it is assumed that DP of the silicate anions in the rock melt is also inversely proportional to the number of the broken Si-O-Si bonds.

The number of the broken bonds in the rock melt due to the addition of water is a function of the amount of water (Taniguchi, 1974). Then, the following relationship should be valid:

$$DP = K/f(W_{\text{H}_2\text{O}}) \quad (2)$$

where K is a constant, $f(W_{\text{H}_2\text{O}})$ is a monotone increasing function of $W_{\text{H}_2\text{O}}$, the water content. On the other hand, the following relationship exists between the molecular weight and the glass transformation temperature of organic polymer (Haisa, 1967):

$$T_g = T_{g\infty} \cdot (1 - \varepsilon/M_p) \quad (3)$$

where $T_{g\infty}$ and ε are constants, and M_p average molecular weight of polymer.

The relationship between the molecular weight and the degree of polymerization is as follows:

$$M_p = DP \cdot M_m \quad (4)$$

where M_m is the molecular weight of monomer. We assume that the relationship (3) holds for the case of rock melt. Substituting the equations (2) and (4) into the equation (3), we obtain:

$$\begin{aligned} T_g &= T_{g\infty} \{1 - \varepsilon/[K \cdot M_m/f(W_{\text{H}_2\text{O}})]\} \\ &= T_{g\infty} - K' \cdot f(W_{\text{H}_2\text{O}}) \end{aligned} \quad (5)$$

where $K' = \varepsilon \cdot T_{g\infty}/K \cdot M_m$. Since ε , $T_{g\infty}$, K and M_m are positive values, K' is always positive. Then equation (5) indicates that the plot of T_g against the water content gives a straight line or a smooth curve, along which T_g decreases with increase of water.

Interpretation of experimental results

Figure 3 shows the relationship between T_g and the amount of water remained at T_g . Roughly speaking, T_g decreases linearly with increase of the water content, in spite of the difference of the experimental condition. The experimental equation for the relation

Fig. 3. The relationship between T_g and the amount of water remained in the sample at T_g .

obtained by the least squares method is as follows:

$$T_g = 778 - 223W_{H_2O} \quad (6)$$

The equation (6) is in harmony with equation (5). Comparing the equation (6) with (5), we can obtain the following equations.

$$T_{g\infty} = 778^\circ\text{C} \text{ and} \\ f(W_{H_2O}) = (223/K') \cdot W_{H_2O}.$$

The value $T_{g\infty}$, which is T_g of anhydrous melt, is similar to that determined on the basis of the mean specific heat measurement (790°C) for anhydrous rhyolitic glass by Bacon (1977). These results suggested that the two assumptions mentioned previously were valid, i.e., the average degree of polymerization of the silicate anions in the rock melt was inversely related to the amount of water and the equation (3) was held between the average molecular weight

Fig. 4. The relationship between T_g and the amount of water released between T_g and 950°C . Abbreviations are the same as in Fig. 3.

and T_g .

Generally, it is well known that volcanic glasses expand abruptly at about $950^\circ\text{--}1000^\circ\text{C}$ when being heated (Hirosue *et al.*, 1972; Taniguchi, 1974). Figure 4 shows the relationship between T_g and the amount of water released at a temperature range from T_g to 950°C . This water is considered to have the tendency to be released easily from the rock melt at lower temperatures. It is obvious from the comparison of Figs. 3 and 4 that a stronger correlation is observed between T_g and the amount of water in Fig. 4 than in Fig. 3. The correlation determined under other experimental conditions was also excellent. Assuming that the correlation is a quadratic, the experimental equations calculated by the least squares method are shown in Table 3. It is obvious that T_g is affected by the experimental conditions although the quantity

Table 3. Experimental equations for the relations between T_g and the water released between T_g and 950°C.

Sample grain size (mesh)	Heating rate (°C/min)	Experimental equation
48 - 100	10	$T_g = 908W_{H_2O}^2 - 795W_{H_2O} + 744$
100 - 150	10	$T_g = 391W_{H_2O}^2 - 567W_{H_2O} + 749$
150 - 200	10	$T_g = 31W_{H_2O}^2 - 443W_{H_2O} + 758$
48 - 100	5	$T_g = 349W_{H_2O}^2 - 524W_{H_2O} + 738$
48 - 100	20	$T_g = 689W_{H_2O}^2 - 693W_{H_2O} + 742$

of water in the sample is the same. On the other hand, it was difficult to find a definite relation between T_g and the amount of water released at above 950°C (see Table 2). These experimental results indicate that water released between T_g and 950°C has a stronger effect on T_g than total water remained at T_g or water released at above 950°C.

Taniguchi (1972) demonstrated that the infra-red absorption peak in the region of 3450 cm^{-1} due to the presence of water shifted to the higher wave number with increasing temperature in heat treatments of the volcanic glass. Generally speaking, the relation between the wave number (ν) and the force constant (f) of the stretching vibration of a diatomic molecule is formulated as follows:

$$\nu = (1/2\pi c) \cdot (f/\mu)^{1/2} \quad (7)$$

where c =light velocity and μ =reduced mass.

As is obvious from the equation, the wave number increases with an increase of the force constant. Consequently, water released at lower temperature had smaller force constant. The water might dissociate easily from the network at low temperature, moved through the network and then destroyed the Si-O-Si bonds by the collision with the bonds. These phenomena may have an effect on decreasing T_g . On the other hand, since water released at above 950°C had a large force constant, the water

could not dissociate at low temperature and could have only a small effect upon T_g .

SUMMARY AND CONCLUSIONS

In the present experiments, the glass transformation temperature of rhyolitic rock melts has been studied in connection with water contents on the basis of the TGA-DTA, and we can draw the following conclusion.

(1) T_g of the rhyolitic rock melt was influenced considerably by water in the melt.

(2) T_g ranged from 490° to 760°C in the present experiments, and decreased linearly with increase of water (< 1.1 wt. %) in the melt at T_g . The experimental equation for the relation is $T_g = 778 - 223W_{H_2O}$.

(3) The average degree of polymerization of silicate anions in the rock melt may be inversely proportional to the amount of water.

(4) The equation $T_g = T_{g\infty} \cdot (1 - \varepsilon/M_p)$ may be useful to the relation between the average molecular weight of silicate anions in the rock melt and T_g .

(5) The stronger correlation was observed between T_g and the water released between T_g and 950°C than that between T_g and total water remained at T_g or water released at above 950°C.

(6) Since the water released at lower temperatures ($T_g \sim 950^\circ\text{C}$) had the smaller force constant of OH bonding, it dissociated easily from the network structure at lower temperatures, destroying the Si-O-Si bonds.

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流紋岩質岩石溶融体のガラス転移温度に及ぼす水の影響

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流紋岩質火山ガラスを試料にして熱分析 (TGA-DTA) を行い、ガラス転移温度 (T_g) を決定した。全ての DTA 曲線は $490^{\circ}\sim 760^{\circ}\text{C}$ の範囲内にガラス転移による吸熱ピークを示した。 T_g は T_g において試料内に残留する水の量に逆比例する。この事は水によってメルト内の珪酸陰イオンの平均重合度が減少する事を意味している。又、 T_g と $T_g\sim 950^{\circ}\text{C}$ の間に系外に放出される水の量との相関は、 T_g 以上ないし 950°C 以上で放出されるものに比べ極めて良い。この事はメルト構造における水の力の定数の違いによって説明される。すなわち定数の小さな水はより低温においてメルト構造から解離し、熱運動を行いつつ系外に向って拡散し酸素橋を破壊する。その為に T_g は低下する。