Low-temperature thermal effects in natural volcanic glasses due to strain.

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Summary. Sharp exothermic peaks occurring at about 90° C during D.T.A. treatment of natural volcanic glasses are described and are shown to be due to release of external strain. This is probably triggered by loss of surface water. No systematic variation in strain could be found in glass of different geological histories, but strain is found to decrease during natural weathering of volcanic glasses. Differences in weatherability of natural glasses may be related to degree of surface strain.

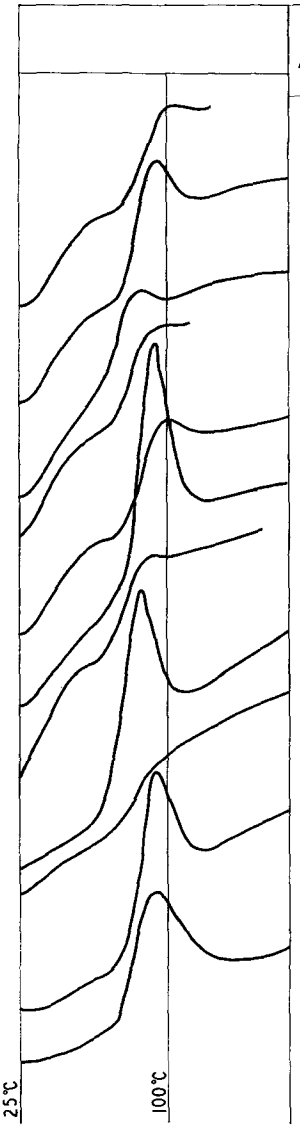
DURING the course of a petrological investigation of a series of recent (A.D. 150 to 8000 B.C.) volcanic ash showers from the central North Island of New Zealand, it was found desirable to assess the degree of weathering of the shower materials (essentially rhyolitic pumice). These varied from fresh pumice to samples showing considerable hydrous alteration. It was found possible to correlate stages of weathering with quantitative measurements of water loss, and differential thermal analysis (D.T.A.) of high sensitivity was used to identify the nature of the water loss. Almost all the samples showed, during heating, sharp exothermic peaks at between 80° and 90° C. The cause of such peaks was not obvious and there appears to be no account of them in the literature. An account of their nature and a tentative interpretation in terms of strain are therefore given below.

The twelve samples used are listed in table I, together with their localities and their approximate ages. The differential thermal analysis equipment employed for most of the work was of the type described by Berkelhamer (1944), with stainless steel sample-block, ignited Al_2O_3 as reference material, heating rate of approximately 10° C per minute, and chromel-alumel differential thermocouples used with a sensitive recording galvanometer.

TABLE I. Nature, locality, and approximate ages of samples. Numbers are those used by Baumgart (1954) and Healy (1962), and refer to the stratigraphical position of the showers within the Taupo Ash Sequence. The map references refer to the North Island 1 mile to the inch series of topographical maps.

Sample.	Thickness where collected.	Locality.	Approximate age (years B.P.).
Ash fall deposits			
Member 5	8 in.	N 94·589347, 2 miles SE. of Taupo	< 2100
Member 7	7 in.	,,	1900
Member 14C	2 in.	,,	3100
Waimihia (*a*) member (15)	19 in.	,,	3400
Member 24B	4 in.	,,	> 8850
Waimihia (*b*) member (15)	12 in.	N 94·560439, 4 miles N. of Taupo	3400
Kaharoa Ash	2 ft	N 86·955868	800
Pumice breccia deposits			
Rhyolite Block member (2)	14 in.	N 94·589347, 2 miles SE. of Taupo	1800
Waitahanui Breccia	> 100 ft	East shore of L. Taupo between Waitahanui and Hinemaiai rivers	3150
Obsidian			
Inclusion in Shower 14A	—	N 94·589347, 2 miles SE. of Taupo	3100
Inclusion in Shower 16	—	,,	> 3400
Ignimbrite glass			
Basal zone of 700 ft sheet	—	N 57·367519, near Matamata	Pliocene-Pleistocene

Possible causes of low temperature exothermic effect. Possible explanations of the exothermic peak included low-temperature oxidation, devitrification or crystallization, and release of strains in the glass. Silicate analysis, however, showed that no easily oxidizable material was present, and furthermore, preliminary D.T.A. patterns showed that the effect persisted under some conditions after the samples had been ignited at 700° C. Further, X-ray powder diffraction patterns of heated samples showed no evidence of any crystalline phase. These results seem to exclude oxidation or crystallization as an explanation, but release of strains in the glass seemed a possible cause and it was tested in the first place as follows.



RUN NUMBER	PREVIOUS THERMAL TREATMENT OF SAMPLE		
	TEMPERATURE HEATED TO	TEMPERATURE COOLED FROM	COOLING RATE
11	560	560	SLOW
10	330	330	RAPID
9	123	123	RAPID
8	450	450	SLOW
7	330	330	SLOW
6	230	180*	RAPID
5	710	710	SLOW
4	750	480*	RAPID
3	640	640	SLOW
2	500	452*	RAPID
1	UNTREATED SAMPLE		

FIG. 1. D.T.A. records of a sample of crushed Waimihia (*a*) pumice that had undergone a succession of heating and cooling cycles. The cooling was done in two ways, slowly by allowing the sample to cool naturally in the furnace, and rapidly by withdrawing the sample from the furnace. Asterisks indicate that the sample was cooled slowly to the temperature indicated, and then allowed to cool rapidly to room temperature.

Effects of heat on crushed samples. A sample of crushed (< 60 mesh) Waimihia pumice (Healy, 1962) was placed in the apparatus and subjected to a series of heating and cooling cycles, these being recorded as D.T.A. patterns. The cooling was done in either of two ways: either rapidly, by withdrawing the sample from the furnace and allowing to cool in the air, or slowly, by allowing the sample to cool naturally in the furnace, this taking approximately 6 hours from 500° C to room temperature. The sample itself was not touched at any stage during this first experiment. Results are shown in fig. 1 from which the following four deductions may be made: the intensity of the peak can be reduced after slow cooling, and can be reintroduced after rapid cooling; the peak can only be reduced to a minimum after slow cooling from a temperature of about 640° C (see run 3, fig. 1); the peak can be reintroduced by rapid cooling from a temperature as low as approximately 180° C (see run 6, fig. 1); and the peak occurs immediately following the endothermic peak due to loss of loosely absorbed surface water (about 60° C).

The above results appear to support the possibility that the exothermic effect in the crushed samples is caused by release of strains induced in the glass during rapid cooling. Ross and Smith (1955), however, have shown that strain is induced through the natural hydration of volcanic glasses (as in the formation of perlite from obsidian), and it is possible that much of the effect found in natural glasses is due to this.

In the second phase of the work, larger samples of crushed Waimihia pumice were heated in a separate furnace before obtaining D.T.A. patterns. Samples treated in this way were heated more slowly and held at a high temperature for longer periods than was the case during D.T.A. treatment. Fig. 2 shows the D.T.A. records of a sample (*a*) that had been heated at 500° C for about 20 hours and cooled to air temperature slowly (approximately 17 hours); of a sample (*b*) briefly heated to 500° C and slowly cooled to air temperature over a period of 5 hours; and of a sample (*c*) briefly heated to 620° C and rapidly cooled. It will be seen that the upward drift in patterns (*b*) and (*c*) does not appear in the case of sample (*a*), which had undergone the prolonged heating. Similar reduction in drift after prolonged heating was shown by five additional samples. The drift in samples (*b*) and (*c*) is tentatively interpreted as due to energy of internal strain in the glass being released at an increasing rate with increasing temperature. On this basis, the absence of drift in sample (*a*) would be interpreted as due to the release of strain during the prolonged heating, a process of annealing. It was thought that rapid air and water quenching of samples after prolonged

heating at 500° C would induce considerable strains. Fragmentation of the glass, however, occurred, with release of strains.

From fig. 2 it appears initially that the magnitude of the peak in sample (*a*) is comparable with that in sample (*c*). Careful consideration, however, shows that increased drift in the record of sample (*c*) tends to

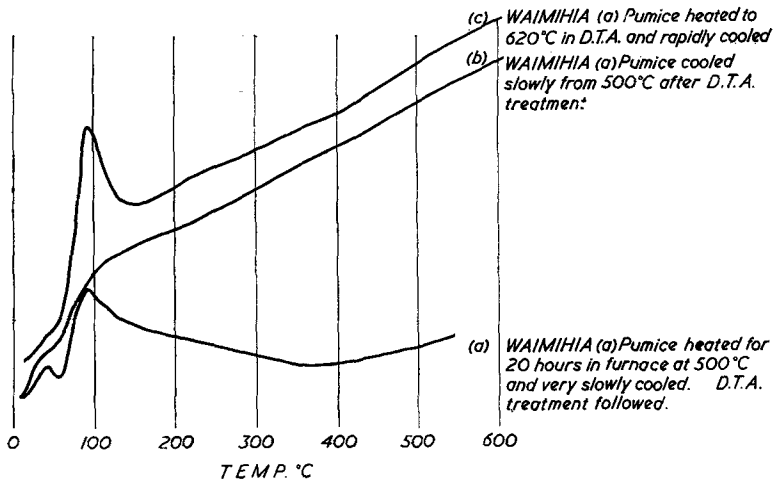


FIG. 2. D.T.A. records of crushed Waimihia (*a*) pumice that has undergone different heat treatments. Record (*a*) indicates a greatly reduced background drift after the sample had been heated for 20 hours at 500° C prior to D.T.A. treatment.

give a reduced impression of the magnitude of its peaks, and on measurement of peak heights it is found that the value of the peak of sample (*a*) is less than half that of sample (*c*).

Effect of crushing sample. As these experiments were performed on crushed samples, it was desirable to ascertain the effects of the crushing. This was done by using solid pumice fragments, the sample thermocouple being threaded through the centre of the fragment along a very small drillhole. A Gallenkamp furnace was used for these runs. It was found that the 80 to 90° C peak was magnified some fourfold, and it was impossible to reduce this peak through slow cooling; this is attributed to the geometrical form of the vesicles in which the external stress would be developed. It seems that in the case of a cavity, stress induced on the inside surface by cooling would be difficult to dissipate and thus would be largely reversible during heating and cooling cycles. The corresponding endothermic effect expected during cooling has not yet been

looked for because of the greater difficulty of obtaining controlled cooling rates of the samples. It is clear, however, that the exothermic effect was not produced by crushing.

Because of the above results it was considered desirable to investigate the presence and extent of strain in glasses with different geological histories and in glasses at various stages of weathering.

Evidence of strain in glasses

Glasses with different geological histories. In fig. 3 are shown D.T.A. patterns of two obsidians occurring as accessory inclusions within the Taupo ash showers and an ignimbrite glass from the base of the ignimbrite sheet, Matamata, New Zealand. Comparing the patterns of these with the crushed pumice of fig. 1, and the samples of ash shower and pumice breccia material in fig. 4, two points of interest emerge: the very high background drift; and the lack of a well-defined 80° to 90° exothermic peak, although, as previously discussed, this could be due to the high drift. Neither obsidian nor ignimbrite glasses contain internal vesicles; they thus have a small surface area compared with the pumice type of glass, so that high surface strain would not be expected. The high drift in these glasses was tentatively interpreted as due to internal strain, but when the samples were heated at 500° C or 900° C for 20 hours each, followed by very slow cooling, the subsequent D.T.A. patterns were identical with those of the untreated samples, with no reduction of drift. It was concluded from this that the high drift in these samples was due to the larger effective particle-size, which was responsible for a higher rate of heat conduction to the thermocouple in the sample than to that in the reference material. Thus drift is not a sign of internal strain unless it can be reduced by annealing.

Glasses with varying degrees of weathering. D.T.A. records of fine fractions ($\frac{1}{2}$–$\frac{1}{16}$ mm) from selected pumice beds are shown in fig. 4. These show a sequence of successive degrees of weathering in the glasses, the least altered being two pumice breccias of glowing-avalanche origin. The remainder are true ash showers.

The onset of weathering is indicated by a slight endothermic effect near 500° C (incipient kaolin), this becoming more pronounced in the most advanced stages of weathering, and being due unmistakably to halloysite. In the three most hydrated stages the endothermic peaks near 110° C due to halloysite also increase in intensity with increased weathering. From fig. 4 it can be seen that, in a general way, the inten-

sity of the 80° to 90° C exothermic peak decreases with increased weathering. The two patterns of showers 24 and Waimihia both show distinct 90° C exothermic peaks within the broader endothermic reaction,

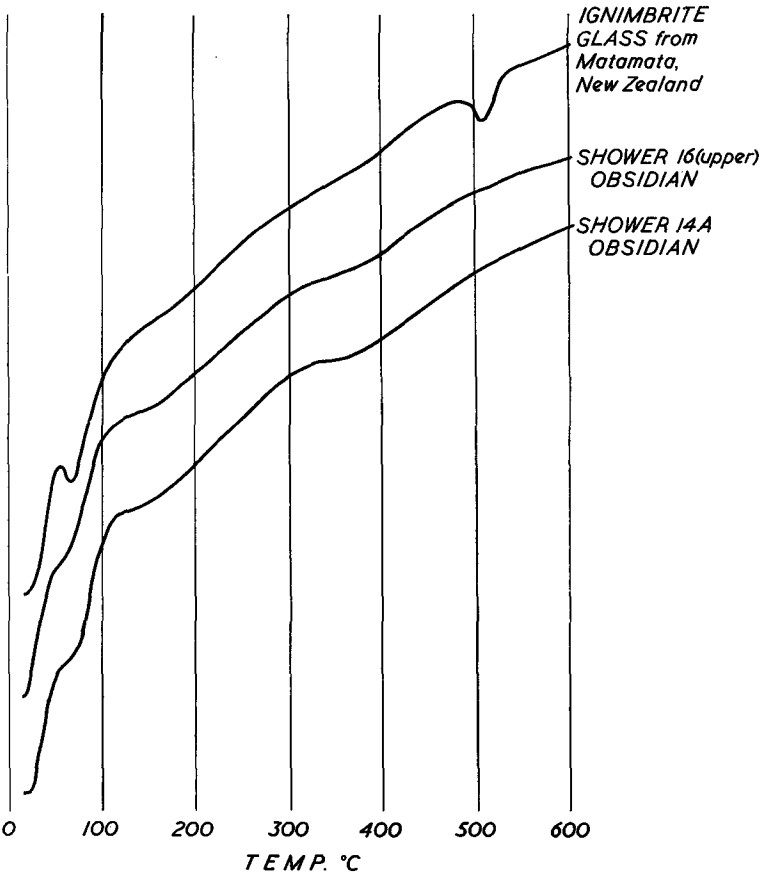


FIG. 3. D.T.A. records of two obsidians and an ignimbrite glass. The high background drift could not be reduced by prolonged heating prior to D.T.A. treatment. The low temperature exothermic peaks are not strongly developed.

and this is here interpreted as residual external strain. The most intensely weathered specimen (shower 26) shows no evidence of residual strain. A further point of interest noted during this study is that the glass from the finer fractions of the showers has a considerably smaller development

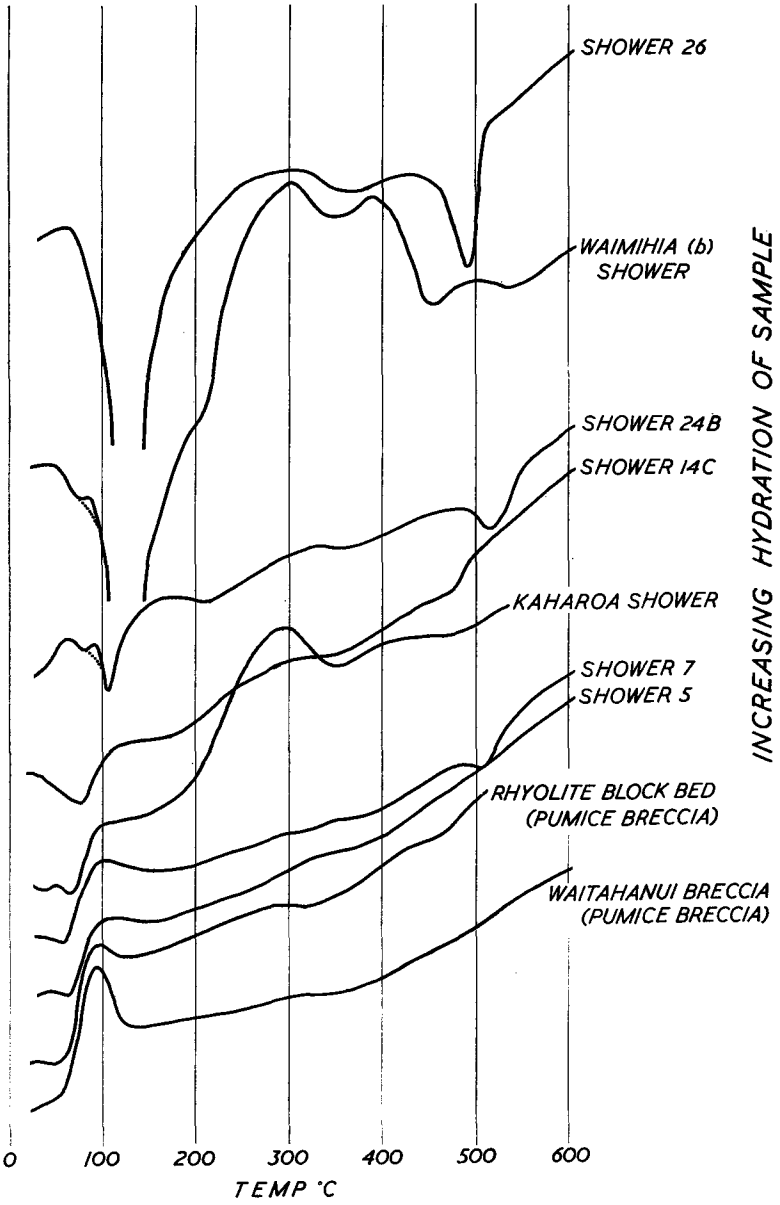


FIG. 4. D.T.A. records of a series of natural glasses at different stages of weathering. There is a gradual reduction of the 90° C exothermic peak with increased weathering.

of external strain than the glass from the corresponding coarser fractions. This is believed to be due to the glass from the finer fractions having undergone more complete hydration during weathering than the larger glass fragments.

Significance of strain in natural glasses. The data described give an explanation of the exothermic effects in D.T.A. patterns of samples containing volcanic glass. If, as seems likely, natural glasses have different degrees of strain according to their conditions of cooling, this could result in different rates of weathering.

One problem, repeatedly encountered in a study of ash deposits and the soils containing them, is that unweathered glassy material sometimes occurs in the presence of other minerals showing a relatively advanced stage of weathering, and under conditions where glass of similar composition is usually weathered to secondary hydrated minerals. It seems probable that unstrained glass would have considerably more resistance to weathering than strained glasses. The latter would be subject to attack in areas of strain in a manner resembling strain-accelerated corrosion of metals.

Conclusions.

From these experiments we conclude that:

On heating volcanic glasses there is evidence of a sharp exothermic reaction due to release of external strain, and a gradual exothermic reaction due to the slow release of internal strain.

Release of external strain is apparently triggered by loss of surface water.

External strain decreases as weathering increases.

Vesicular glasses tend to have a high external and relatively low internal strain.

As external strain is related to surface water adsorption, it has significance in weathering mechanisms.

Zones of weakness in glass caused by strain would be more readily attacked than unstrained glass in a manner somewhat resembling stress-corrosion of metals.

Different degrees of strain may explain great differences in weatherability in natural glasses in soils, these differences apparently being unrelated to composition.

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