Heat capacity of hydrous basaltic glasses and liquids

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ABSTRACT

We determined the heat capacities of four series of glasses and liquids of basaltic and basaltic andesite compositions from remelted volcanic rock samples and Fe-free synthetic analogues. The samples are low-alkali, Ca- and Mg-rich aluminosilicates with non-bridging oxygen to tetrahedrally-coordinated cation ratios (NBO/T) ranging between 0.33 and 0.67. Differential scanning calorimetry measurements were performed at atmospheric pressure between room temperature and ~100 K above the glass transition for hydrous samples and up to ~1800 K for dry samples. The water contents investigated range up to 5.34 wt.% (16.4 mol%). Water does not measurably affect the heat capacity of glasses. We derived a new value of the partial molar heat capacity of water in silicate glasses of $\overline{C}_{P,H_2O}^{glass} = 82.804 + 10^{-3}\ T - 48.274 \times 10^{-5}\ T^{-2}$ (J/mol K) using our new data in combination with literature data on more and less polymerized compositions. The increase in heat capacity at the glass transition is of the order of ~30–40% and generally increases with increasing water content. The onset of the glass transition in hydrous samples occurs below the Dulong–Petit limit of 3R/g atom. The configurational heat capacity, i.e., the magnitude of the change in heat capacity observed at the glass transition, generally increases as polymerization decreases and as water content increases. We obtained a partial molar heat capacity of water in silicate liquids of basaltic composition of ~86 J/mol K. This value is comparable to the partial molar values for the major oxides which range from ~79 to 230 J/mol K. The partial molar heat capacity of water in silicate liquids appears to be compositionally-dependent, increasing as melt polymerization decreases. Such a dependence is certainly linked to the speciation and structural roles of water in complex silicate melts, however, a single value of ~93 J/mol K could reproduce the heat capacity of hydrous liquids of a wide range of NBO/T (0–1.51) at temperatures up to ~100 K above the glass transition and water contents of 0–3.76 wt.% with a root-mean square deviation of only 3.23 J/mol K.

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1. Introduction

Water is present to some degree in all glasses, whether man-made or naturally-occurring. It is particularly important in geologic glasses formed by rapid cooling of lava at volcanic arcs, where water gets released by dehydration of hydrous minerals into the overlying mantle wedge during the subduction of oceanic plates, triggering melting and production of hydrous basalt. Water contents can be up to 6 wt.% or more [1]. Quantifying the effects of water on the physical and thermodynamic properties of the hydrous magmas produced at arcs is required in order to accurately model magmatic and volcanic processes.

There are very few data on the heat capacity of hydrous aluminosilicate glasses and liquids [2–5], and thus the compositional dependence of heat capacity and the effects of water speciation on heat capacity are

not well understood. Water is known to lower the glass transition temperature dramatically in silicate systems, a dynamic transition readily observable as a discontinuity in heat capacity.

Two previous studies investigated the effect of water on heat capacity for geologically-relevant, multi-component compositions. Polymerized compositions, with non-bridging oxygen to tetrahedrally-coordinated cation ratios (NBO/T) ranging from 0 to 0.21, were studied by Bouhifd et al. [2] and Bouhifd et al. [3] studied two highly depolymerized compositions with NBO/T ratios of 0.86 and 1.51. Bouhifd et al. [2] determined the partial molar heat capacity of water in polymerized glasses to be independent of composition and to be well described by a single expression of the Maier–Kelley form for all water contents investigated. The partial molar heat capacity of water in glass therefore seems to also be independent of water speciation in the glass above room temperature. They later used the same expression to describe the partial molar heat capacity of water in highly depolymerized glasses [3]. In all cases, they observed that water depresses the temperature of the glass transition and increases the

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configurational heat capacity at the glass transition relative to dry compositions.

Here we report new measurements of the heat capacity of hydrous basaltic glasses and liquids which are important magmatic compositions in the Earth's mantle and crust, to test whether the partial molar heat capacity of water is really independent of silicate composition, at least for complex, multicomponent materials. We show that water has a negligible effect on the heat capacity of glasses, but measurable effects on the configurational heat capacity, on the glass transition, and on the heat capacity of liquids, which appear to depend on the melt polymerization.

2. Experimental methods

2.1. Sample synthesis and characterization

The anhydrous glasses were obtained via two methods. Two crystal-rich lava samples were collected on Fuego volcano, Guatemala, crushed and melted at 1500 °C, quenched to a glass, then crushed and remelted again two more times to obtain homogeneous glasses. Fe-free analogues to a natural basalt from Fuego volcano and a natural basaltic andesite from Pacaya volcano, also in Guatemala, were obtained by reproducing the whole-rock compositions of samples GU-4-309 (basalt) and VP743 (basaltic andesite) compiled in the Central American Geochemistry database [6]. Oxide and carbonate powders were mixed in the appropriate proportions but all the Fe (calculated as FeO) was replaced by MgO on a molar basis to conserve the NBO/T of the original natural composition. The powders were mixed in acetone, the acetone burned off, then the mixtures were decarbonated by heating slowly to 1200 °C. After decarbonation, the mixtures were melted at 1500 °C in Pt crucibles, quenched to a glass, then crushed and remelted again two times two ensure homogenization. Sample compositions are reported in Table 1 and compared with literature samples in Fig. 1. The basaltic and basaltic andesite samples in this study have greater M^{2+}/M^{+} ratios than previously studied samples [2,3]. Previously studied samples include polymerized albite, granite, phonolite, and trachyte (NBO/T of 0, 0, 0.19, and 0.21, respectively), and highly depolymerized tephrite and foidite (NBO/T of 0.86 and 1.51, respectively). The basalt and basaltic
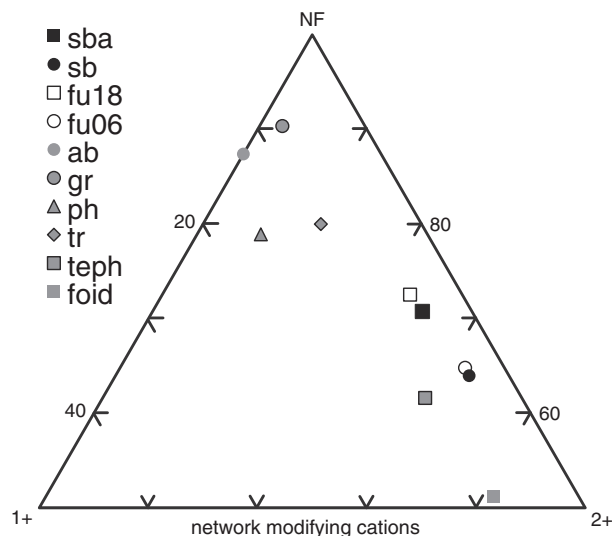

Fig. 1. Comparison of the sample compositions in this study with literature samples from Bouhifd et al. [2,3]; ab: albite, gr: dk89, ph: phonolite, tr: trachyte, teph: tephrite, foid: foidite. Proportions of network formers ($SiO_2 + Al_2O_3 + TiO_2$) and network modifiers ($2+$: MgO + FeO + CaO) or charge balancers ($1+$: $Na_2O + K_2O$) in moles. Note that the $1+$ and $2+$ axes are truncated at 50.

andesite samples in this study are moderately depolymerized, with NBO/T ratios of 0.33 for the natural basaltic andesite fu18, 0.64 for the natural basalt fu06, and of 0.40 for sba, and 0.67 for sb.

Table 1
Compositions (wt.%) of the samples used in this study.

Sample	sba	sb	fu18	fu06
Description	Synthetic	Synthetic	Fuego	Fuego
	Basaltic andesite	Basalt	Basaltic andesite	Basalt
SiO_2	54.42(0.35)	51.46(0.35)	53.08(0.41)	49.40(0.50)
TiO_2	1.37(0.06)	1.16(0.06)	0.88(0.05)	0.96(0.05)
Al_2O_3	20.49(0.23)	18.62(0.92)	20.42(0.30)	17.57(0.21)
FeO_{total}	<d.l.	<d.l.	7.50(0.26)	10.56(0.38)
MnO	<d.l.	<d.l.	<d.l.	<d.l.
MgO	8.40(0.18)	14.87(0.60)	3.21(0.09)	7.46(0.16)
CaO	10.39(0.29)	9.33(0.24)	8.94(0.19)	8.97(0.21)
Na_2O	3.76(0.17)	3.28(0.36)	3.93(0.21)	3.10(0.25)
K_2O	1.06(0.05)	0.71(0.04)	0.83(0.05)	0.60(0.05)
P_2O_5			0.20(0.08)	0.16(0.07)
Total	99.90	99.44	98.99	98.79
NBO/T	0.40	0.67	0.33	0.64
AE/A[a]	5.47	8.85	3.31	6.13
A/NM[b]	0.15	0.10	0.23	0.14
Al/Si[c]	0.44	0.43	0.45	0.42
Fe^{2+}/Fe_{total}[d]			0.48	0.46
gfw (g)[e]	62.84	60.28	65.48	63.48
n[f]	3.005	2.897	3.042	2.908

Standard deviation on 30 measurements in parentheses.
[a] AE = MgO + CaO and A = $Na_2O + K_2O$ in mole percent.
[b] NM = A + AE in mole percent.
[c] Al/Si in cation units.
[d] Value for dry starting glasses.
[e] Gram formula weight for 1 mole of oxides, assuming 0.01 wt.% H_2O.
[f] Number of atoms per gram formula weight.

Table 2
Sample characterization.

Sample	Core	gfw[a] g	n[b]	H_2O wt.%[c]	H_2O mol%[c]	Weight mg	ρ[d] kg/m³
sba dry		62.83	3.005	0.01	0.03	25.24	2608(1)
sba-10	Top	62.07	3.005	0.50(19)	1.72(65)	24.79	2624(1)
sba-11	Calorimetry	61.39	3.005	0.95(19)	3.24(65)	36.95	2618(2)
sba-04	Calorimetry	59.86	3.005	2.00(17)	6.64(63)	31.17	2619(1)[e]
sba-03	Calorimetry	58.59	3.005	2.92(19)	9.49(62)	23.21	2600(2)[e]
sba-07	Calorimetry	57.47	3.005	3.76(27)	11.99(86)	41.97	2557(2)
sba-08	Top	56.10	3.004	4.83(17)	15.04(53)	25.62	2534(1)
sba-13	Center	55.47	3.004	5.34(17)	16.44(52)	23.95	2541(1)
sb dry		60.27	2.897	0.01	0.03	37.48	2675(1)
sb-11	Calorimetry	59.40	2.899	0.63(16)	2.08(53)	38.14	2691(1)
sb-12	Calorimetry	58.48	2.901	1.31(16)	4.25(52)	32.20	2680(2)
sb-16	Calorimetry	57.60	2.903	1.98(15)	6.33(48)	38.43	2655(1)
sb-14	Calorimetry	56.29	2.907	3.02(16)	9.43(50)	47.96	2633(1)
sb-18	Bottom	55.40	2.909	3.76(16)	11.56(49)	14.80	2614(1)
sb-17	Bottom	54.35	2.911	4.65(16)	14.03(48)	23.78	2593(1)
fu18 dry		65.46	3.042	0.01	0.04	31.66	2655(1)
fu18-04	Calorimetry	63.86	3.040	0.96(15)	3.40(53)	35.33	2654(2)
fu18-03	Calorimetry	63.36	3.040	1.27(16)	4.47(56)	34.02	2652(2)
fu18-07	Calorimetry	63.08	3.039	1.44(14)	5.04(49)	26.70	2652(1)
fu18-01	Calorimetry	62.03	3.039	2.11(16)	7.26(55)	31.97	2634(1)
fu18-09	Calorimetry	60.68	3.037	3.00(16)	10.10(54)	35.76	2622(3)
fu18-02	Calorimetry	60.61	3.037	3.05(16)	10.26(54)	32.67	2613(2)
fu18-05	Top	59.17	3.036	4.05(16)	13.30(53)	27.87	2592(1)
fu18-08	Calorimetry	58.11	3.035	4.81(17)	15.51(55)	49.42	2578(1)
fu06 dry		63.46	2.908	0.01	0.04	29.49	2766(2)
fu06-07	Calorimetry	61.64	2.912	1.18(16)	4.04(55)	29.21	2762(1)
fu06-06	Calorimetry	61.25	2.913	1.44(16)	4.89(54)	40.66	2760(2)
fu06-03	Calorimetry	60.01	2.915	2.29(16)	7.63(53)	22.32	2741(2)
fu06-04	Calorimetry	59.43	2.916	2.70(15)	8.90(49)	20.50	2687(2)
fu06-05	Calorimetry	58.89	2.918	3.09(16)	10.10(52)	29.55	2739(4)
fu06-10	Calorimetry	58.87	2.918	3.10(20)	10.13(65)	34.21	2741(2)

[a] Gram formula weight for 1 mole of oxides.
[b] Number of atoms per gram formula weight.
[c] Uncertainty on water content in parentheses (last two significant figures).
[d] Density of compacted samples in the case of hydrous samples. Standard deviation on 5 density measurements in parentheses.
[e] Samples synthesized at 5 kbar. All other hydrous samples synthesized at 3 kbar.