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EVIDENCE FOR A TEKTO-SILICATE STRUCTURE AND DOMINANCE OF Fe(III) OVER Fe(II) IN SILICIC VOLCANIC GLASSES OF THE NEVADA TEST SITE

R. G. Warren

More than 400 individual analyses have been obtained by electron microprobe for silicic glasses in 58 samples of tuff and lava from the Nevada Test Site (NTS). These samples comprise a wide range in chemical and petrographic types, including calc-alkaline and peralkaline rock types, and include most of the volcanic units of the NTS.¹ Locations and brief petrographic descriptions are given for representative samples in Table 1.

Analytical Procedure

Each sample was examined under the petrographic microscope and areas most suitable for microprobe analysis of glasses were selected. All such areas must be free of alteration, dust, and microlitic inclusions within a 40 x 40 micron area. Several types of glass fragments may be present in each tuff sample, including small glass shards, pumice fragments, and large, rounded or angular glass fragments (perlite); several fragments of each type present were analyzed in each sample. Each analysis was performed using a 40 x 40 micron raster with a beam current of 10 nanoamps. Under such conditions, consecutive analyses of the same area indicated negligible sodium loss. In some samples, such areas as large as 40 x 40 microns may not exist, and it is necessary to analyze using a 10 x 10 micron raster, constantly moving the sample beneath the beam. Such analyses are possible only for the often highly elongate walls of pumice tubes, which allow movement for hundreds of microns in a single direction. Even under such conditions, a small, but consistent loss of sodium is evident and such analyses should be avoided, if possible. Feldspar standards were utilized for Na, K, Ca, Ba, Si, and Al analyses, ilmenite for Mn, and a clinopyroxene for Mg, Fe, and Ti. All analyses are corrected for differential matrix effects.³

Results

Analytical totals for the 99 sets of averaged analyses from the 58 samples range from 89.7 to 98.1%. SiO₂ contents (uncorrected for H₂O content) range from 65.8 to 75.8%. Representative analyses are shown in Table 2. In Table 3, elemental concentrations are represented as the number of molecules per 24 oxygens. For all samples, within the expected limits of analytical accuracy, the following relationships are found for the molecular concentrations:

$$[O] = 2[Si + Ti + Al + Fe]$$

$$[Al+Fe] = [Na + K + 2(Ca + Ba + Mn)]$$

Median values and their standard deviations for the elemental sums above are listed in Table 4.

Discussion and Conclusions

The above molecular relationships are valid throughout a wide range in glass type and chemistry (Tables 2 and 3) as well as rock type (Table 1), and apparently define a general relationship for natural glasses of silicic composition. This relationship is explained most simply by postulating a tectosilicate structure for such glasses in which Si, Ti, Al, and Fe(III) occupy 4-coordinate (network forming) sites. Occupancy of such sites by Al and Fe(III) produces a negative charge that is exactly balanced by the total positive charge of Na, K, Ca, Ba, and Mn, which occupy higher coordinate (network modifying) sites. It should be noted that if Fe is calculated as Fe(II) it cannot appear in the first equation and would appear on the right-hand side of the second equation because Fe(II) cannot reasonably be assigned to the 4-coordinate site. Certainly, the lowest analytical totals (see Table 2) result from relatively high water contents. However, the molecular relationships are not affected by low totals and so it is clear that water does not greatly modify the glass structure, even though much of the water may be structurally bound, as in zeolites.

Laboratory studies of glasses from binary and multicomponent systems are consistent with the structural relationships hypothesized above. Infinitely branched silicates occur in binary mixtures of SiO_2 and oxides of a network modifying cation (such as Na_2O , K_2O , CaO , etc) when the mole fraction of SiO_2 exceeds 0.44.⁴ A pronounced viscosity maximum at $\text{Al/Na}=1$ was found for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, independent of SiO_2 concentration.⁵ This was attributed to existence of a network structure. Recent Mössbauer studies have shown that Fe (III) occupies a 4-coordinate site.⁶

The existence of a well-defined structure for natural silicic glasses is of great importance for three reasons:

(1) The relationships among elements defined by the structure provides the microprobe analyst with a measure of the quality of natural silicic glass analyses. Due to absorption of variable amounts of water, the analytical total does not provide such a measure.

(2) Earlier NIS workers have concluded that Si has been leached by groundwater from glasses of most NIS volcanic rocks, and therefore glass compositions have been substantially modified from magmatic compositions.^{7,8} These conclusions are invalid because they are based on whole rock chemical analyses of glassy tuffs, which contain ash that differs chemically from shards and other glass fragments.⁹ However, it is possible that magma might contain excess Na and K, which are subsequently lost from glass during secondary hydration. The additional, non-bridging oxygen required in a structure containing excess Na and K would be replaced by two hydroxyl groups upon hydration. Such

alteration, however, would not affect elements that occupy 4-coordinate sites and concentrations of such elements in the glass would reflect magma chemistry.

(3) Clearly, the tendency for glasses to form a tektosilicate structure is very strong. Rocks that have chemical compositions represented almost entirely by tektosilicate normative components (albite, orthoclase, and quartz) are very abundant; their compositions define the "granite minimum". If natural silicic glasses indeed represent unaltered, quenched magmas, then it is probable that the structure of the silicate liquid plays a major role in guiding the evolution of silicate magmas towards the "granite minimum".

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TABLE 1.--Locations and condensed petrographic descriptions for representative samples of NIS volcanic rocks.

Sample	Sample type ^a	Nevada State Coordinates(ft)		USGS ^b quad	Unit symbol ^c	Rock type ^d	Alteration ^e	% phenocrysts	
		N	E					felsic ^f	mafic ^g
Rw19w-1	O	902610	606630	AT	TMR1	nwt	Gl	15	0.07 (Biot)
Ue19p-1261	C	912382	598307	DHF	TPCu	nwt	Gl	3.1	0.13 (Biot>Cpx>Hbld)
Ue19p-1461	C	912382	598307	DHF	TRPP	l	Gl	11	0.35 (Biot>>Cpx)
Rw18a-5	O	887850	619510	AT	TRAU2	b	Gl	17	4.7 (Biot>Hbld>>Opx)
Ue19p-1790	C	912382	598307	DHF	TRAM	b	Gl	2.6	0.06 (Cpx>Hbld>Opx)
U19ab-1930-1940	da	911400	599378	DHF	TRAM	b	Zc, mGl	4.3	0.03 (Hbld>Biot)
TTR-2	O	876600	488790	TC	TTT	vt	Gl, μ Gr	15	0.56 (Cpx>Biot>Hbld)
Rw18a-3	O	892040	614370	AT	TBG	b	Gl, mZc	0.00	0.00

a) O = outcrop, C = core, da = drill cuttings that are representative of unit.

b) AT = Ammonia Tanks 7.5', DHF = Dead Horse Flat 7.5', TC = Thirsty Canyon 15'.

c) Symbols are for petrologic units of Warren.

d) b = bedded tuff, t = ash-flow tuff (nw = nonwelded, mw = moderately welded, v = vitrophyric), l = lava.

e) Gl = vitric, Zc = zeolitic (clinoptilolite), μ Gr = microgranophyric, "m" indicates a minor amount of the indicated component.

f) Felsic phenocrysts are quartz, sanidine, anorthoclase, and plagioclase.

g) Mafic phenocrysts are biotite (Biot), hornblende (Hbld), clinopyroxene (Cpx), orthopyroxene (Opx), and olivine (Ol), present in the indicated relative concentrations.

TABLE 2.--Electron microprobe analyses of glass in representative samples of NTS volcanic rocks, weight per cent basis. (All n analyses of a particular glass type are averaged. Glass types are: s = shard, pu = pumice, pe = perlite, l = lava.)

Sample	n	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	BaO	Na ₂ O	K ₂ O	Total
RW1Sw-1	3s	74.5	0.11	11.7	0.57		0.00	0.16	0.00	3.69	5.25	96.0
	3pu	73.7	0.13	11.9	0.40		0.00	0.28	0.00	3.68	5.30	95.4
Ue19p-1261	8s	73.5	0.09	11.8	0.87	0.12	0.00	0.25	0.00	4.30	4.62	95.6
	6pu	73.8	0.09	11.7	0.87	0.12	0.00	0.30	0.00	4.08	4.75	95.7
Ue19p-1461	4l	72.0	0.17	12.3	0.90		0.04	0.39	0.00	3.97	5.20	95.0
RW18a-9	3s	69.9	0.15	11.1	0.91	0.11	0.16	0.97	0.04	2.80	4.31	90.5
	2pu	70.1	0.17	11.2	0.92	0.07	0.16	1.01	0.07	2.84	4.33	90.9
Ue19p-1790	3pe	69.7	0.13	11.5	1.05		0.00	0.39	0.00	3.16	5.26	91.2
	3pu	69.1	0.09	11.4	1.09		0.00	0.37	0.00	3.01	5.28	90.3
U19ab-1930-1940	4pu	68.6	0.07	11.4	0.94		0.02	0.43	0.00	2.87	5.36	89.7
TTR-2	3s	65.8	0.46	15.1	3.90		0.28	0.87	0.07	5.52	6.05	98.1
	2pu	72.0	0.20	13.5	1.09		0.06	0.39	0.00	4.49	6.10	97.8
RW18a-3	4pu	68.3	0.22	10.1	3.59	0.09	0.00	0.14	0.00	4.64	4.68	91.8
	8s	68.1	0.22	10.1	3.47	0.07	0.00	0.15	0.00	4.92	4.39	91.4

TABLE 3.--Elemental contents for glass analyses of Table 2, calculated as the number of molecules per 24 oxygens. (Symbols for glass types are identical to those used in Table 2).

Assumed coordination number =										Summed values		
Sample	n	4				>6				Cn=4	Al+Fe	charge, Cn>6
		Si	Ti	Al	Fe	Mn ^a	Ca	Na	K			
RW19w-1	3s	10.064	0.011	1.896	0.056	0.000	0.022	0.965	0.902	12.027	1.952	1.911
	3pu	10.025	0.013	1.900	0.038	0.000	0.040	0.967	0.915	11.976	1.936	1.961
Uel9p-1261	8s	9.991	0.008	1.892	0.088	0.012	0.036	1.134	0.799	11.979	1.980	2.029
	6pu	10.021	0.008	1.870	0.087	0.012	0.040	1.071	0.820	11.986	1.957	1.995
Uel9p-1461	4l	9.889	0.015	1.996	0.092	0.004	0.055	1.055	0.911	11.994	2.090	2.084
RW18a-9	3s	10.008	0.015	1.874	0.095	0.039	0.148	0.776	0.785	11.992	1.969	1.935
	2pu	9.999	0.015	1.889	0.096	0.032	0.150	0.782	0.785	11.999	1.985	1.931
Uel9p-1790	3pe	9.953	0.012	1.938	0.111	0.000	0.057	0.876	0.958	12.014	2.049	1.948
	3pu	9.964	0.008	1.938	0.116	0.000	0.055	0.839	0.971	12.026	2.054	1.920
U19ab-1930-1940	4pu	9.963	0.005	1.953	0.101	0.002	0.065	0.806	0.992	12.022	2.054	1.932
TTR-2	3s	9.074	0.046	2.449	0.403	0.057	0.125	1.473	1.062	11.972	2.852	2.899
	2pu	9.702	0.020	2.134	0.106	0.009	0.052	1.170	1.043	11.962	2.240	2.335
RW18a-3	4pu	9.841	0.022	1.706	0.385	0.009	0.020	1.294	0.858	11.954	2.091	2.210
	8s	9.837	0.022	1.713	0.375	0.007	0.020	1.376	0.806	11.947	2.088	2.276

a = also includes Ba and Mg

TABLE 4.--Median values and standard deviations of summed values defined in Table 3 for complete sample set. (All values based on 24 oxygens. Complete sample set consists of 402 analyses from 58 samples.)

	<i>Cn</i> =4	Al+Fe	Charge, <i>Cn</i> ≥6
Median summed value	11.992	1.957	1.949
±2σ { population	0.026	0.082	0.131
{ median	0.001	0.004	0.007