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MAJOR-ELEMENT, TRACE-ELEMENT, AND VOLATILE CONCENTRATIONS IN SILICATE MELT INCLUSIONS FROM THE TUFF OF PINE GROVE, WAH WAH MOUNTAINS, UTAH

by

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INTRODUCTION

This open-file report provides a complete data set of the compositions of silicate melt inclusions from the 22-Ma tuff of Pine Grove, in the Wah Wah Mountains of SW, Utah. It is intended to complement several manuscripts on the Pine Grove system that are currently being prepared for publication.

The geology of these volcanic rocks, found within the Miocene Blawn Formation (Abbott and others, 1983), has been described in detail by Keith (1982), Keith and others (1986), and Keith and Shanks (1988). The analyzed samples were collected by the first author during May 1993 with help from the second author and Dr. Jeffrey Keith of Brigham Young University.

The silicate melt inclusions consist of quenched melt (now glass) that was originally trapped in growing quartz phenocrysts during crystallization within the magma reservoir, prior to eruption. The host phenocryst acts as a pressure vessel during eruption, preventing the trapped melt from outgassing. Therefore, these inclusions can preserve the dissolved volatile concentrations in the melt at the time of entrapment. Roedder (1984) provides a complete introduction to melt inclusions and their analysis.

SAMPLES

Keith et al. (1986) divided the tuff of Pine Grove into an "air fall unit" of Plinian fallout tephra and three overlying pyroclastic-flow units: the "basal unit", "pink unit", and "upper unit." Other volcanic rocks associated with the Pine Grove system include rhyolite domes extruded subsequent to the pyroclastic eruptions, cobbles of which are found in a conglomeratic layer that overlies the eruptive sequence. All inclusions except PU3 ("pink unit") came from the Plinian fallout found at the base of the tuff of Pine Grove. This unit consists of a clast-supported framework of lapilli, about 0.5 to 2.0 cm in diameter. Nearly all pumiceous glass has been altered to clay. Quartz and feldspar phenocrysts are generally not cracked. Nearly all melt inclusions in the "air fall unit" are glassy. Most have very small bubbles (<0.1 vol.% of the inclusion) or lack bubbles entirely. Inclusions connected to the surface of the host crystal by capillaries and those within fractured phenocrysts are usually devitrified or finely vesiculated or both. In general, these inclusions are opaque, principally due to vesiculation.

In contrast, inclusions from the "pink" and "upper" units contain large bubbles (> 1 vol. %) and many appear to be intersected by cracks. There are fewer opaque (melt) inclusions than in the "air fall unit", but more inclusions that are only slightly devitrified. Very few inclusions from the "pink" and "upper" units were analyzed because of the difficulty in finding inclusions >30 μm in diameter without cracks. The one analyzed inclusion from the "pink unit" (PU3) had a large bubble and a H_2O concentration consistent with leakage.

Fluid inclusions are also found in these samples, and will be discussed in greater detail in future reports.

TABLE 1. CHARACTERISTICS OF PINE GROVE MELT INCLUSIONS

INCLUSION	SIZE (μm)	THICKNESS (μm)	BUBBLES (number: size in μm)
PGAF 4	85x80	72	1:10
PGAF 5	85x85	75	2: 7,12
PGAF 6	120x105	58	None
PGAF 8	100x100	98	3 :5 to 10
PGAF 12	150x130	134	None
PGAF 17	90x82	70	1:14
PGAF 18.1	80x80	67	4: largest is 10
PGAF 18.2	72x70	67	1:5
PGAF 19	120x100	53	1:10
PGAF 20	90x90	70	2:7,10
PGAF 21	115x105	100	3:10,5,5
PGAF 22.1	95x95	76	1:15
PGAF 22.2	100x100	76	3:10
PGAF 25	95x95	57	1:15
PGAF 26	170x150	75	4:5
PGAF 28	95x70	65	5:5
PGAF 29	105x105	72	2:3
PGAF 30	155x60	47	None
PGAF 31	205x115	107	4:5
PGAF 32	155x100	55	None
PGAF 33.1	150x50	71	3:10,10,5
PGAF 33.2	180x140	71	1:10
PGAF 35	90x70	55	None
PGAF 36	100x90	72	1:15
PGAF 37	85x85	82	1:15
PGAF 38	100x75	52	1:12
PGAF 39	90x85	71	1:15
PGAF 40	105x85	58	1:15
PGAF 41	105x100	59	3:5
PGPU3	90x85	72	1:45

PGAF represents Pine Grove "air fall unit", whereas PGPU denotes the "pink unit". PGAF 18, 22 and 33 each contained two inclusions. The inclusion size is approximated as a parallelepiped with the two listed dimensions corresponding to the length and width. The actual thickness of the inclusion, in most cases, falls between these other two dimensions. The listed thickness corresponds to the measured thickness of the doubly polished inclusion and its host crystal.

FTIR: ACQUISITION AND UNCERTAINTIES

All Fourier transform infrared (FTIR) spectroscopic analyses were done on a Nicolet 60SX with attached Spetra-Tech microscope at Lawrence Livermore National Laboratory according to the methods of Newman et al. (1986). Doubly polished inclusions of glass within quartz phenocrysts were placed in the path of infrared radiation. The beam path was constrained by use of two aperatures, placed above and below the sample, allowing microanalysis of small inclusions. In all cases, the apertures were opened so that an area of the inclusion greater than 25 µm x 25 µm was sampled. The largest inclusions permitted passage of an 80 µm x 80 µm beam through the entire thickness of the sample. Therefore, unlike electron and ion microprobes that sample less than a few cubic microns of material, FTIR analysis allows quantification of a significant volume fraction of the inclusion.

Between 512 and 1024 scans were collected with an MCT-A detector cooled with liquid nitrogen. Absorbance was measured at 2350 cm^{-1}, 4500 cm^{-1}, and 5200 cm^{-1} to quantify molecular CO_2, hydroxyl (OH), and molecular H_2O (H_2Om), respectively, dissolved in the glass. Air in the sample chamber was purged with pure N_2 gas to dilute the ambient atmospheric CO_2 to low values. Because gaseous CO_2 produces a doublet at 2350 cm^{-1}, it can be differentiated readily from molecular CO_2 dissolved in the glass, which results in a single peak. Replicate analyses of both CO_2-poor and CO_2-rich inclusions allow us to estimate that the effect of atmospheric CO_2 in the sample chamber should affect our results by < 10 ppm.

Backgrounds were drawn manually and quantification was done by measuring peak height. The formula for calculating concentrations was:

$$\text{Wt.\% X} = \frac{\text{Abs} * \text{mw}}{\rho * \varepsilon * d}$$

where X is the species being analyzed, mw is the molecular weight of the species, Abs and ε are the absorbance and extinction coefficient, respectively, at the relevant wavelength, and ρ and d are sample density and thickness (Newman et al., 1986). Thicknesses were measured with a 543 Series digital micrometer made by Mitutoyo Mfg. Co., Ltd.
The relevant extinction coefficients (ε) are listed below:

Species	Wavenumber	ε	Reference
CO_2	2350 cm^{-1}	1077±80 l/mol·cm	Blank, 1993
H_2O_m	5200 cm^{-1}	1.61±.05 l/mol·cm	Newman et al., 1986
OH	4500 cm^{-1}	1.73±.02 l/mol·cm	Newman et al., 1986

TABLE 2: FTIR DATA

SAMPLE	d(µm)	ABS(5200)	ABS (4500)	H_2Om (wt.%)	OH (wt.%)#	H_2Ot(wt.%)	H_2O 2 sigma	ABS (2350)	CO_2 (ppm)	CO_2 2 sigma
PGAF4	72	0.0788	0.0104	5.33	0.65	5.98	0.40	0.2548	629	65
PGAF5	75	0.0853	0.0114	5.53	0.69	6.22	0.38	0.2254	534	51
PGAF6	58	0.0738	0.0087	6.19	0.68	6.87	0.48	0.2704	828	84
PGAF6	98	0.1300	0.0160	6.46	0.74	7.19	0.41	0.2387	433	41
PGAF12	134	0.1472	0.0196	5.35	0.66	6.01	0.33	0.2512	333	30
PGAF17	70	0.0845	0.0110	5.87	0.71	6.59	0.43	0.2604	661	65
PGAF18.1	67	0.0858	0.0132	6.23	0.89	7.12	0.47	0.2261	600	59
PGAF18.2	67	0.0813	0.0110	5.90	0.74	6.64	0.43	0.2202	584	58
PGAF19	53	0.0708	0.0084	6.50	0.72	7.22	0.54	0.2002	671	75
PGAF20	70	0.0888	0.0114	6.17	0.74	6.91	0.50	0.1932	490	50
PGAF21	100	0.1182	0.0168	5.75	0.76	6.51	0.39	0.1452	258	24
PGAF22.1	76	0.1038	0.0144	6.65	0.86	7.50	0.48	0.2184	511	49
PGAF22.2	76	0.0935	0.0120	5.99	0.72	6.70	0.41	0.0268	63	8
PGAF25	57	0.0796	0.0116	6.80	0.92	7.72	0.55	0.2586	806	84
PGAF26	75	0.0960	0.0130	6.23	0.78	7.01	0.42	0.1866	442	43
PGAF28	65	0.0876	0.0124	6.56	0.86	7.42	0.47	0.1038	284	28
PGAF29	72	0.0935	0.0135	6.32	0.85	7.17	0.44	0.2388	589	57
PGAF30	47	0.0604	0.0088	6.25	0.85	7.10	0.53	0.0944	357	41
PGAF31	107	0.1452	0.0216	6.60	0.91	7.52	0.41	0.1305	217	20
PGAF32	55	0.0788	0.0108	6.97	0.89	7.86	0.54	0.1608	519	53
PGAF33.1	71	0.0935	0.0130	6.41	0.83	7.24	0.44	0.1128	282	27
PGAF33.2	71	0.0928	0.0130	6.36	0.83	7.19	0.44	0.0832	208	21
PGAF35	55	0.0724	0.0104	6.41	0.86	7.26	0.50	0.0819	265	27
PGAF36	72	0.0958	0.0133	6.47	0.83	7.30	0.45	0.0411	101	10
PGAF37	82	0.1055	0.0145	6.26	0.80	7.06	0.41	0.4488	972	91
PGAF38	52	0.0746	0.0116	6.98	1.01	7.99	0.57	0.0292	100	17
PGAF39	71	0.1003	0.0145	6.87	0.92	7.80	0.48	0.324	811	78
PGAF40	58	0.0806	0.0116	6.76	0.91	7.67	0.51	0.112	343	35
PGAF41	59	0.0833	0.0108	6.87	0.83	7.69	0.51	0.059	178	18
PGPU3	72	-	-	-	-	1.43*	0.15	0.1424	344	33

OH calculated as weight % H_2O.   *H_2O calculated from absorbance at 3570 cm^{-1} peak.

Abbreviations in Table 2 correspond to the following:

d(μm)	The thickness of the sample in micrometers.
ABS	Absorbance (unitless) at a given wavelength.
H_2O_t	Total Water: H_2O_m + OH
H_2O 2 sigma	Error (2σ) calculated by propagating all uncertainties associated with analysis:

ε	listed above
ρ	2300±100 g/l
d:thickness	X μm ± 3 μm
peak height	error varied

ELECTRON MICROPROBE ANALYSIS

All analyses were done on the JEOL 8900 at the U.S. Geological Survey in Menlo Park, CA. Standards and conditions are listed in Table 3. Samples were initially analyzed as alloys; i.e., not as oxides. Use of an, LDE1 synthetic crystal allowed quantification of oxygen, permitting one to obtain 100% totals on hydrous glass (Armstrong, 1988b, Nash, 1992). Because the low-energy x-rays emitted by oxygen are readily absorbed by the carbon coat, it is important to have a similar coat thickness on sample and standard. Therefore, the inclusion-bearing quartz host was used as the standard for oxygen for each melt inclusion. The standard for Si was rhyolitic glass (RLS 132: Macdonald et al., 1992). Each inclusion was analyzed two times; once for major elements (Si, Al, K, Na, F, and O) and once for minor elements (F, Cl, Mg, Ca, P, Mn, S, Ti). The first analysis was done with a 7.5-nA beam focussed to a 40-μm spot. The second analysis utilized a 30-nA beam focussed to a 20-μm spot. Each analyzed element was tested to ensure that the count rate for its emitted x-rays did not decrease with time, due to elemental migration. These tests were performed on hydrous melt inclusions from the tuff of Pine Grove.

The K-ratios (counts sample/counts standard) for all elements were input into CITZAF (Armstrong, 1988a) and element concentrations were calculated off line. The CITZAF output is listed in Table 4. These values were then recalculated to show the percent oxides within the melt inclusions, both absolute and recalculated to 100% volatile-free (Table 5).

Table 6 shows the estimated counting uncertainties (2σ) in wt.% and minimum detection limits for PGAF6, which should be nearly identical to those for other samples. Uncertainty was determined by the following formula:

$$\sigma = \frac{\sqrt{n}*X}{n}$$

where n = the total number of counts and X is the calculated concentration. Minimum detectable peaks were assumed to be three standard deviations (of the background) above the background.

TABLE 3: ELECTRON MICROPROBE STANDARDS AND ANALYSIS CONDITIONS

Element	O	Fe	Na	K	Al	Si	F
Spectrometer	1	2	3	4	5	3	1
Crystal	LDE1	LIF	TAP	PET	TAP	TAP	LDE1
BG+	15	4	3	3	5	5	2.5(3 on std)
BG-	15	4	3	3	5	5	2.5(3 on std)
peak search	yes	yes	No	yes	yes	yes	No
count time	20	20	10	20	15	10	30
nA	7.5	7.5	7.5	7.5	7.5	7.5	30
beam size(μm)	40	40	40	40	40	40	20
standard	quartz from host of inclusion	synthetic fayalite	Tiburon albite	OR1 (orthoclase)	Tiburon albite	RLS 132 rhyolite glass	F-phlogopite

Element	S	Mg	Ca	Cl	Ti	Mn	P
Spectrometer	2	3	4	5	2	4	5
Crystal	PET	TAP	PET	PET	LIF	LIF	PET
BG+	3	5	5	4	3(5 on Std)	5	5
BG-	3	5	5	4	3(5 on Std)	5	5
peak search	No	No	No	No	No	No	No
count time	30	30	30	30	30	30	30
nA	30	30	30	30	30	30	30
beam size(μm)	20	20	20	20	20	20	20
standard	Barite	MgO	An100 glass	Sodalite	TiO2	Mn2O3	Apatite

TABLE 4: ELECTRON MICROPROBE RESULTS AS ELEMENTS

Element (wt.%)	PGAF4	PGAF6	PGAF8	PGAF12	PGAF17	PGAF18.1	PGAF18.2	AF19	PGAF20
O	53.11	52.87	53.88	52.96	52.7	52.47	51.17	53.31	52.58
F	0.3188	0.3723	0.2346	0.3565	0.3220	0.3321	0.3285	0.3723	0.3666
Na	2.89	2.98	2.96	3.12	2.86	3.07	2.44	3.03	2.72
Mg	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al	6.74	6.80	6.54	6.80	6.73	6.79	6.81	6.45	6.78
Si	33.03	33.16	32.02	33.18	33.44	33.18	34.1	32.16	33.25
P	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
S	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cl	0.0586	0.0629	0.0331	0.0544	0.0484	0.057	0.0477	0.0594	0.0561
K	3.46	3.45	3.33	3.42	3.63	3.27	3.48	3.23	3.25
Ca	0.2500	0.2357	0.1436	0.2408	0.2240	0.2039	0.2244	0.2302	0.2473
Ti	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Mn	0.0941	0.1112	0.0737	0.0924	0.1129	0.0941	0.0975	0.0907	0.0873
Fe	0.5489	0.4972	0.4609	0.5304	0.5230	0.5745	0.4823	0.5418	0.4826
Total	100.50	100.54	99.68	100.75	100.59	100.04	99.18	99.47	99.82

Element(wt.%)	PGAF21	PGAF22.1	PGAF22.2	PGAF25	PGAF26	PGAF28	PGAF29	AF30	PGAF31
O	50.92	52.70	52.48	52.57	52.83	51.93	52.35	53.38	53.19
F	0.3433	0.2987	0.2161	0.3051	0.3703	0.3327	0.3653	0.4087	0.3496
Na	3.04	2.98	3.04	2.9	2.7	3.83	3.12	2.98	3.16
Mg	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al	6.75	6.76	6.79	6.38	6.79	6.55	6.75	6.80	6.75
Si	33.46	33.44	33.34	33.7	33	33.84	33.31	33.77	33.07
P	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
S	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cl	0.0613	0.0637	0.0604	0.0579	0.0662	0.0647	0.0586	0.0544	0.0603
K	3.41	3.5	3.36	3.1	3.82	3.21	3.39	3.41	3.30
Ca	0.2140	0.1773	0.0889	0.1705	0.2272	0.1871	0.2123	0.226	0.203
Ti	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Mn	0.0984	0.0821	0.0616	0.0702	0.1095	0.0804	0.0975	0.087	0.098
Fe	0.5595	0.5120	0.4605	0.5527	0.5267	0.5969	0.5781	0.53	0.46
Total	98.85	100.51	99.90	99.81	100.44	100.62	100.23	101.65	100.64

Note: bdl = below detection limit

TABLE 4 (CONTINUED): ELECTRON MICROPROBE RESULTS AS ELEMENTS

Element(wt.%)	PGAF33.1	PGAF33.2	PGAF36	PGAF37	PGAF39	PGAF40	PGAF 41
O	51.99	51.24	53.09	53.2	53.43	52.61	53.44
F	0.3858	0.3257	0.2223	0.3626	0.3545	0.3396	0.3247
Na	3.30	3.20	3.08	2.63	3.00	2.94	3.08
Mg	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al	6.87	6.73	7.09	6.56	6.67	6.84	6.88
Si	33.96	34.28	32.42	32.16	31.93	33.60	33.22
P	bdl	bdl	bdl	bdl	bdl	bdl	bdl
S	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cl	0.0613	0.052	0.0552	0.0712	0.0594	0.0621	0.0606
K	3.43	3.44	3.31	3.57	3.24	3.36	3.41
Ca	0.233	0.177	0.097	0.240	0.218	0.2355	0.1622
Ti	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Mn	0.091	0.079	0.070	0.103	0.094	0.1095	0.0919
Fe	0.45	0.48	0.51	0.47	0.53	0.5339	0.5194
Total	100.77	100.00	99.94	99.36	99.53	100.63	101.18

Note: bdl = below detection limit

TABLE 5: ELECTRON MICROPROBE RESULTS AS OXIDES

Oxide (wt.%)	PGAF4	PGAF6	PGAF8.1	PGAF12	PGAF17	PGAF18.1	PGAF18.2	PGAF19	PGAF20
SiO2	70.65	70.93	69.20	70.97	71.53	70.97	72.94	68.79	71.12
TiO2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al2O3	12.73	12.85	12.32	12.85	12.71	12.83	12.86	12.18	12.81
FeO	0.71	0.64	0.52	0.68	0.67	0.74	0.62	0.70	0.62
MgO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MnO	0.149	0.176	0.119	0.146	0.179	0.149	0.154	0.144	0.138
CaO	0.350	0.330	0.243	0.337	0.313	0.285	0.314	0.322	0.346
Na2O	3.90	4.02	3.81	4.21	3.86	4.14	3.29	4.08	3.67
K2O	4.17	4.16	4.02	4.12	4.37	3.94	4.19	3.89	3.92
P2O5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cl(ppm)	590	630	370	540	480	570	480	590	560
F(ppm)	3190	3720	2670	3570	3220	3320	3290	3720	3670
S(ppm)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	93.04	93.54	90.54	93.72	94.00	93.44	94.75	90.54	93.05

Oxide (wt.%)	PGAF4	PGAF6	PGAF8.1	PGAF12	PGAF17	PGAF18.1	PGAF18.2	PGAF19	PGAF20
SiO2	75.93	75.82	76.39	75.69	76.06	75.92	76.96	75.94	76.43
TiO2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al2O3	13.68	13.73	13.60	13.70	13.52	13.72	13.57	13.45	13.76
FeO	0.76	0.68	0.58	0.73	0.72	0.79	0.65	0.77	0.67
MgO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MnO	0.160	0.188	0.132	0.156	0.191	0.159	0.163	0.159	0.149
CaO	0.376	0.352	0.268	0.359	0.334	0.305	0.331	0.356	0.372
Na2O	4.19	4.29	4.21	4.49	4.10	4.43	3.47	4.51	3.94
K2O	4.48	4.44	4.44	4.40	4.65	4.21	4.42	4.30	4.21
P2O5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cl(ppm)	630	670	410	580	520	610	500	660	600
F(ppm)	3430	3980	2950	3800	3420	3550	3470	4110	3940
S(ppm)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	100	100	100	100	100	100	100	100	100

TABLE 5 (CONTINUED): ELECTRON MICROPROBE RESULTS AS OXIDES

Oxide (wt.%)	PGAF21	AF22.1	PGAF22.2	PGAF25	PGAF26	PGAF28	PGAF29	PGAF30	PGAF31
SiO2	71.57	71.53	71.31	72.08	70.59	72.38	71.25	72.23	70.74
TiO2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al2O3	12.75	12.77	12.83	12.05	12.83	12.37	12.75	12.85	12.75
FeO	0.72	0.66	0.59	0.71	0.68	0.77	0.74	0.69	0.60
MgO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MnO	0.156	0.130	0.098	0.111	0.173	0.127	0.154	0.138	0.154
CaO	0.299	0.248	0.124	0.239	0.318	0.262	0.297	0.315	0.284
Na2O	4.10	4.02	4.10	3.91	3.64	5.16	4.21	4.02	4.26
K2O	4.11	4.22	4.05	3.74	4.60	3.87	4.08	4.11	3.98
P2O5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cl(ppm)	610	640	600	580	660	650	590	540	600
F(ppm)	3430	2990	2160	3050	3700	3330	3650	4090	3500
S(ppm)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	94.11	93.94	93.38	93.20	93.27	95.34	93.91	94.82	93.18

Oxide (wt.%)	PGAF21	PGAF22.1	PGAF22.2	PGAF25	PGAF26	PGAF28	PGAF29	PGAF30	PGAF31
SiO2	76.02	76.13	76.34	77.32	75.65	75.90	75.83	76.16	75.91
TiO2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al2O3	13.55	13.59	13.73	12.93	13.75	12.97	13.57	13.54	13.68
FeO	0.76	0.70	0.63	0.76	0.73	0.81	0.79	0.72	0.64
MgO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MnO	0.165	0.138	0.104	0.119	0.186	0.133	0.164	0.146	0.166
CaO	0.318	0.264	0.133	0.256	0.341	0.274	0.316	0.333	0.305
Na2O	4.35	4.28	4.39	4.19	3.90	5.41	4.48	4.24	4.57
K2O	4.37	4.49	4.33	4.01	4.93	4.06	4.35	4.33	4.27
P2O5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cl(ppm)	650	680	650	320	710	680	620	570	650
F(ppm)	3650	3180	2310	3270	3970	3490	3890	4310	3750
S(ppm)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	100	100	100	100	100	100	100	100	100

TABLE 5 (CONTINUED): ELECTRON MICROPROBE RESULTS AS OXIDES

Oxide (wt.%)	PGAF33.1	PGAF33.2	PGAF36	PGAF37	PGAF39	PGAF40	PGAF41	PGAF Mean	1 sigma
SiO2	72.64	73.32	69.35	68.79	68.30	71.87	71.06	71.04	1.32
TiO2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	-
Al2O3	12.98	12.71	13.39	12.39	12.60	12.92	13.00	12.72	0.28
FeO	0.58	0.62	0.65	0.60	0.68	0.69	0.67	0.66	0.06
MgO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	-
MnO	0.143	0.125	0.111	0.163	0.149	0.173	0.145	0.144	0.021
CaO	0.325	0.247	0.136	0.336	0.305	0.329	0.227	0.285	0.059
Na2O	4.45	4.31	4.15	3.55	4.04	3.96	4.15	4.04	0.35
K2O	4.13	4.15	3.99	4.30	3.90	4.05	4.11	4.09	0.18
P2O5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	-
Cl(ppm)	610	520	550	710	590	620	610	580	70
F(ppm)	3860	3260	2220	3630	3550	3400	3250	3340	460
S(ppm)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	-
Total	95.70	95.86	92.05	90.56	90.39	94.39	93.75	93.38	1.54

Oxide (wt.%)	PGAF33.1	PGAF33.2	PGAF36	PGAF37	PGAF39	PGAF40	PGAF41	PGAF Mean
SiO2	75.89	76.45	75.30	75.93	75.54	76.12	75.78	76.06
TiO2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Al2O3	13.56	13.26	14.54	13.68	13.94	13.69	13.86	13.62
FeO	0.60	0.65	0.71	0.66	0.76	0.73	0.71	0.71
MgO	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
MnO	0.150	0.130	0.121	0.179	0.165	0.184	0.155	0.154
CaO	0.340	0.258	0.147	0.371	0.338	0.349	0.242	0.306
Na2O	4.65	4.50	4.51	3.91	4.47	4.20	4.43	4.32
K2O	4.32	4.32	4.33	4.75	4.32	4.29	4.38	4.38
P2O5	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cl(ppm)	640	540	600	790	660	660	650	610
F(ppm)	4030	3400	2410	4000	3920	3600	3460	3690
S(ppm)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Total	100	100	100	100	100	100	100	100

TABLE 6: PRECISION OF ELECTRON MICROPROBE ANALYSES

Element IN PGAF 6	Concentration	2-σ counting uncertainty	Minimum detection limit
O	52.9 wt.%	0.6 wt.%	990 ppm
F	3720 ppm	100 ppm	370 ppm
Na	2.98 wt.%	0.17 wt.%	300 ppm
Mg	<70 ppm	-	70 ppm
Al	6.80 wt.%	0.11 wt.%	150 ppm
Si	33.16 wt.%	0.31 wt.%	330 ppm
P	<80 ppm	-	80 ppm
S	<60 ppm	-	60 ppm
Cl	630 ppm	70 ppm	90 ppm
K	3.45 wt.%	0.09 wt.%	160 ppm
Ca	0.236 wt.%	0.008 wt.%	350 ppm
Ti	<160 ppm	-	160 ppm
Mn	0.111 wt.%	0.012 wt.%	630 ppm
Fe	0.50 wt.%	0.05 wt.%	500 ppm

Oxide IN PGAF 6	Concentration	2-σ counting uncertainty	Minimum detection limit
SiO_2	70.9 wt.%	0.7 wt.%	700 ppm
TiO_2	<270 ppm	-	270 ppm
Al_2O_3	12.85 wt.%	0.21 wt.%	280 ppm
FeO	0.64 wt.%	0.07 wt.%	640 ppm
MgO	<120 ppm	-	120 ppm
MnO	0.176 wt.%	0.020 wt.%	1000 ppm
CaO	0.330 wt. %	0.011 wt.%	490 ppm
Na_2O	4.02 wt.%	0.23 wt.%	400 ppm
K_2O	4.16 wt.%	0.11 wt.%	190 ppm
P_2O_5	<180 ppm	-	180 ppm
Cl	630 ppm	70 ppm	90 ppm
F	3720 ppm	100 ppm	370 ppm
S	<60 ppm	-	60 ppm

Reproducibility and accuracy can be estimated by the data in Table 7. Column 2 lists the mean of six analyses for minor elements (Ti, Mg, Mn, Ca, P, Cl, F, and S) on PGAF41. Because four of these elements were below detection limit, the 2-σ variation of the group is listed for four elements only (in Column 3). Columns 4 corresponds to the mean of three analyses of RLS 132, a rhyolitic glass. The published analysis for this sample (from Macdonald et al., 1993) is listed in Column 5.

TABLE 7: ELECTRON MICROPROBE REPRODUCIBILITY AND ACCURACY

1	2	3	4	5
Oxide (Wt.%)	PGAF41(n=6)	PGAF41 2-σ variation	RLS 132 (n=3)	RLS 132 pub.
SiO_2	75.8	-	75.9	75.7
TiO_2 (ppm)	<270	-	1930	2100
Al_2O_3	13.86	-	11.43	11.44
FeO_t	0.71	-	2.34	2.13
MgO (ppm)	<120	-	570	500
MnO	0.155	0.042	0.200	0.15
CaO	0.242	0.012	0.098	0.12
Na_2O	4.43	-	5.26	5.25
K_2O	4.38	-	4.65	4.53
P_2O_5 (ppm)	<180	-	250	100
Cl (ppm)	650	50	1770	1850
F (ppm)	3460	440	880	2100
S (ppm)	<60	-	<60	-
Total	100.0	-	100.4	100.0

The only element that shows a large difference between the analyzed and published value is F; however, we believe that this difference may be due to heterogeneity in the standard RLS 132, as the published F analysis was done by a bulk method. We conclude this for several reasons: 1) As shown in subsequent tables, the SIMS and electron microprobe analyses of the Pine Grove inclusions are in good agreement. 2) The SIMS analyses of RLS 140 and a macusanite glass gave F concentrations within 20 percent of the published values. 3) The microprobe standard for F, is end-member fluor-phlogopite, and thus of known composition. 4) Analysis of other rhyolitic glasses by electron microprobe gave F concentrations very similar to published values.

In addition to the data listed in Tables 4 and 5, we also analyzed a sample of the "upper unit" that was welded during emplacement of an overlying trachybasalt, shortly after deposition of the tuff of Pine Grove (Keith et al., 1986). The matrix is dense and glassy, as opposed to most of the Pine Grove tephras, which contain matrix that has been altered to friable clay. The relative proportion of elemental oxygen to cations indicates that the sample contains about 3.2 wt.% H_2O. The glass contains high K and low Na, Fe, Ca, Mn, Cl, and F relative to glass inclusions from the "air fall" and "pink" units.

TABLE 8: COMPARISON OF MELT INCLUSIONS AND HYDRATED MATRIX:

Oxide in wt.%	Mean of PGAF Inclusions	Hydrated Matrix	Hydr. Matrix Normalized
SiO_2	76.1	73.7	76.2
TiO_2	bdl	bdl	bdl
Al_2O_3	13.62	13.11	13.55
FeO	0.71	0.25	0.27
MgO	bdl	bdl	bdl
MnO	0.154	0.131	0.135
CaO	0.306	0.135	0.139
Na_2O	4.32	3.30	3.42
K2O	4.38	6.05	6.25
P_2O_5	bdl	bdl	bdl
Cl (ppm)	610	bdl	bdl
F (ppm)	3690	620	640
S (ppm)	bdl	bdl	bdl
Total	100	96.7	100

SECONDARY ION MASS SPECTROMETRY (SIMS)

For the analysis of melt inclusions by SIMS, a primary ion beam of $^{16}O^-$ struck the sample at approximately 17 keV. It was focussed to a spot ~12-15 μm in diameter at currents of 1 to 1.5 nA. Positive secondary ions were accepted into the mass spectrometer from a 20-μm-diameter circular area defined by the 25-μm transfer optic lens and a 750-μm field aperture. We studied ^{1}H, ^{7}Li, ^{9}Be, ^{11}B, ^{19}F, ^{26}Mg, ^{30}Si, ^{47}Ti, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{98}Mo, ^{120}Sn, ^{133}Cs, ^{138}Ba, ^{184}W, ^{232}Th, and ^{238}U. Only secondary ions with initial kinetic energies of 75±20 eV ejected from the crater were allowed into the mass spectrometer. This degree of "energy filtering" effectively eliminates complex molecular ions from the mass spectrum. However, dimers are incompletely removed, so that there is a contribution of ^{18}OH to the ^{19}F signal corresponding to approximately 600 ppm F. No other molecular ion contributed to the elements analyzed at levels greater than approximately 1 ppm. Errors in the analyses arise from counting statistics and exact knowledge of standard glass compositions. The former were less than 10% for Li, Be, B, Ti, Rb, and Y. Lower count rates were observed for the other elements, resulting in higher 2-σ counting uncertainties. The calibration factors were determined using bulk-analyzed siliceous glasses including NBS 610 and several natural glasses.

The SIMS data are listed in Table 9. If more than one SIMS analysis was done on an inclusion, the mean is reported. Five replicate analyses were done on PGAF6 for the elements Li, Be, B, Ti, Rb, Mo, Sn, Cs, and Th. Table 9 lists the mean and 1-σ variation (in parentheses) for those five analyses under the column for PGAF6. The mean of all PGAF inclusions (and its 1-σ variation) is also listed in Table 9.

TABLE 9. SIMS RESULTS

Element (ppm)	PGAF6(n=5)	PGAF12	PGAF17	PGAF18.1	PGAF18.2	PGAF22.1
Li	176(32)	222	183	152	174	212
Be	11.7(2.2)	14.2	10.0	9.3	8.7	11.9
B	52(6)	52	45	39	43	54
F	4870	-	4230	-	-	-
Mg	42	-	49	-	-	-
Ti	89(24)	90	101	96	95	79
Rb	473(42)	437	390	409	479	439
Sr	0.2	-	0.3	-	-	-
Y	77	-	80	-	-	-
Mo	3(2)	3	3	4	3	3
Sn	25(23)	12	2	2	8	21
Cs	21.7(4.6)	18	16	23	20	20
Ba	0.9	-	0.5	-	-	-
W	14	-	5	-	-	-
Th	22(4)	17	29	25	25	21
U	20	-	12	-	-	-

Element (ppm)	PGAF22.2	PGAF25	PGAF26	PGAF28	PGAF30	PGAF31	PGAF33.1
Li	128	185	5	244	170	148	157
Be	9.1	10.7	9.6	11.4	10.5	-	-
B	48	48	45	52	50	52	53
F	3390	3690	4220	4160	-	4580	4830
Mg	43	32	40	37	-	28	33
Ti	92	84	76	72	65	69	77
Rb	460	461	451	459	504	458	473
Sr	1.3	0.3	0.2	0.3	-	0.1	0.2
Y	76	79	78	77	-	79	77
Mo	3	2	2	3	2	6	1
Sn	10	13	5	13	28	21	4
Cs	18	19	20	21	18	21	21
Ba	0.6	0.8	0.2	0.8	-	0.0	0.5
W	7	8	6	11	-	10	11
Th	23	20	26	16	21	20	20
U	17	17	17	17	-	17	19

TABLE 9 SIMS RESULTS (CONTINUED)

Element (ppm)	PGAF33.2	PGAF36	PGAF39	PGAF 40	PGAF41	PGAF Mean and 1-σ variation	PGPU3.1
Li	101	163	173	165	169	163(51)	67
Be	11.5	12.8	10.2	9.9	12.0	10.2(3.0)	-
B	52	49	48	44	49	48.6(4.0)	45
F	-	3520	4100	3750	4520	4189(458)	3386
Mg	-	35	20	35	30	36.0(7.5)	59
Ti	71	82	83	88	77	82.6(10.2)	123
Rb	487	433	502	512	506	463(33)	452
Sr	-	0.1	0.2	0.4	0.2	0.3(0.3)	0.3
Y	-	72	81	93	78	79(5)	90
Mo	3	3	4	4	2	3(1)	1
Sn	12	8	18	44	7	14(11)	25
Cs	21	15	16	28	19	19.7(2.9)	17.2
Ba	-	0.7	0.8	0.8	0.6	0.5(0.3)	0.3
W	-	6	5	13	12	8.4(3.7)	10
Th	19	20	19	25	20	21.6(3.3)	22
U	-	16	19	22	18	17.4(2.2)	15

Table 10 lists the 2-σ counting uncertainties for PGAF39; these values should be representative of uncertainties for all melt inclusion analyses listed in Table 9. They were calculated in the same manner as those for the electron microprobe. The other two columns in Table 10 show the mean of two SIMS analyses of RLS 140 and the value reported in the literature (Macdonald et al. 1992). This shows that for most elements, the SIMS values are accurate to within 10 relative percent of the published values.

TABLE 10: SIMS COUNTING UNCERTAINTIES AND ACCURACY

Element PGAF 39 (ppm)	PGAF 39	2-σ counting uncertainty	RLS 140 (n=2)	RLS 140 Macdonald et al. (1992)
Li	173	3	36	36
Be	10.2	0.8	3.3	3.7
B	48	3	44	-
F	4100	350	379	450
Mg	20	4	644	547
Ti	83	14	888	833
Rb	502	22	145	155
Sr	0.2	0.2	35	33
Y	81	4	20	22
Mo	4	3	7	6.6
Sn	18	12	7	2.6
Cs	16	4	7	5.4
Ba	0.8	0.6	347	310
W	5	2	5	1.8
Th	19	4	25	-
U	19	4	6	7.1

REFERENCES

Abbott, J.T., Best, M.G., and Morris, H.T., 1983, Geologic Map of the Pine Grove-Blawn Mountain Area, Beaver County, Utah: U.S. Geological Survey Miscellaneous Investigations Series I-1479.

Armstrong, J.T., 1988a, Accurate quantitative analysis of O and N with a multilayer crystal, *in* D.E. Newbury, ed., Microbeam Analysis -1988: San Francisco Press, San Francisco, p. 301-304.

Armstrong, J.T., 1988b, Quantitative analysis of silicate and oxide minerals. Comparison of Monte-Carlo, ZAF, and Phi-Rho-Z procedures, *in* D.E. Newbury, ed., Microbeam Analysis -1988: San Francisco Press, San Francisco, p. 239-246.

Blank, J.G., 1993, An experimental investigation of the behavior of carbon dioxide in rhyolitic melt: Pasadena, California, California Institute of Technology, Ph.D. thesis, , 210 p.

Keith, J.D., 1982, Magmatic evolution of the Pine Grove porphyry molybdenum system, southwestern Utah: Madison, Wisconsin, University of Wisconsin, Ph.D. thesis, 246 p.

Keith, J.D., and Shanks, W.C. III, 1988, Chemical evolution and volatile fugacities of the Pine Grove porphyry molybdenum and ash flow tuff system, southwestern Utah, *in* Taylor, R.P., and Strong D.F., eds., Recent Advances in the Geology of Granite-Related Mineral Deposits: Canadian Institute of Mining and Metallurgy Special Volume 39, p.402-423.

Keith, J.D., Shanks, W.C. III, Archibald, D.A., and Farrar, E., 1986, Volcanic and intrusive history of the Pine Grove porphyry molybdenum system, southwestern Utah: Economic Geology, v. 81, p.553-577.

Macdonald, R., Smith, R.L., and Thomas, J.E., 1992, Chemistry of the subalkalic silicic obsidians: U.S. Geological Survey Professional Paper 1523, 214p.

Nash, W.P., 1992, Analysis of oxygen with the electron microprobe: Applications to hydrated glass and minerals: American Mineralogist, v. 77, p. 453-456.

Newman S., Stolper, E.M., and Epstein, S., 1986, Measurement of water in rhyolitic glasses: calibration of an infrared spectroscopic technique: American Mineralogist, v. 71, p. 1527-1541.

Roedder, E., 1984, Fluid Inclusions: Mineralogical Society of America Reviews in Mineralogy, v. 12, 644 p.