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for

Magmatic Degassing Histories from Apatite Volatile Stratigraphy

by

Boyce, J.W., and Hervig, R.L.

A description of the Sample Preparation, Analytical, and Numerical Modeling protocols used for this work, including one figure. Also included is a table of measured H, F, and Cl concentrations.

Sample Preparation.

Apatite crystals from the Cerro Galan ignimbrite were provided by C. Shirnick, GEOMAR. Sample I3H was prepared by mounting in dental acrylic and polished by hand to expose C-axis parallel core sections. The crystal was removed from the acrylic and cleaned by ultrasonication, then mounted for SIMS analysis by pressing into indium metal in a hydraulic press. Indium mounting eliminates epoxy or other hydrocarbon-based materials from the sample, reducing the background of H species in the SIMS, while high-pressure pressing of the indium assures a flat mount surface. All other samples were mounted in Araldite™ epoxy and polished. After application of a gold coating, the sample was allowed to pump down in the SIMS overnight prior to analyses to minimize H background values.

Analytical Protocol.

The elemental ratio measurements described here were made using the Cameca 6f secondary ion mass spectrometer (SIMS) in the School of Earth and Space Exploration at Arizona State University. Using a 5-12nA $^{16}O^-$ primary beam, we measured positive primary ions $^{1}H^+$, $^{12}C^+$, $^{19}F^+$, $^{28}Si^+$, $^{31}P^+$, $^{37}Cl^+$ (except in the case of CG-I3H, where $^{35}Cl^+$ was measured), and $^{43}Ca^+$. The primary beam was focused to ~20µm, then rastered over a 20µm x 20µm area to reduce surface contamination. Further reduction of contamination was accomplished by including a pre-analytical sputtering time of 120-240 s before each analysis. Only ions from the central 8µm of the sputtered region were allowed into the mass spectrometer. Spacing between craters was 5-7µm, resulting in significant overlap of sputtered regions during the series of analyses. Only secondary ions with 75±20 eV excess kinetic energy were detected. Ratios were converted to concentrations using apatite standard materials from Durango, Mexico, Sludyanka, Russia, and Mud Tanks, Australia. Measured ratios in apatite standards are generally reproducible to better than 1.5% (2σ). While a Cs^+ primary beam coupled with detection of negative secondary ions would have increased intensities for most of the isotopes of interest, our line scans resulted in overlapping craters. Too much of the conducting gold coat was removed to allow such closely spaced analyses to be obtained using Cs^+, and the O^- primary beam gave sensitivities well in excess of that required.

All data were reduced using $^{31}P^+$ as a reference isotope. Conversion from measured isotope ratios ($X/^{31}P$) was accomplished by using a suite of apatite standard materials with independently measured OH, F, and Cl contents. Apatite from Durango, Mexico; Mud Tank, Australia; and Sludyanka, Russia were typically measured at the beginning and end of each analytical session, with literature values used to calculate calibration slopes for each element. Internal agreement for each standard is typically better than 10% from session to session over the course of several months, and it is likely that some of this scatter is due to real compositional variations within single megacrysts. Calibration curves obtained using O^- primary ions were tested for consistency by comparison with measurements made using Cs^+ on the same samples, resulting in a linear relationship ($r^2 > 0.999$) between ratios derived using different primary ions.

Uncertainties for each analysis are calculated using standard error-propagation equations, and incorporate uncertainty from counting statistics, as well as from the linearity of the calibration curve and the uncertainties in the standard compositions used to derive the calibration curves.

Numerical Modeling Protocol.

The diffusion timescales described in the text were determined by a forward-modeling approach, using a 1-D finite-difference method analogous to those described in Press et al.(1992). As diffusion in the **c**-axis direction is $>10^2$ times faster than in the **a**-axis direction, a 1-D semi-infinite half-space geometry with a no-slope boundary condition at the core was utilized. Initial conditions were set as described in the text (see Figure DR-1), as a square wave function with local minima at OH = 0 ppm, and neighboring maxima varied until models mimicking the form of the measured OH were obtained with the minimum amount of misfit between the model and the data. A second model with less extreme minima and maxima was also created and used for comparison.

For each set of initial conditions (Figure DR-1), we forward model the diffusion profile using a constant temperature = 800°C and diffusivities from Brenan (1993). At each time-step, the misfit between the measured OH values and the numerical approximation (averaged over 8µm-wide bins, to allow a comparison with the 8µm analyzed regions) is calculated by a weighted sum of the square of the individual misfits. The model with the lowest misfit is determined to be the best-fit time. The fact that models with OH = 0 (Figure DR-1a) cannot under any circumstances fit the data as well as one with more reasonable (less extreme) initial conditions (Figure DR-1b) suggests that the OH = 0 models are not terribly realistic. Nevertheless, they provide an absolute maximum residence time, which is all we require for our purposes.

Figure DR-1. Diffusion models used to determine maximum timescales for the survival of observed OH zoning in apatite. Dashed line represents initial conditions of diffusion model, grey boxes are OH measurements (as in Figure 2), and heavy black-outlined boxes are the best-fit results of the diffusion model, binned into 8µm boxes. A) Model for most extreme initial values, with local minima set to OH = 0. B) Better fit model using less extreme values, given as an example of more likely original zoning.

Table DR-1. Concentrations of H, F, and Cl, with 2σ uncertainties, including and excluding calibration errors.

References

Brenan, J. (1993). "Kinetics of fluorine, chlorine, and hydroxyl exchange in fluorapatite." Chemical Geology **110**: 195-210.

Press, W. H., S. A. Teukolsky, et al. (1992). Numerical Recipes in C: The Art of Scientific Computing. Cambridge, Cambridge University Press.

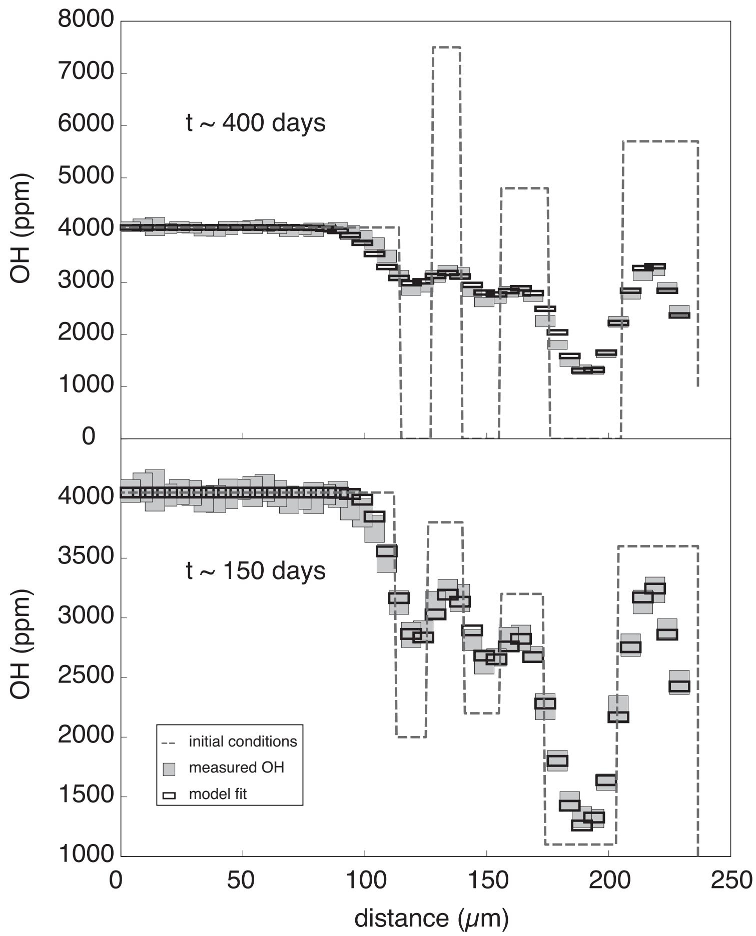
8000
7000
6000
5000
4000
3000
2000
1000
0
t ~ 400 days
OH (ppm)
4000
3500
3000
2500
2000
1500
1000
t ~ 150 days
OH (ppm)
initial conditions
measured OH
model fit
0
50
100
150
200
250
distance (μm)

FIgure DR-1

Table DR-1

CG-E1A

OH (ppm)	2σ*	2σ**	Cl (ppm)	2σ*	2σ**	F (ppm)	2σ*	2σ**
2459	203	284	3925	1141	1151	30529	2196	3449
2913	158	297	3756	994	1019	30008	1166	2863
3234	216	347	3775	773	850	30091	1604	3073
3133	199	332	4074	734	846	30569	1380	3000
2771	188	299	4554	773	913	31277	1674	3198
2244	206	270	5534	650	918	32522	1779	3346
1623	136	192	6280	948	1183	33106	1603	3300
1318	154	178	6214	953	1181	33773	1999	3557
1329	177	191	6018	930	1148	33488	1607	3331
1466	155	189	5616	898	1092	33422	1889	3471
1803	175	223	5384	881	1060	33346	1514	3276
2256	219	278	4646	772	920	32609	1430	3180
2696	127	269	4412	729	870	31661	2030	3425
2832	213	316	4527	663	835	31561	1646	3204
2818	204	311	4976	683	888	31696	1842	3319
2669	144	273	5631	644	924	31825	1597	3200
2621	184	287	5517	1045	1193	31877	1564	3187
2814	176	297	5000	735	925	31586	2012	3409
3166	228	348	4574	650	830	30865	1429	3045
3236	171	327	4430	852	962	30155	2005	3305
3112	223	342	5010	698	901	30142	1145	2865
2894	161	297	5437	830	1029	30702	1348	2996
2857	212	317	5370	782	990	30228	1949	3276
3128	197	330	4971	710	906	29608	1603	3037
3498	237	377	4687	570	789	29526	1552	3004
3743	223	389	4823	740	913	29761	1611	3053
3879	236	405	5091	746	941	29902	1908	3229
3952	264	424	5028	774	954	29837	1359	2933
4034	215	407	5029	863	1018	29834	1832	3180
4032	171	390	5052	825	992	29514	1630	3044
4003	263	427	5143	974	1110	29367	1079	2777
3999	179	390	4981	895	1037	29233	1274	2848
3990	228	409	5046	602	842	28794	1632	2993
4041	219	410	4996	609	842	29015	1988	3216
4088	224	415	5045	713	914	29683	1670	3078
4057	255	427	5053	770	954	29336	1500	2964
4077	168	393	5095	785	967	29516	1748	3110
4039	249	423	4976	533	795	29289	1700	3066
3996	226	409	5048	752	941	29386	1417	2926
3996	217	405	4889	867	1010	28850	1874	3135
4047	208	406	4970	674	881	28720	1204	2777
4056	211	407	4748	815	960	28282	1994	3169
4029	185	395	4911	722	908	28398	1596	2944
4068	346	477	4960	909	1046	28535	1201	2761
4092	244	424	4841	1057	1151	28260	1526	2896
4063	191	400	4893	716	903	28522	1764	3047

CG-I3H

OH (ppm)	2σ*	2σ**	Cl (ppm)	2σ*	2σ**	F (ppm)	2σ*	2σ**
1773	261	453	5639	843	1511	47722	2115	9958
873	158	262	5315	793	1425	34341	1277	7118
483	88	191	5612	619	1407	32926	1395	6857
563	106	204	5248	777	1404	33485	1614	7016
1245	86	309	4127	613	1110	32429	850	6667
1801	176	430	3496	384	891	31422	939	6476
2087	104	469	4130	534	1076	31702	1429	6620
2091	160	481	4916	424	1195	31004	1297	6454
2643	188	594	4261	547	1107	29532	987	6102
3021	118	656	4540	426	1118	29533	1366	6175
2756	190	617	5236	514	1291	29745	1193	6181
2496	146	556	4956	579	1259	30071	1273	6263
2885	232	653	4391	504	1116	29661	1593	6255
2911	204	650	4764	809	1329	30191	1634	6370
2536	318	614	5311	499	1302	30249	1215	6287
2417	146	541	4841	630	1257	29189	1329	6098
2869	319	677	4474	519	1138	28418	1259	5930
3284	181	719	4469	538	1145	27550	1185	5741
3629	249	803	4592	595	1193	27352	802	5635
3620	556	917	4530	748	1253	26659	3484	6457
3691	129	792	4573	398	1116	27395	1524	5790
3673	208	802	4703	559	1200	27673	1811	5926
3717	197	809	4726	545	1199	28043	1127	5828
3755	214	820	4774	486	1187	28102	1277	5871
3761	217	822	4780	640	1250	27431	1503	5792
3847	267	850	4714	673	1252	28043	1320	5869
3894	235	852	4783	653	1256	28372	1623	6009
3898	182	842	4665	728	1269	28085	1337	5881
3864	229	845	4750	526	1196	27109	1591	5752
3840	227	839	4745	525	1195	27309	1374	5736
3767	213	822	4751	529	1198	27766	1023	5753
3716	237	817	4693	562	1199	26799	1390	5639
3799	242	835	4816	580	1231	27365	1373	5746
3765	151	810	4712	952	1399	27225	1188	5677
3789	220	828	4725	515	1187	27297	1302	5716
3744	196	814	4788	528	1205	27505	917	5683
3714	146	799	4776	634	1246	27264	1211	5690
3862	251	850	4979	521	1241	28283	1229	5897
3973	218	864	4854	617	1254	28494	1311	5956
3858	174	833	4819	388	1164	27711	1326	5804
3740	226	819	4706	607	1220	26902	1225	5621
3673	190	798	4696	718	1269	26747	1565	5674
3775	223	826	4721	550	1200	27036	1274	5658

CG-E1D

OH (ppm)	2σ*	2σ**	Cl (ppm)	2σ*	2σ**	F (ppm)	2σ*	2σ**
3978	233	411	4566	661	854	26934	1517	2802
4134	192	408	5057	842	1033	29748	2117	3356

4296	229	436	4992	682	887	29630	1728	3110
4189	259	444	4720	654	846	27269	1209	2668
4132	191	403	4340	729	867	26363	1151	2571
4064	252	426	4445	699	837	26652	1417	2657
3882	203	389	4490	764	958	26767	1310	2774
3793	193	386	4594	638	839	27028	1264	2671
3661	218	379	4603	652	852	26937	1567	2866
3505	244	383	4686	624	826	27319	1401	2734
3477	175	345	4825	675	881	27702	1660	2927
3216	178	332	5031	615	879	28481	1306	2756
3068	186	322	5211	842	1017	29671	1560	3005
2931	248	341	5520	866	1061	30587	2065	3279
2974	200	317	5578	707	958	31495	1948	3356
3081	202	334	5134	755	943	29931	1680	3101
3077	249	352	4736	771	943	27922	1149	2697
3039	193	320	4476	819	939	27005	1960	3046
2882	206	317	4534	763	883	27636	1394	2812
2699	190	294	4685	697	864	27900	1399	2821
2604	167	281	4660	733	903	27459	1487	2814
2566	185	286	4463	817	942	27409	1444	2787
2493	198	287	4737	789	935	27431	1376	2771
2403	164	258	5005	737	912	27817	1582	2836
2428	161	263	5081	626	846	27353	1886	3023
2566	174	277	4793	884	1012	26584	1991	3091
2748	214	318	4583	838	913	26479	1745	2929
2677	202	299	4223	715	816	26080	2092	3063
2380	186	276	4301	848	933	26751	1475	2798
1950	144	219	4533	875	986	27439	1829	2999
1616	171	208	4633	811	948	28065	2017	3203
1390	152	185	4846	729	910	28650	1710	2985
1289	196	200	5058	843	1017	28968	1454	2915
1263	184	189	5027	966	1095	29679	1864	3000
1259	149	173	4639	743	865	29995	1563	3056
1194	141	167	4593	641	831	30516	2005	3282
1183	171	176	4379	696	836	30877	1954	3325
1077	145	158	4292	736	873	31209	1767	3121
1049	126	151	4288	700	822	30958	2171	3422

CG-E1E

OH (ppm)	**2σ***	**2σ****	**Cl (ppm)**	**2σ***	**2σ****	**F (ppm)**	**2σ***	**2σ****
4581	415	554	4604	676	850	26616	1882	2986
4474	318	490	4825	595	818	28839	1902	3151
4843	560	667	5121	724	928	30092	2557	3662
4699	488	609	4853	532	782	28184	1851	3075
4672	272	482	4860	448	736	28377	1547	2917
4716	403	556	5008	666	880	29126	1713	3061
4859	333	526	4879	579	813	28957	2258	3385
4844	278	497	4915	583	819	29023	1509	2945
4836	340	528	4703	608	814	27660	1231	2706
4801	272	491	4883	519	778	28460	933	2649

4944	248	492	5037	424	742	29137	1256	2832
4875	186	463	5053	407	736	28545	1528	2919
4863	183	461	4893	421	727	28147	827	2588
4839	175	456	4897	418	725	27906	881	2586
4903	209	473	4930	394	717	28424	1197	2750
4946	197	472	4880	304	673	28446	1092	2708
4989	232	489	4759	495	752	28139	945	2627
5021	193	477	4796	514	767	27915	1078	2660
5072	157	470	4724	525	766	28094	1042	2660
4941	216	479	4639	435	708	28226	963	2641
5116	264	512	4615	563	778	29015	900	2683
4553	198	441	4453	491	720	27448	1400	2771
4153	205	412	4524	533	751	26293	1231	2600
4022	226	411	4531	649	826	26116	1044	2503
4147	210	414	4424	396	666	27385	1233	2686
4109	146	388	4497	573	773	27176	1047	2589
4195	177	405	4547	523	748	27756	1271	2732
4495	182	431	4413	532	740	28104	1562	2904
4568	232	456	4469	478	714	28939	1343	2857
4068	219	412	4787	531	776	28172	1317	2786
3760	184	373	4719	557	784	27359	935	2560
3897	178	382	4494	430	690	28629	1301	2813
3909	126	366	4282	558	744	28690	887	2652
3394	186	346	4528	473	717	29388	1114	2792
2742	143	278	4818	498	760	29546	1112	2804
2495	125	253	4649	702	872	30153	1012	2815
2334	112	236	4444	545	751	29202	1268	2842
1912	128	209	4811	630	838	29224	1143	2791
1489	88	164	5160	489	788	30426	1114	2876
1322	116	162	4773	514	764	30807	1131	2912
1243	89	147	4133	446	663	31081	917	2859
1170	98	144	3767	475	645	30770	1364	3008
1110	67	131	3837	517	677	31411	951	2897
903	73	119	4104	443	659	31666	1652	3216
443	72	91	4617	774	919	29634	3584	4417
384	98	93	6850	830	1154	35268	2555	3996
371	77	88	6597	1032	1270	31454	1780	3268
388	130	102	6847	687	1066	33072	2328	3704

CG-E1C

OH (ppm)	**2σ***	**2σ****	**Cl (ppm)**	**2σ***	**2σ****	**F (ppm)**	**2σ***	**2σ****
3613	308	423	4286	848	947	26511	1857	2964
3774	271	414	4324	694	838	27801	1642	2926
3683	261	402	4369	683	835	28075	1128	2693
3420	340	429	4195	798	902	28024	1342	2786
3378	224	361	4443	741	881	28470	1733	3026
3555	243	384	4289	837	939	28389	1316	2802
3531	304	415	4255	733	860	27421	1244	2694
3611	198	367	4325	694	838	26711	1599	2823
3747	193	376	4232	685	824	26758	1471	2757

3900	262	419	4409	807	926	27424	2119	3194
3960	208	398	4348	699	843	27246	1596	2860
4011	289	441	4295	438	675	26922	1325	2694
4007	340	469	4211	681	819	26624	1233	2627
3886	565	613	4124	601	758	26261	2182	3162
3722	264	407	4181	635	785	26782	1777	2933
3887	477	550	4367	913	1003	27678	2077	3182
3777	303	432	4232	665	810	27378	1657	2904
3772	249	403	4400	662	823	27608	1632	2907
3718	395	484	4394	628	800	27677	1984	3123
4330	307	474	4433	907	1003	28432	1850	3092
3896	375	483	4093	777	879	26425	1522	2760
4049	271	434	4284	741	868	26997	1627	2860
3855	247	408	4292	460	687	27337	1130	2636
3836	278	423	4437	662	826	28099	1644	2949
3697	282	414	4421	892	990	27974	1951	3122
3495	191	356	4291	698	838	27562	1567	2868
3599	251	391	4223	828	927	27654	1732	2967
3798	291	427	4034	616	760	27838	1410	2805
3666	259	400	3962	765	859	28513	1233	2773
3566	300	415	3872	625	752	28112	1776	3025
3614	265	399	3922	770	859	28186	2105	3235
3768	233	395	3946	665	786	27371	1892	3044
4073	242	422	3861	582	722	26947	1257	2663
4306	269	453	3937	594	737	27125	1131	2620
4132	270	440	3943	570	721	27079	2173	3208
3982	337	466	4026	763	862	27244	1384	2748
3693	199	374	3930	749	844	27880	1717	2975
3516	253	386	4090	651	788	27645	1304	2739
3599	208	371	3949	637	766	27579	1491	2828
3550	246	385	3990	619	758	27486	1649	2908
3392	308	408	3885	573	718	27983	2064	3194
3220	326	407	4296	614	782	28352	1601	2943
3227	270	374	4348	594	773	28240	1995	3167
3769	273	415	4270	474	693	28149	1368	2808
4416	271	462	4112	628	775	27410	1855	3024
4582	298	487	4109	727	843	27207	1813	2984
4249	285	456	4359	807	922	28076	1602	2924
3419	332	424	4260	630	789	28779	997	2698
2447	253	311	4158	547	726	29664	1615	3047
1540	182	208	3818	598	729	29566	1740	3108
1003	118	140	3581	389	578	29613	1548	3009
873	113	130	3589	503	646	29822	1561	3031
706	115	119	3848	812	885	30116	1505	3025
517	108	104	3938	593	736	29643	1469	2971
393	90	92	4305	724	857	30489	1432	3018
361	100	92	4694	671	855	30924	2088	3409
412	116	100	4921	682	882	32390	2236	3601
425	139	107	5138	823	998	32987	2094	3556

456	109	101	5063	888	1039	32977	2212	3626
385	115	97	5182	908	1064	32015	1542	3187
316	147	100	5322	1124	1239	31456	1835	3298

* Uncertainty estimate based on counting statistics of measured ratios. This is the uncertainty most appropriate for comparing measurements within a single profile.

** Uncertainty estimate including calibration error. This is the most appropriate estimate of uncertainty to use to compare different traverses.