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Experimental investigation of H$_2$O and Cl$^-$ solubilities in F-enriched silicate liquids; implications for volatile saturation of topaz rhyolite magmas

Abstract To interpret the degassing of F-bearing felsic magmas, the solubilities of H$_2$O, NaCl, and KCl in topaz rhyolite liquids have been investigated experimentally at 2000, 500, and ≈1 bar and 700° to 975 °C. Chloride solubility in these liquids increases with decreasing H$_2$O activity, increasing pressure, increasing F content of the liquid from 0.2 to 1.2 wt% F, and increasing the molar ratio of ((Al + Na + Ca + Mg)/ Si). Small quantities of Cl$^-$ exert a strong influence on the exsolution of magmatic volatile phases (MVPs) from F-bearing topaz rhyolite melts at shallow crustal pressures. Water- and chloride-bearing volatile phases, such as vapor, brine, or fluid, exsolve from F-enriched silicate liquids containing as little as 1 wt% H$_2$O and 0.2 to 0.6 wt% Cl at 2000 bar compared with 5 to 6 wt% H$_2$O required for volatile phase exsolution in chloride-free liquids. The maximum solubility of Cl$^-$ in H$_2$O-poor silicate liquids at 500 and 2000 bar is not related to the maximum solubility of H$_2$O in chloride-poor liquids by simple linear and negative relationships; there are strong positive deviations from ideality in the activities of each volatile in both the silicate liquid and the MVP(s). Plots of H$_2$O versus Cl$^-$ in rhyolite liquids, for experiments conducted at 500 bar and 910°–930 °C, show a distinct 90° break-in-slope pattern that is indicative of coexisting vapor and brine under closed-system conditions. The presence of two MVPs buffers the H$_2$O and Cl$^-$ concentrations of the silicate liquids. Comparison of these experimentally-determined volatile solubilities with the pre-eruptive H$_2$O and Cl$^-$ concentrations of five North American topaz and tin rhyolite melts, determined from melt inclusion compositions, provides evidence for the exsolution of MVPs from felsic magmas. One of these, the Cerro el Lobo magma, appears to have exsolved alkali chloride-bearing vapor plus brine or a single supercritical fluid phase prior to entrapment of the melt inclusions and prior to eruption.

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Introduction

Magmatic-hydrothermal fluids, which are also known as magmatic volatile phases (MVPs), play an important role in many igneous processes. MVPs are responsible for driving volcanic eruptions, degassing volatiles from the inner Earth to the atmosphere, altering rocks and generating a wide variety of mineral deposits, and influencing magmatic evolution by modifying the compositions and textures of phenocrysts and melts in igneous environments. MVPs have been the object of intense scientific scrutiny in the past decade. For example, recent work has shown that F-poor felsic liquids exsolve one or more MVP(s) if the liquid contains 0.2 to 0.3 wt% Cl$^-$ (Webster 1997). This extensive level of research notwithstanding, there is still a great deal to learn about magmatic degassing, such as the timing and mechanism of MVP exsolution and MVP evolution.

To better understand processes of MVP release from SiO$_2$- and F-rich rhyolitic magmas, we have conducted new hydrothermal experiments at pressures and temperatures representative of shallow crustal magmatic and volcanic conditions. These experiments constrain the solubilities of Cl$^-$ and H$_2$O in three, volatile phase-saturated, F-enriched liquids of rhyolite composition that are very similar to those of silicate melt inclusions from tin rhyolites of central Mexico. We have directed particular attention to melt inclusions from the Cerro el Lobo tin rhyolite, located in San Luis Potosi, Mexico; compositions of these inclusions are compared with those of the F-bearing experimental glasses to determine the MVP-saturated state of this magma and other tin and topaz rhyolite magmas. The Cerro el Lobo magma was chosen for comparison because other compositional characteristics of the melt inclusions led Webster et al. (1996) to suggest that this magma exsolved one or more

MVP(s) before the inclusions were entrapped in quartz phenocrysts, and these new experimental data allow us to test this hypothesis.

Methods

Experimental methods

In this study, Cl^- and H_2O solubilities were determined for 2 molten topaz rhyolites containing 0.2 and 1.2 wt% F (i.e., SM61A and SM 8009 from Spor Mountain, Utah; Table 1). These new solubility data have been combined (Table 2) with published experimental results for a third sample of topaz rhyolite from Spor Mountain (i.e., SM 1) that contains 1.25 wt% F (Webster and Holloway 1990).

A 1:1 molar mixture of reagent grade NaCl and KCl was added to the rock powders and mixed in an agate mortar and pestle for at least 60 min for all experiments involving SM8009 and SM61A except for run 95–9D. The rock powders were not fused to glass prior to use. Less than 2 mg of H_2O and ≤ 2 mg of NaCl + KCl were added for every 15–20 mg of rock powder in each experiment. The chloride salts were added as a 1:1 molar mixture of NaCl:KCl to minimize the variability of the molar ($Na_2O/(Na_2O + K_2O)$) ratio of the run product glasses. The experiments were conducted in sealed $Pd_{30}Ag_{70}$ and Au capsules.

The H_2O contents of the experimental charges were varied by the following techniques: drying some rock powder-chloride mixtures in open capsules overnight at either 110° or 500 °C, running undried mixtures, and adding up to several mg of distilled-deionized H_2O. The intrinsic H_2O contents of the topaz rhyolite starting materials were determined by fusing the rock powders in sealed precious metal capsules and analyzing the glasses by ion microprobe. The H_2O contents of the alkali chlorides were determined by measuring weight loss during heating of the salt powders at high temperature.

Most experiments were conducted in an internally heated pressure vessel (IHPV) at the American Museum of Natural History using the experimental techniques of Webster (1992a,b). The rock powder-chloride $\pm$ H_2O mixtures were run at 500 and 2000 bar (Fig. 1) and $703 \pm 10°$ to 973 ± 10 °C for periods ranging from 78 to 283 h (Table 2). All IHPV runs were quenched isobarically. The oxygen fugacity was not specifically buffered during the experiments, but it was controlled by the inherent oxygen fugacity of the IHPV. The O_2 buffering capacity of the IHPV was determined with a H_2 sensor; the vessel imposes a f_{H_2} that is roughly equivalent to that of the $Mn_{1-x}O$-Mn_3O_4 solid oxygen buffer at 820 °C and 2000 bar *for runs with a water activity of one.*

A single Cl^- solubility experiment was conducted in air, i.e., at 1 atm confining pressure, by heating a Au capsule containing a rock-chloride mixture in a muffle furnace. Temperature was monitored with a chromel-alumel thermocouple, and temperature variations are estimated at ≤ 20 °C. This experiment was quenched in air to room temperature within several seconds. The internal run pressure is not well constrained because the capsule, which was puffed up after quenching, could have contained pressures greater than 1 atm without bursting. Run pressure is believed to be near 1 bar.

Analytical methods

Electron microprobe

The run product glasses were analyzed for Si, Al, Na, K, Ca, Fe, Mn, Ti, Mg, F, and Cl at 15 keV and 10 nA beam current on an ARL-SEMQ electron microprobe using wavelength-dispersive techniques (see Webster and Duffield 1991). All glasses contain salt-bearing vesicles so these analyses required careful attention. Bulk glass compositions were determined in one set of analyses (6 to 10 per glass) with a defocussed electron beam (≈ 20 μm diameter) and peak count times of 20 to 40 s. The samples were moved relative to the defocussed beam during analysis to minimize Na and F migration. The Cl concentrations were determined in a second set of

Table 1 Compositions of silicate melt inclusions from Cerro el Lobo, San Luis Potosi, Mexico, and natural topaz rhyolite starting materials used in Cl^- solubility experiments

Constituent	Topaz Rhyolite SM1[a]	Topaz Rhyolite SM8009[b]	Topaz Rhyolite SM61A[c]	Melt Inclusions[d]
SiO_2	72.90	71.79	74.57	72.8 ± 1.0
Al_2O_3	13.80	14.00	13.02	14.0 ± 0.9
CaO	0.40	0.51	0.81	0.87 ± 0.10
Na_2O	4.60	4.52	3.46	4.48 ± 0.27
K_2O	5.10	4.95	5.47	4.75 ± 0.38
FeO[e]	1.01	1.04	1.10	1.06 ± 0.17
MgO	***[f]	***[f]	0.18	0.01 ± 0.01
TiO_2	0.04	0.03	0.27	0.05 ± 0.03
MnO	0.04	***[f]	0.04	0.03 ± 0.02
F	1.25	1.15	0.19	0.43 ± 0.29
Cl	0.15	0.14	0.07	0.20 ± 0.03
H_2O[g]	1.0	2.1	2.7	1.2 ± 0.9
TOTAL	100.29	100.23	101.88	100.00
Molar (A/CNK)[h]	0.99	1.02	0.99	0.99 ± 0.01
Molar (N/NK)[i]	0.58	0.58	0.49	0.59 ± 0.02
Molar (ANCM/S)[j]	0.35	0.36	0.31	0.36 ± 0.02

[a] Topaz rhyolite sample from Spor Mountain, Utah; analytical methods in Webster and Holloway (1990).
[b] Topaz rhyolite sample from Spor Mountain, Utah; F and Cl analysis of fused glass by electron microprobe and other constituents determined by ICPMS.
[c] Topaz rhyolite sample from Spor Mountain, Utah; sample provided by Eric Christiansen. Analytical methods described in Christiansen et al. (1984).
[d] Composition of 21 melt inclusions in quartz phenocrysts from Cerro el Lobo, San Luis Potosi, Mexico, determined by electron microprobe analysis (Webster et al. 1996).

[e] Total iron as FeO.
[f] Concentration of constituent < 0.01 wt%.
[g] Water content determined by SIMS (Webster et al. 1996).
[h] Molar ratio of $[Al_2O_3/(CaO + Na_2O + K_2O)]$ in starting material.
[i] Molar ratio of $[Na_2O/(Na_2O + K_2O)]$ in starting material.
[j] Molar ratio of $[(Al + Na + Ca + Mg)/Si]$ in starting material.

Table 2 Summary of experimental run conditions and results

Experiment Number	Pressure (kbar)	Temperature (°C)	Duration (h)	Natural Starting Material[a]	Cl⁻ in Glass (wt%)[b]	Computed Cl⁻ in "Fluid" (wt%)[c]	Molar A/CNK[d] of glass	Molar N/NK[e] of glass	Molar ANCM/S[f] of glass	H₂O (wt%)[g] in glass	F (wt%) in glass	Computed D[h]_Cl
13[i]	2.00	800	261	SM1	0.05 ± .01	0.63 ± .05	1.13	0.61	0.41	5.8	1.12	13
14[i]	2.00	800	261	SM1	0.06 ± .01	0.60 ± .05	1.12	0.59	0.39	5.8	1.08	10
93-3	2.17	973	78	SM8009	0.47 ± .05	53 ± 5	1.01	0.57	0.40	1.1	1.30	110
94-1D	2.00	703	283	SM8009	0.59 ± .02	33 ± 20	0.92	0.51	0.36	2.7	1.23	56
96-2A	1.99	942	283	SM8009	0.09 ± .01	22 ± 13	1.01	0.57	0.35	6.2	1.12	240
96-2C	1.99	942	283	SM8009	0.34 ± .01	34 ± 4	0.93	0.56	0.36	5.7	1.15	100
96-2D	1.99	942	283	SM8009	0.26 ± .01	11 ± 6	1.00	0.58	0.35	4.7	1.14	42
96-4B	1.99	750	139	SM8009	0.34 ± .01	42 ± 4	1.20	0.38	0.29	3.9	0.94	120
95-9B	0.50	930	257	SM61A	0.32 ± .02	56 ± 4	1.07	0.40	0.30	2.1	0.14	180
95-9C	0.50	930	257	SM61A	0.35 ± .01	47 ± 4	1.03	0.43	0.30	2.3	0.10	130
95-9D	0.50	930	257	SM61A	0.02 ± .01	2 ± 1	1.07	0.49	0.30	3.0	0.08	100
95-9E	0.50	930	257	SM61A	0.33 ± .02	53 ± 4	1.02	0.42	0.30	3.0	0.15	160
95-9F	0.50	930	257	SM61A	0.31 ± .02	5 ± 3	0.97	0.50	0.30	1.4	0.13	16
95-10F	0.49	910	268	SM61A	0.37 ± .01	15 ± 15	0.97	0.49	0.30	3.5	0.18	41
95-10A	0.49	910	268	SM8009	0.14 ± .01	1 ± 1	0.90	0.59	0.36	2.9	0.94	7
95-10B	0.49	910	268	SM8009	0.36 ± .03	54 ± 4	1.02	0.47	0.34	0.7	1.12	150
95-10D	0.49	910	268	SM8009	0.42 ± .01	3 ± 2	0.85	0.58	0.36	2.8	1.19	7
95-9G	0.50	930	257	SM8009	0.41 ± .04	57 ± 4	0.95	0.48	0.34	2.1	0.86	140
95-10E	0.49	910	268	SM8009	0.39 ± .03	22 ± 22	0.82	0.60	0.36	3.4	1.08	56
95-10G	0.49	910	268	SM8009	0.35 ± .01	4 ± 2	0.83	0.59	0.35	3.0	1.19	11
95-10H	0.49	910	268	SM8009	0.20 ± .02	5 ± 2	0.86	0.58	0.36	2.8	1.15	25
1atm-97-2A	≈0.001[j]	1045	105	SM8009	0.40 ± .04	n.d.[k]	1.02	0.55	0.36	0.2	1.2	n.d.[k]

[a] Starting materials are a mixture of reagent grade NaCl and KCl and one of three natural topaz rhyolites (SM1, SM61A, and SM8009; see Table 1).
[b] Cl⁻ concentration (±1σ precision) of run product glass determined by electron microprobe; see text for methodology.
[c] Computed Cl⁻ concentration (±1σ precision) of volatile phase or phases coexisting with silicate liquids. For experiments at pressures and temperatures requiring two volatile phases, the reported Cl⁻ contents of "fluid" represent Cl in vapor plus brine. See text for methodology. Chloride in "fluid" was measured by chloridometer for runs 13 and 14 (Webster and Holloway 1990).
[d] Molar [Al₂O₃/(CaO + Na₂O + K₂O)] of run product glass.
[e] Molar [Na₂O/(Na₂O + K₂O)] of run product glass.
[f] Molar [(Al + Na + Ca + Mg)/Si] of run product glass.
[g] Water concentration of run product glass determined by SIMS. The ±1σ precision is based on multiple analyses of a single glass and ranges from 0.2 to 0.5 wt%. See text for methodology.
[h] Computed distribution coefficient for Cl⁻ (wt% Cl⁻ in "fluid"/wt% Cl⁻ in melt). For experiments involving two volatile phases, the distribution coefficient represents ((wt% Cl⁻ in vapor + wt% Cl⁻ in brine)/wt% Cl⁻ in melt).
[i] Experiments of Webster and Holloway (1990).
[j] Experiment conducted in sealed gold capsule at 1 atm confining pressure; if capsule contained small overpressure without bursting, then internal pressure may have been greater than, but near, one atm ≈ one bar.
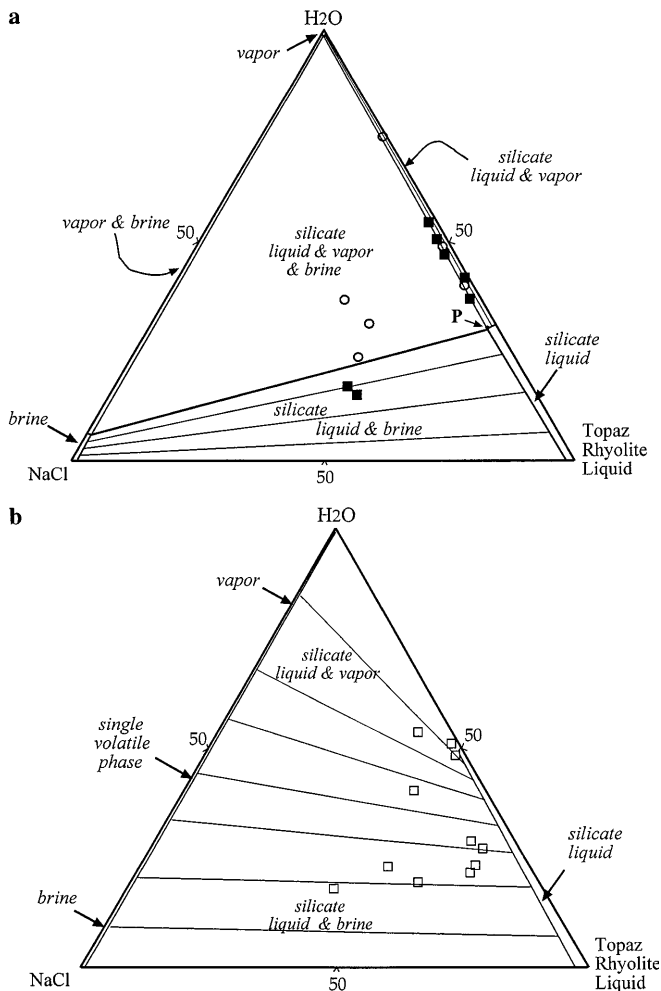[k] Parameters not determined.

Fig. 1a,b Interpretive phase diagram for the pseudoternary system topaz rhyolite-NaCl-H₂O. Phase fields include volatile phase-free topaz rhyolite liquids and fields with liquids saturated in one or two volatile phases. Bulk compositions of the charges for both starting compositions (*square* SM8009, *circle* SM61A) are plotted relative to interpreted phase relations at 500 bar and ≈900 °C (**a**) and 2000 bars and ≈950 °C (**b**). At 2000 bar, silicate liquid SM8009 apparently coexisted with one volatile phase only. At 500 bar, at least three experiments involving SM61A included silicate liquid and two volatile phases, and nearly all SM8009 runs involved silicate liquid and one volatile phase. Concentrations are in mole percent; all chloride in system is computed on a NaCl-equivalent basis. Point *P* is the composition of silicate liquid coexisting with two volatile phases. As described in text, these phase relations are based on extrapolation of experimental results of Bodnar et al. (1985) for 2000 bar, and Bodnar et al. (1985) and Chou (1987) for 500 bars

analyses (10 to 30 analyses per glass with 60 to 120 s count times) on vesicle-free areas of glass with a ≤2 μm diameter beam; the samples were held stationary during analysis. Replicate analyses on the same area of glass indicate that Cl is not mobile under the electron beam at these conditions.

Natural Cl-bearing obsidians of known composition were probed to determine analytical accuracy and precision. Accuracy for Cl is good and equivalent to that reported previously (Webster and Duffield 1991). The predicted precision for a single Cl analysis with 60 s count times, based on counting statistics, ranges from 3% to 1% relative for glasses containing 0.2 to 0.6 wt% Cl, respectively, and the measured analytical precision for Cl in an obsidian containing 0.2 wt% Cl is ≤5% relative. The determination of low

analytical variability for Cl in the run product glasses indicates that Cl is homogeneously distributed in the glasses.

Ion microprobe

The glasses were analyzed for H, Cl, Na, Si, and K by secondary ion mass spectrometry (SIMS) using a Cameca IMS 3f ion microprobe at the Woods Hole Oceanographic Institution (Tables 1, 2). Five to fifteen replicate analyses were conducted on each glass, and all glasses are homogeneous as defined by precisions ≤6% relative. The primary ion beam was typically 15 to 20 μm in diameter. All constituents were analyzed as high-energy ions, and only secondary ions with excess kinetic energies in the 75 ± 25 eV range were analyzed. Details on analytical techniques and standard glasses are described by Webster and Duffield (1991).

The ion yields for Na, K, and Cl were determined for all run product glasses, and they fall well within the ranges expected for felsic glasses. Moreover, the Cl concentrations determined by SIMS show good agreement, within error, with those determined by electron microprobe.

Computational methods

The Cl⁻ contents of the volatile phases in these experiments were computed (Table 2) using the method of Webster and Holloway (1990) and by accounting for H₂O and Cl⁻ initially present in the rock powders, H₂O in fluid inclusions located in the grains of NaCl and KCl, and Cl⁻ and H₂O intentionally added to some charges. For experiments at pressures and temperatures involving two volatile phases, the reported Cl⁻ concentration of the "fluid" actually represents the Cl⁻ content of vapor plus brine. It should be noted that for several runs the sole sources of H₂O were the water-bearing salts and rock powders (additional H₂O was not intentionally added to the charges); due to the large inherent weighing errors on sub-milligram quantities the computed Cl⁻ contents of these "fluids" exhibit comparatively poor precision.

Experimental results and discussion

All run product glasses are vesicular, and the vesicles contain the quenched residue of the MVP(s) (i.e., aqueous liquid, vapor, a trace of silicate material ± alkali chloride crystals). Most glasses are free of crystals, but a few contain a trace of quartz and/or feldspar phenocrysts.

H₂O and Cl⁻ solubility in topaz rhyolite liquids

For silicate liquids saturated with respect to NaCl-, KCl-, and H₂O-bearing volatile phases, the solubilities of H₂O and Cl⁻ in these F-bearing liquids are similar (Fig. 2) in many ways to those observed previously for H₂O and Cl⁻ in molten haplogranite at 500 and 2000 bars (Webster 1997). The solubility of H₂O varies inversely with that of Cl⁻ in topaz rhyolite liquids (Fig. 2, upper graph) and in F-free haplogranite liquids (Fig. 2, lower graph). Moreover, as was observed for H₂O-deficient haplogranite liquids, the solubility of Cl⁻ in H₂O-poor topaz rhyolite liquids varies only marginally with changing pressure. Although Cl⁻ solubility decreases with declining pressure, the influence of pressure is small over the range ≈1 bar to 2000 bar and the
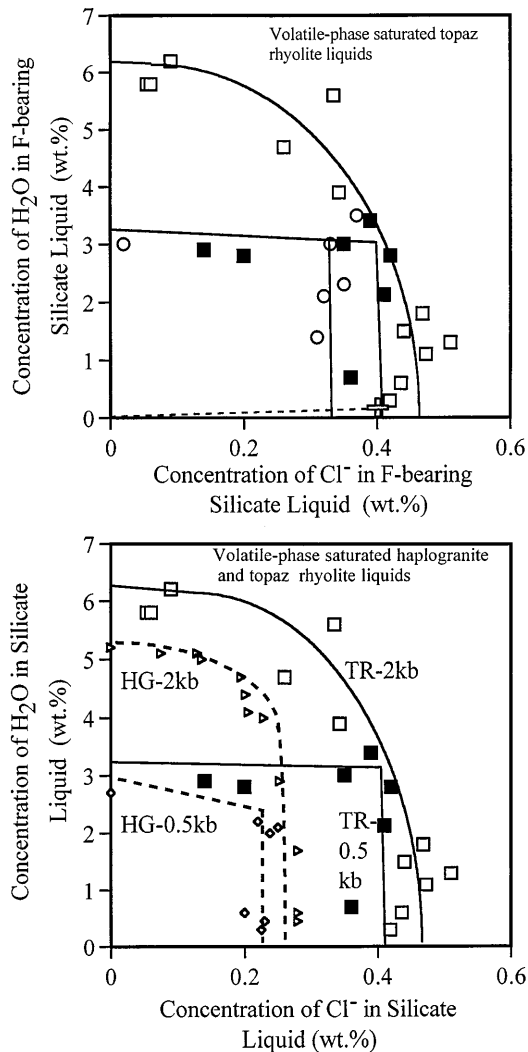
maximum solubility of H_2O in a Cl-free liquid by simple linear and negative relationships (Fig. 2); rather, the MVP saturation curves connecting the y and x intercepts exhibit strong convex curvature away from the origin. Such curvature implies that there are strong positive deviations from ideality in the activities of each volatile in the silicate liquid and in the MVP(s) at 500 bar; these deviations diminish with increased pressure as shown by the 2000 bar data. This is consistent with the results of Shmulovich and Graham (1996), who observed strong positive deviations from ideality for H_2O in aqueous NaCl solutions in equilibrium with albite liquid at 1000 bar and 700°–900 °C and more ideal mixing behavior for H_2O at 4000 bar.

The absolute maximum solubilities of H_2O and Cl^- in melts of natural, F-bearing rhyolites differ from those in haplogranite liquids. At 2000 bar, for example, the H_2O solubility of Cl-free topaz rhyolite SM8009 is approximately 20% greater than that of Cl-free haplogranite liquid, and the Cl^- solubility of H_2O-free topaz rhyolite liquid is roughly twice that of H_2O-free haplogranite liquid. The solubility of H_2O in F-bearing liquids like these has been addressed (Webster and Holloway 1990; Holtz et al. 1993) and will not be discussed further. Prior experimental work on NaCl- and KCl-saturated felsic silicate liquids showed that Cl^- solubility increases with increasing F content and increasing values of the [(Al + Na + Ca + Mg)/Si] ratio (i.e., the molar ANCM/S) in the liquid (Webster 1997). Both the F content and the molar ANCM/S of topaz rhyolite SM8009 are greater than those of the haplogranites studied previously (Webster 1997), and we attribute the enhanced solubility of Cl^- in this molten topaz rhyolite to be a result of these differences in composition.

Fig. 2 Plots showing solubility of H_2O and Cl^- in silicate liquids saturated in one or two volatile phases. Solubilities for topaz rhyolite liquids are shown in *upper graph* at 2000 bar and 750°–990 °C (*open square* SM8009), 500 bar and 910°–930 °C (*open circle* SM61A, *filled square* SM8009), and ≈1 bar (*open cross*). In the lower graph, solubilities for topaz rhyolite liquids are compared with those for haplogranite liquids (*triangle* 2000 bar, *diamond* 500 bar) at 800°–1075 °C. Haplogranite solubility data (*dashed curves*, labeled *HG*) are from Webster (1997); topaz rhyolite data (*solid curves*, labeled *TR*) are from this study and Webster (1997). Curves designate stable compositions of silicate liquids saturated with a magmatic volatile-phase or phases. Chloride solubilities in silicate liquids increase with increasing pressure, increasing abundance of F, and increasing molar [(Al + Na + Ca + Mg)/Si] with all other variables equal. Associated precision ($\pm 1\sigma$) is roughly equivalent to twice the size of each symbol

Phase relations in the pseudo-ternary system: NaCl-H_2O-topaz rhyolite liquid

We have converted the abundances of H_2O, silicate liquid, and total Cl^- (on an equivalent wt% NaCl basis) in the starting materials to mole fractions and plotted them on interpretive, pseudo-ternary phase diagrams for 500 bar (≈900 °C) and 2000 bars (≈950 °C) in order to determine the number of volatile phases that were stable during each of these experiments (Fig. 1). It is important to note that using silicate liquid as one of the components assumes that this phase dissolved congruently in the volatile phase(s) and that the liquid compositions did not change (i.e., each run product glass has roughly the same composition). It is also noteworthy that: (1) although the positions of the tie lines are interpretive they are consistent with the compositions of silicate liquid-volatile phase pairs, (2) the solubility of silicate liquid in molten NaCl at these conditions is unconstrained and we have assumed this solubility to be negligible (i.e., < 1 wt%) at both pressure conditions, (3) the solubilities of topaz rhyolite liquid in an aqueous volatile phase that we used are consistent with the solubilities determined

difference in Cl^- solubility is not statistically significant between 500 bar and ≈1 bar. Furthermore, plots of H_2O versus Cl^- in haplogranite and topaz rhyolite liquids show similar trends. At 2000 bar the solubility data for both liquids can be fit by smooth curves whereas at 500 bar the solubility plots show distinct breaks-in-slope.

In F-poor and F-bearing felsic liquids, the maximum solubility of Cl in a H_2O-poor liquid is not related to the

experimentally by Webster (1990) and Luth and Tuttle (1969), and (4) the phase relations shown for bulk compositions in which a silicate liquid was stable are also interpretive and are not based on direct observation of the number of volatile phases present during the experiments.

Phase relations on the silicate-free NaCl-H$_2$O join for 500 bar pressure (Fig. 1a) were extracted from the experimental data of Bodnar et al. (1985) and Chou (1987) that are consistent with the observations of Sourirajan and Kennedy (1962). For invariant conditions involving three phases, i.e., silicate liquid, vapor, and brine, we assume that the silicate liquid composition is located at point P (i.e., at the sharp bend in the phase boundary for the silicate liquid-only field). This distinctive 90° or near 90° break-in-slope pattern, also shown in graphs of H$_2$O versus Cl (Figs. 1, 2), is assumed to be a result of immiscibility in the MVPs (Webster 1997), based on the results of previous experimental studies of alkali chloride-enriched systems at comparatively high temperature and low pressure where two MVPs are stable (Shinohara et al. 1989; Webster 1992a; Lowenstern 1994; Shinohara 1994).

Phase stability on the binary NaCl-H$_2$O join for 2000 bar pressure (Fig. 1b) is based solely on Bodnar et al.'s (1985) extrapolation of the phase relations observed at lower temperatures and pressures. These data suggest that only one volatile phase is stable for all NaCl contents of the system at 2000 bar and these temperatures. This interpretation contrasts with the extrapolations of Chou (1987), which suggest that vapor and brine are stable with roughly 25 to 55 wt% NaCl at 2000 bars and temperatures ≤950 °C in the system NaCl-H$_2$O. We have chosen the results of Bodnar et al. (1985), because subsequent studies (Joyce and Holloway 1993; Webster 1997) imply that only one volatile phase is stable at 2000 bar and temperatures of 850° to 950 °C for NaCl- ± KCl-bearing aqueous systems. The locations of the bulk compositions of the charges for the 2000 bar runs in NaCl-, H$_2$O-, silicate liquid-space imply that topaz rhyolite liquid SM8009 coexisted with either H$_2$O-rich vapor, alkali chloride-rich brine, or a fluid of intermediate composition at this pressure.

The bulk compositions of the charges for most 500 bar experiments plot in two-phase fields (i.e., the silicate liquid plus vapor and the silicate liquid plus brine fields of Fig. 1) or along the boundary for 2-phase and 3-phase conditions. This suggests that silicate liquid coexisted with either vapor or brine for most of the runs. This interpretation is problematic because several of the experiments involved significant weighing errors, which may have caused their bulk compositions to plot in the two-phase fields incorrectly. Nevertheless, it appears that most 500 bar runs involved silicate liquid plus vapor or brine. Under these conditions, phase-rule constraints indicate that the compositions of the silicate liquid and the associated volatile phase were unbuffered and were free to change as a function of the starting Cl$^-$/H$_2$O ratio of the charge.

Conversely, the bulk compositions of three of the experimental charges for SM8009 plot well within the three-phase field, which suggests that the silicate liquid in these runs coexisted with vapor and brine. The presence of a third phase at temperatures ≥900 °C is important because phase-rule constraints indicate that the activities of Cl$^-$ and H$_2$O in the silicate liquid and coexisting volatile phases must have been fixed at these conditions (Shinohara 1994). Within the three-phase field, the compositions of the silicate liquid and the coexisting volatile phases will vary only if pressure and/or temperature change (Candela and Piccoli 1995; Piccoli and Candela 1995). Thus, even though the Cl$^-$/H$_2$O ratios of the bulk compositions for these three experimental charges were different, only the relative proportions of liquid and volatile phases may change. The activities of Cl$^-$ and H$_2$O in the silicate liquid and volatile phases were fixed and equivalent to those of the phases located at the three corners of the 3-phase field.

It is clear (Figs. 1, 2) that the maximum H$_2$O and Cl$^-$ concentrations of the three 500 bar vapor- and brine-saturated topaz rhyolite liquids (SM8009) that are situated near the break-in-slope were not buffered or constrained to the same extent as those of the three 500 bar haplogranite liquids saturated in vapor and brine at similar temperature conditions (also located at a break-in-slope). The 500 bar haplogranite glasses containing ≤0.25 wt% Cl$^-$ and roughly 2 wt% H$_2$O are tightly clustered at the break-in-slope, whereas the Cl$^-$ and H$_2$O concentrations of the SM8009 glasses exhibit greater variability. These topaz rhyolite glasses also show small but distinct variations in their F concentrations, molar A/CNK [Al$_2$O$_3$/(CaO + Na$_2$O + K$_2$O)] ratios, and molar ANCM/S ratios, which contrasts with the minimal compositional variability shown by the haplogranite liquids, and we suspect that the poor clustering of the topaz rhyolite liquids is a result of these compositional differences.

Discussion

Volatile phase saturation of tin/topaz rhyolite magmas

Theoretical constraints, experimental research, and recent improvements in our knowledge of volatile abundances in felsic magmas are consistent with the exsolution of volatile phases in volcanic systems "early", i.e., well before eruption. Simple computations indicate that the dominant minerals crystallizing from granitic magmas, i.e., quartz and feldspar, will remove vanishingly small quantities of H$_2$O, CO$_2$, F, Cl, B, and S from silicate melts, and as a result, residual melts will become rapidly and increasingly enriched in these constituents as magmatic evolution progresses. This is true even if we account for the loss of volatiles in melt to hydrous phenocrysts that may be present. A MVP exsolves when *the combined vapor pressures of all magmatic volatiles* exceed the lithostatic pressure, and that is why F-poor

and F-enriched felsic liquids will exsolve H_2O- and Cl-bearing MVPs with as little as 1 wt% H_2O and 0.2 to 0.5 wt% Cl in the liquid at 2000 bar.

The compositions of silicate melt inclusions provide constraints on pre-eruptive abundances of volatiles and other mobile constituents in natural silicate melts (Roedder 1984; Webster and Duffield 1991, 1994; Lowenstern 1995). We have compared the concentrations of Cl^- and H_2O in more than 120 melt inclusions entrapped in quartz phenocrysts from five tin/topaz rhyolites with their abundances in the experimentally-prepared topaz rhyolite glasses, to seek evidence of MVP saturation during the evolution of these rhyolite magmas (Fig. 3). Melt inclusion-bearing phenocrysts were separated from rock samples collected at Cerro el Pajaro and Cerro el Lobo, Mexico; Spor Mountain and Honeycomb Hills, Utah; and Taylor Creek, New Mexico. We have focussed on inclusions containing < 1.5 wt% F because this is similar to the range of F in the run product glasses and because the F content of silicate liquids influences the solubilities of Cl^- (Webster 1997) and H_2O in silicate liquids (Holtz et al. 1993). Liquids containing more than 1.5 wt% F should dissolve comparatively more Cl^- and H_2O before saturating in and exsolving volatile phases.

We assume that each melt inclusion represents a microscopically-sized aliquot of topaz rhyolite melt and that the average abundances of volatiles in the melt inclusions represent the average volatile abundances of the rhyolite melts prior to eruption. We also offer the cautionary note that the apparent pre-eruptive H_2O concentrations may be somewhat low due to diffusion of H_2

or H_2O from the inclusions through the host phenocrysts or through volatile loss along cracks in phenocrysts after inclusion entrapment (Lowenstern 1995). Specifically, diffusive loss of H_2 from the melt inclusions may have occurred as the hot volcanic materials were cooled after eruption. Moreover, some melt inclusions from Taylor Creek and from the Mexican localities contain abundant crystals, and consequently, it was necessary to rehomogenize these inclusions to crystal-free glasses by heating the phenocrysts in our laboratory prior to analysis. Diffusive loss of H_2 could also have taken place during the rehomogenization process.

The melt inclusion compositions (Fig. 3) imply that the pre-eruptive abundances of H_2O in these rhyolite melts ranged from < 1 to > 5 wt% and that most micro-aliquots of melt from these magmas apparently contained from 0.1 to 0.4 wt% Cl^-. Although the Cl^- abundances are lower than the H_2O concentrations by an order of magnitude, these Cl^- contents are significant because, in general, they are similar to the Cl^- abundances of the volatile phase-saturated, F-enriched felsic liquids of our experiments.

In particular, comparison of the apparent pre-eruptive concentrations of H_2O and Cl^- in the Honeycomb Hills melt phase with the experimentally-determined solubility limits for H_2O and Cl^- in topaz rhyolite liquids indicates that the Honeycomb Hills magma may have exsolved MVPs over a wide range in pressure and, in particular, that some fractions of magma were MVP-saturated at pressures > 500 bar. Moreover, the first MVP(s) (e.g., either a single aqueous, alkali chloride fluid or coexisting vapor and brine) to exsolve from this F-enriched rhyolite melt could have been strongly enriched in Cl^-. This is apparent from the comparatively high Cl/H_2O ratios of many of the melt inclusions and the observation that many inclusions plot near the Cl-enriched portions of the H_2O-Cl^- solubility curves. This argument assumes, however, that the Cl^-/H_2O ratios are not artificially high because the H_2O contents were reduced by diffusive loss of H_2 or H_2O from the melt inclusions after entrapment.
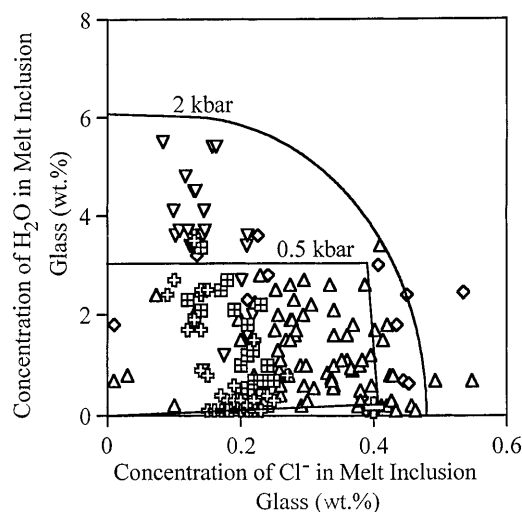

Fig. 3 Plot of Cl^- and H_2O concentrations of > 120 melt inclusions entrapped in quartz phenocrysts from tin and topaz rhyolites: Cerro el Pajaro, Mexico (*cross*), Cerro el Lobo, Mexico (*lined box*), Honeycomb Hills, Utah (*downward triangle*), Taylor Creek Rhyolite, New Mexico (*upward triangle*), and Spor Mountain, Utah (*diamond*) (Webster et al. 1991, 1996; Webster and Duffield 1991). Melt inclusion compositions imply that some fractions of Honeycomb Hills magma should have been saturated in one or more MVPs at 2000 bar. Most melt inclusions imply that many first-formed MVPs should have been enriched, comparatively, in alkali chlorides; see text for discussion

Volatile phase saturation of Cerro el Lobo magma prior to eruption

Although most silicate melt inclusions from the F-bearing rhyolites (Fig. 3) display considerable dispersion in their abundances of Cl^- and H_2O, melt inclusions from the tin rhyolite of Cerro el Lobo, Mexico, show a restricted range in Cl abundance and a distinct negative correlation between Cl^- and H_2O (Fig. 4). Prior investigation of Cerro el Lobo melt inclusions led investigators to suggest that this F-enriched, rhyolite-forming magma had either reacted or equilibrated with a MVP before the melt inclusions were entrapped in quartz phenocrysts (Webster et al. 1996). In that study, five rhyolite samples were collected at Cerro el Lobo which is located approximately 6 km ENE of Tepetate,
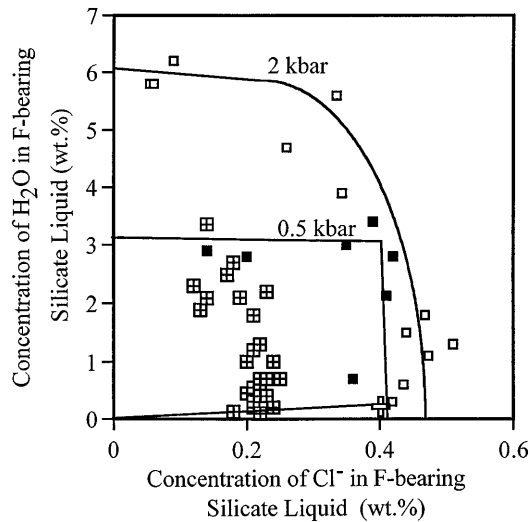
Fig. 4 Comparison of Cl⁻ and H_2O concentrations of Cerro el Lobo melt inclusions (*lined box*) with solubilities of Cl⁻ and H_2O in topaz rhyolite liquids (symbols as in Fig. 2) saturated in one or more MVPs. The melt inclusions show a negative correlation between Cl⁻ and H_2O and a limited range in Cl⁻ contents, which is similar to the behavior of these volatiles in MVP-saturated topaz rhyolite liquids. This correspondence suggests that the Cerro el Lobo liquid was saturated in one or more MVPs prior to eruption but the generally low Cl⁻ contents are problematic; see text for discussion.

San Luis Potosi, Mexico. Four of the samples were collected along a vertical traverse up the face of a cliff on the southeast side of the volcanic dome, and the fifth sample was collected at the crest of the dome roughly several hundred meters away from the cliff locality. Of the four cliff samples, one was taken from the vitrophyric base of a northeast-directed flow and the other three samples were collected progressively upwards and through the core of the flow. Webster et al. (1996) constrained relative chemistratigraphic relationships at Cerro el Lobo by assuming that the sample from the vitrophyric base represents first-erupted magma and that the overlying rhyolite samples originated from progressively greater depths in the magma reservoir. The compositions of the melt inclusions were determined by electron microprobe and SIMS analysis, and the results (Fig. 5) show: (1) the lowest abundances of Cl⁻, B, and Be and the highest concentrations of H_2O occur in first-erupted magma and (2) the pre-eruptive abundances of Cl⁻, B, and Be in the tin rhyolite liquid increase and the H_2O content decreases while sampling progressively deeper into the magma reservoir. It was concluded that the covariation of Cl⁻, B, and Be with H_2O could not be the result of crystal fractionation of a hydrous mineral, because amphiboles and apatite are not present in these rocks and because biotite occurs only as rare and highly-oxidized phenocrysts. Consequently, it was suggested that a MVP extracted Cl⁻, B, and Be from the upper-

Fig. 5 Plots showing pre-eruptive concentrations of H_2O, Cl⁻, Be, and B in Cerro el Lobo liquid as a function of apparent position in magma reservoir; volatile abundances were determined from melt inclusion compositions as described in text. Positions 4 through 1 are located progressively deeper into magma reservoir. First-erupted liquid contained the highest concentrations of H_2O and lowest abundances of Cl⁻, Be, and B, on average. These relationships are consistent with the observations in Fig. 4, suggesting that MVP(s) may have exsolved from Cerro el Lobo magma before tin rhyolite liquid was entrapped in quartz phenocrysts. One sigma precision for Cl⁻ is shown as *horizontal bars*
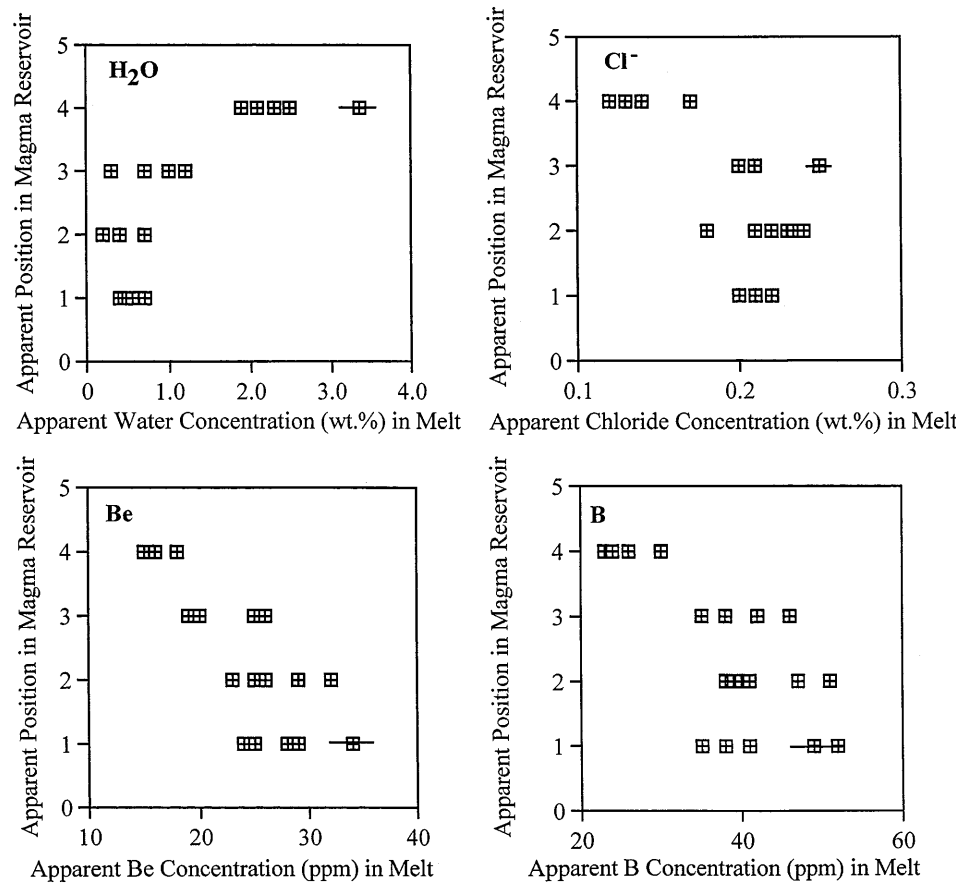
most, H₂O-enriched fraction of magma (Webster et al. 1996).

Comparison of these melt inclusion compositions with the compositions of volatile phase-saturated topaz rhyolite liquids provides additional evidence regarding volcanic degassing of this magma. The negative correlation between Cl^- and H_2O in the Cerro el Lobo melt inclusions is analogous to the trends shown by these volatiles in topaz rhyolite liquids saturated in NaCl- and KCl-bearing volatile phases (Fig. 4), and the abundances of these volatiles in the Cerro el Lobo liquid, prior to eruption, are very similar to those shown by MVP-saturated topaz rhyolite liquids and haplogranite liquids (Fig. 1). The melt inclusions (i.e., the micro-aliquots of Cerro el Lobo liquid) containing < 2 wt% H_2O show a very restricted range in Cl^- concentration (i.e., 0.18 to 0.25 wt%) implying that the Cl^- concentrations of these aliquots of silicate liquid were not free to increase progressively during melt evolution. Instead, they were buffered or fixed by some phase(s) during the chemical evolution of the magma. These inclusions also contain a broad range in H_2O contents implying the magmatic abundances of H_2O were not so constrained. This is consistent with our experimental data demonstrating that the H_2O contents of MVP-saturated topaz rhyolite liquids can vary much more than the Cl^- concentrations for a single pressure condition (Fig. 2). It is important to note that even if the apparent pre-eruptive H_2O concentrations of these inclusions are somewhat low due to diffusive loss of H_2 or H_2O from entrapped liquid or glass, the *relative differences* in H_2O contents of the melt inclusions should be roughly similar to the relative differences in the Cerro el Lobo liquid prior to eruption.

The presence of fixed Cl^- abundances of only 0.2 to 0.24 wt% in the melt inclusions is somewhat inconsistent with the experimental data and, therefore, problematic. The Cl^- solubility experiments show that even at pressures as low as ≈1 bar, extremely H_2O-poor, MVP-saturated silicate liquids containing 1.2 wt% F should dissolve at least 0.4 wt% Cl. Thus, the apparently low Cl^- concentrations of the H_2O-poor Cerro el Lobo inclusions are not a result of MVP saturation at pressures near 1 bar, and hence, must be a result of differences in liquid composition (i.e., Cl^- activity). For example, although the mean ANCM/S ratios of the inclusions are similar to those of sample SM8009, the F contents are not exactly equivalent between the 8009 run glasses and the melt inclusions. Furthermore, our experiments involved NaCl- and KCl-rich MVPs (i.e., high Na and K activities were forced on the system by the experimental procedure used), whereas, the MVP(s) that exsolved from the Cerro el Lobo melt may have contained comparatively lower abundances of Na and K and higher abundances of other cations such as Ca and Fe. We speculate that Cl^- activity of the Cerro el Lobo melt was fixed at values lower than that of our experiments, but the cause of this discrepancy is unknown and requires investigation.

In summary, the correspondence in trends of Cl^- versus H_2O with the experimental results implies that the Cerro el Lobo magma exsolved and equilibrated with one or more magmatic volatile phases prior to eruption. These volatile phase(s) apparently sequestered H_2O, Cl^-, Na, K, B, Be and other constituents from the silicate liquid which explains the distinct covariations involving H_2O, Cl^-, B, and Be in the inclusions (Fig. 5).

Additional evidence for "early" MVP saturation of felsic magmas

Our conclusion that the Cerro el Lobo magma exsolved and equilibrated with MVP(s) prior to eruption is consistent with the results of other melt inclusion studies. For example, "early" exsolution of a MVP from eruptive magmas of intermediate to felsic composition has been documented through recent geochemical investigations of silicate melt inclusions from volcanic units at Long Valley Caldera, California (Anderson et al. 1989), the Valles Caldera, New Mexico (Dunbar and Hervig 1992; Stix and Layne 1996), Pantelleria, Italy (Lowenstern 1994, 1995), and at Mt. Pinatubo, in the Philippines (Gerlach et al. 1995). In each of these studies it was concluded that late-stage crystallization and magma evolution took place in the presence of a volatile-enriched phase or phases; the MVP(s) had exsolved *well before eruption-driven degassing occurred.* Thus, it follows for volatile phase saturation brought on by a reduction in confining pressure, that the abundances of volatiles and other mobile constituents in some silicate melt inclusions may not represent the maximum pre-eruptive concentrations of these components in natural silicate liquids (Lowenstern 1993; Gerlach et al. 1995; many others). Some melt inclusions may represent partially degassed magma, and hence, for future studies it may be necessary to identify and study melt inclusions that were entrapped prior to MVP exsolution.

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