

The exsolution of magmatic hydrosaline chloride liquids

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Abstract

Hydrosaline liquid represents the most Cl-enriched volatile phase that occurs in magmas, and the exsolution of this phase has important consequences for processes of hydrothermal mineralization and for volcanic emission of Cl to the atmosphere. To understand the exsolution of hydrosaline liquids in felsic to mafic magmas, the volatile abundances and (Cl/H₂O) ratios of more than 1000 silicate melt inclusions (MI) have been compared with predicted and experimentally determined solubilities of Cl and H₂O and associated (Cl/H₂O) ratios of silicate melts that were saturated in hydrosaline chloride liquid with or without aqueous vapor in hydrothermal experiments. This approach identifies the minimum volatile contents and the values of (Cl/H₂O) at which a hydrosaline chloride liquid exsolves from any CO₂- or SO₂-poor silicate melt. Chlorine solubility is a strong function of melt composition, so it follows that Cl solubility in magmas varies with melt evolution. Computations show that the (Cl/H₂O) ratio of residual melt in evolving silicate magmas either remains constant or increases to a small extent with fractional crystallization. Consequently, the initial (Cl/H₂O) in melt that is established early during partial melting has important consequences for the exsolution of vapor, vapor plus hydrosaline liquid, or hydrosaline liquid later during the final stages of melt ascent, emplacement, and crystallization or eruption. It is demonstrated that the melt (Cl/H₂O) controls the type of volatile phase that exsolves, whereas the volatile abundances in melt control the relative timing of volatile phase exsolution (i.e., the time of earliest volatile exsolution relative to the rate of magma ascent and crystallization history).

Comparing melt inclusion compositions with experimentally determined (Cl/H₂O) ratios and corresponding volatile solubilities of hydrosaline liquid-saturated silicate melts suggests that some fractions of the eruptive, calc-alkaline dacitic magmas of the Bonnin and Izu arcs should have saturated in and exsolved hydrosaline liquid at pressures of 2000 bars. Application of these same melt inclusion data to the predicted volatile solubilities of Cu-, Au-, and Mo-mineralized, calc-alkaline porphyritic magmas suggests that the chemical evolution of dioritic magmas to more-evolved quartz monzonite compositions involves a dramatic reduction in Cl solubility that increases the probability of hydrosaline liquid exsolution. The prediction that quartz monzonite magmas should exsolve a hydrosaline chloride liquid, that is potentially mineralizing, is consistent with the general observation of metal-enriched, hypersaline fluid inclusions in the *more felsic plutons* of numerous porphyry copper systems. Moreover, comparing the volatile contents of melt inclusions from the potassic, alkaline magmas of Mt. Somma-Vesuvius with the predicted (Cl/H₂O) ratios of hydrosaline liquid-saturated melts having compositions similar to those of the volatile-rich, alkaline magmas associated with the orthomagmatic gold–tellurium deposits of Cripple Creek, Colorado, suggests that hydrosaline chloride liquid should have exsolved at Cripple Creek as the magmas evolved to phonolite compositions. This prediction is consistent with the well-documented role of Cl-enriched, mineralizing hydrothermal fluids at this major gold-mining district.

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1. Introduction

Silicate magmas saturate in volatiles and exsolve a broad spectrum of volatile phases that includes aqueous, aqueous-carbonic, and aqueous-sulfate vapors or liquids; and sulfide, carbonate, phosphate, and/or hydrosaline (Cl- and/or F-rich) liquids. Magmatic hydrosaline chloride liquids (herein abbreviated MHL), which under certain conditions are equivalent to chloride-enriched aqueous liquids, hypersaline brines, or water-bearing salt melts and have been referred to as such (Roedder, 1992; Cline and Vanko, 1995; Candela and Piccoli, 1995; Shinohara, 1994), are fundamentally important to processes of ore formation in Cu-, Mo-, Au-, Sn-, Fe- and W-mineralized magmas. Hydrosaline chloride liquids, with or without a coexisting aqueous vapor, also exsolve from or may even be assimilated by unmineralized magmas, and important examples include the alkaline eruptive systems of Pantelleria (Lowenstern, 1994) and Mt. Somma-Vesuvius (Webster and DeVivo, 2002); granites of Sardinia (Frezzotti, 1990), Norway (Hansteen, 1989), and Ascension Island (Roedder and Coombs, 1967; Webster and Rebbert, 2001); and more rarely in ocean island basalts (Lassiter et al., 2002). Hydrosaline liquids are readily formed through unmixing of a Cl-bearing aqueous fluid into vapor plus hydrosaline liquid (brine), but prior research has also focused on the question of whether or not hydrosaline liquids will exsolve directly from silicate melts in nature (Roedder, 1992; Lowenstern, 1994; Cline and Vanko, 1995). A goal of this study is to address this issue by comparing the results of geochemical modeling that predict Cl concentrations of MHL-saturated silicate melts with the Cl and H₂O concentrations of silicate melt inclusions from some of Earth's most volumetrically significant magmatic systems in order to determine the likelihood and importance of MHL saturation and exsolution in mineralizing and barren magmas.

2. Background

2.1. Phase relations of chlorine-enriched systems

Chlorine-enriched silicate melts may exsolve either: a Cl-bearing aqueous vapor, a MHL, a Cl-bearing

supercritical fluid, or vapor plus MHL. Phase relations for the NaCl–KCl–H₂O systems at low-pressure and low-temperature magmatic conditions have been determined experimentally (Bodnar et al., 1985; Chou, 1987; Sterner et al., 1992), but the stability relationships among the volatile phases in these systems are poorly known for Ca-, Mg-, and Fe-enriched systems at the higher pressure and temperature conditions of silicate magmas. In addition, volatile phase relationships for H₂O-, CO₂-, and Cl-enriched systems at magmatic conditions are not well constrained (Bowers and Helgeson, 1983; Joyce and Holloway, 1993; Duan et al., 2003).

Experimental and theoretical investigations (Shinohara et al., 1989; Shinohara, 1994; Webster, 1997; Webster et al., 1999; Signorelli and Carroll, 2000) have established an accurate means of distinguishing silicate melts coexisting with one volatile phase from melts saturated with two volatile phases (Fig. 1). This schematic diagram compares the concentrations of H₂O and Cl in a silicate melt saturated in one volatile phase (i.e., the solid curve) and those in a silicate melt saturated in either one or two volatile phases (dashed curve). With increasing (Cl/H₂O) in the system, the dashed curve delimits the volatile contents of silicate

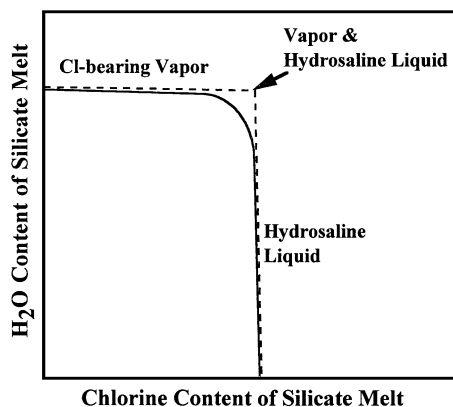


Fig. 1. Schematic plot of H₂O and Cl concentrations of a silicate melt that is saturated in either (solid curve) a single volatile phase that evolves gradually from vapor to hydrosaline chloride liquid as the (Cl/H₂O) ratio of the system increases or (dashed curve) differing volatile phases that sequentially include vapor only, vapor plus hydrosaline liquid, and hydrosaline liquid only with increasing (Cl/H₂O). The dashed curve represents a melt–fluid system that involves subcritical behavior at the sharp break in slope. See text for discussion.

melt coexisting with: vapor only (along the horizontal limb of curve), vapor plus MHL (at the point of intersection of the horizontal and vertical limbs of curve), and MHL only (along the vertical limb of curve). As the relationships involving volatile contents and phase relations have a strong bearing on magmatic degassing, they require further explanation.

The solid curve depicts the change in volatile solubilities of a silicate melt coexisting with a single volatile phase at all conditions. With increasing Cl content in the system, the volatile phase undergoes a progressive increase in (Cl/H₂O) and gradually evolves from vapor to MHL while the (Cl/H₂O) of the silicate melt also increases.

Conversely, for systems that exsolve more than one volatile phase (dashed curve), the Cl contents of the silicate melt and the vapor increase while the H₂O concentration of the silicate melt is relatively constant with increasing Cl in the system. This situation is maintained until the system saturates in aqueous vapor plus MHL at the sharp break in slope. As the Cl content of the system continues to increase, the Cl and H₂O concentrations of the silicate melt, MHL, and vapor are fixed because two volatile phases are stable. Here, the phase rule requires that the volatile activities are held constant while the ratio of (MHL/vapor) increases in response to increasing Cl in the system. Eventually, the Cl content of the system is sufficiently high such that vapor is no longer stable, the melt is saturated in MHL only, and the volatile solubilities of the melt and MHL again begin to change along the vertical limb of the curve. Specifically, the H₂O content of the silicate melt decreases dramatically while the Cl content of the silicate melt increases negligibly. In summary, the sharp break in slope reflects subcritical volatile phase behavior which is favored by conditions of decreasing pressure and/or increasing temperature (Bodnar et al., 1985; Chou, 1987; Sterner et al., 1992). It is also important to understand that, for both conditions and solubility curves (i.e., for supercritical or subcritical volatile phase behavior), the silicate melt is saturated with respect to a MHL under the most Cl-rich conditions.

2.2. Experimental calibration of phase relations

In addition to the strong influence of the (Cl/H₂O) ratio on volatile phase exsolution, melt composition,

temperature, and pressure affect the disposition of the volatile solubility curves and hence control MHL exsolution. Water and Cl solubilities have been determined experimentally for molten granite (Webster, 1997), topaz rhyolite (Webster and Rebbert, 1998), phonolite (Webster et al., 2003a,b), latite, andesite, and basalt (Webster et al., 1999) at 2000 bars (Fig. 2A). Solubility data are also available for several of these melts at 500 bars. Through the compositional range of granite to basalt, Cl solubility in H₂O-poor silicate melts increases over an order of magnitude and H₂O solubility in Cl-poor melts varies within the range of 5 to 7 wt.%. Moreover, as shown previously (Fig. 1) a MHL exsolves from each of these melts when characterized by high (Cl/H₂O) ratios.

To determine the range of (Cl/H₂O) through which granite, phonolite, andesite, and basalt melts saturate in a MHL, bold lines which delimit the stability field of MHL have been overlain on the volatile solubility curves (Fig. 2B). Specifically, a MHL is defined herein as a volatile phase containing at least 25 wt.% Cl (or 41 wt.% NaCl equivalent). The limiting value of this parameter is based on the spread in measured and computed Cl contents of the volatile phases coexisting with the melts of the cited experimental studies (i.e., along the vertical limbs of the solubility curves) (Fig. 2A). For those experiments involving silicate melt, vapor, and MHL, instead of a single volatile phase, the 25 wt.% Cl value represents the average Cl content of the vapor plus MHL. Each bold line is labeled with the minimum (Cl/H₂O) ratio required for exsolution of MHL from the respective melt. For example, volatile phase-saturated granite melts at 2000 bars having compositions similar to that used in the study of Webster (1997) coexist with a MHL for (Cl/H₂O) in melt ratios ≥ 0.05 . Volatile phase-saturated topaz rhyolite melts coexist with a MHL with roughly similar (Cl/H₂O). As the silicate melt compositions become less felsic, however, the minimum (Cl/H₂O) in melt ratio for MHL saturation increases. Volatile phase-saturated phonolite melt requires (Cl/H₂O) ≥ 0.15 , latite and andesite melts require (Cl/H₂O) ≥ 0.35 , and this particular basalt melt requires (Cl/H₂O) ≥ 0.55 .

It is important to understand that the (Cl/H₂O) ratio of a Cl-enriched fluid phase(s) is different from that of coexisting, Cl-enriched silicate melts. Experimental observations and theoretical constraints (Candela,

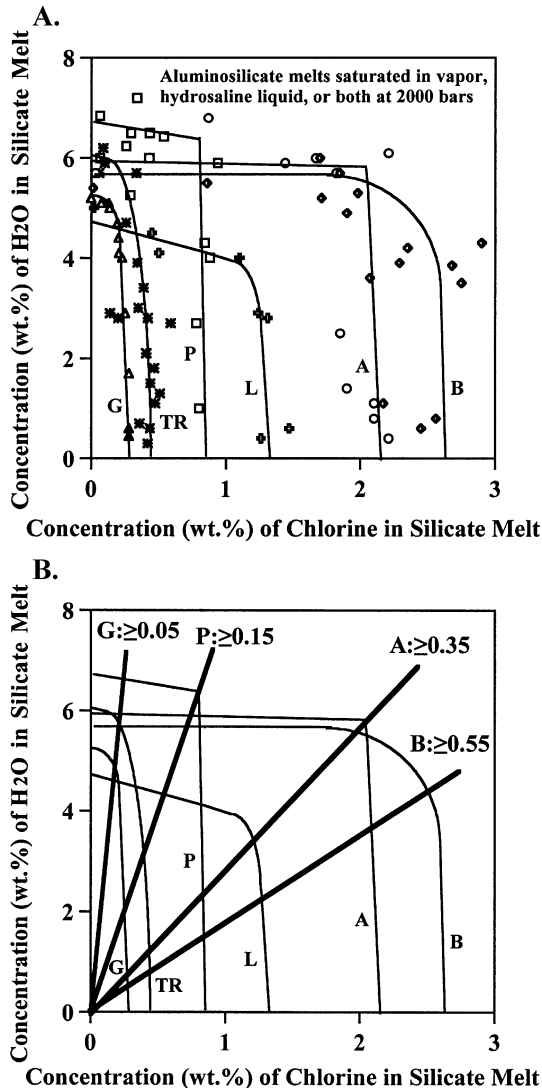


Fig. 2. Plots of (A) H₂O and Cl concentrations of granite (G=triangles), topaz rhyolite (TR=asterisks), phonolite (P=squares), latite (L=open crosses), andesite (A=open circles), and basalt (B=filled diamonds) melts saturated in vapor, vapor plus hydrosaline chloride liquid, or hydrosaline chloride liquid at 2000 bars (Webster, 1997; Webster and Rebbert, 1998; Webster et al., 1999, 2003a,b), and (B) labeled bold lines, overlain on the same solubility curves, that delimit the minimum (Cl/H₂O) weight ratios in melt required for saturation and exsolution of hydrosaline chloride liquid from granite/topaz rhyolite ($G: \geq 0.05$), phonolite ($P: \geq 0.15$), andesite ($A: \geq 0.35$), and basalt ($B: \geq 0.55$) melts at 2000 bars. Vapor plus hydrosaline liquid exsolve at the point of intersection (i.e., the sharp break in slope) for phonolite and andesite melts.

1989; Shinohara, 1994; Webster et al., 1999) clearly indicate that the (Cl/H₂O) of a hydrosaline liquid is typically smaller than that in the melt. For example, the minimum (Cl/H₂O) of an andesite melt saturated in a MHL at 2000 bars (Fig. 2) is 0.35, whereas the (Cl/H₂O) of the coexisting hydrosaline liquid with or without a vapor phase is approximately 0.067 (Webster et al., 1999). In contrast, the most Cl-enriched, hydrosaline liquid-saturated andesite melts of the same investigation were characterized by (Cl/H₂O) as large as 5.5 with a corresponding (Cl/H₂O) of approximately 3.3 in the coexisting hydrosaline liquid (with or without a vapor phase).

The type of magmatic volatile phase that may exsolve also varies with pressure and temperature. For example, H₂O solubilities in Cl-poor silicate melts (Moore et al., 1995) and Cl solubilities in H₂O-poor melts (Webster et al., 2003a,b) decrease with decreasing pressure. The reduction in H₂O and Cl solubilities resulting from a pressure change of 2000 to 500 bars has been determined for granite (Webster, 1997), topaz rhyolite (Webster and Rebbert, 1998), and phonolite melts (Webster et al., 2003a,b), and the influence of pressure on the solubility of these volatiles is most pronounced for H₂O. The minimum (Cl/H₂O) necessary for MHL saturation of phonolite melt increases as pressure decreases from 2000 to 500 bar (Fig. 3). Hence, with all other variables equal, the tendency for a MHL to exsolve within a Cl-enriched silicate magma, as compared to the likelihood of exsolution of a Cl-poor vapor, is greater at higher pressure (greater depth). Temperature also affects MHL stability. For example, experimental investigation of haplogranitic melts (Webster, 1997) at two temperature ranges (i.e., near 800 °C and at 1000–1075 °C) clearly shows that the influence of temperature on H₂O and Cl solubilities and on the minimum (Cl/H₂O) necessary for MHL saturation mimics the solubility behavior shown schematically (Fig. 1). In particular, the volatile solubilities determined for the lower temperature experiments exhibit a gradual change in slope with increasing (Cl/H₂O), whereas the higher temperature solubilities show a distinct break in slope. Consequently, decreasing temperature reduces the minimum (Cl/H₂O) necessary for MHL saturation and, thereby, increases the tendency toward MHL exsolution in silicate magmas containing elevated abundances of H₂O and Cl (i.e., those magmas

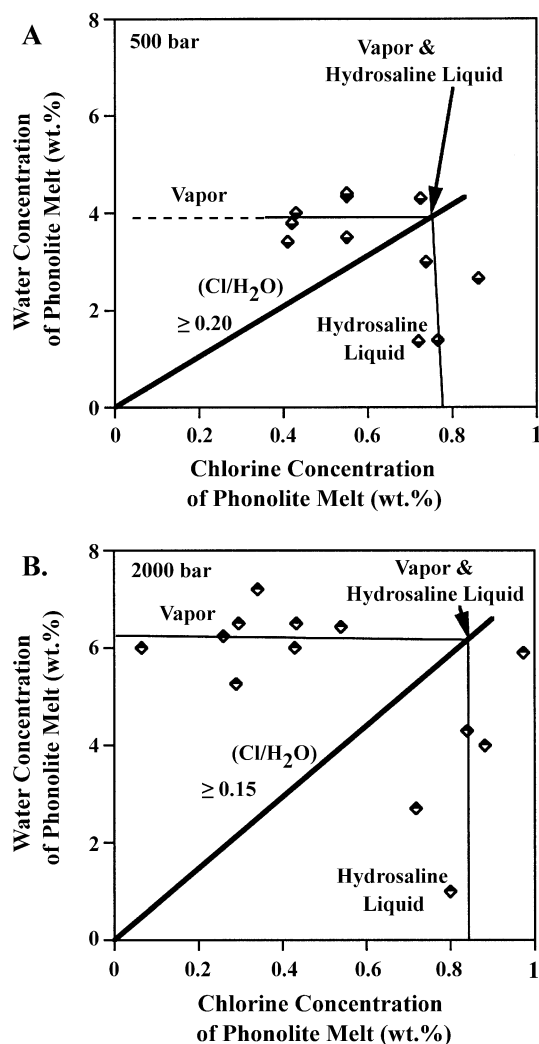


Fig. 3. Plots of H₂O and Cl concentrations of phonolite melt saturated in vapor, vapor plus hydrosaline chloride liquid, or hydrosaline chloride liquid at 500 (A) and 2000 (B) bars (Webster et al., 2003b). Bold lines delimit the minimum (Cl/H₂O) ratios in melt required for saturation and exsolution of hydrosaline chloride liquid at both pressures. Lower pressures require larger (Cl/H₂O) ratios for hydrosaline liquid, versus vapor, exsolution.

containing volatile abundances similar to the values near the break in slope).

2.3. Water and chlorine in silicate magmas

Determining if silicate magma saturates in a MHL requires accurate constraints on (Cl/H₂O) ratios of

silicate melts as well as accurate information on magmatic volatile solubilities as a function of system composition, pressure, and temperature. The compositions of some silicate melt inclusions (MI) provide the volatile contents of magmas (Anderson et al., 1989; Lowenstern, 1995) and, hence, constrain ranges of magmatic (Cl/H₂O) ratios, but as described below the (Cl/H₂O) of a MI is a product of the initial melt (Cl/H₂O), the effects of crystallization and degassing, and the timing of entrapment. I have culled the recent scientific literature and identified studies involving more than 1000 MI from 37 different rhyolitic (and granitic) through basaltic systems (Fig. 4). The H₂O concentrations of nearly all of the MI shown were measured directly, but H₂O was estimated for a small number of inclusions as the difference of (100 wt.-%-electron microprobe total).

The pristine chemistry of some MI can be compromised by a variety of syn- and post-entrapment processes (Roedder, 1984; Lowenstern, 1995, 2003), but in the context of this study only two potential problems are of significant concern. To evaluate the frequency and disposition of *initial* MHL exsolution we require precise knowledge on the maximum concentrations of volatiles in magmas, but in fact, a significant number of MI represent partially degassed magma (Johnston, 1978; Anderson et al., 1989; Stix et al., 1993; Lowenstern, 1994; Gerlach et al., 1994a,b; Stix and Layne, 1996; Raia et al., 2000; Signorelli and Carroll, 2000; Bacon, 2000; Webster and Rebbert, 2001; Webster et al., 2001). Thus, these samples of entrapped magma contain less than the maximum volatile contents that were dissolved in the bulk magma prior to degassing, and the (Cl/H₂O) ratios of the degassed melt have been modified as well. The compositions of such MI may help to establish the final pressure or depth of volatile phase exsolution, but they do not constrain initial volatile exsolution. In addition, a significant number of the MI (Fig. 4) were found in a partially to completely crystallized state and, consequently, required reheating and fusion to glass before analysis. The H₂O contents of reheated MI are reduced through diffusive loss of H₂ and/or H₂O during heating (Roedder, 1984). Thus, reheating MI artificially increases their (Cl/H₂O) ratios to an unconstrained extent. It should be noted, however, that the degree of H₂O loss is not significant for some of the cited studies (Hauri, 2002), and hence some of

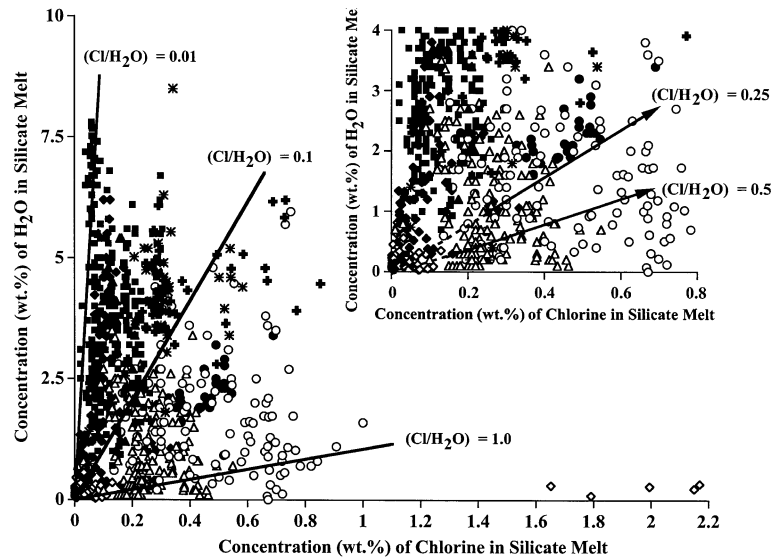


Fig. 4. Plot showing H₂O and Cl concentrations of more than 1000 unheated (filled symbols) and reheated (open symbols) silicate melt inclusions from 36 different magmatic systems. Melt compositions include high-silica rhyolite/granite (squares), high-F rhyolite (triangles), alkaline rhyolite/granite (asterisks), dacite/andesite (crosses), alkaline intermediate to mafic magmas (circles), and basalts (diamonds). The range in (Cl/H₂O) ratios for most melt inclusions is shown by the bold lines. Most reheated melt inclusions contain less H₂O than most unheated inclusions, but this comparison also involves different magma compositions as well as different magmatic systems. Thus, the difference in H₂O may not be solely a result of remelting the inclusions prior to analysis. Inset in upper right shows a magnified view of the data (i.e., melt inclusions containing ≤ 4 and ≤ 0.8 wt.% H₂O and Cl, respectively). The bold lines in the inset figure show the (Cl/H₂O) ratios for the six most Cl-enriched, unheated basalt melt inclusions (melt inclusion data from Harris and Anderson, 1984; Kovalenko et al., 1988; Dunbar et al., 1989; Anderson et al., 1989; Métrich and Clocchiatti, 1989; Webster and Duffield, 1991; Dunbar and Hervig, 1992a,b; Bacon et al., 1992; Métrich et al., 1993; Sisson and Layne, 1993; Webster et al., 1993, 1995, 1996, 2001, 2003a,b; Hervig et al., 1989; Lowenstem, 1994; Webster and Duffield, 1994; Gerlach et al., 1994a,b; Marianelli et al., 1995; Schiano et al., 1995; Manley, 1996; Barclay et al., 1996; Stix and Layne, 1996; Self and King, 1996; Roggensack et al., 1997; Bureau et al., 1998; Sisson and Bronto, 1998; Belkin et al., 1998; Kent et al., 1999; Lima et al., 1999; Marianelli et al., 1999; Bacon, 2000; Gurenko and Schmicke, 2000; Raia et al., 2000; Horn and Schmincke, 2000; Saito et al., 2001; Roggensack, 2001; Signorelli et al., 2001; Hauri, 2002; Lassiter et al., 2002; Straub and Layne, 2003; Webster and Nash, unpublished data).

these data are still useful. In summary, this database involves a broad spectrum of melt compositions that are representative of Earth's magmatic activities, but the Cl and H₂O contents of some MI are less than the true maxima contained in their respective volatile phase-saturated magmas while some of the same as well as other MI exhibit artificially high (Cl/H₂O) due to H₂O loss during reheating.

The MI span a wide range in (Cl/H₂O). Most ratios range from 0.008 to 2.0, but the (Cl/H₂O) of the majority of unheated MI range from 0.008 to 0.25. In general, unheated MI from high-silica rhyolites and primitive basalts exhibit the smallest (Cl/H₂O) ratios, whereas the largest ratios occur in unheated as well as reheated MI from calc-alkaline dacites and andesites (herein referred to as dacite and andesite MI, respectively) and from phonolitic to phonotephritic alkaline

rocks. The comparatively small number of investigations on unheated MI from calc-alkaline dacitic and andesitic magmas shows intriguingly high (Cl/H₂O). Few of these unheated MI, in fact, exhibit (Cl/H₂O) ratios that exceed 0.25, whereas many of the reheated MI do. Unfortunately, it is difficult to determine with confidence which reheated MI contain H₂O contents that are not too different from those of the source magmas and which MI do not, given that many reheated MI exhibit the largest (Cl/H₂O) ratios. Notably, the most Cl-enriched MI reported to date occur in phenocrysts sampled from Austral Islands basalts (Lassiter et al., 2002). These particular MI were reheated and exhibit (Cl/H₂O) ratios that exceed 8. The investigators interpreted the MI to represent magma that reacted with and/or assimilated a hydro-saline brine. Interestingly, the assimilation of alkali

chloride brines by basaltic magmas in oceanic environments has been discussed in other studies (Kent et al., 1999, and references therein).

3. Results and discussion

3.1. Exsolution of hydrosaline liquids in eruptive intermediate magmas of calc-alkaline affinity

Experimentally determined volatile solubility data have been compared with compositionally relevant MI data to successfully identify chemical evidence of MHL-saturation in magmas that erupted as North American topaz rhyolites (Webster and Rebbert, 1998) and magmas forming granitic blocks entrained in Ascension Island volcanic units (Webster and Rebbert, 2001). This approach has been used routinely to constrain vapor or fluid exsolution in H₂O- and CO₂-dominated magmas (Anderson et al., 1989; Lowenstern, 1995; 2003; Stix and Layne, 1996; others), and it is applicable to magmatic systems enriched in other volatiles. For instance, the advent of comparatively new MI data for H₂O- and Cl-enriched, subduction-related, andesitic and dacitic melts of the Pacific Japan, Izu, Aleutian, and Bonin arcs (Schiano et al., 1995; Bacon, 2000; Saito et al., 2001; Straub and Layne, 2003) presents the opportunity to characterize the likelihood of MHL exsolution in intermediate, calc-alkaline magmas. These MI exhibit a range of bulk compositions, so it is necessary to account for chemical evolution of magmas through fractional crystallization in order to understand all aspects of MHL exsolution. In particular, one must address the influence of these compositional differences on Cl solubility, and this is readily accomplished by computing the Cl abundance of MHL-saturated dacitic and andesitic melts (Webster and DeVivo, 2002). Comparison of the measured Cl and H₂O contents of the andesite and dacite MI with modeled Cl solubilities (Fig. 5A), over the range in bulk composition of the MI for MHL-saturated conditions at 2000 bars pressure, shows that the Cl concentrations and average (Cl/H₂O) necessary for MHL saturation in andesitic melts (represented by the bold line) are significantly larger than the Cl contents and (Cl/H₂O) of the andesite MI. This precludes the exsolution of MHL from these andesitic magmas. However, these same

data imply that some andesite MI (i.e., those exhibiting smaller (Cl/H₂O) ratios) represent magma that would have exsolved a water-dominated vapor at these pressures. The isobaric H₂O contents of the different modeled melt compositions are assumed to be about 6 wt.% because of the measured values in Fig. 2B and because this value is roughly consistent with predicted H₂O solubilities (Moore et al., 1995, 1998). It is clear that as andesite melts evolve to dacitic compositions, some dacite MI exhibit Cl contents that approach those required for MHL saturation of melt at pressures near 2000 bars. Thus, these MI represent fractions of dacite melt that would have saturated in and exsolved a MHL once the magma had ascended to a depth that is equivalent to this pressure.

Crystallization of most geologically representative mineral assemblages increases the volatile activities of residual melt fractions while simultaneously changing the bulk composition of residual melt. Isobaric crystallization increases the tendency toward volatile phase exsolution via second boiling, because although apatite, amphiboles, and micas are common igneous phases that contain H₂O (as OH⁻) and Cl, most geologically representative assemblages are dominated by minerals that do not contain H₂O or Cl. Consider the situations in which: (1) a crystalline phase assemblage sequesters no H₂O or Cl, or (2) equal quantities of H₂O and Cl are sequestered by some minerals in the assemblage. In either situation, the H₂O and Cl concentrations in residual melt, represented by the most Cl-enriched dacite MI in Fig. 5B, would increase along a linear trajectory oriented away from the origin. Conversely, as is more typical in nature, the volatile concentrations of the residual melt evolve away from the origin along a curved trajectory oriented toward increasing (Cl/H₂O) if the phase assemblage includes hydrous and/or halogen-bearing minerals (e.g., apatite, amphibole, or mica) that contain more H₂O than Cl. For example, if a silicate melt that is compositionally equivalent to the second most Cl-enriched MI precipitates a phase assemblage containing 80 modal% anhydrous minerals and 20 modal% biotite and/or amphibole (i.e., minerals containing at least 4 wt.% H₂O and no Cl), then the H₂O and Cl contents of the residual melt would evolve along the curve that branches away from the linear trend and toward larger (Cl/H₂O). The most important observations, here, are that both tra-

jectories keep comparatively Cl-enriched melts on the MHL-saturated side of the volatile saturation curves for dacite melt and that the crystallization of hydroxyl-dominated minerals increases the relative tendency for MHL to exsolve, rather than a vapor phase, albeit to a small extent.

These relationships also have relevance for volatile phase exsolution in more primitive silicate magmas. Even though MI from volatile-poor basalt magmas (Fig. 4, inset) typically contain low abundances of H₂O and Cl and display low (Cl/H₂O), some rare basaltic MI do exhibit (Cl/H₂O) of 0.25 to 0.5. And, as discussed previously, the (Cl/H₂O) established during initial melt generation will either be maintained

or will increase during subsequent magma evolution. If the (Cl/H₂O) ratios of primitive melts like those represented by these basaltic MI are sufficiently large, then residual fractions of the corresponding magmas will eventually exsolve a MHL, with or without a coexisting vapor phase, after extensive crystallization and associated increase in volatile abundances. The key point is that the (Cl/H₂O) controls the type of volatile phase that exsolves, whereas the volatile abundances control the relative timing of volatile phase exsolution (i.e., the time of earliest volatile exsolution relative to the rate of magma ascent and the crystallization history).

In summary, these MI indicate that some fractions of the andesite melts which erupted in the Izu and Bonnin arcs would have exsolved Cl-bearing vapors, whereas some fractions of dacite melt would have exsolved a MHL at pressures of or near 2000 bars. This suggests that MHL exsolution may occur in other arc-related andesite and dacite magmas. This also implies that such magmas may saturate in vapor and/or MHL well before eruption because of the pressures and depths involved, and this is consistent

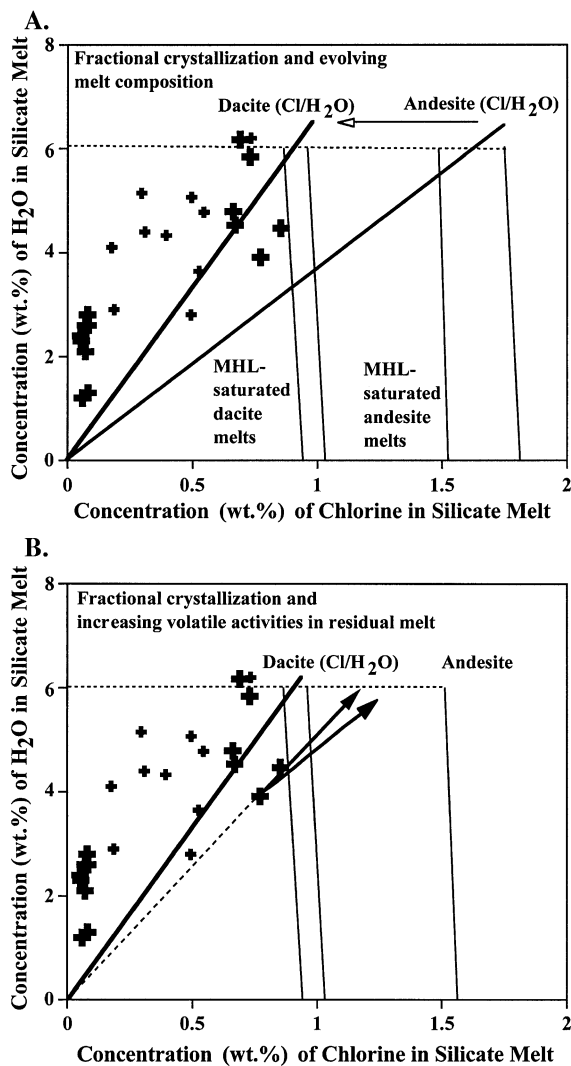


Fig. 5. Plots comparing H₂O and Cl concentrations of unheated melt inclusions from andesites (large crosses) and dacites (small crosses) (Schiano et al., 1995; Bacon, 2000; Saito et al., 2001; Straub and Layne, 2003) from subduction-related volcanoes with the computed 2000-bar solubility of Cl (fine lines) in hydrosaline chloride liquid (MHL)-saturated andesite and dacite melts having bulk compositions equivalent to the magmas represented by these particular melt inclusions. The bold lines delimit the minimum, average (Cl/H₂O) ratios required for MHL saturation of dacite and andesite melts at 2000 bars. Plot (A) shows how compositional evolution of andesite to dacite melt dramatically reduces the minimum Cl concentration needed for MHL exsolution. At least two of the dacite melt inclusions contain (Cl/H₂O) ratios necessary for MHL exsolution in dacite magma. Plot (B) shows how fractional crystallization of melt, represented by the single andesite melt inclusion having the largest (Cl/H₂O) ratio, either: (straight arrow) maintains the (Cl/H₂O) ratio of residual melt through crystallization of a Cl- and H₂O-free mineral assemblage or (marginally curved arrow) increases the (Cl/H₂O) ratio of residual melt through crystallization of 80% Cl- and H₂O-free minerals and 20% biotite and/or amphibole (hydrous phases containing no Cl). In summary, whereas most of these melt inclusions are consistent with the exsolution of an aqueous vapor phase at pressures \leq 2000 bars, the other inclusions show that fractional crystallization reduces the minimum Cl concentration in melt necessary for MHL exsolution while simultaneously increasing the H₂O and Cl contents and either maintaining or increasing the (Cl/H₂O) ratio of residual melt (favoring MHL exsolution).

with prior investigations (Johnston, 1978; Gerlach et al., 1994a,b; Wallace, 2001). Furthermore, the likelihood of MHL exsolution in such magmas is enhanced by fractional crystallization because it: (1) increases volatile abundances in the residual melt and (2) increases the silica and decreases the CaO and MgO concentrations of the residual melt which reduces Cl solubility without influencing H₂O solubility appreciably. These relationships have global relevance, because MHL exsolution will sequester significant levels of magmatic Cl and may ultimately enhance volcanic degassing of Cl to the atmosphere.

3.2. Exsolution of hydrosaline liquids in mineralizing calc-alkaline magmas

Magmatic hypersaline fluid inclusions occur in Cu- (\pm Au- and Mo-) mineralized porphyritic granitoids of calc-alkaline affinity, and these inclusions represent fluids that are instrumental in the dissolution and transport of ore metals (Roedder, 1971; 1992; Kamenetsky et al., 1999; Ulrich et al., 1999). Enhanced solubility of Cu and Au in aqueous, magmatic–hydrothermal fluids, as a direct function of chlorinity, has been demonstrated experimentally and theoretically (Keppler and Wyllie, 1991; Gammons and Williams-Jones, 1995; Candela and Piccoli, 1995; Bai and Koster van Groos, 1999). In this regard, theoretical arguments have also been made to suggest that MHL may exsolve directly from such magmas (Cline and Vanko, 1995; Roedder, 1992). However, it has also been maintained that silicate melts may first exsolve a Cl-bearing, supercritical aqueous fluid that subsequently unmixes to form a brine (i.e., MHL) and coexisting vapor (Cline and Bodnar, 1991; Roedder, 1992; Shinohara, 1994). To determine how likely it is for mineralizing magmas of intermediate composition to directly exsolve a MHL, data on the volatile abundances of such magmas (prior to emplacement and final crystallization) are required. At this time, however, there are few data that constrain H₂O and Cl contents of MI from mineralizing plutonic granite to granodiorite magmas (Yang and Bodnar, 1994).

Most magmatic Cu (\pm Au and Mo) mineralization is associated with porphyritic granitoids ranging in composition from quartz diorite to quartz monzonite, but Cu ores also occur in more felsic rocks (Tittley

and Beane, 1981; Stringham, 1966). In fact, porphyry Cu deposits are generally associated with the more felsic plutons in such systems (Creasey, 1977). Although it is difficult to determine accurate compositions of these igneous units because of the extensive, attendant hydrothermal alteration, Tittley and Beane (1981) show that silica, in most of these granitoids, ranges from 55 to 70 wt.% and (Na₂O+K₂O) from 4 to 8 wt.%. The computed solubility of Cl in MHL-saturated melts of quartz diorite, granodiorite, and quartz monzonite compositions is compared (Fig. 6A) with the observed concentrations of H₂O and Cl in subduction-related dacitic and andesitic MI (Schiano et al., 1995; Bacon, 2000; Saito et al., 2001; Straub and Layne, 2003). This comparison assumes that the latter, volatile-charged eruptive magmas contain similar overall volatile abundances to their mineralizing plutonic counterparts. It is apparent that the MI do not contain sufficient Cl (i.e., ≥ 1.6 wt.%) to match that required for granodiorite and quartz diorite magmas to exsolve a MHL directly. However, the solubility of Cl in MHL-saturated quartz monzonite magmas is nearly equivalent to the Cl contents of the most Cl-enriched andesitic MI, which suggests that the latter magmas may indeed exsolve a MHL. Thus, the observed association of Cu mineralization with comparatively felsic plutons and highly saline fluid inclusions is consistent with the predicted exsolution of MHL from quartz monzonite magmas.

The timing of hydrosaline liquid exsolution in mineralizing magmas has important consequences for the efficiency of ore metal dissolution, transport, and deposition. The solubility of many ore metals is strongly enhanced by the presence of Cl in hydrothermal fluids (Webster et al., 1989; Keppler and Wyllie, 1991; Heinrich et al., 1992; Hedenquist and Lowenstern, 1994; Candela and Piccoli, 1995; Reyf, 1997; Chevychev and Chevycheva, 1997; Bai and Koster van Groos, 1999). In this regard, recent work (Audetat and Pettko, 2003) has shown that several barren granites of northern New Mexico represent magmas that exsolved a fluid relatively early in their crystallization history (i.e., before 30% crystallization), but this study also concluded that these magmas did not generate mineralization primarily because of the low salinity of their exsolving fluids. Moreover, it follows that those magmas exsolving a potentially

mineralizing volatile phase at an early stage in their crystallization history have comparatively more time for the volatile phase to interact with and scavenge ore metals from minerals and residual melt than for magmas characterized by late volatile exsolution. The former magmas should achieve a closer approach to equilibrium between the melt, phenocrysts, and the volatile phase[s] than the latter. This is also consistent with the premise that the efficiency of ore metal dissolution in mineralizing volatile phases is greater if the volatile phase interacts with the magma before a significant quantity of ore metals is sequestered by phenocrysts during fractional crystallization (Cline

and Bodnar, 1991; Yang and Bodnar, 1994). Thus, early exsolution of a MHL will influence melt–phenocryst–volatile phase interactions and may result in more extensive mineralization.

3.3. Exsolution of hydrosaline liquid in mineralizing, potassic intermediate magmas

Mineralized, potassic (alkaline) igneous rocks also contain hypersaline fluid inclusions, and the magmatic systems represented by these rocks are economically significant because they are associated with approximately 20% of the world's large gold deposits (Müller and Groves, 2000). Many of these systems are also genetically linked with silver, base metal, or molybdenum mineralization. The Oligocene, alkaline-

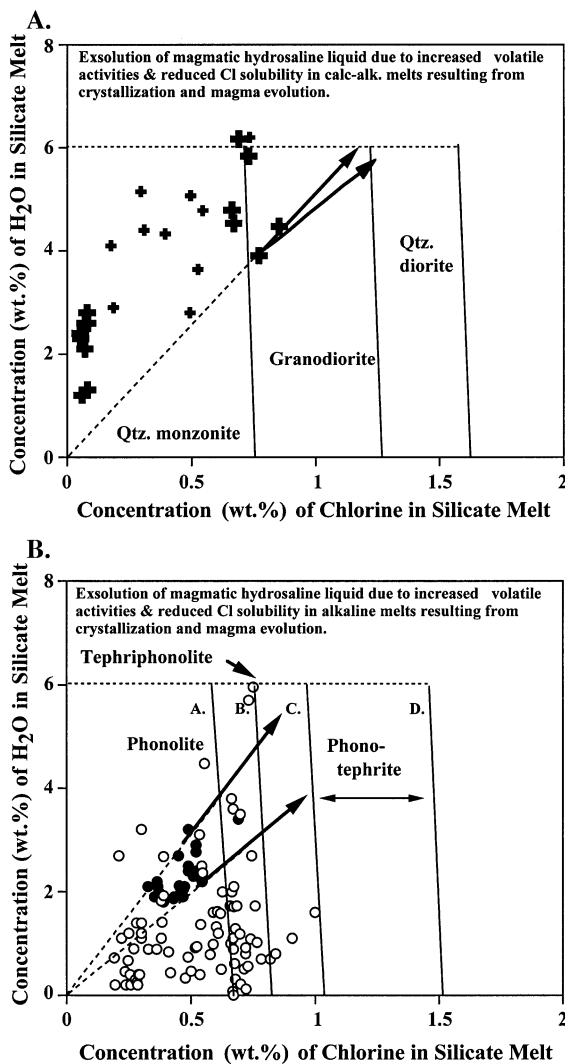


Fig. 6. Plot (A) compares H₂O and Cl concentrations of the andesite and dacite melt inclusions from subduction-related volcanoes (Fig. 5) with the computed 2000-bar solubility of Cl (fine lines) in hydrosaline chloride liquid (MHL)-saturated quartz diorite, granodiorite, and quartz monzonite melts having bulk compositions equivalent to subduction-related, calc-alkaline porphyritic magmas mineralized with copper ± gold and molybdenum. Chemical evolution from quartz diorite to quartz monzonite significantly reduces the minimum Cl content of melt required for MHL exsolution. Crystallization of andesite melts (which are treated, herein, as the volcanic equivalents of potentially mineralized subduction-related plutonic rocks) containing comparatively high (Cl/H₂O) ratios increases the H₂O and Cl contents and either maintains or, more likely, increases the (Cl/H₂O) ratio of residual melt also favoring MHL exsolution. Subduction-related, calc-alkaline magmas of quartz monzonite composition characterized by greater (Cl/H₂O) ratios may be key in the generation of magmatic–hydrothermal copper, gold, and molybdenum mineralization, and this is consistent with the association of mineralization and hypersaline fluid inclusions in numerous systems. Plot (B) compares the H₂O and Cl concentrations of heated (open symbols) and unheated (filled symbols) phonotephrite through phonolite and trachybasalt through phonolite melt inclusions (Marianelli et al., 1995; 1999; Belkin et al., 1998; Lima et al., 1999; Raia et al., 2000; Webster et al., 2001, 2003a,b; Signorelli et al., 2001) from potassic alkaline volcanoes with the computed 2000-bar solubility of Cl (fine lines) in hydrosaline liquid (MHL)-saturated phonotephritic (lines C–D), tephriphonolitic (line B), and phonolitic (line A) melts having bulk compositions equivalent to gold mineralized, alkaline magmas. Chemical evolution from phonotephrite to phonolite significantly reduces the minimum Cl content of melt required for MHL exsolution. Crystallization increases the H₂O and Cl contents and either maintains or, more likely, increases the (Cl/H₂O) ratio of residual melt also favoring MHL exsolution. This is consistent with the presence of Cl-enriched fluid inclusions in gold-mineralized, alkaline magmatic systems.

potassic volcanic rocks of the Cripple Creek Au–Te mining district, Colorado, are a particularly relevant example. The veined ores at Cripple Creek are associated with fluid inclusions that trapped the remnants of CO₂-bearing hydrothermal brines containing up to 40 wt.% NaCl equivalent (Thompson et al., 1985), and the hydrothermal alteration assemblages show ample evidence for magmatic fluorine enrichment (Kelley et al., 1998). Interestingly, the least altered examples of these rocks exhibit bulk compositions that are analogous to those of the potassic and volatile-charged magmas of the Mt. Somma-Vesuvius volcanic complex. The pre-eruptive magma geochemistry and solubility of volatiles in the latter system have been investigated extensively (Marianelli et al., 1995; Belkin et al., 1998; Lima et al., 1999; Signorelli and Carroll, 2000; Raia et al., 2000; Webster and DeVivo, 2002; Webster et al., 2003b), and hence, it is useful to compare the results of volatile solubility experiments and modeled solubilities of MHL-saturated, compositionally relevant alkaline melts with the measured abundances of H₂O and Cl in Mt. Somma-Vesuvius MI.

Fig. 6B weighs the H₂O and Cl contents of Mt. Somma-Vesuvius phonotephrite to phonolite MI against the measured solubility of Cl in MHL-saturated Cripple Creek, Colorado, phonolite melt (line A) and the computed Cl solubilities of MHL-saturated tephriphonolite (line B) and phonotephrite melts (area between lines C and D). The isobaric H₂O contents of these modeled melt compositions are also assumed to remain constant at about 6 wt.%. Clearly, the majority of the reheated MI contain less H₂O than the unheated MI and exhibit (Cl/H₂O) ratios that are indicative of MHL exsolution. Nevertheless, extrapolation of the H₂O and Cl abundances of the unheated MI, which represent the result of crystallization of melts with these volatile contents, generates (Cl/H₂O) ratios that are equivalent to those of the MHL-saturated limbs for the 2000 bar phonolite, tephriphonolite, and phonotephrite volatile solubility curves. Thus, if the pre-eruptive concentrations of H₂O and Cl in the Cripple Creek magmas were similar to those in Mt. Somma-Vesuvius magmas, then the former would have exsolved a hydrosaline liquid as they evolved toward more phonolitic compositions (as the H₂O and Cl concentrations in the residual magma increased simultaneously under isobaric conditions). These sol-

ubility relationships and the potential for early exsolution of a MHL should be considered when interpreting mineralizing processes at Cripple Creek and other Cl-charged, mineralizing, alkaline magmatic systems. For example, the Cu–Au ores of the alkaline Dinkidi porphyry deposit, Philippines, were generated by alkali metal-, Cl-, and S-rich brines exsolved from a monzonitic magma that was associated with less-evolved gabbroic and dioritic to more-evolved monzonitic magmas (Kamenetsky et al., 1999). Here, too, the chemical evolution of more primitive magmas to somewhat alkaline, monzonitic compositions may have played a key role in the exsolution of the mineralizing brines. Moreover, these interpretations are consistent with prior evidence for the presence of MHL in other, non-mineralized alkaline magmas (Frost and Touret, 1989; Lowenstern, 1994; De Vivo et al., 1995).

3.4. *The influence of other variables on magmatic hydrosaline liquid exsolution*

To understand the broader likelihood of MHL exsolution, it is important to consider the influence of other variables on exsolution processes. For instance, a reduction in pressure causes a modest decrease in Cl solubility of MHL-saturated silicate melts and a more significant decrease in H₂O solubility of vapor-saturated silicate melts (Fig. 3). Consequently, higher (Cl/H₂O) ratios are required for MHL saturation with decreasing pressure. Many MI (Fig. 6B) contain Cl and H₂O abundances that are less than those required for volatile phase saturation of a phonolitic melt at 2000 bars. Thus, as batches of phonolite melt with these volatile contents ascend toward the surface, the vapor-saturated limb of the compositionally relevant volatile solubility curve shifts and approaches the volatile contents of the MI much more rapidly than the MHL-saturated limb because of the reduction in pressure. This increases the relative likelihood of vapor saturation rather than MHL saturation of silicate melt.

Temperature also influences the type of volatile phase that exsolves (Fig. 1). As temperature decreases, the break in slope for the volatile solubility curves for silicate melts evolves from a sharp to a more gradual change (in the region where the volatile phase evolves from vapor to MHL). Simultaneously,

this region of the solubility curves shifts progressively toward the origin with decreasing temperature, which means that lower total H₂O and Cl contents are required for volatile phase exsolution for melts with comparatively high Cl and H₂O. Thus, such melts are more likely to exsolve a volatile phase at lower temperature.

The presence of elevated concentrations of volatiles other than H₂O and Cl in magma also has a dramatic effect on volatile exsolution and the assemblage of volatile phases that is stable. Carbon dioxide, for example, influences H₂O solubility in melts (Bowers and Helgeson, 1983; Joyce and Holloway, 1993; Duan et al., 2003), and hence, the timing of volatile phase exsolution in magma (Holloway, 1976; Holloway and Blank, 1994). At the present time, there are insufficient data to model the exsolution of H₂O-, CO₂-, and Cl-enriched volatile phases at magmatic conditions. Nevertheless, the limited experimental and modeled data that are available indicate that the presence of even minor concentrations of CO₂ in magmatic systems increases the stability of MHL plus immiscible CO₂-dominated vapor. Thus, CO₂ enhances the stability of MHL in nature. Conversely, the minimal experimental data on ore-metal and trace-element partitioning between aqueous-carbonic fluids and silicate melts that are available (Webster et al., 1989) indicate that increasing abundances of CO₂ actually diminish the dissolution of trace and ore metals in Cl-bearing fluids. Similarly, preliminary results from an experimental study of volatile solubilities in H₂O-, SO₂-, and Cl-bearing phonolite melt demonstrate that elevated abundances of SO₂ in melt dramatically reduce Cl solubilities (Webster and De Vivo, unpublished data).

4. Summary

Hydrosaline liquids exsolve from magmas ranging from rhyolite to dacite as well as from their plutonic equivalents. The exsolution of a MHL is controlled, predominantly, by the solubilities of Cl and H₂O in silicate melts and less so by changes in pressure or temperature. Chlorine solubility in silicate melt varies strongly with composition and can be computed with a new solubility model and compared with the Cl

contents of silicate melt inclusions to constrain MHL exsolution in nature.

Comparisons, like these, indicate that some fractions of subduction-related, calc-alkaline dacitic magmas should exsolve a MHL at pressures of 2000 bars, but there are surprisingly few melt inclusion data that are relevant to the comparatively large number of subduction-related andesite and dacite melts on Earth. These comparisons demonstrate that these magmatic systems cannot be modeled by focusing exclusively on the dominant magmatic volatiles (i.e., H₂O, CO₂, and SO₂). Chlorine is also important in such magmas. Far more MI data are needed to understand degassing processes in non-felsic, explosively erupting systems.

Comparison of these same, albeit limited, MI data with predicted, 2000-bar Cl solubilities of Cu-mineralized porphyritic systems suggests that a potentially mineralizing MHL should exsolve from magmas of quartz monzonite composition, and this is consistent with observations on hypersaline fluid inclusions from copper porphyries. Here, too, the volatile contents of MI from compositionally relevant systems must be determined to better constrain mineralizing processes. Moreover, comparison of the volatile abundances of MI from the potassic eruptive units of Mt. Somma-Vesuvius with the computed Cl solubilities of phonolitic and more primitive magmas like those associated with gold- and tellurium-mineralization at Cripple Creek, Colorado, suggests that chemical evolution of these magmas to phonolitic compositions should saturate the latter melts in a potentially mineralizing MHL at pressures of 2000 bars.

This method of investigating MHL exsolution is applicable to other silicate magmas assuming that the volatile contents of compositionally relevant, silicate melt inclusions are available. However, volatile phase exsolution is a strong function of the activities of all volatiles in magmatic systems, and improved experimental constraints on the solubilities of Cl, H₂O, SO₂, and CO₂ are also required.

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