

Chlorine solubility in evolved alkaline magmas

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Abstract

Experimental studies of Cl solubility in trachytic to phonolitic melts provide insights into the capacity of alkaline magmas to transport Cl from depth to the earth's surface and atmosphere, and information on Cl solubility variations with pressure, temperature and melt or fluid composition is crucial for understanding the reasons for variations in Cl emissions at active volcanoes. This paper provides a brief review of Cl solubility experiments conducted on a range of trachytic to phonolitic melt compositions. Depending on the experimental conditions the melts studied were in equilibrium with either a Cl-bearing aqueous fluid or a subcritical assemblage of low-Cl aqueous fluid + Cl-rich brine. The nature of the fluid phase(s) was identified by examination of fluid inclusions present in run product glasses and the fluid bulk composition was calculated by mass balance. Chlorine concentrations in the glass increase with increasing Cl molality in the fluid phase until a plateau in Cl concentration is reached when melt coexists with aqueous fluid + brine. With fluids of similar Cl molality, higher Cl concentrations are observed in peralkaline phonolitic melts compared with peraluminous phonolitic melts; over all the Cl concentrations observed in phonolitic and trachytic melts are approximately twice those found in calc-alkaline rhyolitic melts under similar conditions. The observed negative pressure dependence of Cl solubility implies that Cl contents of melts may actually increase during magma decompression if the magma coexists with aqueous fluid and Cl-rich brine (assuming melt-vapor equilibrium is maintained). The high Cl contents (approaching 1 wt% Cl) observed in some melts/glasses from the Vesuvius and Campi Flegrei areas suggest saturation with a Cl-rich brine prior to eruption.

Key words *alkaline magmas – solubility – chlorine – supercritical fluid*

1. Introduction

Chlorine generally occurs as a minor component in most magmas and fumarolic gases. However, it has been observed that the release of Cl from volcanoes to the atmosphere during eruptions and quiescent degassing may contribute to thinning of the ozone layer and the production of acid rain (Johnston, 1980; Devine

et al., 1984; Symonds *et al.*, 1988; Albritton, 1989). In addition, recent developments of spectroscopic methods to measure Cl and S emissions at active volcanoes offer the possibility to use measured variations in Cl and S emissions to better understand the subsurface movements of magmas and eruption likelihood (*e.g.*, Francis *et al.*, 1998; Love *et al.*, 1998; Duffell *et al.*, 2003; Edmonds *et al.*, 2003). However, such applications require adequate knowledge of the factors controlling Cl distribution between melt and fluid(s) in decompressing magmas.

In recent years the study of volatiles in melt (now glass) inclusions has provided a wealth of data about Cl abundance in silicate melts under magmatic conditions (*e.g.*, Lowenstern, 1995, and references therein). These data provide information on the amount of Cl dissolved in the melt at the time of melt inclusion entrapment.

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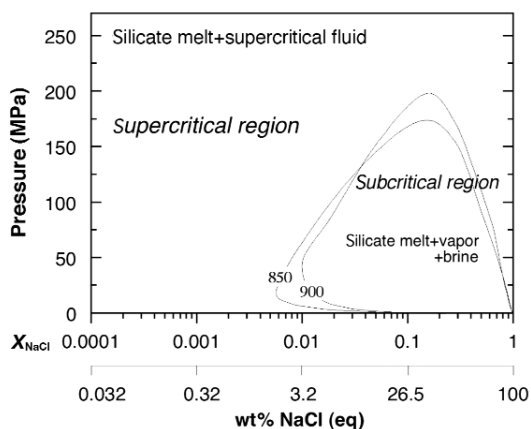


Fig. 1. Pressure- X_{NaCl} diagram of the system NaCl- H_2O with 850 and 900°C isotherm (redrawn after Anderko and Pitzer, 1993a). The polythermal projection of the 3-phase vapor+brine+halite equilibrium onto the pressure-composition section is from Bishoff (1991) and Anderko and Pizer (1993a). Experiments with bulk Cl contents that fall within the solvus will coexist with both an aqueous fluid phase (containing a small amount of Cl) and a salt-rich brine.

Although the absolute amount of Cl in magmas is difficult to estimate, the knowledge of solubility limits is of fundamental importance for interpretation of glass inclusion Cl abundance. In many cases, solubility data provide an upper limit on the volatile content of melts and they also provide indirect information about the presence of Cl-bearing fluid(s) within the magma body.

This paper reviews some recent work involving experimental determination of the solubility and the fluid/melt partitioning of chlorine in hydrous, evolved alkaline magmas at shallow crustal depths (<~8 km). Cl solubility behavior at crustal pressures differs somewhat from that of water and carbon dioxide because in Cl-rich systems the silicate melts may also coexist with a Cl-rich brine. Most experimental studies of Cl solubility in hydrous systems have added Cl to the experimental samples using aqueous (Na, K) Cl solutions (Shinohara *et al.*, 1989; Métrich and Rutherford 1992; Webster, 1992a,b; Student and Bodnar 1999; Signorelli and Carroll, 2000, 2001, 2002). This approach allows description

of the behavior of Cl-bearing fluid using the well-known system NaCl- H_2O (Sourirajan and Kennedy 1962; Bodnar *et al.*, 1985; Chou, 1987; Anderko and Pitzer 1993a,b). For H_2O -rich solutions, the binary phase relations (fig. 1) show a single fluid phase of variable composition at high pressures or low Cl concentrations. Published experimental data for silicate melts coexisting with low-Cl fluids, or with supercritical Cl-bearing fluids show that Cl partitions strongly into aqueous fluids relative to silicate melts by a factor of ~20 to 300 (*e.g.*, Holland, 1972; Kilinc and Burnham, 1972; Webster, 1992a,b; Kravchuk and Keppler, 1994; Student and Bodnar, 1999). Webster (1992a,b) has also found that Cl concentration in rhyolitic melts coexisting with a single aqueous fluid phase with low Cl content (<20 wt% Cl) decreases as pressure increases from 200 to 800 MPa and the fluid/melt partition coefficient for Cl increases with increasing pressure.

However, with increasing concentration of Cl in the solution at pressures below ~200 MPa, the binary system H_2O -NaCl is characterized by an immiscibility gap (subcritical region; see fig. 1) within which a Cl-poor, aqueous fluid coexists with a Cl-rich, hydrosaline brine. Within the subcritical region, the compositions of aqueous fluid and brine are invariant at constant pressure and temperature, which means that Cl and H_2O concentrations in the fluids and the coexisting silicate melt will be fixed (Gibbs' phase rule). A constant Cl content in the glass (flat distribution or plateau) for further addition of Cl to the system is the typical expression of the melt being saturated with both a hydrosaline liquid and an H_2O -rich aqueous fluid and it is assumed to define the solubility limit for Cl in the hydrous silicate melt (Malinin *et al.*, 1989; Shinohara *et al.*, 1989; Métrich and Rutherford, 1992; Webster, 1992a,b; Signorelli and Carroll, 2000, 2001, 2002). Experiments carried out in this region (coexisting silicate melt + aqueous fluid + brine) for hydrous rhyolitic melts have documented that: 1) chlorine does not partition strongly into the water-rich fluid phase and the aqueous fluid/melt partition coefficient is ~5 at 100 MPa (Webster and Holloway, 1988; Shinohara *et al.*, 1989; Métrich and Rutherford, 1992; Candela and Piccoli, 1995; Williams, 1995); 2) there is a

positive correlation between the fluid/melt distribution coefficient and total pressure (Shinohara *et al.*, 1989; Malinin *et al.*, 1989); and 3) chlorine solubility, that is the maximum amount of Cl in a melt coexisting with a brine + aqueous fluid assemblage, depends strongly on melt composition (*e.g.*, Webster and De Vivo, 2002) and pressure. The solubility varies from a few thousand ppm to ~1 wt%, being higher in peralkaline rhyolites (pantellerites) relative to metaluminous compositions (Shinohara *et al.*, 1989; Métrich and Rutherford, 1992) Results presented in this review paper extend these observations to consider trachytic and phonolitic melts, which have much higher Cl solubilities than typical calcalkaline rhyolitic melt compositions.

Silicate melts can be saturated with respect to a fluid phase (*e.g.*, H₂O, CO₂, noble gases) or a mineral phase (*e.g.*, anhydrite or pyrrhotite for S-bearing magmas). The solubility of Cl is a more complex and ambiguous term since the silicate melt can be saturated with respect to mineral, liquid and fluid phases (*e.g.* halite, pure liquid NaCl or a Cl-rich brine, Cl₂, HCl or Cl-bearing aqueous fluids). Throughout this paper, the term solubility is used to refer to the maximum amount of Cl that can be dissolved in the silicate melt when it is saturated with an immiscible aqueous fluid + brine assemblage at a given set of conditions. The distribution of Cl between a melt and an aqueous phase is generally expressed in the literature as Nernst-type partition coefficients ($D_{m/aq, Cl}$, where m=melt, aq=aqueous fluid). However, only components that can vary independently in a phase or a system have a real distribution coefficient (Candela and Piccoli, 1995) and this is not strictly true for Cl (although it would be true for components such as NaCl, KCl, etc.; *e.g.*, see Candela and Piccoli, 1995; Frank *et al.*, 2003). However, given the lack of knowledge concerning Cl speciation in the fluid phase, a simple Nernst-style partition coefficient is often used in discussion of melt-fluid partitioning of Cl.

2. Pressure and Cl solubility

The solubility of Cl in phonolitic melts equilibrated with Cl-bearing fluids over a range

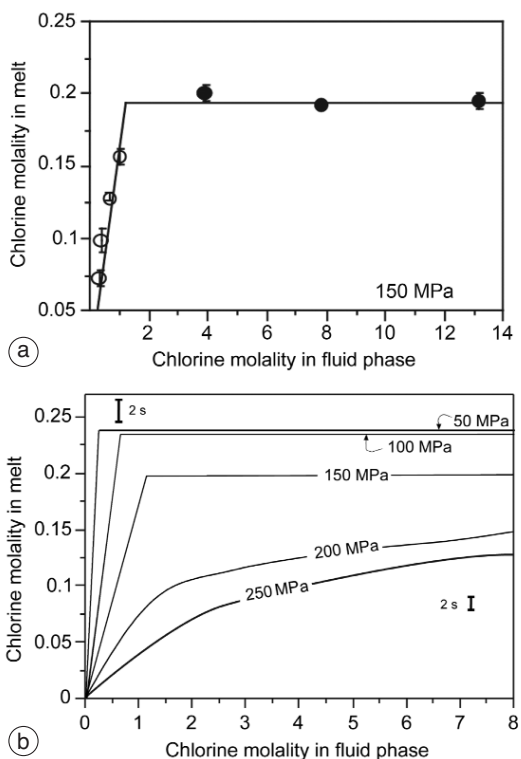


Fig. 2a,b. Variation of the chlorine molality in the melt with the calculated chlorine molality in a single fluid phase (for brine-saturated conditions this is an «apparent molality» because the melt coexists with both Cl-poor aqueous fluid and Cl-rich brine). a) Chlorine molality ($C_{m,Cl}$) of MB phonolitic melts versus Cl molality at $P=150$ Mpa, $T=850^{\circ}\text{C}$. Experiments carried out in the two-phase field (melt + aqueous fluid) are represented as open circles and those in the three-phase field (melt + aqueous fluid + hydrosaline brine) are represented as solid circles. b) Summary of variation of the chlorine molality in the melt with the chlorine molality in a single fluid phase (experimental data points not shown). The vertical bars show the two-sigma standard deviations on analyses of chlorine in the silicate melt $C_{m,Cl}$ (moles/kg) $C_{m,Cl}$ (ppm)/35450 (data from Signorelli and Carroll, 2000).

of pressures and fluid Cl contents, as determined by Signorelli and Carroll (2000), is shown in fig. 2a,b. The melt composition used in these experiments is given in table I and experimental details are given in Signorelli and

Table I. Composition (wt%) on water free basis of experimental starting materials.

Sample	Montaña Blanca MB	Vesuvius Ves	Phlegraean Fields CI	Vesuvius VS	Vulsini O	Zikwala ER	Seite Cidades SM	Synthetic phonolite D
SiO ₂	59.5	57.3	62.1	62.9	59.9	68.3	64.6	58.7
TiO ₂	0.66	0.19	0.44	0.37	0.55	0.53	0.63	
Al ₂ O ₃	19.0	21.7	18.60	18.00	17.9	13.8	16.9	24.5
FeO*	3.34	2.23	3.30	3.07	4.00	5.81	3.00	
MnO	0.2	0.13	0.24	0.16	0.12	0.28	0.20	
MgO	0.33	0.23	0.35	0.46	1.06	0.16	0.35	
CaO	0.79	2.94	1.77	2.68	4.34	0.75	0.63	
Na ₂ O	10.09	5.68	5.64	4.09	2.87	5.90	7.79	11.30
K ₂ O	5.56	9.53	7.32	8.10	8.78	4.11	5.63	5.50
P ₂ O ₅	0.07	0.04	0.02	0.04	0.17	0.06	0.07	
Cl	0.35	0.55	0.59	0.55	0.16	0.08	0.21	
F	0.09	0.4	0.34	0.19	0.37	0.10	0.17	
LOI	0.45	3.10	2.50	1.40	2.60	0.57	0.20	
[2] AI	1.2	0.91	0.92	0.86	0.79	1.03	1.12	1.0
[3] A/CNK	0.8	0.87	0.91	0.88	0.81	0.89	0.84	1.0

Major elements, Cl and F for MB have been determined by XRF. FeO* = total Fe as FeO; for Ves analysis Cl and F determined by potenziometry; LOI = Loss On Ignition; [2] Agpaiteic Index = [(Na₂O+K₂O)/Al₂O₃] molar ratio; [3] molar [(Al₂O₃/CaO+Na₂O+K₂O)] ratio (see for details Signorelli and Carroll, 2000, 2002); alkali exchange and partial crystallization in some experiments resulted in slightly different experimental melt compositions, as documented in Signorelli and Carroll (2000, 2002).

Carroll (2000); all of the experiments involved equilibration of silicate melt with (Na, K) Cl solutions of variable initial chloride molality and fluid compositions at the end of the experiments was calculated by mass-balance. These experiments may contain two types of fluid inclusions trapped in the quenched glass: type-I inclusions contain both a vapor bubble and a liquid phase, whereas type-II fluid inclusions contain a vapor bubble, liquid and one or more daughter minerals (salts). The minerals contained in these inclusions are believed to be alkali chlorides, possibly with other chlorides (*e.g.*, CaCl₂ and FeCl₂). Only experiments from below 200 MPa are found to contain both type-I and type-II inclusions. Experiments above 200 MPa contain only type-II inclusions. The experiments carried out between 50 and 150 MPa display the common behavior of a positive linear correlation between Cl in glass and in the

fluid phase, when Cl molality in the fluid phase is below $\sim 2m$ Cl, and then a flat distribution where further increases in the total amount of Cl in the system do not increase Cl in the glass (fig. 2a). The experiments at 200 and 250 Mpa show a parabolic increase in melt Cl content with increasing Cl in the fluid (*i.e.*, the rate of increase in melt Cl content slows in experiments with more Cl-rich fluids). Figure 2b shows the isobaric trends for all of the data superimposed on the same diagram ($T=850-875^\circ\text{C}$). This comparison clearly shows that as pressure increases there is a decrease in the slope of the straight line (melt coexists with single fluid of variable Cl content; positive slope) and a shift of the pivot point between the straight line and the plateau (melt coexists with both aqueous fluid and brine) towards more Cl-rich fluids until the sharp break of slope between them turns into a smooth passage be-

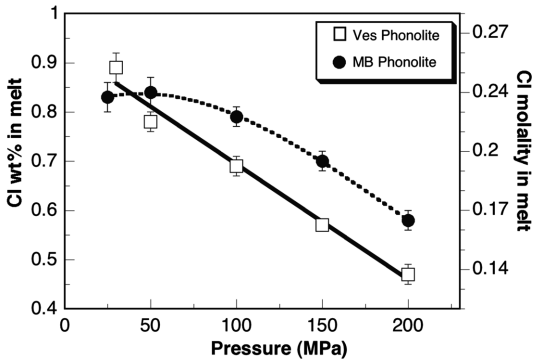


Fig. 3. Chlorine solubility in phonolitic melts saturated with aqueous fluid+brine *versus* pressure. Solid circles and open squares represent MB (Montaña Blanca, Tenerife) and Vesuvius phonolitic glasses ($\pm 1\sigma$ standard deviation), respectively (data from Signorelli and Carroll, 2000).

tween 200 and 250 MPa. These results indicate that the melt Cl content decreases as pressure increases when the melt is saturated with both an aqueous fluid phase and a brine phase, as shown in fig. 3 for 2 phonolitic compositions (Vesuvius 79 A.D. and Montaña Blanca, Tenerife; supercritical values taken from solubility at 2 molal Cl in fluid). The lack of change in melt Cl contents for the MB phonolite at pressures below 100 Ma is probably due to the fact that this composition begins to crystallize at the lowest pressures investigated and the changes in melt composition result in decreased Cl solubilities, as predicted by the model of Webster and De Vivo (2002) and discussed further below. The Cl contents of the brine and aqueous fluid phases coexisting with these melts at any pressure (below the top of the miscibility gap) can be estimated from the H₂O-NaCl binary

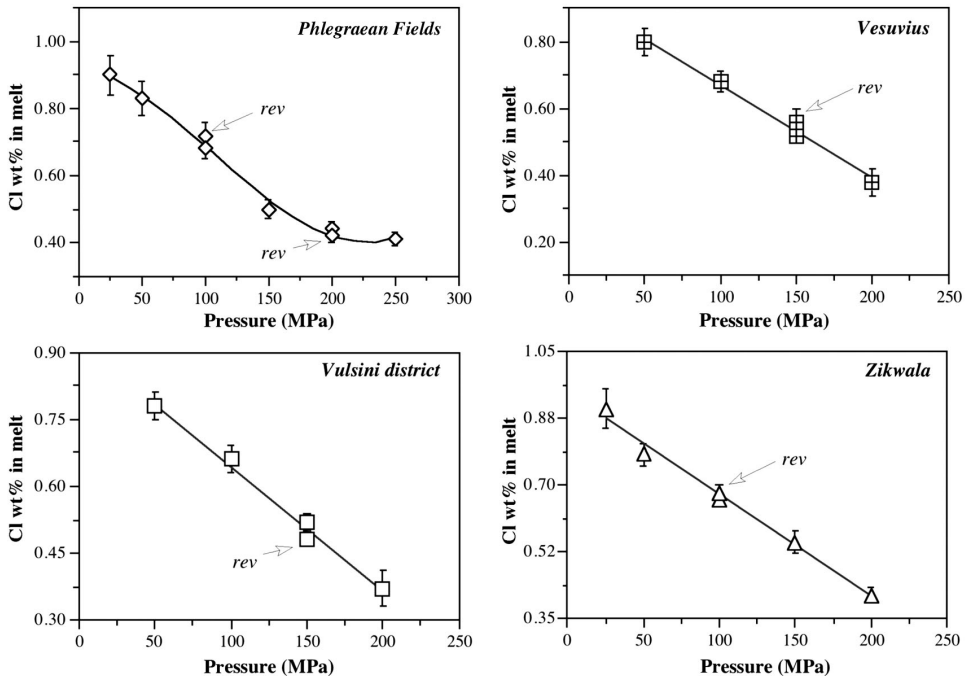


Fig. 4. Chlorine solubility ($\pm 1\sigma$ standard deviation) in trachytic (Signorelli and Carroll, 2002) and phonolitic melts (Signorelli and Carroll, 2000) saturated with aqueous fluid+brine *versus* pressure. «This study» refers to Signorelli and Carroll (2002). Original melt compositions are given in table I and «rev» refers to reversal experiments.

shown in fig. 1. As indicated in fig. 1, the brine phase actually becomes more Cl-rich as pressure decreases and this may explain why the melt also becomes more Cl-rich as pressure decreases – if the Cl activity in the brine increases as pressure decreases, then the Cl activity in the coexisting melt also increases as pressure decreases (see also thermodynamic-molar volumes discussion in Signorelli and Carroll, 2002). The effect of KCl (and other chlorides) on the field of immiscibility has not been considered due to lack of data but studies at lower temperature (400-600°C) suggest that the addition of KCl tends to enlarge the field of immiscibility but does not change the general geometry of the binary (Anderko and Pitzer, 1993b).

Cl solubility in trachytic melts saturated with both an aqueous fluid phase and a brine phase shows variation with pressure very similar to that observed for phonolitic melts, as shown for a variety of trachytic melts in fig. 4 (data from Signorelli and Carroll, 2002). The compositions of the trachytic melts studied are reported in table I and the variations in Cl solubility with melt composition are discussed below.

3. Melt composition and Cl solubility

Experimental studies involving hydrous rhyolitic to phonolitic melts equilibrated with an aqueous vapor and a hydrosaline liquid have shown that the behavior of chlorine in the melt is a strong function of the melt composition and in general Cl solubilities are higher in more Si-poor melts (*e.g.*, Métrich and Rutherford, 1992; Carroll and Webster, 1994 and references therein; Webster *et al.*, 1999; Signorelli and Carroll, 2001, 2002; Webster and De Vivo, 2002). Métrich and Rutherford (1992) found that the peraluminous-peralkaline character of a silicate melt, expressed as molar ratio of $\text{Na}_2\text{O}+\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ (= Al saturation Index, AI), has a large effect on Cl solubility in hydrous rhyolitic melts, as shown in fig. 5. A change of melt composition from metaluminous rhyolite to peralkaline pantellerite yields a more than 3-fold increase in Cl solubility (fig. 5). On the other hand, Signorelli and Carroll (2001), working with a peraluminous rhyolitic compo-

sition, found that Cl solubility is higher in peraluminous rhyolites than in metaluminous rhyolites and the increase of Cl solubility with peraluminosity is possibly even more pronounced than the changes observed with increasing peralkalinity (*e.g.*, at 100 MPa, brine + aqueous fluid saturation, peraluminous rhyolite with AI=0.8 has 0.64 wt% Cl). These results suggest a minimum (~3000 ppm) in Cl solubility in metaluminous rhyolites and higher Cl solubilities in both peralkaline and peraluminous compositions. Cl solubility in hydrous phonolites also depends on peralkalinity of the melt (Signorelli and Carroll, 2000) and the results of Signorelli and Carroll (2002) for a close-to-metaluminous phonolite (fig. 6) suggest a possible minimum (~0.48 wt%) in Cl solubility in metaluminous phonolites. The higher Cl solubility in metaluminous phonolite with respect to metaluminous rhyolite is probably due to the lower silica activity of phonolitic melts, as suggested by various previous studies that document increasing Cl solubility with decreasing silica activity (Kotlova *et al.*, 1960; Iwasaki and Katsura, 1967; Webster, 1997a,b; Webster and Rebbert, 1998; Webster *et al.*, 1999; Webster and De Vivo, 2002); note that decreasing silica activity is also correlated with increasing activities of network-modifying cations, as discussed further below. In fig.

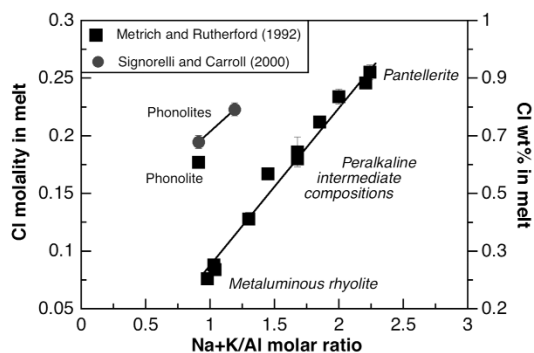


Fig. 5. Solubility of chlorine at 100 MPa as a function of molar (Na+K)/Al ratio for natural rhyolites and phonolites saturated with an aqueous fluid + hydrosaline brine (data from Metrich and Rutherford, 1992; and Signorelli and Carroll, 2000).

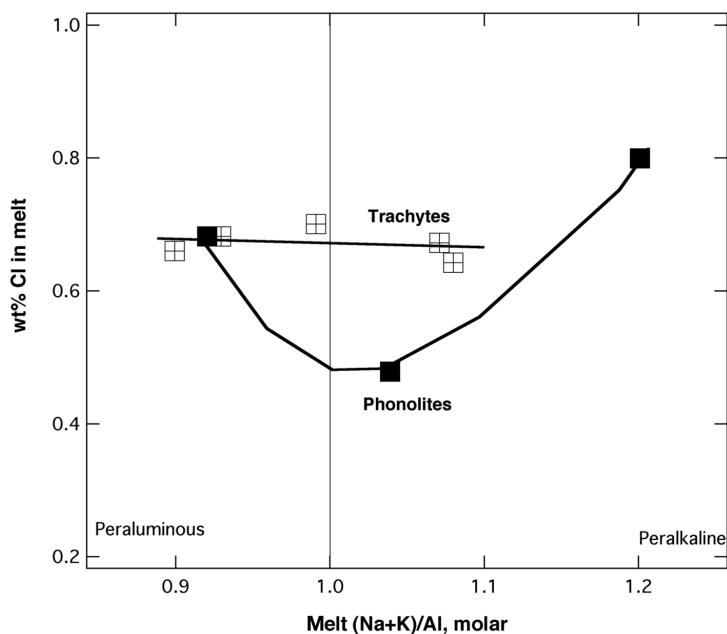


Fig. 6. Solubility of chlorine (± 1 standard deviation) at 100 Mpa, 850-875°C as a function of molar [(Na+K)/Al] ratio for natural trachytes (open symbols, from Signorelli and Carroll, 2002), and natural and synthetic phonolites (filled symbols, from Signorelli and Carroll, 2000) saturated with an aqueous fluid + hydrosaline liquid.

6 the results of Signorelli and Carroll (2002) for trachytic compositions with variable alkali/alumina are also shown. The most evident difference between the trachytic and phonolitic melts is that the trachytes don't show any minimum and Cl solubility is constant at approximately 0.67 wt% over the range of agpaite index investigated (0.9-1.08). Apparently, the peraluminous-peralkaline character of the trachytic melt has little influence on Cl solubility, in contrast to the significant variations seen in phonolitic and rhyolitic compositions.

A possible explanation of the lack of variation in Cl solubility with peralkalinity comes from the recent study of Webster and De Vivo (2002) concerning the effects of melt composition on Cl solubility in a wide range of silicate melt compositions (41 different compositions, all at 200 MPa, 786-1193°C). Webster and De Vivo (2002) modelled the effects of melt composition on brine-saturated melts containing up

to 3.2 wt% H₂O using the idea of association coefficients that express the effect of the molar abundance of each melt component (cations + F⁻) on Cl solubility (positive association coefficients indicate a component increases Cl solubility, negative values indicate components that reduce Cl solubility). They found that the affinity of individual cations for Cl decrease in the order Mg~Ca>Fe>Na>K>network-forming Al>Li~Rb~Cs; F has a positive effect on Cl solubility. However, the relation between composition and solubility is more complex in peralkaline and peraluminous melts (because of possible variations in the structural role of Al), and the effects of Ca, Mg and Al are greater in mafic melts than in more silica-rich melts. Details of this model are explained in Webster and De Vivo (2002) and the good agreement between their model predictions and measured Cl solubilities at 200 MPa for a wide range of melt compositions is shown in fig. 7. The fact that

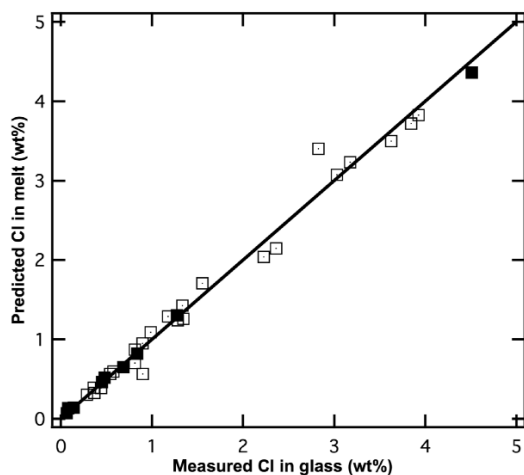


Fig. 7. Correlation between measured Cl solubilities and those predicted by the model of Webster and De Vivo (2002). All melts are saturated with a Cl-rich brine at 200 MPa pressure and temperatures of 786–1193°C. Filled symbols show experiments used to generate the model association coefficients and open symbols show melt compositions for which the Cl solubility was calculated using the model association coefficients. Typical 1- σ analytical precision for measured Cl contents are on the order of 0.05 to 0.1 wt%.

Mg, Ca and Fe have significantly greater effects on Cl solubilities than do K and Na may help explain why the Cl solubilities in trachytes studied by Signorelli and Carroll (2002) appear to be independent of alkali/alumina ratio. Following the results of Webster and De Vivo (2002), the higher abundances of Mg, Ca and Fe in the trachytes overwhelm the effects of varying alkali/alumina, thus there is no significant variation in Cl solubility; such effects might be more apparent in more extremely peralkaline or peraluminous trachytes. Extrapolation of the results of Webster and De Vivo (2002) to other pressures, and consideration of the effects of melt H₂O content on Cl solubility still need to be investigated. The use of association coefficients to quantify how melt composition variations affect Cl solubilities appears promising, but the approach is not completely general because numerous additional correc-

tions are needed depending on the types of melts considered (*e.g.*, peralkaline, peraluminous – see Appendix in Webster and De Vivo, 2002).

4. Volcanological implications

All studies of Cl solubility in hydrous rhyolites, phonolites and trachytes in the presence of subcritical (Na, K) Cl-H₂O fluids have shown that Cl solubility decreases regularly as the pressures rises. The higher Cl solubility in phonolites and trachytes with respect to rhyolites, however, suggests that evolved alkaline magmas can transport larger amounts of chlorine to the earth's surface. This reservoir of chlorine may be potentially emitted to the atmosphere if significant Cl is lost during cooling, crystallization and degassing of volcanic products.

The composition of high-temperature gases released from volcanoes depends on factors such as gas solubility in the silicate melt and vapor/melt partitioning and separation during the generation and rise of magmas. Giggenbach (1996) has proposed a model for equilibrium degassing (*i.e.*, closed-system degassing) that takes into account these factors. However, this model requires that volatile solubilities approach Henry's Law behavior and that the solubilities decrease with decreasing pressure (as observed for H₂O, CO₂, noble gases). The negative correlation of melt Cl concentration with pressure means that Cl solubility behavior in brine-saturated magmas cannot be treated as simply as other volatile species, at least when high melt Cl contents suggest brine saturation. The solubility of Cl may also be complicated by the formation of non-volatile alkali chlorides and HCl^o at low pressure. Alternatively, various authors have convincingly demonstrated that the potential distribution of Cl in magmatic fluids depends on the shape of the immiscibility solvus of NaCl-H₂O system (or a similar «salt»-H₂O system) at low pressures and magmatic temperatures (*e.g.*, Hedenquist and Lowenstern, 1994; Shinohara, 1994; Hedenquist, 1995). During decompression and/or crystallisation of a magma at low (<200 MPa) pressures it may be-

come saturated with both a low-density vapor and a high-density brine (first and/or second boiling; see Webster and De Vivo, 2002). As described by Hedenquist and Lowenstern (1994), the low density phase will contain components such as H₂O, CO₂, SO₂, H₂S, HCl and the higher density brine phase will contain alkali salts, metals, water and sulphates. The shape of solvus in the NaCl-H₂O binary (fig. 1) predicts that upon further isothermal decompression, the vapor and the brine will progressively become less and more saline, respectively.

Once information on Cl solubility in silicate melts is available, indirect evidence for immiscibility between silicate melts and H₂O-NaCl fluids is provided by the study of Cl concentrations in glass inclusions present in magmatic phenocrysts. These inclusions are small samples of silicate melt trapped during crystal growth and they represent the most accessible samples of non-degassed magma (*e.g.*, Roedder, 1984; Lowenstern, 1995, and references therein; Signorelli *et al.*, 2001; Webster and De Vivo, 2002). Alternatively, matrix glasses from rapidly erupted and cooled pumices (*e.g.*, from Plinian eruptions) may provide useful information on some volatiles (*e.g.*, Gardner *et al.*, 1998; Signorelli and Capaccioni, 1999; Signorelli *et al.*, 2001). For example, data collected from the literature on Cl contents of phonolitic glass inclusions and matrix glasses are presented in fig. 8. The content of Cl in these evolved alkaline melts is quite variable, ranging from 0.18 to 1.03 wt%. The highest abundance of Cl occur in volcanic products from Vesuvius (1.03 wt%), whereas the lowest pertain to Laacher See (0.18 wt%), Montaña Blanca (~0.35 wt%) and Tambora (~0.2 wt%). Provided that the magma was fluid saturated and the magmatic reservoir was located at pressures below about 200 MPa, the similarity of natural and experimental data for Vesuvius suggests that most Vesuvian phonolitic melts were saturated with respect to a hydrosaline liquid (brine). If these assumptions are also valid for Laacher See, Montaña Blanca and Tambora, the comparison between natural and experimental data suggests that these systems could not have been saturated with a hydrosaline brine prior to eruption. The comparison of Cl in glass inclusions and degassed matrix glasses, when

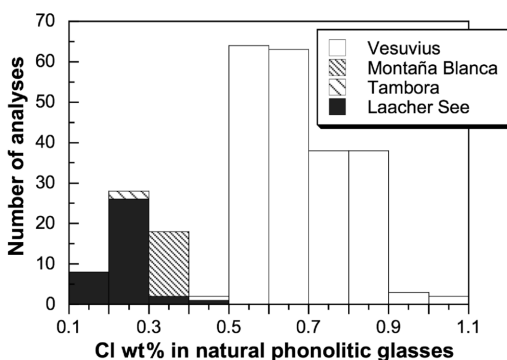


Fig. 8. Histogram of chlorine content of glass inclusions and matrix glasses from phonolites. The data are from the following volcanic systems: Vesuvius (Cornell and Sigurdsson, 1987; Mues-Schumacher, 1994 and unpubl.; Cioni *et al.*, 1995, 1998; Signorelli and Capaccioni, 1999; Signorelli *et al.*, 1999), Tambora (Devine *et al.*, 1984), Montaña Blanca (Signorelli, unpubl.) and Laacher See (Harms and Schmincke, 2000).

possible, suggests that Cl may be retained in the silicate melts during the Plinian phase of phonolitic eruptions (Cl degassing is slow on the eruption timescale). This is not the case of the Laacher See and Tambora eruption where chlorine has apparently shown a volatile behavior, with Cl content in matrix glasses lower than in glass inclusions (Devine *et al.*, 1984; Harms and Schmincke, 2000). There is a sharp gap between the field observation and the laboratory experiment concerning the behavior of chlorine during syn-eruptive decompression. Recently, Gardner *et al.* (1998) have shown that at fast decompression rates, Cl cannot diffuse out efficiently, although water can. On the contrary, when the erupted material cools more slowly Cl is lost, presumably as a result of groundmass crystallization.

The observed variations in Cl solubility with pressure for brine-saturated melts may be used to estimate pre-eruptive pressures of the most evolved magmas produced during the Campanian Ignimbrite (CI) eruption (Signorelli *et al.*, 2001), assuming that the system was saturated with both brine and aqueous fluid. As shown in fig. 9, experiments at 25 to 200 MPa using an

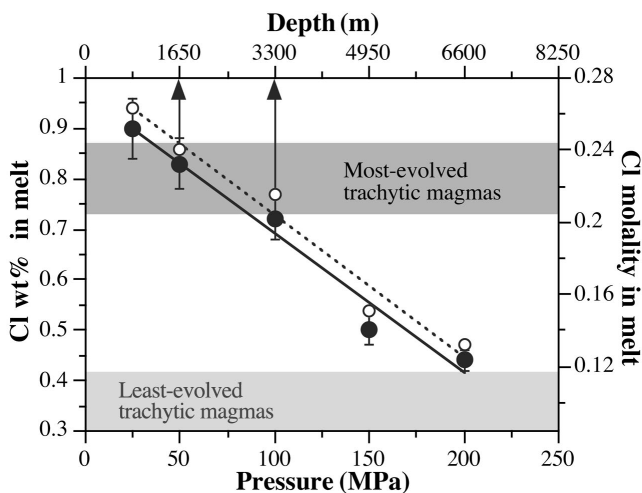


Fig. 9. Chlorine solubility in trachytic melts saturated with aqueous fluid+brine *versus* pressure (MPa). Solid and open circles represent original and water-free values ($\pm 1\sigma$ standard deviation), respectively. Shaded areas represent the Cl distribution in matrix glasses (most-evolved trachytic magma) and glass inclusions (least-evolved trachytic magma). The arrows indicate the inferred depth of the CI magma chamber (from Signorelli *et al.*, 2001).

evolved trachyte from the CI eruption show that the high Cl contents of these magmas correspond to minimum pre-eruptive pressures of 50-100 MPa, or depths of only 2-4 km, if the magmas were saturated with both an aqueous fluid phase and a brine prior to eruption, and neglecting possible effects of other components such as CO_2 (Signorelli *et al.*, 2001). In fact, the high Cl contents of these magmas can only be explained if the magmas were brine-saturated prior to eruption. Higher pressures could be possible if the magmas coexisted with only a brine and not an aqueous fluid phase but preliminary data on water fugacities calculated from the compositions of coexisting biotite-magnetite-sanidine present in the CI rocks also suggest water fugacities of 70-130 MPa, consistent with a relatively shallow, vapor-saturated system (Fabrizio and Carroll, unpubl.).

5. Conclusions

Experimental data concerning chlorine solubility in phonolitic to trachytic melts and va-

por/melt and hydrosaline brine/melt partitioning of Cl under magmatic conditions provide insights concerning the geochemical behavior of Cl in evolved alkaline melts. The results summarized in this study are directly applicable to volcano monitoring by allowing better interpretation of the origins of variations in measured halogen emissions from alkaline magmatic systems. In more general terms, the experimental data on Cl solubility as a function of magma composition and pressure will provide better constraints on the volcanic degassing of Cl and help in the identification of eruptive products preserved in the geologic record which may have been associated with large Cl emissions. This will aid studies seeking to correlate the record of climatic variability with the record of volcanic eruptions and will allow better estimation of past volcanic input to the atmosphere.

At pressures and temperatures outside the vapor-brine immiscibility field of the $\text{NaCl-H}_2\text{O}$ system, the concentration of Cl in alkaline melts depends on the activity of Cl in the fluid phase. Under conditions within the vapor-brine immiscibility field, the concentration of Cl in melt is

constant and is buffered by the coexistence of aqueous vapor and hydrosaline brine. Cl partitioning between hydrosaline liquid and melt and Cl solubility exhibit a strong negative dependence on the pressure, whereas Cl partitioning between aqueous vapor and melt shows a positive correlation with pressure. These features may be attributed to the shape of the immiscibility field of the NaCl-H₂O system. When compared with experimental results on rhyolites, the solubility of Cl in phonolites and trachytes is approximately twice as high under similar conditions. These results demonstrate that Cl solubility in hydrous evolved melts is a strong function of melt composition and higher solubilities can be expected in alkali-rich, low silica activity compositions. The strong dependence of Cl solubility on pressure in magmas saturated with aqueous fluid + brine means that melt Cl contents might be useful for estimating minimum pre-eruptive pressures, as illustrated for the most evolved (and presumably highest-level) compositions observed in the Campanian Ignimbrite eruption. Additional work is still needed to address the effects of melt composition on Cl solubility over a range of pressures and temperatures and to quantify the effects of other volatile components (*e.g.*, F, CO₂) on Cl solubility. The release of Cl during explosive eruptions may also be influenced by degassing kinetics and this represents another area where more experimental data are needed if we wish to model Cl release in active volcanic systems.

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