



Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data

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Received 1 November 2003; received in revised form 9 April 2004; accepted 15 July 2004

Abstract

Owing to advances in microanalytical techniques over the last 15 years, there is a growing database on the volatile contents of subduction-related magmas as recorded in melt (glass) inclusions trapped in phenocrysts in volcanic rocks. Basaltic magmas from subduction zones show a wide range of water contents, ranging from as high as 6–8 to <0.5 wt.% H₂O. Variations are related in some places to primary factors such as proximity to the arc front or extent of subduction-related mantle enrichment inferred from trace element systematics. Some low values of H₂O in melt inclusions result from shallow degassing before crystallization and entrapment of inclusions. The dissolved CO₂ contents of melt inclusions from basaltic arc lavas range from below detection (~25 ppm) to nearly 2500 ppm. This variability is caused by degassing of low-solubility CO₂ before inclusions are trapped. The estimated primary CO₂ content of arc basaltic magma inferred from global arc volcanic CO₂ emissions and magma flux is >3000 ppm, suggesting that no melt inclusions sample undegassed arc magmas. The Cl and S contents of arc basaltic magmas are greater than midocean ridge basalts, indicating that these volatiles are also recycled from subducted sediment and altered oceanic crust back into the mantle wedge. Comparison of the fluxes of volatiles subducted back into the mantle along subduction zones and returned from the mantle to the surface reservoir (crust, ocean, and atmosphere) via magmatism suggests that there is an approximate balance for structurally bound H₂O and Cl. In contrast, ~50% of subducted C appears to be returned to the deep mantle by subduction, but uncertainties are relatively large. For S, the amount returned to the surface reservoir by subduction zone magmatism is only ~15–30% of the total amount being subducted. Dacitic and rhyolitic magmas in arcs contain 1–6 wt.% H₂O, a range that overlaps considerably with the values for basaltic magmas. Either basaltic parents for these differentiated magmas are relatively H₂O-poor, or intermediate to silicic arc magmas form through open-system processes involving variable amounts of crustal melting, mixing with basalt and basaltic differentiates, and fluxing of CO₂-rich vapor from mafic magma recharged into silicic magma bodies. Consideration of H₂O–CO₂ relations and gaseous SO₂ emissions for intermediate to silicic arc magmas shows that such magmas are typically vapor-saturated during crystallization in the middle to upper crust. Gas emissions thus reflect migration and accumulation of volatiles within complex open magmatic systems.

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Keywords: volatiles; subduction zone; melt inclusion

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1. Introduction

Subduction of altered oceanic crust and sediment plays a fundamental role in the geochemical cycles of the major volatiles (H, C, S, and Cl) as well as many other elements on Earth. However, because volatiles are almost completely degassed during subaerial eruption, it is difficult to measure preeruption volatile concentrations directly. One way around this problem is to analyze tiny samples of undegassed melt trapped inside of phenocrysts. Because the crystalline host for the inclusions is relatively rigid, they act as tiny pressure vessels and prevent the trapped melt from degassing, even though the bulk magma decompresses to surface pressure during eruption. Advances in microanalytical techniques [Fourier transform infrared spectroscopy (FTIR) and secondary ion mass spectrometry (SIMS)] for precise determination of H₂O and CO₂ in melt inclusions have led to a growing body of data on the volatile contents of subduction-related magmas. These developments have been complemented by important advances in experimental petrology, geodynamics, and the geochemistry of light

element and isotopic tracers that have helped to further elucidate the complex pathways and processes by which volatiles are recycled through subduction zones and back to the Earth's surface reservoir (crust, oceans, and atmosphere).

It was originally proposed by Coats (1962), before the advent of plate tectonic theory, that the origin of volcanic rocks in the Aleutians entailed the transport of water in sediments and basaltic oceanic crust to depths >100 km along a major thrust fault. He proposed that "water and material of granitic composition were sweated out of these materials and were added to a molten fraction of basaltic composition that was interstitial to peridotite of the mantle". In the 1970s, Anderson (1973, 1974a,b) developed the "water-by-difference" technique based on electron microprobe analysis of melt (glass) inclusions trapped in phenocrysts and suggested that water contents of mafic arc magmas could be as high as 7 wt.% H₂O. He also found high Cl contents by electron microprobe analysis of melt inclusions. Although his results for water were not widely accepted at the time, subsequent development of precise techniques for

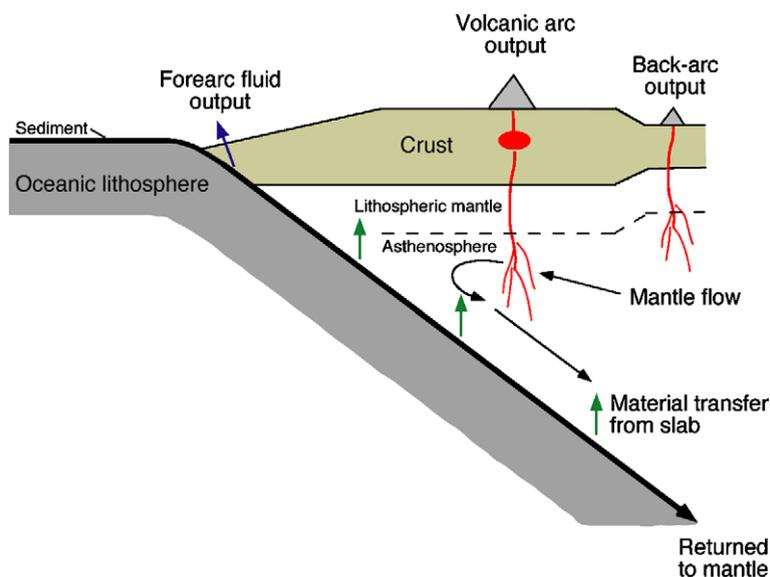


Fig. 1. Schematic view of volatile recycling and magma generation in subduction zones. Sediment and altered basaltic oceanic crust transport volatiles into subduction zones. Pore water is largely expelled from rock and sediment within the first 5–10 km depth (e.g., Moore and Vrolijk, 1992). Structurally bound H₂O and other volatiles can be transported to greater depth and are partially to completely released via metamorphic devolatilization reactions, after which they ascend into the overlying mantle, resulting in hydration and partial melting. Some portion of subducted volatiles may be retained by minerals in the slab and returned to the deep mantle.

direct measurement of H₂O in melt inclusions has shown that arc basaltic magmas can have relatively high H₂O (6–8 wt.%; e.g., Sisson and Layne, 1993; Roggensack et al., 1997; Grove et al., 2002). These results lend support to a model of subduction zone magmatism based on experimental-phase equilibrium studies, trace elements, and isotope geochemistry that involves fluxing of the mantle wedge with H₂O derived from the slab (Fig. 1; McBirney, 1969; Fyfe and McBirney, 1975; Anderson, 1982; McCulloch and Gamble, 1991; Luhr, 1992; Stolper and Newman, 1994; Pearce and Peate, 1995). They also support the idea that transport of an H₂O-rich component from slab to wedge is the major process by which major, trace, and other volatile elements are recycled in subduction zones.

In this paper, I review (1) data on volatiles in melt inclusions in both mafic and silicic arc magmas, and (2) estimates of the flux of volatiles returned to the Earth's mantle in subduction zones vs. volatile outputs via arc magmatism. For general reviews from an experimental perspective on the role of H₂O in arc magmatism and the release of volatiles from subducted materials, the reader is referred to Ulmer (2001) and Poli and Schmidt (2002).

2. Techniques for measuring magmatic volatiles

Constraints on magmatic volatile contents come from both direct and indirect means. Direct analysis of melt inclusions in phenocrysts and quenched submarine basaltic glass with microanalytical techniques makes it possible to measure H₂O and CO₂ (FTIR, SIMS) and S, Cl, and F (SIMS, electron microprobe). Indirect techniques for estimating H₂O contents include comparing natural-phase assemblages and melt compositions with results of experimental-phase equilibrium studies (e.g., Rutherford et al., 1985) and mineral–melt equilibria based on thermodynamic models calibrated with experimental data (Housh and Luhr, 1991; Sisson and Grove, 1993). An important difference between melt inclusion results and these indirect methods is that the latter require that equilibrium be achieved between crystals and liquid in a bulk sample, whereas inclusions give data specific to the formation conditions of individual crystals. Data for melt

inclusions commonly show evidence for mixing of crystals that grew in melts of different compositions (e.g., Anderson, 1976; Anderson et al., 2000; Kent and Elliot, 2002) indicating that many bulk samples of volcanic rock never experienced full crystal–liquid equilibration before eruption.

Volcanic gases provide complementary information about volatile contents of magmas and volatile fluxes from volcanoes. However, because magma degassing is a complex process and the compositions of gases are frequently modified by cooling, reequilibration, contamination, and reaction with wallrocks or fluids, it is often difficult to interpret gas data in terms of original magmatic concentrations. Sulfur dioxide is the easiest of the main magmatic volatiles to measure in volcanic plumes because its concentration is relatively high compared to ambient atmospheric values. Numerous remote measurements of SO₂ fluxes from active volcanoes have been made, including both ground-based and airborne use of the UV correlation spectrometer (COSPEC) since the early 1970s and the satellite-based Total Ozone Mapping Spectrometer (TOMS; Fig. 1) since 1978 (Krueger et al., 2000; see: <http://skye.gsfc.nasa.gov>). Measured SO₂ fluxes from arc volcanoes using these techniques provide essential information on the flux of S returned from the mantle via arc magmatism. Fluxes of other major volatiles (CO₂, H₂O, and Cl) can be estimated by combining measured SO₂ fluxes with analyses of volcanic gases to constrain CO₂/SO₂, H₂O/SO₂, and Cl/SO₂ ratios (e.g., Hilton et al., 2002). Direct measurements of CO₂ flux exist for some arc volcanoes (e.g., Gerlach, 1991; Gerlach et al., 1997).

3. Melt inclusions: formation and postentrapment modification

Melt inclusions form in crystals when some process interferes with the growth of a perfect crystal. This can occur from a variety of mechanisms, including skeletal growth due to strong undercooling or nonuniform supply of nutrients, and formation of reentrants by resorption followed by additional crystallization (Lowenstern, 1995). Compositional boundary layers form adjacent to growing crystals, so a primary concern in melt inclusion studies is

whether the trapped melt accurately represents the bulk melt surrounding the crystal at the time of entrapment, or has been affected by boundary layer enrichment or depletion (Roedder, 1984). Lu et al. (1995) combined diffusion theory with analytical data for rhyolitic melt inclusions from the Bishop Tuff and demonstrated that compositional gradients have a negligible effect on the compositions of melt inclusions $>50\ \mu\text{m}$ in diameter. The diffusive effect is negligible because the growth of crystals is controlled by the concentration of major constituents in the adjacent melt. A nonnegligible depletion in such a major constituent in the melt adjacent to a growing crystal would lead to cessation of crystallization. Other constituents that have diffusivities greater than the major elements, particularly fast-diffusing components like H_2O , will not develop significant concentration gradients (Lu et al., 1995; Watson, 1996). However, analyses of small inclusions ($<50\ \mu\text{m}$ in diameter) should be viewed in light of potential boundary layer effects.

A number of processes can potentially modify the composition of melt inclusions after they are trapped inside the crystal host (Fig. 2; see Danyushevsky et al., 2002 for a thorough review). During continued cooling, crystallization of the included melt continues along the melt–crystal interface, depleting the melt in constituents that enter the crystalline phase and enriching it in elements incompatible in the crystal. Diffusive exchange can also occur between the melt

and the crystal, and this particularly affects the Fe contents of many melt inclusions in olivine (Danyushevsky et al., 2000; Gaetani and Watson, 2000, 2002). Most importantly for volatile studies, the much greater thermal contraction of the melt relative to the crystal host during postentrapment cooling results in formation of a vapor bubble (shrinkage bubble) that can significantly deplete the melt in CO_2 because of its low solubility (Anderson and Brown, 1993; Cervantes et al., 2002). During ascent and eruption, volatiles can be lost if the host crystal ruptures around the inclusion (Fig. 2). The resulting depressurization in the inclusion results in the formation of one or more vapor bubbles, and such inclusions can typically be recognized by thin films of glass that form where melt is injected into the cracks. Finally, during slow cooling in lava flows or domes, melt inclusions crystallize, and additional volatiles can be lost if the inclusion host is cracked or H diffuses through the host. Such diffusive loss of H from inclusions has been recognized on the basis of measured D/H ratios in basaltic melt inclusions from Hawaii (Hauri, 2002), and has been observed during laboratory reheating experiments (Anderson, 1974a; Danyushevsky et al., 2002). Given the many possible postentrapment processes, it is critical in volatile studies of melt inclusions to fully characterize the textural features of inclusions before sectioning and analysis so that textural data can be integrated with compositional information to assess postentrapment effects.

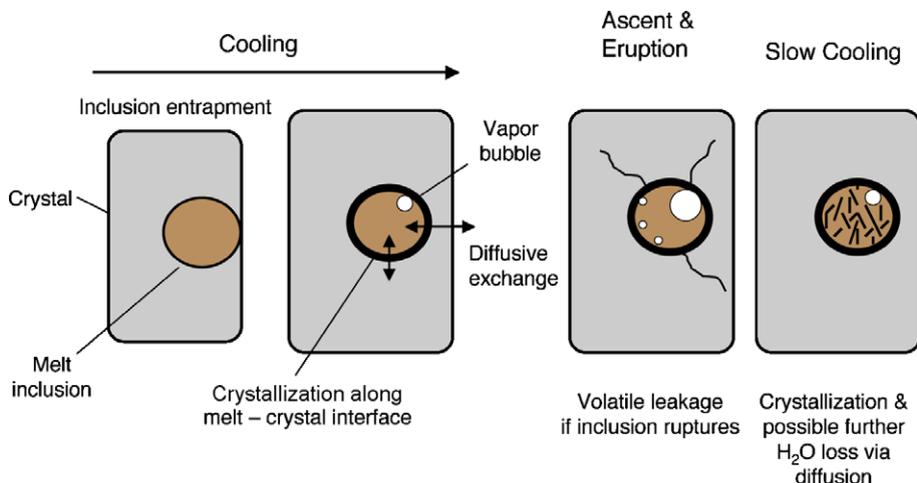


Fig. 2. Postentrapment modification of melt inclusions (see text for details).

4. Volatile contents of basaltic arc magmas

The following summary and discussion are largely restricted to data for melt inclusions from basaltic arc magmas that have been analyzed for major volatiles including CO₂. Although experimental-phase equilibrium studies have yielded important insights on the H₂O contents of arc magmas (e.g., Baker and Eggler, 1987; Luhr, 1990; Sisson and Grove, 1993; Moore and Carmichael, 1998; Pichavant et al., 2002), a review of the relevant experimental literature is beyond the scope of this paper. The reason for restricting the data to those inclusions analyzed for CO₂ is that it is the least soluble of the major volatiles, and hence the first to be lost by degassing (Fig. 3; Dixon and Stolper, 1995; Newman et al., 2000). Thus,

the presence of CO₂ in melt inclusions is an indication of high-pressure entrapment and likely minimal loss of H₂O, Cl, and S by degassing before inclusion entrapment or by postentrapment cracking of the host.

4.1. Water

Water is the most abundant volatile component recycled in subduction zones (e.g., Ito et al., 1983). Water contents of arc melt inclusions have a wide range of values, from 5 to 6 wt.% H₂O for inclusions from Nicaragua (Cerro Negro), central Mexico, and the Marianas, to <0.5 wt.% for Galunggung, Indonesia (Fig. 3; Table 1). Values as high as 8–10 wt.% H₂O have been found in melt inclusions in high-Mg andesites from the Shasta region of California (Grove

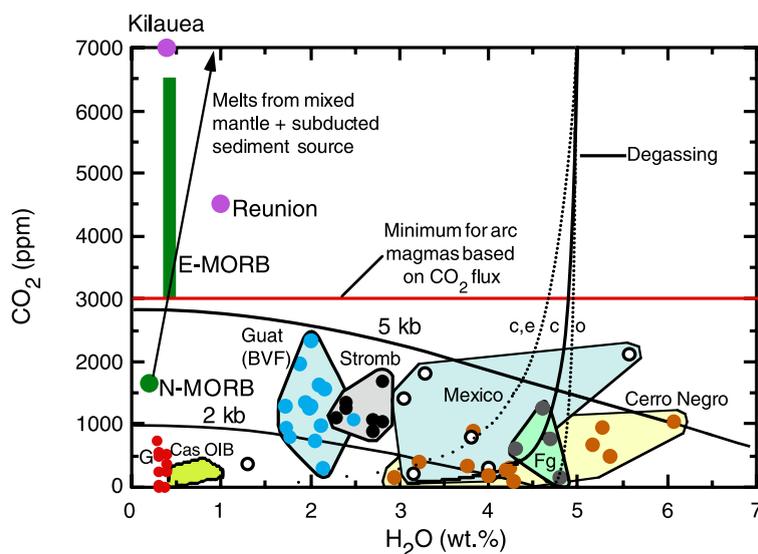


Fig. 3. H₂O vs. CO₂ for melt inclusions from arc basalts. Data are shown for Cerro Negro (Roggensack et al., 1997), Fuego (Fg; Roggensack, 2001), Guatemalan volcanoes behind the volcanic front (Guat BVF; Walker et al., 2003), the Trans-Mexican Volcanic Belt (Luhr, 2001; Cervantes and Wallace, 2003a,b), Stromboli (Metrich et al., 2001), Cayuse Crater, a cinder cone with OIB-like trace element composition from the Oregon Cascades (Cas OIB; M. Rowe, unpublished data), and Galunggung volcano, Indonesia (G; Sisson and Bronto, 1998). For Cerro Negro, only inclusions from the 1992 explosive eruption are plotted; partially degassed inclusions from the effusive 1995 eruption are not shown. Note that a Mexican sample with OIB-like composition has low H₂O (open circle with 1.3 wt.% H₂O) like the Cayuse Crater inclusions. Shown for comparison are the primary CO₂ contents of N-MORB (Marty and Tolstikhin, 1998) and E-MORB (Hekinian et al., 2000) magmas, and Kilauea basaltic magma (Gerlach et al., 2002). Also shown is the CO₂ content of basaltic magma from Reunion based on rare high-pressure melt inclusions (Bureau et al., 1999). Vapor saturation isobars are shown for 2 and 5 kb pressure. The minimum value estimated for primary CO₂ in arc magmas is ~3000 ppm and is derived using the global arc CO₂ flux (Hilton et al., 2002) and the maximum estimated value for flux of magma from mantle to crust in arcs (Crisp, 1984). Arrow shows the H₂O and CO₂ contents of model basaltic magmas derived from an N-MORB mantle source that has been enriched by bulk addition of subducted sediment. The sediment CO₂/H₂O ratio used is the global average from Hilton et al. (2002). Degassing curves are shown for a magma with 5 wt.% H₂O and 7000 ppm CO₂ (calculated using Newman and Lowenstern, 2002). Curves are shown for open-system (o) and closed-system (c) degassing. Also shown is a degassing path for magma that starts with 3 wt.% excess vapor (c,e).

Table 1
Volatile contents of some arc and back-arc basaltic magmas

| Location | Material | H ₂ O (wt.%) | CO ₂ (ppm) | S (ppm) | Cl (ppm) | References |
|---------------------------|----------|----------------------------|--------------------------|------------|-------------|------------|
| Cascades (Shasta region) | MI, exp | <1 to >8 | | 1000–3000 | 400–2200 | 1–3 |
| Batan Island, Philippines | MI | | | 1720–3200 | 1790–2900 | 4 |
| Galunggung, Indonesia | MI | 0.2–0.4 | 0–750 | 350–2900 | 700–1600 | 5,6 |
| Central Mexico | MI | 1.3–5.2 | 250–2100 | 1000–6000 | 700–1900 | 7 |
| Cerro Negro, Nicaragua | MI | 3.1–6.1 | 0–1040 | 300–1300 | 700–1500 | 8 |
| Aeolian Islands, Etna | MI | | | 1200–3200 | 200–2900 | 9 |
| Mariana arc | MI | 1.4–3.3 | 0–600 | | 100–4100 | 10,11 |
| Mariana Trough | GL | 0.5–2.1 | 0–170 | | 80–840 | 12 |
| N-MORB | GL | 0.1–0.5 | 100–300 | 800–1500 | <100 | 13–15 |

MI=melt inclusion; GL=submarine glass; exp=experimental-phase equilibria.

References: (1) Anderson (1974a); (2) Sisson and Layne (1993); (3) Grove et al. (2002); (4) Metrich et al. (1999); (5) Sisson and Bronto (1998); (6) de Hoog et al. (2001a); (7) Cervantes and Wallace (2003a); (8) Roggensack et al. (1997); (9) Metrich and Clochchiatti (1996); (10) Newman et al. (2000); (11) Kent and Elliot (2002); (12) Stolper and Newman (1994); (13) Dixon and Stolper (1995); (14) Wallace and Carmichael (1992); (15) Michael and Cornell (1998).

et al., 2002; Grove, personal communication). The H₂O variations appear in some cases to be related to primary factors such as proximity to the arc front or relationship to degree of subduction-related mantle enrichment. In assessing variations with distance from the trench, it is important to note that the lower end of the range of H₂O for arc basalts overlaps with values for submarine basaltic glasses from back-arc basins such as the Marianas back arc and Lau Basin, in which H₂O contents vary from 0.5 to 2 wt.% (Stolper and Newman, 1994; Kent et al., 2002). This is consistent with the interpretation that subduction input of H₂O to the mantle wedge decreases with increasing slab depth and lateral distance from the trench.

It is particularly important to recognize the effects of shallow degassing before melt inclusion H₂O contents are interpreted in terms of primary variability. An excellent example comes from the 1992 and 1995 eruptions of Cerro Negro volcano, Nicaragua (Roggensack et al., 1997). The 1992 eruption was explosive, producing a 7-km-high sustained ash column, whereas the 1995 eruption was mainly effusive after an initial phase of discrete ash explosions (<2 km in height). Melt inclusions in olivine from the 1992 eruption contain generally higher H₂O (mostly 4.0–6.1 wt.%) and CO₂ (mostly 300–1040 ppm) than inclusions from the less energetic 1995 eruption (mostly <3.5 wt.% H₂O and <400 ppm CO₂). Otherwise, the inclusions have similar K₂O contents and major element compositions, suggesting that the

H₂O variations are due to degassing and not primary variability. Roggensack et al. (1997) interpreted these results to indicate that olivine in the magma erupted in 1995 crystallized at shallower depths (based on lower vapor saturation pressures) at which pressure much or all of the CO₂ was degassed and some H₂O was lost. Similar patterns have been observed in basaltic melt inclusions from Stromboli volcano, Italy (Metrich et al., 2001), and in basaltic andesite melt inclusions from Parícutin volcano, Mexico (Luhr, 2001). Extreme examples in which nearly all H₂O is degassed before olivine growth and melt inclusion entrapment have been documented from the Chichináutzin volcanic field in central Mexico (Cervantes and Wallace, 2003a,b). Such degassing prior to inclusion entrapment is not surprising in H₂O-rich magmas because much of the crystal growth may be driven by H₂O loss rather than cooling.

Variations in volatile content with distance from the trench were studied in Guatemala by Walker et al. (2003). At arc front volcanoes, H₂O contents are 1–6.2 wt.% at Fuego and about 2 wt.% at Pacaya, but the Pacaya inclusions have CO₂ below detection limit, so the low H₂O values could be the result of partial degassing before inclusion entrapment. The variability observed for Fuego is a result of mixing between undegassed and degassed magma just before eruption, and the primary H₂O contents of the basaltic magmas are probably 4–5 wt.% (Roggensack, 2001). Most monogenetic basaltic cinder cones located up to 80 km behind the volcanic front have H₂O contents

similar to Pacaya (~2 wt.%; Walker et al., 2003). The results therefore show no consistent across arc variation, but the highest H₂O contents (Fuego) are found only at the arc front.

Quantitative relations between H₂O and incompatible trace elements in arc and back-arc basaltic magmas have been demonstrated for only a few regions. Compositional variability of basaltic magmas from the Mariana Trough back arc can be explained by melting of a depleted midocean ridge basalt (MORB) mantle that has been variably enriched with an H₂O-rich component, presumably derived from the subducted slab (Stolper and Newman, 1994). However, the melting region beneath the Marianas back arc is spatially distant from the inclined seismic zone, and therefore the composition of this slab component probably reequilibrated with the mantle during transport (Stolper and Newman, 1994). Recently, the relations for back-arc magmas have been extended to include the Marianas arc (Newman et al., 2000; Kelley et al., 2001). In the Mount Shasta region of the Cascades, H₂O contents of primitive magmas vary from <1 to >8 wt.%, and there is a strong link between H₂O, large ion lithophile elements (LILE) and light rare earth element (LREE) (Grove et al., 2002). Another example of the relationship between H₂O content (and other volatiles) and trace element enrichment of the sub-arc mantle wedge comes from the Chichináutzin volcanic field in central Mexico (Cervantes and Wallace, 2003a). Melt inclusion H₂O contents in this region vary from 1.3 to 5.2 wt.%. Enrichment of H₂O relative to Nb correlates positively with K/Nb, Ba/Nb, and La/Nb, indicating a clear link between H₂O and trace element enrichment of the mantle wedge. These results show that fluxing of the wedge with an H₂O-rich component from the subducted slab is important in the formation of magmas that are enriched in LILE and LREE relative to high-field-strength element (HFSE).

Some arc basaltic magmas are relatively H₂O-poor (Fig. 3) and are inferred therefore to be the result of decompression melting caused by upwelling in the mantle wedge (Sisson and Layne, 1993). A well-documented example comes from the 1982–1983 eruptions of Galunggung volcano, Indonesia, where basaltic melt inclusions contain 0.3–0.4 wt.% H₂O (Sisson and Bronto, 1998). The inclusions contain relatively high CO₂, S, and Cl, so degassing of

magma before olivine growth and inclusion entrapment seems unlikely as an explanation for the low H₂O contents. Some H₂O-poor arc magmas have trace element geochemical patterns similar to those of ocean island basalts (OIBs), suggesting that they come from a mantle source that has not been significantly enriched in H₂O and trace elements by subduction processes (Fig. 3). In contrast, the H₂O-poor arc magmas from Galunggung have trace element characteristics, such as high Ba/Nb, that are generally attributed to enrichment of the mantle wedge by a hydrous component derived from the subducted slab (Gill, 1981; Brenan et al., 1995; Pearce and Peate, 1995; Keppler, 1996). The very high Cl/H₂O ratio of the Galunggung melt inclusions (see below) suggests that hypersaline brine could have carried the subduction elemental signature into the mantle wedge without significantly enriching the wedge in H₂O (Sisson and Bronto, 1998).

D/H ratios of undegassed melt inclusions are a potential tracer for water recycling in subduction zones but are challenging to measure by ion probe techniques (Hauri, 2002). Fractionation factors for D/H between fluid and hydrous minerals indicate that D should be partitioned into a fluid phase relative to H during dehydration of subducted oceanic crust (Suzuoki and Epstein, 1976; Hauri et al., 2002). This should result in elevated δD values for subduction-related magmas. Based on analyses of geothermal waters and high-temperature gases at active volcanoes, it has been proposed that δD values of H₂O in subduction zone magmas are in the range from –30‰ to –10‰, higher than MORB values (–50‰ to –60‰; Taran et al., 1987; Giggenbach, 1992; Taran et al., 1995). Similarly, fumarolic gas samples from the Mount St. Helens dacite dome indicate a value of –33‰ for primary magmatic water (Shevenell and Goff, 1993). These results are consistent with data for δD in Mariana Trough and Lau Basin basaltic glasses that suggest a δD value of about –25‰ for the H₂O-rich subduction-derived component (Poreda, 1985; Stolper and Newman, 1994).

4.2. Carbon dioxide

Studies of CO₂ recycling in subduction zones have relied on isotopic data for volcanic gases from arc volcanoes and submarine basaltic glasses from back-

arc basins (Varekamp et al., 1992; Sano and Marty, 1995; Sano and Williams, 1996; Fischer et al., 1998; Nishio et al., 1998; Snyder et al., 2001; Hilton et al., 2002). Sources of C in arc basaltic magmas include subducted carbonate sediments and carbonate in altered oceanic crust ($\delta^{13}\text{C} \sim 0\text{‰}$), organic material in marine sediments ($\delta^{13}\text{C} < -20\text{‰}$), and indigenous mantle C ($\delta^{13}\text{C} = -6.5 \pm 2.5\text{‰}$; Sano and Marty, 1995). Fumarolic gases from arc volcanoes have $\delta^{13}\text{C}$ of -1‰ to -10‰ (Poreda and Craig, 1989; Sano and Marty, 1995; Sano and Williams, 1996; Fischer et al., 1998; Snyder et al., 2001). The $\delta^{13}\text{C}$ values and $\text{CO}_2/{}^3\text{He}$ ratios of both fumarolic gases and submarine basaltic glasses have been interpreted to indicate the presence of CO_2 from sources other than the mantle wedge, and thus to provide evidence of C recycling from subducted sediment (Sano and Marty, 1995; Sano and Williams, 1996; Fischer et al., 1998; Nishio et al., 1998; Snyder et al., 2001; Hilton et al., 2002; Shaw et al., 2003).

Dissolved CO_2 contents in melt inclusions from basaltic arc lavas range from below detection (~ 25 ppm) to nearly 2500 ppm (Fig. 3; Table 1). There are no systematic variations with H_2O or other volatile contents, and CO_2 values for a given suite or eruption can be quite variable despite little variation in H_2O . This variability and the common occurrence of low values are probably caused by degassing before entrapment of melt inclusions (Fig. 3). This is caused by the much lower solubility of CO_2 relative to H_2O in silicate melts, which can result in degassing of CO_2 without significant loss of H_2O (Dixon and Stolper, 1995; Newman et al., 2000). However, as is evident from Fig. 3, it is also possible for some H_2O to be lost if a melt starts with a relatively high initial CO_2 content. These observations for CO_2 and an assessment of volcanic gas data (Anderson, 1975) suggest that arc basaltic magmas are typically saturated with a CO_2 -rich vapor phase in the crust. Because magmas are probably vapor-saturated, the H_2O and CO_2 data for melt inclusions can be used to infer pressure of crystallization and inclusion entrapment. The range in the data indicates that olivine crystallization in basaltic arc magmas commonly occurs between 2 and 5 kb pressure. This pressure range is in general agreement with results of experimental-phase equilibrium studies (Sisson and Grove, 1993; Moore and Carmichael, 1998).

The CO_2 contents of arc melt inclusions are comparable to estimates of the primary CO_2 content of normal midocean ridge basalt (N-MORB) that are based on $\text{CO}_2/{}^3\text{He}$ measurements of MORB glasses and the ${}^3\text{He}$ flux from the midocean ridge system to the ocean, but are much less than estimates for enriched MORB and basaltic magmas from some mantle plumes (Fig. 3). However, because the melt inclusions are likely to have been trapped after significant degassing of CO_2 had occurred, they provide little constraint on the primary CO_2 contents of arc magmas. An estimate of the primary CO_2 content of arc magmas can be made using the total annual CO_2 flux from arc volcanoes and an estimate of the global rate of addition of mafic magma to arcs. Using a maximum likely value for the magma flux to arcs ($8.5 \text{ km}^3/\text{year}$; Crisp, 1984) yields a minimum primary CO_2 content for arc magmas of ~ 3000 ppm CO_2 , higher than all of the melt inclusion values (Fig. 3). Given that the rate of arc magma production is likely to be $2\text{--}4 \text{ km}^3/\text{year}$ (Crisp, 1984; Carmichael, 2002; Dimalanta et al., 2002), the primary CO_2 contents of arc magmas are likely to be in the range from 0.6 to 1.3 wt.% CO_2 (see also Fischer and Marty, this volume). These estimates suggest that all arc basaltic melt inclusions represent melts trapped after significant loss of CO_2 has occurred by degassing.

The $\text{CO}_2/\text{H}_2\text{O}$ ratios of subducted sediment and altered oceanic crust (Plank and Langmuir, 1998; Hilton et al., 2002) are much higher than the $\text{CO}_2/\text{H}_2\text{O}$ ratio of arc basaltic magmas based on the range of measured H_2O values (Fig. 3) and the primary CO_2 contents estimated above. This suggests that CO_2 must be preferentially retained in subducted materials relative to H_2O . If carbonate minerals remain stable in subducted sediment and oceanic crust during metamorphic dehydration reactions, then CO_2 might preferentially be retained in the slab and subducted deeper into the mantle. Thermodynamic modeling suggests that decarbonation of sedimentary carbonate at depths beneath arc volcanoes ($\sim 80\text{--}180$ km) will only occur if there is infiltration of H_2O -rich fluids into the subducted sediment (Kerrick and Connolly, 2001). The likely source of such fluids would be from dehydration of subducted oceanic crust.

It has been proposed, based on high CO_2 emissions, that andesitic arc volcanoes are essentially “ventholes” allowing subducted volatiles to be

returned to the surface and that a free volatile-rich fluid phase is present all the way down to the zone of arc–magma generation (Giggenbach, 1992). In principle, my estimates of the primary CO_2 contents of arc basaltic magmas could be used to estimate depths of initial vapor saturation. Unfortunately, the solubility of CO_2 at high pressure is poorly known because the presence of H_2O appears to enhance CO_2 solubility at pressures >5 kb relative to H_2O -free melts (Holloway and Blank, 1994; King and Holloway, 2002). Available solubility data suggest that H_2O -bearing melts with 0.6–1.3 wt.% CO_2 would become vapor-saturated at depths of about 20–50 km, but uncertainties on these estimates are large. Nevertheless, the results suggest that arc basaltic magmas may be vapor-saturated at lower crustal to upper mantle depths.

4.3. Chlorine

Chlorine contents of arc basaltic melt inclusions are mostly between 500 and 2000 ppm Cl and are significantly higher than uncontaminated MORB (Fig. 4; Table 1), probably as a result of subduction recycling of seawater Cl (Schilling et al., 1978; Ito et al., 1983). Surprisingly, there is no systematic

variation of Cl with H_2O , and Cl contents of ~ 1000 ppm are found in samples ranging from 0.3 to 6 wt.% H_2O . The Cl contents of the melt inclusions are all significantly less than the amount required to saturate a basaltic melt with hydrosaline melt (brine) at the pressures indicated by the H_2O – CO_2 data (Webster et al., 1999), so Cl would have been partitioned between melt and an H_2O – CO_2 –Cl–S vapor phase. Elevated Cl contents are also found in back-arc basalts, reaching values as high as 1700 ppm in Lau Basin basalts (Valu Fa Ridge) that have not been affected by shallow contamination with Cl from a seawater-derived component (Kent et al., 2002).

Geochemical modeling of the addition of an H_2O -rich component to a depleted mantle wedge can be used to estimate the Cl content of subduction-derived material. Stolper and Newman (1994) estimated that the H_2O -rich component added from the slab to the mantle beneath the Mariana Trough back-arc region contained 1.2 wt.% Cl, equivalent to ~ 4 wt.% NaCl brine (following Kent et al., 1999, 2002, brine compositions are recalculated as the equivalent salinity in the H_2O –NaCl–KCl system). Similar modeling using data for basaltic glasses from the Lau Basin suggests comparable values for the subduction-derived

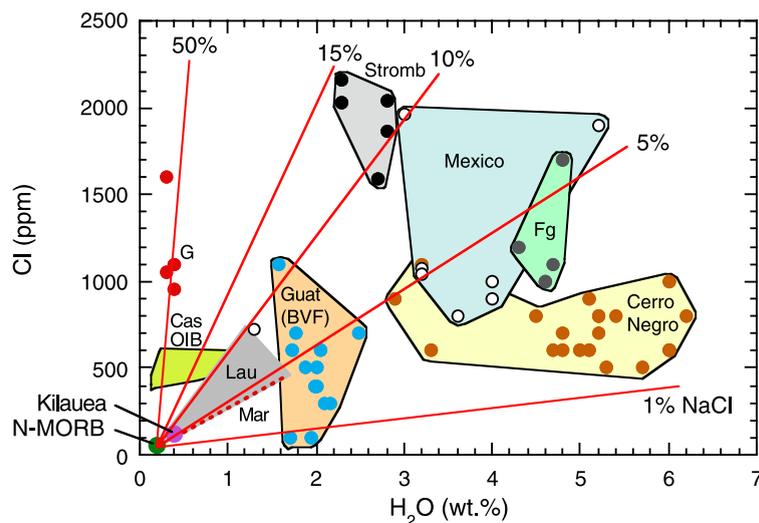


Fig. 4. H_2O vs. Cl for melt inclusions from arc basalts. Data sources and abbreviations as in Fig. 3. Field for Lau Basin back-arc basalts is from Kent et al. (2002). The average Cl/ H_2O ratio for Mariana Trough basalts (Stolper and Newman, 1994) is shown as a dashed line and coincides with the low end of values for the Lau Basin. Lines show basaltic melt compositions produced by addition of fluid with 1, 5, 10, 15, and 50 equivalent wt.% NaCl to an N-MORB mantle source. Melt inclusion data have not been corrected for varying degrees of olivine fractionation, and thus do not represent primary magma values, but such correction should only affect the absolute concentrations and not the Cl/ H_2O ratios.

H₂O-rich component, 4–10 wt.% NaCl brine (Kent et al., 2002). The high Cl contents and very wide range of Cl/H₂O ratios observed for arc basaltic melt inclusions require that Cl is a major component, present at weight percent levels, in fluids derived from the subducted slab and that there is a comparable wide range in Cl/H₂O (2–50% NaCl brine) in such fluids (Kent et al., 2002). The wide range of Cl/H₂O ratios requires that Cl and H₂O are strongly fractionated from one other either during devolatilization of the slab or during migration of slab-derived fluids through the mantle wedge. Such fractionation could plausibly result from formation of hydrous minerals in the mantle wedge. However, it has been argued that Cl–H₂O fractionation must occur during fluid expulsion from the slab or migration through the mantle prior to melting because the relatively large degrees of melting that create subduction zone basaltic magmas would likely exhaust hydrous phases from the residual mantle (Kent et al., 2002).

Knowledge of Cl in hydrous fluids transferred from slab to wedge is important not only for global geochemical cycles but also because the solubility of

many elements in high-temperature aqueous fluids is strongly dependent on Cl. In particular, there is considerable debate about whether Re and Os are transferred from slab to wedge in hydrous fluids (Brandon et al., 1996; Alves et al., 1999; McInnes et al., 1999; Borg et al., 2000; Chesley et al., 2002; Righter et al., 2002). Experimental data on Os partitioning show that Os contents of fluids are dependent on Cl (Xiong and Wood, 2002). However, for the estimated fluid Cl contents summarized above, hydrous subduction zone fluids would contain very little Os (~10 ppt), consistent with data from arc magmas (Righter et al., 2002).

4.4. Sulfur

Evidence for S recycling in subduction zones comes from melt inclusions in arc basaltic magmas, which have S contents (mostly 900–2500 ppm S) that are commonly higher than MORB of comparable FeO^T (Fig. 5; Table 1). The high S contents of many arc basaltic magmas require that they have higher f_{O_2} relative to MORB magmas. At the oxygen fugacities

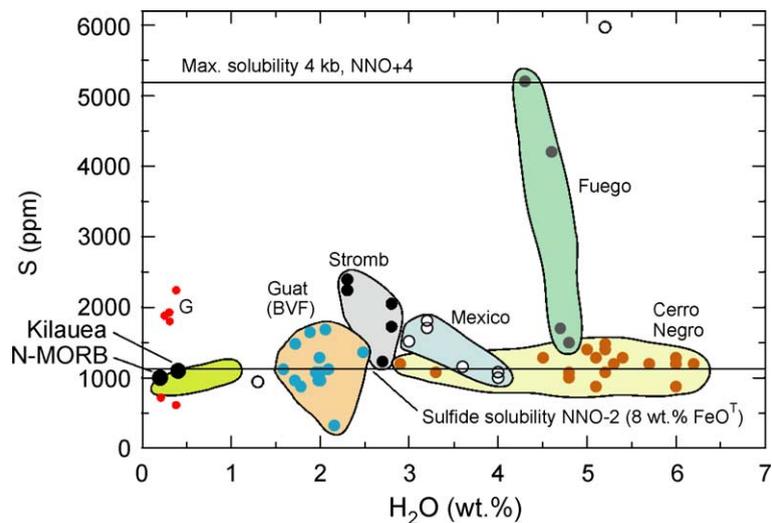


Fig. 5. H₂O vs. S for melt inclusions from arc basalts. Data sources and abbreviations as in Fig. 3. N-MORB value is from Wallace and Carmichael (1992) and is for samples with 8–10 wt.% FeO^T. Values for H₂O and S in Kilauea tholeiite are based on Clague et al. (1995). Note that for clarity, the circled field for Mexican samples has not been extended to encompass two melt inclusions, which plot near the high and low end of the range for the global dataset. Sulfide solubility line shows 1 bar value for basaltic melt (1150 °C, 8 wt.% FeO^T) at an oxygen fugacity 2 log units more reduced than the Ni–NiO buffer (NNO-2). Saturation limit was calculated using the thermodynamic model of Wallace and Carmichael (1992) updated to incorporate the temperature dependence from Mavrogenes and O'Neill (1999). Maximum solubility of sulfate in El Chichón trachyandesite at 4 kb and NNO+4 is from Luhr (1990).

of MORB magmas (<FMQ), sulfur contents of basaltic melts are controlled by saturation with immiscible sulfide (Fe–S–O) liquid (Wallace and Carmichael, 1992) such that S contents are ≤ 1200 ppm for melts with ≤ 10 wt.% FeO^T. Sulfur solubility in silicate melts increases dramatically with increasing oxygen fugacity as the speciation of S dissolved in the melt changes from predominantly S²⁻ to S⁶⁺ (Carroll and Rutherford, 1987, 1988; Luhr, 1990). Experiments on S solubility in basaltic melts at high f_{O_2} are lacking, but experimental data for the El Chichón trachyandesite indicate a maximum solubility of ~ 5000 ppm S for anhydrite-saturated melts at 1000 °C and an oxygen fugacity 4 log units above the NNO buffer (Luhr, 1990). Given that S⁶⁺ solubility has a strong positive dependence on temperature, maximum values for basaltic melts at >1000 °C are likely to be even higher. That arc basaltic magmas have higher oxygen fugacities than MORB magmas is supported by Fe³⁺/Fe²⁺ data for volcanic rocks (Wallace and Carmichael, 1999), measurements of S K α wavelengths in basaltic melt inclusions (Metrich et al., 1999; Luhr, 2001), and analysis of mantle xenoliths (Brandon and Draper, 1996).

Estimated mantle source concentrations for arc magmas are 250–500 ppm S (Metrich et al., 1999; de Hoog et al., 2001a), higher than MORB estimates of 80–300 ppm S (Chaussidon et al., 1989), requiring enrichment of S in the mantle wedge above subducting slabs. Sulfur isotope data for fumarolic gases, submarine basaltic glasses, and subaerial whole rock samples suggest recycling of seawater sulfate (Ueda and Sakai, 1984; Woodhead et al., 1987; Alt et al., 1993; Imai et al., 1993; Metrich et al., 1999; de Hoog et al., 2001b), although it should be cautioned that high $\delta^{34}\text{S}$ values could also, in part, reflect shallow degassing processes (e.g., Mandeville et al., 1998; Goff et al., 2000). The high S contents of many arc basaltic magmas, elevated $\delta^{34}\text{S}$ values, and higher f_{O_2} relative to MORB all suggest that percolation of slab-derived fluids in the mantle wedge causes both oxidation and addition of S to the mantle. Such high S contents cannot be derived from low- f_{O_2} MORB-type mantle because of solubility constraints imposed by sulfide saturation (Mavrogenes and O’Neill, 1999). Whether residual sulfides are present during mantle melting is also important for understanding PGE and chalcophile element abundances in arc

magmas (Richter et al., 2002). Geochemical modeling based on melt inclusions from the Chichináyutzin volcanic field, Mexico, suggests that several weight percent S is present in the H₂O-rich component transferred from the slab to the wedge (Cervantes and Wallace, 2003a).

5. Volatile fluxes

5.1. Fluxes of major volatiles from subduction-related magmatism

Numerous estimates have been published for the fluxes of the major volatiles returned from the mantle to the surface reservoir (crust, atmosphere, and oceans) by arc magmatism (Stoiber and Jepsen, 1973; Ito et al., 1983; Varekamp et al., 1992; Andres and Kasgnoc, 1998; Hilton et al., 2002). There are basically two different approaches for making such estimates (Fig. 6). The first is to use measured fluxes of SO₂ and CO₂ from arc volcanoes and then scale the results to all active arc volcanoes worldwide. The strength of this approach is that it utilizes actual flux measurements. How to scale the results up to all active arc volcanoes is less certain, but different scaling approaches have yielded fairly similar results, such that the global flux of SO₂ to the atmosphere from arc magmatism is relatively well constrained (Fig. 6). The global CO₂ flux is less well constrained because there is much less data available for CO₂ emissions from arc volcanoes (Gerlach, 1991), but the estimates summarized in Fig. 6 are in excellent agreement with global CO₂/³He systematics (Varekamp et al., 1992; Marty and Tolstikhin, 1998).

Given the abundant data on SO₂ fluxes, the fluxes of other components such as H₂O, CO₂, and Cl can be estimated if ratios of these elements to SO₂ are determined by analysis of fumarolic gases from the volcanoes where the flux measurements are made (Fig. 6). Disadvantages of this approach are that gas–magma separation processes are complex, resulting in fractionation of species with different solubilities, and gas compositions can be changed considerably during postrelease nonmagmatic processes. As a result, fumarolic gas ratios may not be representative of the original magma from which the gases are derived. This

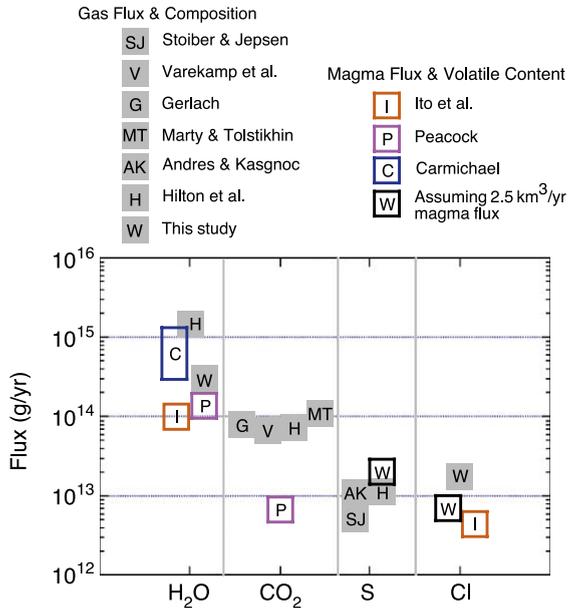


Fig. 6. Estimates of volatile fluxes (outputs) associated with arc magmatism. Estimates are categorized by method, and are based on either (1) measured SO₂ and CO₂ fluxes or fluxes combined with fumarolic gas analyses, or (2) magma flux from mantle to crust and primary magmatic volatile concentrations. Estimates are from Stoiber and Jepsen (1973), Ito et al. (1983), Peacock (1990), Gerlach (1991), Varekamp et al. (1992), Andres and Kasgnoc (1998), Marty and Tolstikhin (1998), Carmichael (2002), and Hilton et al. (2002). Values estimated in this study (*W*) are calculated as follows: H₂O—global CO₂ flux from arc volcanoes (Hilton et al., 2002) and an H₂O/CO₂ ratio of 4 based on relations discussed for Fig. 3; S—magma flux of 2.5 km³/year (Carmichael, 2002) and an average basaltic S content of 1300 ppm; Cl (open square)—magma flux of 2.5 km³/year and an average basaltic Cl content of 1000 ppm. Cl (solid square)—see text for description.

is particularly a problem for H₂O because fumarolic gases are commonly contaminated by meteoric water. Another major advantage of the gas flux method is that flux estimates for individual arcs or arc segments can be made provided a sufficient number of active volcanoes have been studied. This makes it possible to compare different arcs and to see if variations in the amount or composition of sediment being subducted into different arcs correlate with volatile fluxes from arc magmatism (Hilton et al., 2002).

The other basic approach for estimating fluxes of volatiles from arc magmatism is to use data on primary magmatic volatile contents and the flux of mantle-derived magma to the crust in arc regions (e.g., Ito et al., 1983; Peacock, 1990; Carmichael, 2002).

This approach is generally hampered by larger uncertainties than the gas flux approach. In particular, primary magmatic CO₂ concentrations are poorly known, as described previously, because the low solubility of CO₂ causes much of it to be degassed from magma at relatively high pressure. Concentrations of the more soluble volatiles, H₂O, S, and Cl, are being increasingly well constrained by melt inclusion analyses, but as shown above, they can be quite variable both within and between individual volcanoes. Finally, the flux of mantle-derived magmas into the crust at convergent margins is fairly uncertain, primarily because the ratio of extrusive to intrusive rocks is poorly constrained (Crisp, 1984; Reymer and Schubert, 1984; Dimalanta et al., 2002). Given all the uncertainties in the different approaches for estimating volatile fluxes, the best course is to look for consistency between the various estimates. The extent of agreement or disagreement between the various types of estimates can help to better constrain magma fluxes, primary magmatic volatile contents, and gas–magma separation processes.

Estimates of H₂O flux from arc magmatism by Ito et al. (1983) and Peacock (1990) are about 1 × 10¹⁴ g/year, but these values are likely to be too low because they used a conservative value for average H₂O content of arc basaltic magma of 1 wt.%. Carmichael (2002) used a range of values from 6 to 16 wt.% H₂O, constrained by experimental-phase equilibrium and crystal content data, combined with a global arc magma flux of 2.5 km³/year constrained by Nd–Hf isotopes to estimate a range from 4 × 10¹⁴ to 11 × 10¹⁴ g/year H₂O. The upper end of this range agrees with the estimate of Hilton et al. (2002), which is based on the global CO₂ flux from arc volcanoes and an assumed H₂O/CO₂ ratio of 50. However, the range of measured H₂O values (Fig. 3) and my estimates for the primary CO₂ contents of arc basaltic magmas suggests that this value is too high, and that an H₂O/CO₂ ratio of ~4 is more appropriate. Thus, I believe that the best estimate for H₂O flux from arc magmatism is ~3 × 10¹⁴ g/year.

Sulfur and Cl fluxes can also be estimated using the magma flux and magmatic volatile content approach. Using a global arc magma flux of 2.5 km³/year (Carmichael, 2002) and an average S content of 1300 ppm (Fig. 6) yields an arc S flux of 1.8 × 10¹³ g/year S. This value is slightly higher

than, but within uncertainty of, some estimates based on measured SO₂ fluxes from arc volcanoes (Fig. 6). This agreement is perhaps a bit surprising because significant amounts of S degassed from arc magmas undoubtedly become sequestered in the crust in sulfide and sulfate deposits. Thus, it might be expected that the flux of S from mantle to crust carried by arc magmas might greatly exceed the flux of gaseous S lost from arc volcanoes. The best value for global arc S emission based on measured gas fluxes is probably 1×10^{13} g/year S (Hilton et al., 2002) because it uses the most rigorous scaling analysis. Accepting this value and my estimate above (1.8×10^{13} g/year S) based on S concentration and magma flux suggests that ~40–50% of the total S returned to the crust via arc magmatism remains locked up in sulfide and sulfate deposits, with the remainder being vented to the atmosphere.

The Cl flux from arc magmatism was estimated by Ito et al. (1983) to be 4.5×10^{12} g/year based on melt inclusion data and estimated arc magma flux. Using a global arc magma flux of 2.5 km³/year and a magmatic Cl concentration of 1000 ppm (Fig. 4) yields a comparable estimate of 7×10^{12} g/year (Fig. 6). For comparison, I used the average Cl/CO₂ ratio (0.25) of analyzed fumarolic gases from arc volcanoes (Symonds et al., 1994; T. Fischer, written communication) and the CO₂ flux from Hilton et al. (2002) to estimate a Cl flux of 1.8×10^{13} g/year (Fig. 6). However, as with use of H₂O/CO₂, this is likely an overestimate of magmatic values. The much higher solubility of Cl relative to CO₂ causes Cl to be retained during high-pressure degassing such that gases derived from later low-pressure degassing have higher Cl/CO₂ than primary magmatic values. Based on the estimates summarized above, the Cl flux from arc magmatism appears to be relatively well constrained at $\sim 4\text{--}7 \times 10^{12}$ g/year.

5.2. Comparison of subduction input vs. output for major volatiles

A major goal of subduction zone studies is to quantify the fluxes of volatiles subducted back into the mantle along subduction zones and returned from the mantle to the crust and atmosphere via magmatism (Javoy et al., 1982; Ito et al., 1983; Marty and Jambon, 1987; Peacock, 1990; Bebout, 1996).

Knowledge of the flux of volatiles back into the mantle at subduction zones relies on estimates of the amount and composition of sediment being subducted and the amount of volatiles that are stored in the altered oceanic crust. The largest source of uncertainty in such estimates is knowing how much subducted sedimentary pore water and other volatiles are squeezed out of sediment and returned to the accretionary wedge or shallow crust (Ito et al., 1983). Most workers have assumed, based on data for accretionary prisms (e.g., Moore and Vrolijk, 1992), that contributions from pore fluids are expelled at relatively shallow depths such that only structurally bound volatiles in sediment and oceanic crust are devolatilized beneath the magma generation zone in arcs. In a recent compilation, Hilton et al. (2002) have made very detailed estimates for volatile fluxes into subduction zones for individual arcs using, in part, a geochemical database for compositions of subducted sediments (Plank and Langmuir, 1998). Another major source of uncertainty in comparing volatile inputs with outputs is that data for outputs in back-arc regions are far too sparse to incorporate back-arc fluxes, which could be significant, into the global estimates for arc magmatism (Hilton et al., 2002).

Several studies have concluded that there is a large imbalance, by about a factor of 10, between the amount of H₂O subducted to mantle depths and the amount returned to the surface by arc magmatism (Fig. 7; Ito et al., 1983; Peacock, 1990; Bebout, 1996). This potential imbalance has important implications for the origin and permanence of the oceans because it would cause the mass of water to be subducted back into the mantle in ~1 Ga (Fyfe and McBirney, 1975). However, the return flux estimated in the studies mentioned above relied on a conservative value for the average H₂O content of arc basaltic magmas and therefore probably underestimate the return flux of H₂O by arc magmatism. In contrast, the recent compilation by Hilton et al. (2002) suggested that much more H₂O was returned to the surface than was subducted as structurally bound H₂O in minerals. They suggested that either there were additional major sources of H₂O in the mantle wedge or arc crust, or that the excess H₂O was meteoric in origin but incorporated into magma at high temperatures. As summarized above, my assessment of the primary

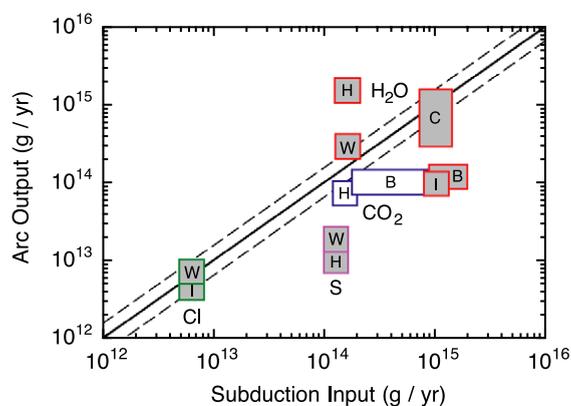


Fig. 7. Comparison of subduction input vs. output for major volatiles. Abbreviations and data sources as in Fig. 6. Estimates for H_2O and CO_2 labelled B are from [Bebout \(1996\)](#). Estimates for this study (*W*) are plotted against inputs from [Hilton et al. \(2002\)](#) for H_2O and *S* and [Ito et al. \(1983\)](#) for *Cl*. Dashed lines show $\pm 50\%$ uncertainty about the 1:1 correlation line. For clarity, the CO_2 data are shown without gray shading.

CO_2 contents of arc basaltic magmas suggests that [Hilton et al. \(2002\)](#) used too high a value for the $\text{H}_2\text{O}/\text{CO}_2$ ratio. [Carmichael's \(2002\)](#) estimate for return flux of H_2O to the surface and my estimate based on $\text{H}_2\text{O}/\text{CO}_2$ relations (Fig. 3) and the global CO_2 flux suggest that there is an approximate balance between the amount of structurally bound H_2O that is subducted and the amount of H_2O returned to the surface by arc magmatism, especially when one considers the range of uncertainty in the flux of H_2O into the mantle (Fig. 7). The suggestion that subducted sediments and altered oceanic crust are efficiently dehydrated during subduction, such that little H_2O is returned to the deep mantle, is consistent with data on the H_2O contents of mantle plume-derived basalts that are inferred to contain a component of deeply recycled, H_2O -poor material ([Dixon et al., 2002](#)). It should be emphasized, however, that despite the apparent approximate balance between subducted structurally bound H_2O and the return flux via arc magmatism, uncertainties in both fluxes are still relatively large. This allows for the possibility that significant amounts of H_2O are released beneath forearc regions, causing serpentinization of forearc mantle wedges ([Brocher et al., 2003](#)), or migrate upwards through tectonically active continental crust by diffuse porous flow ([Ingebritsen and Manning, 2002](#)).

Detailed estimates of C recycling in subduction zones are possible because C isotopic compositions of fumarolic gases can be used to distinguish the relative proportions of different C sources ([Hilton et al., 2002](#)). These estimates suggest that, globally, about 50% of subducted C is returned to the Earth's surface by arc magmatism (Fig. 7). For seven arcs that have been studied in detail for C isotopes, the majority (50–85%) of the CO_2 released by arc volcanoes is derived from subducted marine limestone, carbonate sediment, and carbonate in altered oceanic crust, with most of the remainder being supplied from reduced organic C in subducted sediment ([Hilton et al., 2002](#)). Only 3–22% is estimated to come from the mantle wedge. It should be noted, however, that these estimates are particularly sensitive to the values assumed for the mantle $\text{CO}_2/{}^3\text{He}$ ratio and the sedimentary $\delta^{13}\text{C}$ value and, to a lesser extent, to the assumption that there is no significant C isotope fractionation during slab decarbonation, fluid migration, and melting within the mantle wedge, or shallow degassing ([Hilton et al., 2002](#)). The conclusion that only $\sim 50\%$ of subducted C is returned to the Earth's surface by arc magmatism is consistent with thermodynamic modelling showing that carbonate stability in the subducting slab and sediment will allow significant C to be transported back into the deep mantle, particularly where convergence rates are fast and the subducted lithosphere is old and therefore relatively cold ([Kerrick and Connolly, 2001](#)).

The estimated flux of *S* returned to the mantle is about four to seven times greater than the amount returned to the surface reservoir by arc magmatism (Fig. 7). This is true whether one uses the arc *S* output based on magmatic *S* content and magma flux, which potentially accounts for *S* retained in sulfides and sulfates in the crust rather than degassed to the atmosphere, or the flux based on measured SO_2 fluxes from arc volcanoes (Fig. 7).

In contrast to *S*, the subduction input of *Cl* appears to be balanced by the output of *Cl* due to arc magmatism (Fig. 7; [Schilling et al., 1978](#); [Ito et al., 1983](#)). This suggests that large amounts of *Cl* are probably not returned to the deep mantle, a result that is consistent with studies of the *Cl* contents of mantle plume-related basaltic magmas in which there is a component of deeply recycled lithosphere ([Dixon and Clague, 2001](#); [Lassiter et al., 2002](#)).

6. Volatiles in intermediate to silicic arc magmas

In addition to melt inclusion studies of volatile contents in mafic arc magmas, there is a growing body of data for volatiles in intermediate to silicic (andesite, dacite, and rhyolite) arc magmas. Such data are valuable not only for understanding volcanic emissions and eruptive behavior of volcanoes but also for understanding differentiation processes in convergent plate margins. Water contents of dacitic to rhyolitic melt inclusions in arc volcanic rocks vary greatly, from ~1 to 6 wt.% H₂O (Fig. 8). The variations in H₂O content show no obvious relationship to composition, in contrast to intracontinental high-silica rhyolitic suites, which show increasing H₂O with degree of differentiation as inferred from compatible and incompatible trace elements (Lowenstern, 1994; Gansecki, 1998; Wallace et al., 1999). However, in some subduction-related suites, such as the dacitic ignimbrites from Northern Chile, small increases in H₂O correlate with trace element indicators of differentiation,

suggesting that H₂O increases during fractional crystallization (Schmitt, 2001).

Carbon dioxide concentrations in the melt inclusions range from near detection limits (about 10–20 ppm) to a little over 400 ppm CO₂ (Fig. 8). The combined H₂O–CO₂ data demonstrate that these silicic magmas have sufficient dissolved CO₂ to cause them to be vapor-saturated at pressures of 0.5–2.5 kb. In some cases, these pressures show excellent agreement with pressure estimates derived from experimental-phase equilibrium studies (Pinatubo - Rutherford and Devine, 1996; Katmai - Coombs et al., 2001), providing strong evidence that the magmas were vapor-saturated during crystallization.

An interesting observation from comparing Figs. 3 and 8 is that there is a large degree of overlap between the H₂O contents of basaltic and silicic arc magmas. This is surprising if silicic magmas are generated by fractional crystallization from basaltic magma as the melt H₂O content would be expected to increase during this process, even if the magma is vapor-saturated during crystallization (Fig. 9). How-

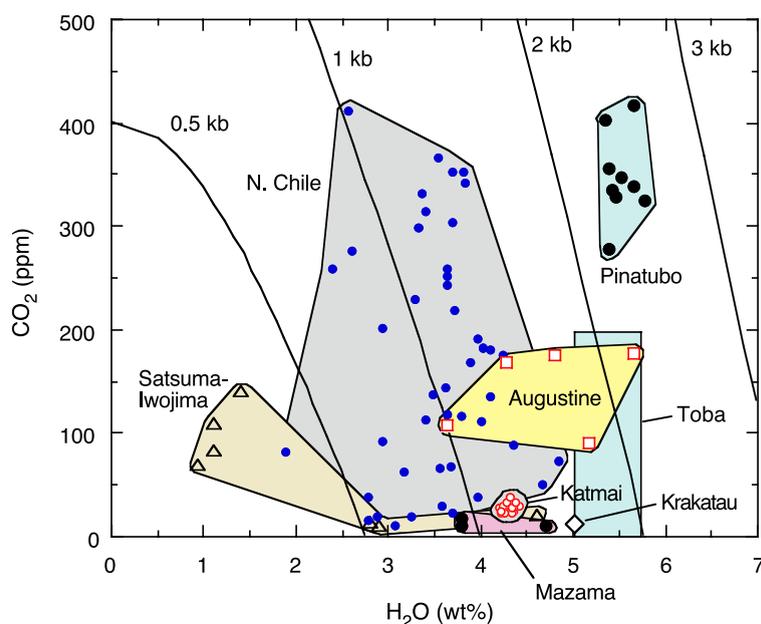


Fig. 8. H₂O vs. CO₂ for melt inclusions from arc dacites and rhyolites. Data are shown for the Toba Tuff (Newman and Chesner, 1989), Mt. Mazama (Bacon et al., 1992), Pinatubo (Wallace and Gerlach, 1994), Krakatau (Mandeville et al., 1998), Satsuma-Iwojima (Saito et al., 2001), dacitic ignimbrites from the Altiplano-Puna, Northern Chile (Schmitt, 2001), Augustine (Roman et al., in review), and Katmai (Wallace, unpublished data). Vapor saturation isobars are shown for 0.5, 1, 2, and 3 kb pressure.

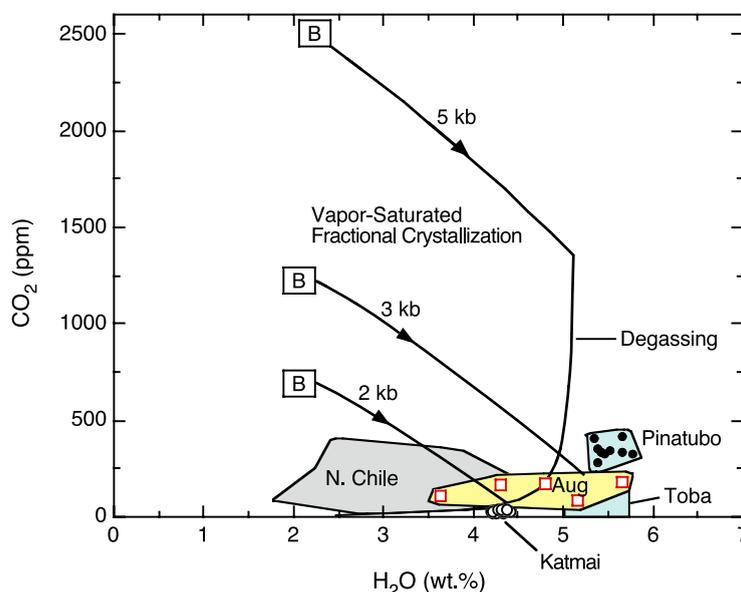


Fig. 9. H₂O vs. CO₂ variations during formation of differentiated magma from basaltic parents (B) by vapor-saturated fractional crystallization at 2, 3, and 5 kb pressure. Approximately 60–70% fractional crystallization is necessary to drive residual liquids from an initial H₂O of 2.25 to 4–5 wt.%. Degassing curve shows the degassing path for magma formed by fractional crystallization at 5 kb, and is calculated for a closed system. If intermediate to silicic magma in arcs is formed primarily by fractional crystallization from a mafic parent at middle to upper crustal pressures (2–5 kb), then the parental melts must generally have H₂O at the lower end of the range shown in Fig. 3 to account for the H₂O–CO₂ relations of silicic arc magmas. The reason for this is that during isobaric fractional crystallization of vapor-saturated magma, H₂O increases in the residual liquid, but CO₂ is preferentially lost to the vapor phase because of its lower solubility. Significant amounts of H₂O will not be degassed from such differentiating magmas until CO₂ is largely degassed from the melt, at which point the melt becomes saturated with nearly pure H₂O vapor and no additional increase in H₂O occurs with further crystallization.

ever, most of the H₂O-rich melt inclusions from mafic arc magmas come from relatively differentiated, low-MgO basalts, so the high H₂O values reflect effects of significant fractionation. Such magmas probably form by high-pressure fractionation of clinopyroxene-rich assemblages from basaltic parents, which prevents significant increases in melt SiO₂ with differentiation (T. Sisson, written communication). Differentiation of similar parent magmas at lower pressures primarily involves olivine+plagioclase fractionation, yielding derivative liquids with high H₂O and intermediate SiO₂ contents. Thus, an intermediate H₂O basaltic parent that fractionates in the mantle or base of the crust can yield high-H₂O, low-SiO₂ differentiates (similar to most of the high-H₂O basaltic melt inclusions), whereas in the middle to upper crust, it would yield high-H₂O, high-SiO₂ differentiates.

Another process that probably contributes to the overlapping range of H₂O in arc basaltic and silicic

magmas is that the silicic magmas are formed largely by crustal melting (Hildreth, 1981; Lange and Carmichael, 1996; Annen and Sparks, 2002) and that their volatile contents reflect a combination of volatiles derived from crustal protoliths and delivered during recharge of basaltic magma into more silicic magma bodies (Wallace et al., 2003). Recharge and degassing of CO₂-rich mafic magma into the lower parts of silicic magma bodies could also reenrich the CO₂ contents of intermediate to silicic magmas that have partially degassed H₂O at relatively low pressures. Such an open system process could cause many silicic arc magmas that have lost some H₂O by degassing to still contain significant dissolved CO₂. Data for SO₂ fluxes from arc volcanoes (see next section below) show evidence of open system gas fluxing through intermediate to silicic magma bodies, so such a process is likely to be quite common.

Chlorine contents of dacitic to rhyolitic melt inclusions in arc volcanic rocks vary from 900 to

2200 ppm (Fig. 10). In some suites (Katmai, Taupo), correlated increases in Cl and H₂O correspond to increasing degrees of fractionation. However, in these cases, Cl increases less rapidly than H₂O, suggesting that the magmas were vapor-saturated during differentiation such that some Cl was lost from the melt to the vapor phase. A similar approach was used by Anderson (1973), who used data on Cl and K₂O in melt inclusions in olivine to infer that basaltic andesite and andesitic magmas in subvolcanic reservoirs are commonly vapor-saturated. Comparison of the Cl contents of intermediate and silicic arc magmas with experimental-phase relations for H₂O–Cl-bearing systems (Webster, 1997) shows that most arc dacitic and rhyolitic magmas do not contain sufficient Cl for the melts to be saturated with a concentrated brine or hypersaline melt (Fig. 10). A notable exception are dacites from Augustine volcano, Alaska, which have high enough Cl to become saturated with both H₂O–CO₂–Cl vapor+H₂O–NaCl brine during decompression. Vol-

canic gases from Augustine are known to be unusually Cl-rich compared to most other arc volcanoes (Symonds et al., 1990), suggesting such high magmatic Cl contents are relatively rare.

Sulfur solubility in silicate melts is strongly dependent on temperature, and the maximum amount of S that can be dissolved is usually limited by saturation of the melt with a sulfide and/or sulfate phase (Carroll and Rutherford, 1987; Luhr, 1990). Arc dacitic and rhyolitic magmas are commonly sulfide-saturated (pyrrhotite, chalcopyrite, monosulfide and intermediate solid solutions). At higher oxygen fugacities, sulfate becomes the main dissolved S species in the melt, and melts can be saturated with anhydrite (Carroll and Rutherford, 1987; Luhr, 1990). In some cases such as the 1991 Mt. Pinatubo dacite, both sulfides and anhydrite are present (Hattori, 1996). Sulfur contents in dacitic and rhyolitic melt inclusions decrease with decreasing preeruptive temperature (Fig. 11). Most values fall between the experimentally derived solubility

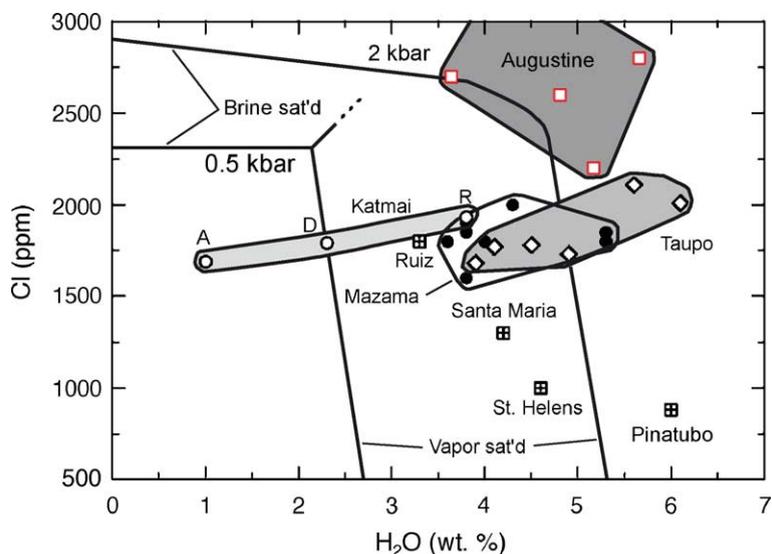


Fig. 10. H₂O vs. Cl for melt inclusions from arc dacites and rhyolites. Data are shown for Mount St. Helens (Rutherford et al., 1985), Taupo (Dunbar et al., 1989), Katmai andesite (A), dacite (D), and rhyolite (R) (Westrich et al., 1991), Mazama (Bacon et al., 1992), Nevado del Ruiz (Layne et al., 1992), Santa Maria, Guatemala (Roggensack et al., 1992), Pinatubo (Gerlach et al., 1996), and Augustine (Roman et al., in review). Phase relations at 0.5 and 2 kb are based on experimental data (800–1075 °C) for rhyolitic melt from Webster et al. (1999). At 0.5 kb, below the critical pressure for H₂O–NaCl fluids at 800 °C, silicate melt can coexist with vapor or brine (hydrosaline melt), or both, depending on the melt Cl content. At 2 kb, above the critical pressure, only a single H₂O–NaCl phase exists, but the presence of CO₂ in natural melts will expand the vapor+brine stability field (Lowenstern, 2000). Note that rhyolitic melt inclusions from Augustine have high-enough Cl for the melts to become saturated with vapor+brine during decompression. Increases in Al, Na, Mg, and Ca dramatically increase the Cl content of brine-saturated melts, so brine saturation in dacitic melts would occur at much higher Cl contents than are shown. Variations in silicate melt composition, however, have little effect on the H₂O contents of vapor-saturated melts.

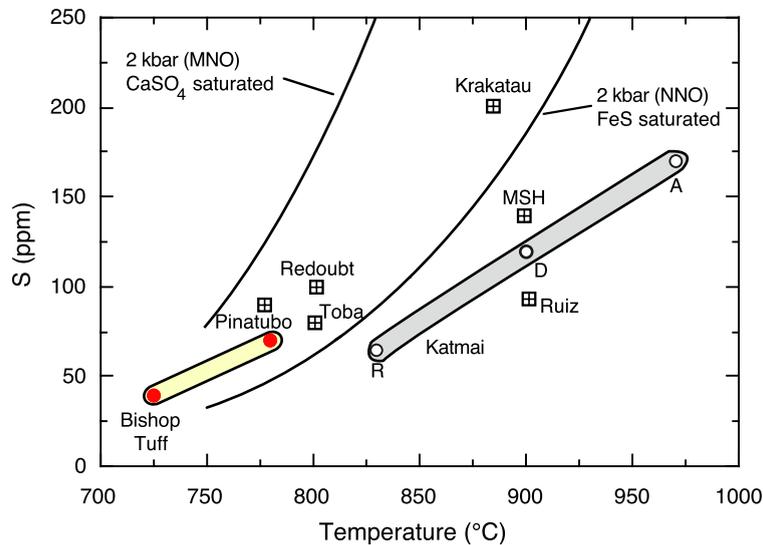


Fig. 11. Preeruptive temperature vs. S for arc dacites and rhyolites. Data sources are given in Figs. 8 and 10. Curves show the solubility of S in pyrrhotite-saturated (NNO buffer) and anhydrite-saturated (MNO buffer) trachyandesite melts at 2 kb (Luhr, 1990). Data for the Bishop Tuff, shown for comparison, are from Wallace et al. (1999).

curves for anhydrite-saturated (MNO buffer) and pyrrhotite-saturated melts (NNO buffer) at 2 kb pressure or fall below the pyrrhotite-saturation curve, consistent with expectations based on the range of oxygen fugacities for these melts (Fig. 11). The very low-dissolved S contents imposed by solubility constraints result in strong partitioning of S into a coexisting H_2O -rich vapor phase, such that most of the total S in low-temperature vapor-saturated magma resides in the vapor (Wallace et al., 2003).

6.1. Fluxes of SO_2 from arc volcanoes and the “excess” sulfur problem

Much of the data for SO_2 fluxes from arc volcanoes that are used to infer global volatile output from arcs come from intermediate composition volcanoes, whereas the magma flux and volatile content approach to understanding volatile outputs are derived from basaltic magmas. This makes it essential to understand the way in which volatiles are “processed” through crustal magmatic systems to gain better insight into global fluxes. Comparison of remote sensing and petrologic data on volatiles over the last several decades has highlighted some major gaps in our understanding of both the abundance of

the different volatiles and the ways in which they are transported through magmatic systems and released to the atmosphere by degassing.

It is possible to use data for S in melt inclusions to make an estimate of the S released by a volcanic eruption if the total volume of erupted magma is known from field studies. However, such estimates assume that the only S released during an eruption is S that was originally dissolved in the melt phase of the magma. When these “petrologic” estimates are compared with remotely sensed SO_2 emissions (COSPEC and TOMS), a very large mass balance problem arises, which has come to be known as the “excess” sulfur problem (Rose et al., 1982; Andres et al., 1991). The amount of dissolved S in magmas before eruption is usually much too low (by a factor of 10–100) to account for the total mass of SO_2 released during the eruption (Fig. 12). All andesitic, dacitic, and rhyolitic eruptions in arc environments have excess S emissions, but basaltic eruptions from hot spot volcanoes (e.g., Hawaiian, Iceland) generally do not (Fig. 12). Some subduction zone basaltic volcanoes, like the 1972 eruption of Pacaya, do not show large excess S emissions, but persistently degassing, open-vent systems like Masaya and Stromboli show very large excesses of S released compared with the volume of lava or tephra actually erupted.

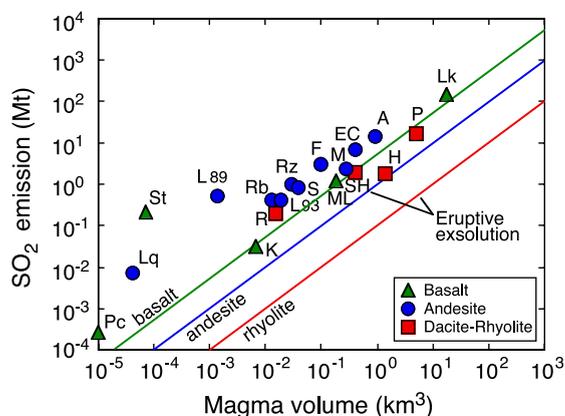


Fig. 12. Volcanic SO_2 emissions, in megatons ($1 \text{ Mt} = 10^{12} \text{ g}$), vs. total volume of erupted magma. SO_2 emissions were measured using remote sensing methods. Most of the remote sensing data are from TOMS, except for Etna, Fuego, Kilauea, Lonquimay, Pacaya and Stromboli (COSPEC), Agung (stratospheric optical depth measurements), and Laki (atmospheric turbidity data). Uncertainties of $\pm 50\%$ for both SO_2 emission and eruptive volume are less than to slightly greater than the size of the symbols. Uncertainties in SO_2 emission data are generally considered to be about $\pm 30\%$ for the TOMS data and $\pm 20\text{--}50\%$ for COSPEC. Data are shown for the following eruptions: (A) Agung, 1963; (EC) El Chichon, 1982; (F) Fuego, 1974; (H) Cerro Hudson, 1991; (K) Kilauea, annual average; (L89) Láscar, 1989; (L93) Láscar, 1993; (Lk) Laki, 1783–1784; (Lq) Lonquimay, 1989; (ML) Mauna Loa, 1984; (M) Mount St. Helens, 1980; (Pc) Pacaya, 1972; (P) Pinatubo, 1991; (Rb) Rabaul, 1994; (R) Redoubt, 1989–1990; (Rz) Ruiz, 1985; (S) Spurr, 1992; (St) Stromboli, annual average. References to data sources can be found in Wallace et al. (2003). Shown for comparison are predicted relationships between SO_2 emission and eruptive volume for rhyolitic, andesitic, and basaltic melts calculated by assuming that the only SO_2 released during the eruption is from S that is originally dissolved in silicate melt. Note that the SO_2 emissions for all eruptions, with the exception of Mauna Loa, Kilauea, and Laki, are at least one order of magnitude greater than predicted for the appropriate bulk composition by syneruptive degassing of dissolved S only.

The large emissions from open-vent systems are undoubtedly caused by shallow separation of gas from melt, which occurs readily in low-viscosity basaltic magmas. However, the cause of excess S emissions during sustained explosive eruptions of more silicic magma is most likely related to the presence of an exsolved C–O–H–S vapor phase in the magma before eruption (Luhr et al., 1984; Andres et al., 1991; Westrich and Gerlach, 1992; Wallace et al., 2003). Because of the strong temperature control on S solubility, such low-temperature silicic magmas have most of their S partitioned into a multicomponent

vapor phase, which would presumably be present as bubbles dispersed throughout magma in crustal storage reservoirs. This allows eruptions of silicic magma to release large amounts of SO_2 derived from the vapor phase even though such magmas have very low concentrations of dissolved S. The large amounts of volatiles implied by remote sensing data suggest that exsolved vapor accumulates in the apical regions of magma bodies during repose periods between eruptions or may get trapped below hydrothermal caps above the body. The presence of an exsolved vapor phase in crystallizing magma bodies may also play an important role in triggering volcanic eruptions. Based on isotopic and other data, the ultimate source of S and CO_2 in the vapor phase is likely to be from mafic magma, as it is well established that silicic magma reservoirs are created and sustained through long-term intrusion of mantle-derived basaltic magma into the crust (Smith, 1979; Hildreth, 1981; Shaw, 1985).

7. Concluding remarks

An important observation that is becoming increasingly apparent with the advent of large geochemical databases is that different arcs erupt significantly different magma series, on average. For example, Izu-Bonin, Tonga-Kermadec, and Aleutian magmas west of Katmai are distinctly Fe-rich relative to magmas in arcs such as the Andes, central Honshu, the Trans-Mexican Volcanic Belt, and much of the Cascades. These more Fe-rich magmas range into classic island arc tholeiites, that are quite different from calc-alkaline basalts. In the Aleutians, associated fractionated magmas at Veniaminof, Fisher Caldera, and Seguam occur as very thin, nearly aphyric, dacitic lava flows that lack hydrous phenocrysts (T. Sisson, written communication). These must have been hot, relatively H_2O -poor, low- f_{O_2} magmas, and they are associated with tholeiitic basalt and basaltic andesite parents. As data on the abundance and isotopic compositions of major volatiles in arc magmas become increasingly abundant, a fruitful focus of future research will be to examine how regional variations in subducted volatiles and the pathways and processes by which they are recycled to the mantle wedge play a role in determining magma composition and flux.

Acknowledgements

I would like to thank Toby Fischer for inviting me to participate in the SOTA 2003 conference and Bill Leeman for inviting this review. Reviews by T. Fischer, T. Sisson, and A. McBirney, and discussions with A.T. Anderson and I.S.E. Carmichael helped to improve the manuscript and are all gratefully appreciated. I am particularly thankful to Tom Sisson for his comments on magma differentiation processes and compositional differences between arcs; the latter formed the basis for the concluding section of this paper.

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