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Volcanic SO₂ emissions and the abundance and distribution of exsolved gas in magma bodies

P.J. Wallace*

Ocean Drilling Program, Texas A & M University, College Station, TX 77845, USA

Abstract

The mass of sulfur dioxide (SO₂) released by most explosive volcanic eruptions greatly exceeds the amount originally dissolved in the erupted volume of silicate melt. Several lines of evidence suggest that this discrepancy is due to the presence of SO₂-bearing gas bubbles in the magma before the time of eruption. Comparison of remote sensing data for SO₂ emissions with conventional petrologic estimates suggests that the discrepancy can be resolved if andesitic and dacitic magmas contain about 1–6 wt% exsolved gas, equivalent to 5–30 vol%, prior to eruption. Such large mass fractions of exsolved gas in pre-eruptive magma are consistent with previously published physical models in which crystallization-induced gas exsolution gradually increases overpressuring of a magma reservoir, eventually triggering an eruption. Simple mass balance models for SO₂ emissions from magma bodies in which there is an upwards increasing gradient in exsolved gas mass fraction (i.e. gas-rich at the top) yield SO₂ vs. eruptive volume trends that are similar to those observed for eruptions ranging in size from 0.01 to 10 km³ of magma. Despite the many uncertainties involved, these patterns are consistent with the hypothesis that subvolcanic magma reservoirs are separated from volcanic vents by cupolas of gas-rich magma that supply much of the gas released in explosive eruptions. The volume fraction of exsolved gas inferred from SO₂ data for the upper regions of many pre-eruptive magma bodies (~30 vol%) is similar to the percolation threshold at which gas bubbles become sufficiently interconnected to allow permeable gas flow through a bubble network. Thus this value may reflect a physical limitation on the maximum exsolved gas volume fraction that can occur at the roof zone of a magma reservoir because any additional gas would be lost by advective flow through the permeable bubble network. Andesitic and dacitic magma in crustal reservoirs are probably gas saturated due to recharge and underplating by basaltic magma that is saturated with H₂O–CO₂–S gas. Comparison of repose times, eruptive volumes, and basaltic magma supply rates for a spectrum of volcanic systems suggests a relatively steady state flux of S from Earth's mantle to atmosphere through many andesitic and dacitic magma systems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sulfur dioxide emission; Exsolved gas; Magma bodies

1. Introduction

The volatile constituents H₂O, CO₂, and S play an important role in the evolution and eruption of magmas. In addition, SO₂ injected into the stratosphere by explosive eruptions is converted into

H₂SO₄ aerosols that can affect both climate and atmospheric chemistry (Lamb, 1970; Hammer et al., 1980; Self et al., 1981; McCormick et al., 1995). Numerous measurements of SO₂ fluxes from active volcanoes have been made using remote sensing techniques (see review by Symonds et al., 1994), including both ground and air-based use of the ultraviolet correlation spectrometer (COSPEC) and the satellite-based Total Ozone Mapping Spectrometer (TOMS).

* Tel.: +1-979-845-0879; fax: +1-979-845-0876.

E-mail address: wallace@odpemail.tamu.edu (P.J. Wallace).

Comparison of such SO₂ emission data with petrologic studies of dissolved S in magmas based on analyses of quenched melt inclusions trapped inside phenocrysts has led to a conundrum, known as the 'excess' S problem, concerning S mass balance during volcanic eruptions (Stoiber and Jepson, 1973; Rose et al., 1982; Andres et al., 1991). Concentrations of dissolved S in magmas before eruption are commonly far too low (by 1 to 2 orders of magnitude) to account for the total mass of SO₂ released during the eruption as measured by remote sensing techniques (Fig. 1). Excess eruptive S is observed in most eruptions for which remote sensing and melt inclusion data are available, and in particular, is characteristic of explosive eruptions of intermediate and silicic magma in subduction zone settings (Andres et al., 1991). In contrast, basaltic eruptions from divergent plate boundaries and hot spots, such as Hawaiian and Icelandic volcanoes, often do not show evidence of excess S emissions (Fig. 1).

Most SO₂ emission estimates that are based on melt inclusions in volcanic phenocrysts assume that the only S released during an eruption is S that was originally dissolved in the silicate liquid (melt) portion of the magma. However, there is a growing body of evidence, based on petrologic, remote sensing, and volcanic gas data, that a large proportion of the SO₂ released during explosive eruptions may actually be contained in a gas¹ phase before eruption (Anderson, 1975; Luhr et al., 1984; Sigurdsson et al., 1990; Andres et al., 1991; Gerlach et al., 1994, 1996; Wallace and Gerlach, 1994; Gerlach and McGee, 1994; Giggenbach, 1996). As a result, eruptions of exsolved-gas-rich silicic magmas can release large amounts of SO₂ derived from pre-eruptive exsolved gas, despite the fact that such magmas generally have very low concentrations of dissolved S. Techniques for quantifying the mass fraction of exsolved gas in magma before eruption are thus important for understanding SO₂ flux data used for forecasting eruptions and for assessing the potential impacts of volcanic

eruptions on Earth's climate and atmosphere. In addition, exsolved gas in crystallizing magma bodies can trigger volcanic eruptions (Blake, 1984; Tait et al., 1989; Woods and Pyle, 1997) and contributes to some magmatic-hydrothermal ore deposits (Burnham, 1979a; Hedenquist and Lowenstern, 1994). The purpose of this paper is to quantify the abundance and distribution of pre-eruptive exsolved gas in a number of magmatic systems from which there have been recent, relatively well-studied eruptions. In the following sections, I begin by reviewing petrologic evidence for pre-eruptive gas saturation in magmas and methods for constraining the concentration of S in the exsolved gas phase.

2. Pre-eruptive gas saturation and volatile gradients in magma bodies

Water, CO₂, S-species, and Cl are the most abundant volatile constituents present in magmas. These volatiles may be present both as dissolved species in silicate melt and exsolved in a separate gas phase. If the sum of partial pressures of the dissolved volatiles in a silicate melt is equal to the local confining pressure, then a separate multicomponent gas phase will be in equilibrium with the melt (Verhoogen, 1949), presumably in the form of bubbles. If a magma is gas-undersaturated, then volatiles will be present in solution only, and their concentrations will be controlled by crystal-liquid differentiation processes. Although gas can be exsolved by isobaric crystallization (second or resurgent boiling), gas may also be redistributed within magma bodies due to its greater buoyancy relative to surrounding silicate melt and crystals (e.g. Candela, 1991), or to the dynamics of magma transport (e.g. Wilson, 1998). Thus for a gas saturated magma, the mass fraction of exsolved gas is not strictly limited by pressure or solubility such that a gas-rich magma could have a bulk volatile content that is greatly in excess of what could be dissolved in the melt at upper crustal pressures (≤ 3 kbar).

Dissolved H₂O concentrations for many silicic magma bodies have been estimated using thermodynamic calculations for biotite-sanidine-magnetite equilibrium (e.g. Hildreth, 1977; Whitney and Stormer, 1983; Luhr et al., 1984). In the case of the Bishop Tuff, this method has also been used to infer a gradient

¹ In this paper, I use the word 'gas' as defined by Verhoogen (1949), to describe the lowest density phase that is in equilibrium with silicate melt + crystals. This serves to distinguish the gas phase from an immiscible hydrous saline melt (fluid) that may coexist with silicate melt + crystals + gas under certain conditions of temperature, pressure, and bulk composition (Roedder, 1992).

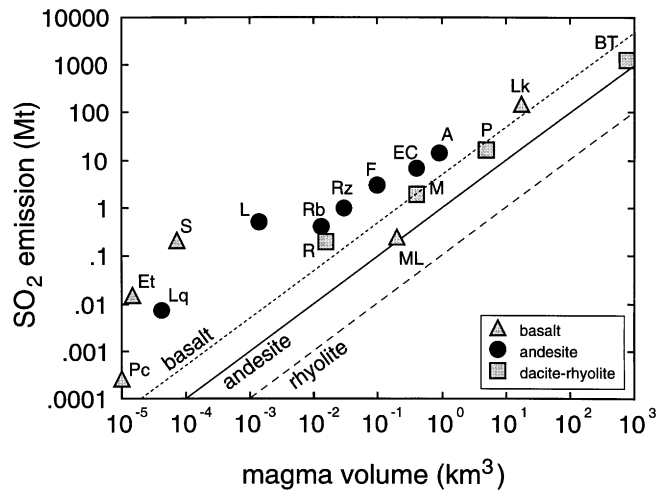


Fig. 1. Volcanic SO_2 emissions, in megatons ($1 \text{ Mt} = 10^{12} \text{ g}$), vs. total volume of erupted magma. Data are taken from Gerlach and Graeber, (1985), Andres et al. (1991) (and references therein), Bluth et al. (1993), Allard et al. (1994), Gerlach et al. (1994), Gerlach and McGee (1994), Self and King (1996), Roggensack et al. (1996), and Thordarson et al. (1996). SO_2 emissions were measured using remote sensing methods except for the eruption of the Bishop Tuff (BT; see text). Most of the remote sensing data are from the TOMS, except for the data for Fuego (determined by COSPEC), Agung (estimated from stratospheric optical depth measurements), and Laki (estimated from information on atmospheric turbidity). Uncertainties of $\pm 50\%$ for both SO_2 emission and eruptive volume are less than or 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 (see discussion in Symonds et al., 1994). Data are shown for the following eruptions: (A) Agung, 1963; (EC) El Chichon, 1982; (Et) Etna, 1975; (F) Fuego, 1974; (L) Láscaar, 1989; (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, 1989–90; (Rz) Ruiz, 1985; (S) Stromboli, annual average. Data for silicic bulk compositions (dacitic to rhyolitic) are shown by squares, intermediate-compositions (andesitic) by filled circles, and basaltic compositions by triangles. Shown for comparison are predicted relationships between SO_2 emission and eruptive volume for rhyolitic (dashed line), andesitic (solid line), and basaltic (short dashed line) 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 and Laki, are at least one order of magnitude greater than predicted for the appropriate bulk composition by syneruptive degassing of dissolved S only. This clear discrepancy over many orders of magnitude in eruptive volume indicates that a major additional source of S must be involved in all of these eruptions.

in dissolved H_2O , with concentrations increasing upwards in the magma body (Hildreth, 1977). Gradients in dissolved H_2O in silicic magma bodies have more recently been confirmed using ion probe and infrared spectroscopic techniques on melt inclusions in phenocrysts (Anderson et al., 1989; Skirius, 1990; Westrich et al., 1991; Lowenstern, 1993; Wallace et al., 1995). However, changes in eruptive style from Plinian column to pyroclastic flow, sometimes inferred to result from decreases in volatiles, do not appear to be related to differences in pre-eruptive dissolved water (Westrich et al., 1988; Skirius, 1990; Lowenstern, 1993; Wallace et al., 1995). Even effusive (non-explosive) eruptions of silicic magma appear to involve magma with initially high dissolved H_2O concentrations (Eichelberger et al., 1986;

Newman et al., 1988; Westrich et al., 1988; Martel et al., 1998). That such magmas are erupted non-explosively requires that water be lost prior to extrusion, which may occur if magma decompression induces sufficient vesicularity to form a magmatic foam that is highly permeable to gas (Taylor et al., 1983; Eichelberger et al., 1986, 1989, 1995; Westrich et al., 1988; Jaupart and Allegre, 1991; Westrich and Eichelberger, 1994; Woods and Koyaguchi, 1994; Sparks, 1997).

It has commonly been assumed that magmas of intermediate to silicic composition only become gas saturated during shallow ascent and emplacement, during eruptive decompression, or during advanced (pegmatitic) stages of plutonic consolidation. Kennedy (1955), drawing on the earlier thermodynamic analysis of

Verhoogen (1949), argued that saturation with respect to water was only likely to occur at the top of magma chambers due to the variations in $P_{\text{H}_2\text{O}}$ imposed by hydrostatic equilibrium in a magma body with significant vertical extent. However, Anderson (1975) reviewed evidence that some andesitic magmas are gas saturated during their formation from more mafic magma and suggested, based on available CO_2 and SO_2 emission data, that magmas in subvolcanic reservoirs are generally saturated with a multicomponent gas phase. Holloway (1976) recognized that the small but finite solubility of CO_2 in silicic magmas at crustal pressures could result in saturation with an $\text{H}_2\text{O}-\text{CO}_2$ gas phase during all stages in the magmatic evolution of granites, including partial melting, ascent and emplacement, and crystallization.

Significant CO_2 in rhyolitic melts has been detected using infrared spectroscopic techniques on obsidians (Newman et al., 1988) and on melt inclusions in phenocrysts (Anderson et al., 1989; Skirius, 1990; Lowenstern, 1994; Wallace and Gerlach, 1994; Wallace et al., 1995). Negative correlations between CO_2 and incompatible trace elements in the Bishop Tuff suggest that the magma was gas saturated during crystallization, with CO_2 partitioning into a coexisting gas phase (Wallace et al., 1995). Pre-eruptive gas saturation of the dacitic magma erupted at Mount Pinatubo in 1991 has also been demonstrated based on melt inclusion and experimental data (Wallace and Gerlach, 1994; Gerlach et al., 1996; Rutherford and Devine, 1996). The occurrence of high-temperature fluid inclusions in phenocrysts from some silicic volcanic rocks provides further evidence of gas saturation during pre-eruptive crystallization (Roeder, 1992; Lowenstern, 1995). Quantitative modeling for the magma body of the Bishop Tuff using $\text{H}_2\text{O}-\text{CO}_2$ solubility relations reveals a pre-eruptive gradient in exsolved gas, with gas contents varying from ~1 wt% in the deeper regions of the magma body to nearly 6 wt% near the top (Wallace et al., 1995, 1999). Several wt% of exsolved gas has also been inferred for silicic magma at Mono Craters, California, based on H_2O and CO_2 data for rhyolitic obsidians (Newman et al., 1988). Similar amounts of exsolved gas are estimated for the magma bodies of the 1982 El Chichón and 1991 Mount Pinatubo eruptions by assuming that all SO_2 released (measured by remote sensing techniques) was stored in the erupted volume of magma

(Luhr et al., 1984; Luhr, 1990; Wallace and Gerlach, 1994; Gerlach et al., 1996).

Thus it appears that volcanic eruptions release abundant 'excess' SO_2 and that subvolcanic magma bodies contain significant exsolved gas. Two important possibilities therefore arise: (1) to forecast the amount of SO_2 release for certain volcanic eruptions; and (2) to confirm and estimate the amount of exsolved gas in subvolcanic magmas. Critical to doing this, as discussed below, is an assessment of the total mass fraction of S-species that is present in the pre-eruptive gas phase.

3. S abundance and speciation in pre-eruptive gas

The solubility behavior and activity-composition relations of S in silicate melts are complex due to multiple valence states (H_2S , S_2 , SO_2 , SO_3) and the occurrence of non-volatile S-rich phases (e.g. immiscible Fe-S-O liquid, pyrrhotite, anhydrite). Two basic approaches can be used to constrain the mass fraction of S that is present in a pre-eruptive exsolved gas phase. Despite uncertainties inherent in each approach, the two yield a fair degree of consistency, making it possible to place limits on the S content of pre-eruptive magmatic gas.

The first approach involves phase equilibria and thermodynamic modeling to estimate fugacities of SO_2 , SO_3 , H_2S , and S_2 . By combining analyses of pyrrhotite, the relationship between pyrrhotite composition and f_{S_2} (Toulmin and Barton, 1964), and independent estimates of $T-f_{\text{O}_2}-f_{\text{H}_2\text{O}}$ from mineral equilibria, it is possible to calculate the fugacities of all major S-species (Whitney and Stormer, 1983; Whitney, 1984; Luhr et al., 1984; Luhr, 1990). If a gas phase is present, then the calculated fugacities can be converted into mole fractions of the various S-species using fugacity coefficients calculated with the Redlich-Kwong equation of state (Holloway, 1987). Application of this method to the 1980 Mount St. Helens and 1982 El Chichón eruptions yields estimates of 1.9 and 1.2–6.0 mol% S_{total} ($\text{H}_2\text{S} + \text{SO}_2$), respectively, in the pre-eruptive gas phase (Whitney, 1984; Luhr, 1990). The main disadvantage with the thermodynamic approach is that combined uncertainties in the various parameters can easily yield a one order of magnitude uncertainty

in the mass fraction of total S in the coexisting equilibrium gas. In addition, many silicic rocks contain pyrrhotite only as inclusions in phenocrysts (Whitney and Stormer, 1983), which raises a question as to whether it was a stable phase at the time of eruption.

A variant on the thermodynamic approach is to analyze trapped melt (glass) inclusions in phenocrysts for concentrations of dissolved H₂O, CO₂, and S, and use experimental solubility studies and derived thermodynamic models (e.g. Burnham, 1979b; Silver et al., 1990; Blank et al., 1993) to estimate fugacities for each component. Although this method works well for calculating H₂O and CO₂ contents of exsolved magmatic gas (Newman et al., 1988; Skirius, 1990; Wallace and Gerlach, 1994; Gerlach et al., 1996), it is difficult to apply to S because of lack of information concerning activity-composition relations of dissolved SO₄²⁻ in silicate melts. Estimates of S concentration in pre-eruptive gas in the 1991 Mount Pinatubo dacitic magma, based on this method and the experimental data of Baker and Rutherford (1992), suggest somewhere between 0.1 and 4.0 mol% S_{total} (see discussions in Gerlach et al., 1996, and Baker and Rutherford, 1996a). The high end of this range of values agrees well with recent experimental measurements of S partitioning between rhyolitic melt and vapor at oxygen fugacities comparable to that of the Pinatubo dacitic magma (Scaillet et al., 1998).

The second approach for estimating S concentrations in pre-eruptive exsolved gas in magmas is through analysis of volcanic gases. Two major disadvantages of this approach should be kept in mind in the following discussion. First, volcanic gases generally are sampled from fumarolic (non-eruptive) states of activity. As such, they probably represent degassing at much lower pressure than the deeper, pre-eruptive stage relevant to large explosive eruptions. Furthermore, sampled volcanic gases may come from shallowly stored magma that has already partially degassed during earlier eruptive activity. Nevertheless, volcanic gases represent our only real sample of gases evolved from decompressing and crystallizing magma at depth. A second general problem is that much of the variation in H₂O, CO₂ and S concentrations in volcanic gases can be caused by secondary, nonmagmatic processes (Symonds et al., 1994; Giggenbach, 1996). However, techniques exist for evaluating these secondary processes, making it

possible to estimate the original S content of the magmatic gas (e.g. Giggenbach, 1975, 1996; Gerlach, 1979). High-temperature gas discharges from convergent margin andesitic to dacitic volcanoes have mol% S_{total} [= 100 (SO₂ + H₂S)/(H₂O + CO₂ + SO₂ + H₂S)] that varies over two orders of magnitude from 0.04 to 7.3 (Symonds et al., 1994; Giggenbach, 1996). The lowest values of S_{total} tend to be from samples collected from degassed lava domes (Symonds et al., 1994). The remaining values are mostly between 0.3 and 7 mol% S_{total}, corresponding to CO₂/S_{total} of 0.2–10. These values are in good agreement with the estimates from Mount St. Helens and El Chichón based on thermodynamic methods and the estimates for Mount Pinatubo based on melt inclusion volatile concentrations and experimental partitioning studies. The range of values from 0.3 to 7 mol% for S_{total} are also in good agreement with recent experimental determinations of S partitioning between melt and coexisting vapor at relevant oxygen fugacities (Keppler, 1999). Because of the general consistency of S_{total} estimates from thermodynamic calculations, solubility measurements, experimental partitioning studies, and volcanic gas discharges, the range from 0.3 to 7 mol% S_{total} will be used as upper and lower limits in calculations throughout the rest of this paper.

It is important to note that the ratio of SO₂ to H₂S in exsolved magmatic gas is dependent on temperature, pressure, and the fugacities of oxygen and H₂O. Over the range of *T*, *P*, *f*_{O₂}, and *f*_{H₂O} conditions of most intermediate to silicic magmas (Carmichael, 1991), S in pre-eruptive gas will either be predominantly H₂S or will occur as subequal amounts of H₂S and SO₂ (Carroll and Rutherford, 1985; Luhr, 1990). The reduced S in the gas phase probably becomes oxidized to SO₂ during eruptive decompression and subsequent atmospheric transport (Varekamp et al., 1984; Gerlach and Casadevall, 1986; Bluth et al., 1995). In more oxidized magmas, such as the 1991 Mount Pinatubo dacite, most of the S in the pre-eruptive gas phase occurs as SO₂ (Westrich and Gerlach, 1992; Rutherford and Devine, 1996). Throughout the rest of this paper, for reasons of simplicity, the concentration of S_{total} in pre-eruptive exsolved gas will be recalculated to equivalent wt% amounts of SO₂. Thus the range of values discussed above for pre-eruptive exsolved gas in andesitic and

dacitic magmas (0.3–7 mol% S_{total}) is equivalent to approximately 1–20 wt% SO_2 in the gas phase, because most of the gas is low molecular weight H_2O .

3.1. Estimation of SO_2 released by the eruption of the Bishop Tuff

Using the techniques based on thermodynamic analysis and phase equilibria, it is possible to estimate the total amount of S that would be present in pre-eruptive exsolved gas in a magma body given an estimate of the exsolved gas mass fraction. For the large rhyolitic magma body that erupted at 0.76 Ma to form the Bishop Tuff, the exsolved gas content vs. depth profile from Wallace et al. (1995) can be used to predict the total amount of SO_2 that would have been released during the eruption. This can be done by using the exsolved gas gradient together with eruptive volume estimates (Hildreth, 1977; Hildreth and Mahood, 1986; Wilson and Hildreth, 1997), S-species fugacities calculated from magnetite–pyrrhotite equilibrium (Whitney, 1984), and fugacity coefficients calculated using the Redlich–Kwong equation of state. The S concentration in the exsolved gas phase calculated using this method is ~ 1.5 mol% S_{total} (~ 5 wt% SO_2), in good agreement with values calculated by thermodynamic modeling of multicomponent gas composition constrained by pyrrhotite saturation and melt inclusion volatile contents for the Bishop Tuff (B. Scaillet, pers. commun., 1998). This value for mol% S_{total} is significantly higher than previously estimated by Scaillet et al. (1998). The Bishop eruption is thus estimated to have released $\sim 1300 \pm 600$ Mt of SO_2 , of which $\sim 30\%$ probably would have been removed from the plume by adsorption onto ash particles (Rose, 1977; Varekamp et al., 1984; Gerlach and McGee, 1994), and the remaining 900 ± 600 Mt injected into the atmosphere.

4. Exsolved gas contents of magmas inferred from SO_2 emissions

One hypothesis to account for the discrepancies between remote sensing and petrologic (eruptive exsolution) estimates of SO_2 emissions (Fig. 1) is that magmas in crustal storage reservoirs contain significant exsolved gas before eruption. An alternative hypothesis that has frequently been invoked to

explain remote sensing data of SO_2 emissions is that unerupted magma at depth degasses during eruption, thereby contributing SO_2 . These two contrasting hypotheses represent endmembers in a continuum of possibilities involving variable proportions of pre-eruptive exsolved gas and syneruptive loss of gas from unerupted magma. Other potential sources of S, such as decomposition of phenocrystic anhydrite in an eruptive plume (Devine et al., 1984) or vaporization of S-rich hydrothermal brines, are unlikely to be significant (Gerlach et al., 1996). That gas is indeed lost from unerupted magma during shallow emplacement and crystallization associated with activity before and after large explosive eruptions, and during dome extrusion (i.e. open-vent systems), is unquestionable. At issue are the relative contributions of pre-eruptive exsolved gas and syneruptive loss of gas from unerupted magma during sustained Plinian and pyroclastic-flow-generating eruptions. Given the strong case that has been made for a minimal contribution from unerupted magma in several recent, well-studied eruptions (Mount St. Helens, Gerlach and McGee, 1994; Redoubt, Gerlach et al., 1994; Mount Pinatubo, Gerlach et al., 1996), the hypothesis that all SO_2 is derived from erupted magma needs to be quantitatively investigated. Additional detailed consideration of unerupted magma degassing will be discussed in a later section.

If all of the SO_2 released during an eruption is originally contained, as both dissolved and exsolved species, within the volume of erupted magma, then the difference between remote sensing and petrologic estimates can be used to estimate the amount of SO_2 that is contributed by the gas phase. The total mass of SO_2 released during an eruption can be expressed as the sum of SO_2 that is contained in pre-eruptive gas and SO_2 released during decompression from exsolution of dissolved S-species in the silicate melt:

$$\text{SO}_2^{\text{Total}} = \text{SO}_2^{\text{in gas}} + \frac{64}{32} S^{\text{dissolved in melt}}$$

If it is assumed that the remote sensing estimate represents the total amount of SO_2 released during an eruption, then the amount of SO_2 that is contained in pre-eruptive gas can be estimated by combining the remote sensing data ($\text{SO}_2^{\text{Total}}$) with estimates, based on melt inclusions, of the amount of dissolved S that is degassed from the melt during

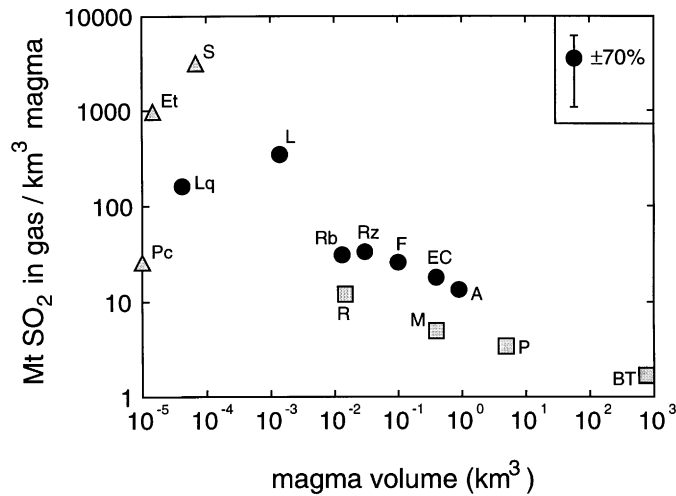


Fig. 2. Mass of SO₂ estimated to be in pre-eruptive exsolved gas vs. eruptive magma volume in recent eruptions for which both remote sensing and petrological data are available (see text for description of methods). Symbols are the same as in Fig. 1. Representative error bar shown at upper right corresponds to an uncertainty of ±70% (relative) based on assumed uncertainties of ±50% for both erupted magma volume and total SO₂ emission.

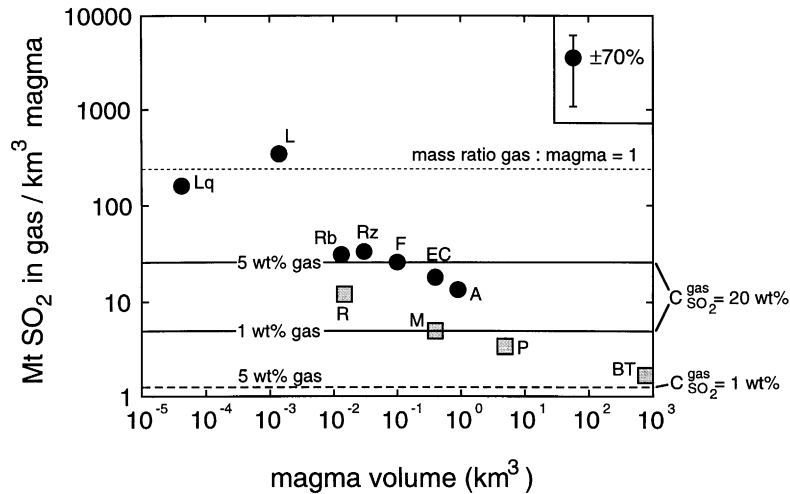


Fig. 3. Mass of SO₂ estimated to be in pre-eruptive exsolved gas vs. eruptive magma volume calculated as in Fig. 2. Dashed and solid lines show the amounts of SO₂ that would be released per unit volume of erupted magma for magmas with pre-eruptive exsolved gas contents of 1 and 5 wt% (concentration of SO₂ in gas = 20 wt%) and 5 wt% (concentration of SO₂ in gas = 1 wt%). These values for total S-species concentrations (expressed as equivalent SO₂) in the exsolved gas phase are chosen to be representative of intermediate to silicic magmas saturated with magnetite + pyrrhotite ± anhydrite (Whitney and Stormer, 1983; Whitney, 1984; Luhr, 1990) and are consistent with analyses of high-temperature gas discharges from convergent margin volcanoes (Symonds et al., 1994; Giggenbach, 1996). The data for basaltic eruptions (Etna, Stromboli, Pacaya) are not shown because basaltic magmas contain gases that are richer in SO₂ than the values adopted here for intermediate to silicic magmas (Gerlach, 1979, 1980; Symonds et al., 1994; Giggenbach, 1996), and hence the exsolved gas contents represented by the horizontal lines are not appropriate. For the two smallest intermediate-composition eruptions (Láscar and Lonquimay), the estimated mass of gas is roughly equivalent to the mass of erupted magma if the exsolved gas has an SO₂ concentration of about 10 wt% SO₂ (short dashed line).

eruption ($S^{\text{dissolved in melt}}$). Normalizing the mass of SO_2 in pre-eruptive gas to the volume of erupted magma (Mt SO_2 in gas/ km^3 magma) provides a useful indicator of the mass of SO_2 contributed from pre-eruptive gas per unit volume of erupted magma (Fig. 2).

Several important features are suggested by the data shown in Fig. 2. First, smaller eruptions appear to have a greater mass of SO_2 per unit volume of magma contributed from a pre-eruptive gas phase than larger eruptions. Second, when eruptions of a given volume are compared, andesitic magmas have a greater amount of SO_2 contributed from pre-eruptive gas than dacitic and rhyolitic magmas. Third, persistently active open-vent basaltic volcanoes (Etna and Stromboli) appear to have extremely large masses of SO_2 contributed from pre-eruptive gas. Such large SO_2 emissions with little or no erupted material from open-vent systems of relatively low viscosity basaltic magma have led to so-called ‘endogeneous growth’ models. In these systems, shallow-stored magma probably degasses without eruption, sinks to deeper levels of the magmatic system, and eventually solidifies to form a high density root beneath the volcano (Francis et al., 1993; Kazahaya et al., 1994; Allard, 1997). Finally, it should be noted that data for Mauna Loa and Laki are not shown in Fig. 2. For these volcanoes, relations between measured SO_2 emissions and total erupted magma indicate that all SO_2 could be produced from exsolution of dissolved S (Fig. 1; see also Andres et al., 1991, and Thordarson et al., 1996).

If the total concentration of S-species in a pre-eruptive gas phase is known or can reasonably be estimated, as discussed in the previous section, then the values shown on the vertical axis in Fig. 2 can be converted into estimated mass fractions of exsolved gas in a magma before eruption. The amounts of SO_2 that would be released per unit volume of erupted magma for various total exsolved gas contents (1 and 5 wt% gas) and exsolved gas S concentrations (1 and 20 wt% SO_2) are shown in Fig. 3. Two of the eruptions shown in Fig. 3 (El Chichón, 1982, and Mount Pinatubo, 1991) have been the focus of detailed analytical and experimental studies in which pre-eruptive exsolved gas mass fractions have been estimated. The El Chichón magma body evidently contained ~ 20 vol% exsolved gas before the eruption, equivalent to ~ 5 wt% gas (Luhr et al., 1984; Luhr, 1990). The Mount Pinatubo magma body

contained about 5–20 vol% exsolved gas, equivalent to about 1–5 wt% gas (Wallace and Gerlach, 1994; Gerlach et al., 1996; Rutherford and Devine, 1996). The estimates for El Chichón and Mount Pinatubo agree well with the values depicted in Fig. 3. It is interesting to note that although the 1982 El Chichón and 1991 Mount Pinatubo eruptions have received considerable attention as being S-rich, the systematics displayed in Fig. 2 show that these eruptions are not anomalous compared with other andesitic and dacitic–rhyolitic eruptions, respectively.

The data and analysis shown in Fig. 3 suggest that intermediate to silicic magmas in eruptions of 0.01 – 10 km^3 of magma appear to contain about 1–6 wt% exsolved gas. Within this range of eruptive volume, smaller volume eruptions contain either systematically higher gas contents, higher proportions of total S in the gas phase, or both. Differences in magma composition and temperature, both of which can strongly affect the solubility of dissolved S (Buchanan et al., 1983; Carroll and Rutherford, 1987; Luhr, 1990; Wallace and Carmichael, 1992; Baker and Rutherford, 1996a), are explicitly accounted for in this calculation, so the patterns shown in Fig. 3 cannot be due to correlations between erupted volume and magma composition or temperature. The correlations shown in Fig. 3 are statistically significant. For the four silicic eruptions, the correlation coefficient (r) for the log transformed data is 0.98; for the seven intermediate-composition eruptions >0.01 km^3 , r is 0.87. Estimated exsolved gas contents for eruptions in the range from 0.01 to 0.1 km^3 are as high as 5–6 wt%. For the two smallest intermediate-composition eruptions (Láscar and Lonquimay), the estimated mass fraction of pre-eruptive gas is much greater, such that the mass of gas is roughly equivalent to the mass of erupted magma (Fig. 3).

5. Contributions of SO_2 from syneruptive degassing of unerupted magma

An alternative hypothesis to the large mass fractions of pre-eruptive exsolved gas inferred above is that during explosive eruptions, unerupted magma at depth degasses and contributes SO_2 . Unfortunately, in most cases where syneruptive degassing of unerupted magma has been invoked, there is little detailed

consideration of mechanisms, mass balance, or the time and length scales over which such a process could occur. Recently, however, the idea has been quantitatively tested using data for several well-studied eruptions. For the 1989–1990 Redoubt and 1991 Pinatubo eruptions, seismic data have been used to interpret the volume of the underlying magma reservoir (Power et al., 1994; Mori et al., 1996). In both cases, the total volumes of unerupted magma that are likely to be present at depth are grossly inadequate to account for the measured SO₂ emissions from major eruptive phases solely by exsolution of dissolved S in unerupted melt (Gerlach et al., 1994, 1996). Similar relationships have been noted for the 1980 eruption of Mount St. Helens (Gerlach and McGee, 1994). It thus appears that for some explosive eruptions, there is an insufficient volume of magma in the underlying reservoir to provide all of the released SO₂ purely by syneruptive degassing of dissolved S from unerupted magma.

An additional problem with the hypothesis that syneruptive degassing of unerupted magma is a significant source for SO₂ is the physical mechanism by which such gas loss could occur. Because gas exsolution is driven by decompression during magma ascent and eruption, it is difficult to envision a process by which gas could separate from deeply-stored but unerupted magma on eruptive timescales. In many regards, the problem of rapid gas loss from a large body of unerupted magma is similar to the problem of how large quantities of H₂O can be lost from ascending silicic magmas in effusive (non-explosive) silicic eruptions (Taylor et al., 1983; Eichelberger et al., 1986; Jaupart and Allegre, 1991; Woods and Koyaguchi, 1994; Eichelberger, 1995). Liquid state diffusion of volatiles dissolved in silicate melt is many orders of magnitude too slow for any appreciable quantity of either H₂O or S to be transferred from unerupted magma at depth on the timescale of an explosive eruption (Shaw, 1974; Baker and Rutherford, 1996b). Furthermore, for relatively viscous intermediate to silicic composition magmas, timescales for buoyant rise of bubbles will be much too slow compared to eruptive timescales (Taylor et al., 1983) to deliver substantial amounts of gas from deep, unerupted magma, into the roof zone of the magma chamber where magma is entering the conduit. Likewise, upward transport rates of magma in the conduit

are too rapid for excess gas accumulation to occur by bubble rise relative to magma in the conduit (Wilson, 1980). Convective processes may be important during repose period degassing in open conduits (e.g. Kazahaya et al., 1994), but they are unlikely to be important on the timescale of an explosive eruption, nor is it clear how such a process would operate during the high magma conduit fluxes characteristic of such eruptions (Wilson et al., 1980).

The most obvious mechanism by which large quantities of S could escape rapidly from a deep (5–10 km) body of unerupted magma would be for decompression to cause sufficient exsolution of volatiles so that gas bubbles form an interconnected network, resulting in a magmatic froth (defined as ≤ 90 vol% gas bubbles; Candela, 1991) with substantial gas permeability. The critical porosity at which vesicles become sufficiently interconnected to allow loss of gas probably lies in the range from 30 to 60 vol% (Eichelberger et al., 1986; Candela, 1991; Klug and Cashman, 1996). For a magma with an initial dissolved water content of 6 wt% H₂O (~ 2 kb), a highly permeable froth would be formed at pressures ≤ 300 –700 bars, equivalent to 60 and 30 vol% porosity, respectively. Similarly, a magma with an initial dissolved water content of 4 wt% H₂O and 800 ppm CO₂ (~ 2 kb) would reach the critical porosity at pressures less than 200–400 bars. Furthermore, to remove sufficient dissolved S from the melt would probably require pressures much lower than 200–700 bars, given the relatively small pressure dependence of S in intermediate and silicic melts (Luhr, 1990). Although wall rocks probably have sufficient strength for a conduit to remain open with magma pressures less than lithostatic (Carrigan et al., 1992; Sparks et al., 1994; Eichelberger, 1995), it is questionable whether this degree of underpressure could be achieved in a deep magma body, initially at ~ 2 kb pressure, while still maintaining an open conduit. In order to maintain an open magma conduit during an eruption, pressures must remain relatively high in the deep reservoir and lower parts of the system (Blake, 1981; Druitt and Sparks, 1984; Tait et al., 1989). This probably precludes substantial decompression-driven degassing of deeply-stored, unerupted magma on the timescale of an explosive eruption.

Notwithstanding the problems discussed above, if pressure in a deep (5–10 km) magma reservoir can

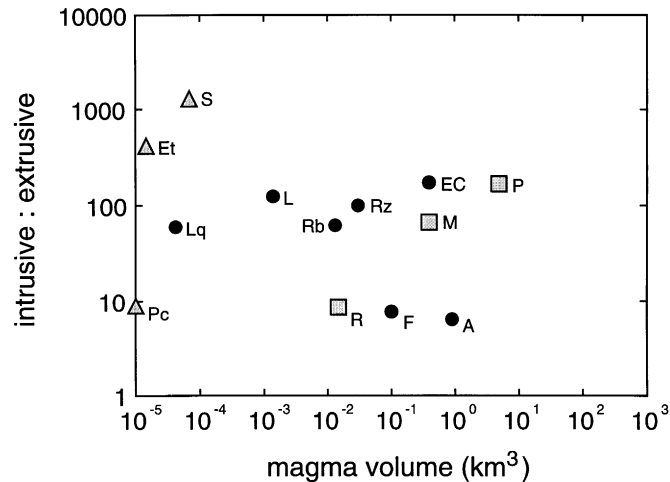


Fig. 4. Intrusive:extrusive ratio for individual eruptions calculated by assuming that all excess SO_2 released during the eruption is derived from syneruptive degassing of unerupted magma. This diagram represents an endmember model for SO_2 emissions that can be compared with the alternative hypothesis, shown in Fig. 2, in which all SO_2 is derived from pre-eruptive exsolved gas dispersed throughout the erupted volume of magma.

drop low enough for rapid formation of permeable magmatic froth on a scale of 10–100 km³ of magma, then the framework presented in Fig. 1 imposes strong constraints on the proportions of unerupted magma that would have to degas in order to account for observed SO_2 emissions. For each eruption considered in Fig. 1, an ‘apparent’ intrusive to extrusive magma volume ratio can be estimated by assuming that all SO_2 comes from syneruptive degassing of dissolved S only (Fig. 4). For the majority of eruptions considered, the apparent intrusive to extrusive ratios predicted in this way vary from 60:1 to 200:1, whereas for four eruptions (Pacaya, Redoubt, Fuego, and Agung), the apparent intrusive to extrusive ratios are much lower. Thus the unerupted magma hypothesis requires both a very large volume of magma at depth and sufficient underpressures in the reservoir during the eruption so that this large magma body is depleted in most of its H_2O and S (and certainly all of its CO_2). Depletion of volatiles from a large body of magma during a single eruption by this process would result in rapid solidification due to the strong effect of water loss on the liquidus and solidus temperatures (Eichelberger, 1995). Such total depletion in volatiles is not consistent with the observed repose periods for many volcanic systems, which can be interpreted to indicate that only a small amount

of volatiles are lost from a magmatic system during a given eruption (e.g. Tait et al., 1989).

A novel variant of the unerupted magma hypothesis was recently proposed by Kress (1997) for the 1991 Mount Pinatubo eruption. When S solubility in silicate melts is examined as a function of oxygen fugacity at constant temperature, there is a solubility minimum near the nickel–nickel oxide buffer (NNO) that corresponds to the change in dissolved S speciation from dominantly reduced S to dominantly oxidized S (Katsura and Nagashima, 1974). It is well accepted that intrusion of a new batch of mafic magma into the Mount Pinatubo magma reservoir triggered the explosive eruption in 1991 (Pallister et al., 1996). Kress (1997) proposed that mixing between reduced basaltic magma saturated with immiscible Fe–S–O liquid and oxidized dacitic magma saturated with anhydrite would have resulted in a hybrid magma with intermediate oxygen fugacity. The hybrid magma is postulated to have been at an oxygen fugacity near the S solubility minimum, causing most dissolved S to exsolve into the vapor phase, and resulting in anhydrite breakdown, which would contribute additional S to the vapor phase. However, the dacitic pumice and ash erupted on 15 June 1991, at Pinatubo contain no basalt, no basalt commingled with dacite, and no intermediate hybrid magma

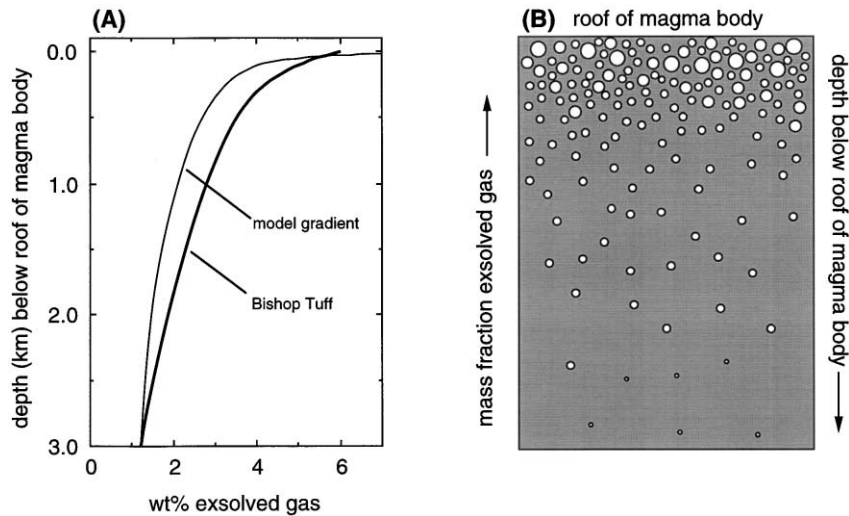


Fig. 5. (A) Model gradient (light solid line) in pre-eruptive exsolved gas content used for calculations shown in Figs. 6 and 7. This gradient was determined by best fit to the data in Fig. 2 for eruptions of $0.01\text{--}10\text{ km}^3$ of magma; that is, the gradient was derived so as to yield straight lines in Fig. 7 that would have the same general trend as the data. Note that the absolute values for wt% exsolved gas are dependent on assumed chamber diameter and gas composition, but the relative shape of the model gradient is independent of any assumed parameters and is determined only by the slope of the data in Fig. 2. The heavy solid line shows the gradient deduced for the pre-eruptive Bishop Tuff magma body using melt inclusion data (Wallace et al., 1995). (B) Schematic showing a magma body with an exsolved gas gradient approximately corresponding to that shown in (A).

(Pallister et al., 1996), so the postulated hybrid magma of Kress (1997) was not erupted. Only the minor volume ($\sim 0.1\text{ km}^3$) of hybrid andesitic magma that erupted in the days prior to the large explosive eruption contained any evidence of magma mixing, and rapidly quenched scoria of this mixed material contained euhedral (unresorbed) anhydrite (Pallister et al., 1996).

The redox hypothesis for the origin of excess SO_2 is problematic because it requires that the initial endmembers are on opposite sides of the S solubility minimum, which occurs near the NNO buffer. However, basaltic magmas from convergent plate margins are typically more oxidized than the value adopted by Kress (1997), and are commonly in the range from NNO to $\text{NNO} + 1$ (Brandon and Draper, 1996; Lange and Carmichael, 1996; Metrich and Clocchiatti, 1996; Luhr, 1997; Wallace and Carmichael, 1999). Such an oxygen fugacity for basaltic magma involved in mixing would place it on the same side of the S solubility minimum as silicic magma, so mixing would not cause S exsolution. Furthermore, the magnitude of the S solubility mini-

um in low temperature, hydrous silicic melts is greatly diminished relative to high-temperature, anhydrous basaltic magmas (cf. Fig. 4 of Carroll and Rutherford, 1987, and Fig. 3 of Katsura and Nagashima, 1974). Indeed, the relations shown by Carroll and Rutherford (1987) suggest that at $T < 900^\circ\text{C}$, there is little or no minimum in S solubility across a wide range of oxygen fugacities.

In summary, the hypothesis that syneruptive degassing of unerupted silicic magma supplies the 'excess' SO_2 observed in sustained explosive eruptions appears to be problematic for two main reasons. First, because of the very large volumes of unerupted magma that would have to degas, and second, because of the very low pressures that would have to be sustained in the deep reservoir feeding the eruption. Furthermore, new intrusion of mafic magma into a silicic magma reservoir shortly before eruption is also problematic as a major source of 'excess' SO_2 because the oxygen fugacities typical of mafic arc magmas are probably close to those of more evolved magmas. Despite these reservations, however, the extent of SO_2 contributions from unerupted magma

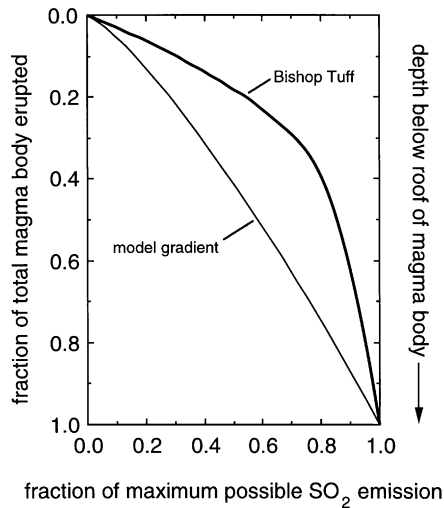


Fig. 6. Fraction of the maximum possible SO_2 emission (i.e. if all magma was erupted) is shown as a function of the fraction of the total magma volume that is erupted for a range of model eruption volumes created by different depths of drawdown in a cylindrical magma body. The shape of the curve for the model gradient is independent of model parameters and is determined solely by the shape of the gradient in Fig. 5(A).

still remains the greatest source of uncertainty in using remote sensing SO_2 data to estimate the amounts of exsolved gas that are in magma bodies prior to explosive eruptions.

6. Models of SO_2 emissions from magma bodies with exsolved gas gradients

Most volcanic eruptions are characterized by emissions of SO_2 that are 10 times or more greater than the amounts that could have been derived from exsolution of dissolved S from the erupted volume of magma. If minimal SO_2 is derived from syneruptive degassing of unerupted magma, then the remote sensing data imply that intermediate to silicic magmas contain about 1–6 wt% exsolved gas (Fig. 3). One hypothesis for the trends observed in Fig. 3 is that magmas in crustal storage reservoirs not only contain exsolved gas before eruption but that there is a vertical gradient in the mass fraction of gas such that the gas mass fraction is greatest in the roof zone of the reservoir (Fig. 5). Evidence for the existence of such a gradient in a magma reservoir is based on H_2O , CO_2 , and trace element concentrations of melt inclusions in quartz phenocrysts from the Bishop Tuff (Wallace et al., 1995, 1999) interpreted in the context of the revised eruption chronology (Wilson and Hildreth, 1991, 1997). For a magma reservoir with such an exsolved gas gradient, the amount of SO_2 released per unit volume of erupted magma varies depending on the maximum depth of drawdown in the magma reservoir (i.e. the depth to which the reservoir is tapped during the eruption; Fig. 6). In the case of the Bishop magma

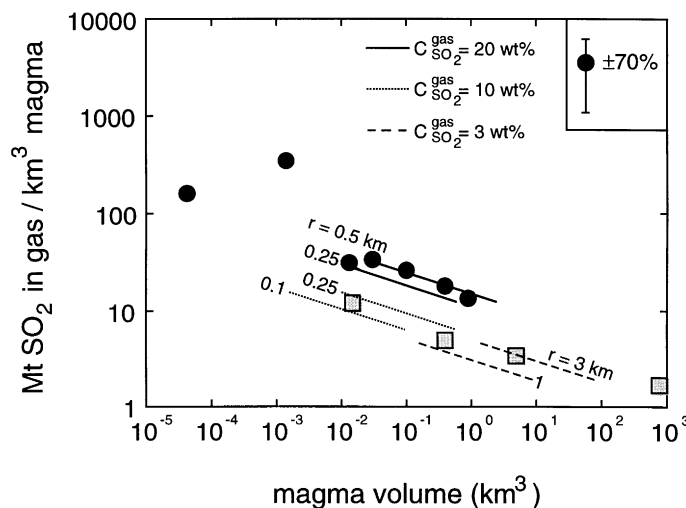


Fig. 7. Mass of SO_2 estimated to be in pre-eruptive exsolved gas vs. eruptive magma volume, as in Fig. 2. Diagonal lines show predicted trends for variable drawdown depths in cylindrical magma bodies with radius of 0.1–4 km based on the gradient shown in Fig. 5(A).

body, the gradient in exsolved gas content is such that the gas-rich cap makes up only $\sim 30\%$ of the total 800 km^3 of erupted magma but contributes $\sim 70\%$ of the total SO_2 emission (Fig. 6). The systematics displayed in Figs. 5 and 6 suggest that if small eruptions preferentially tap the gas-rich top of a larger magma reservoir, then a larger proportion of their total erupted SO_2 should be from pre-eruptive exsolved gas (Wallace, 1997).

This hypothesis can be tested by considering geometrically simple magma bodies of a range of sizes, all of which are characterized by a gradient in exsolved gas content (Figs. 5 and 6). For a cylindrical magma body of a given radius and depth, a wide range of eruptive volumes can result depending on the depth of drawdown during a particular eruption, notwithstanding the complex withdrawal dynamics that may occur in natural magmatic systems. Rather than specifying a particular exsolved gas gradient, it is possible to solve, by inverse methods, for an appropriate gradient based on the observed SO_2 emission data (Fig. 2). Thus the exsolved gas gradient used in the calculations (Figs. 5 and 6) was determined by best fit to the data for eruptions of $0.01\text{--}10 \text{ km}^3$ of magma; that is, the gradient was derived so as to yield straight lines in Fig. 7 that would have the same general trend as the data. Considering that this gradient was derived solely from trends in the data shown in Fig. 2, it is remarkably similar in form to the gradient deduced for the Bishop Tuff magma body by an entirely independent method based on melt inclusion volatile contents (Wallace et al., 1995).

The results of simple models based on variable drawdown depths demonstrate that for a plausible range of magma reservoir sizes, variable depths of magma withdrawal can yield SO_2 emission patterns similar to those that are observed based on remote sensing data (Fig. 7). However, for the smallest volume eruptions shown in Fig. 7 (Láscar and Lonquimay), it is difficult to explain the very high apparent values of SO_2 in gas per km^3 of magma erupted unless the uppermost part of the magma body contains a headspace of gas (e.g. Giggenbach, 1996). A more plausible alternative is that SO_2 emission data for very small volume eruptions reflect separation and concentration of gas relative to magma during ascent and shallow storage. This interpretation is supported by data and physical models for

Vulcanian and Strombolian eruptions, which suggest that segregation of gas at shallow depth leads to episodic explosions (Allard et al., 1991; Blackburn et al., 1976; Chouet et al., 1974; Self et al., 1979; Wilson, 1980). In contrast, sustained Plinian and pyroclastic flow-forming eruptions typically involve larger volumes of magma, and are characterized by high magma flux and rapid ascent from crustal reservoirs ($\sim 5\text{--}10 \text{ km}$ deep), which precludes segregation of gas from magma before fragmentation (Wilson, 1980).

Based on comparison with model trends (Fig. 7), the SO_2 emission vs. eruptive volume data are consistent with the hypothesis that smaller eruptions preferentially tap the gas-rich upper portions of larger magma bodies. Most pyroclastic eruptions greater than $\sim 1 \text{ km}^3$ are compositionally heterogeneous with respect to major and/or trace elements (e.g. Hildreth, 1981), and many that are one to two orders of magnitude smaller show distinct zonation. For example, two of the smaller eruptions shown in Fig. 7 are zoned from dacite to andesite (Ruiz, 0.03 km^3 , and Redoubt, 0.015 km^3). Upward increases in exsolved gas content result in stable density stratification and may thus help preserve major and trace element compositional gradients in magma bodies (Wallace et al., 1995).

It is important to note that for an eruption of a given size there may be as much as one order of magnitude difference in the amount of SO_2 in gas per unit volume of erupted magma (e.g. Mount St. Helens and El Chichón in Figs. 3 and 7). Although this can be explained in part by differences in magma body radius and drawdown depth, variations in other parameters are probably more important: (1) maximum gas content at the top of the magma body; (2) concentration of S in the pre-eruptive gas phase; (3) extent of pre-eruptive gas loss during transport of magma from deep to shallow reservoirs; and (4) influence of reservoir, vent, and conduit geometry on withdrawal dynamics. Amounts of pre-eruptive magmatic gas are likely to vary from one eruption to another, but a main cause of observed variation probably is an upward increase in exsolved gas content. The calculated trends in Fig. 7 are not meant to imply that all magma bodies have similar amounts of gas but merely that gradients in exsolved gas contents can lead to the observed patterns in data for SO_2 emissions. Many

magma bodies are probably characterized by less steep gradients. As the magnitude of the gradient diminishes, the diagonal trends shown in Fig. 7 will flatten out until they become horizontal for a magma with homogeneous gas content (Fig. 3). Ultimately, there are many uncertainties in assessing exsolved gas contents in magma bodies, and the unique characteristics of each of the magmatic systems portrayed in Fig. 3 underscore the need for further detailed studies of individual eruptions. Nevertheless, the models shown in Fig. 7 serve to illustrate how pre-eruptive gradients in exsolved gas contents would, under a simplified set of circumstances, be manifested in volcanic SO₂ emissions.

The exsolved gas gradient used in the modeling was derived so that trends for eruptive volume vs. SO₂ released would yield a straight line with negative slope on a log–log diagram (Fig. 7). Any such solution will yield an exsolved gas mass fraction that decreases logarithmically with depth in the magma chamber, assuming constant SO₂ mass fraction in the gas phase and constant dv/dz , where v is volume withdrawn from the chamber and z is depth. Although such a logarithmic gradient is a continuous function, it results in a gas distribution with two distinct regions, a gas-rich top with a relatively steep gradient, and a gas-poor lower region with relatively constant gas content (Fig. 5). With such a gradient, the upper, gas-rich region occupies a small fraction (~10%) of the total chamber volume. The fraction of the reservoir that consists of gas-rich magma in such a model is in accord with the fraction of a magma body that is likely to be evacuated during a given eruption (Smith and Shaw, 1979; Crisp, 1984; Shaw, 1985). The exsolved gas gradient portrayed in Fig. 5 is somewhat analogous to that used by Blake (1984) and Druitt and Sparks (1984), in which an exsolved gas-rich cap representing a small fraction of the chamber overlies a gas-undersaturated dominant volume. Their modeling suggests that only in large caldera-forming eruptions does less gas-rich magma get expelled from the deeper regions of a magma reservoir as the cauldron block collapses and subsides until lithostatic pressure is reestablished.

There are several methods by which the hypothesis that exsolved gas gradients generally exist in magma reservoirs could be tested. One test would be to use the method developed by Wallace et al. (1995) based

on melt inclusion H₂O, CO₂, and trace element data to study an eruption for which remote sensing data are available. This method works well for the Bishop Tuff magmatic system, in the upper parts of which fractional crystallization was the dominant process responsible for differentiation (Michael, 1983; Lu, 1991), but the method will be difficult to apply in magmatic systems where magma mixing plays an important role. Nevertheless, application of the melt inclusion method to the 1991 Mount Pinatubo yields an estimated exsolved gas content of 3.6 ± 1.2 wt% (Wallace, unpublished data, cited in Wallace et al., 1995), consistent with the range of estimates based on other methods (e.g. Fig. 3). Another way in which the exsolved gas gradient hypothesis could be tested is by using time series data from remote sensing techniques. For example, the 1982 eruption of El Chichón occurred in three closely spaced major pulses that occurred over eight days. Combination of TOMS-derived SO₂ emissions with eruptive volumes for each of the three pulses might make it possible to detect a change in SO₂/km³ of magma over time (S.J. Schaefer, pers. commun.).

7. Gas accumulation and eruption triggering

Physical models of eruption mechanics suggest a basis for expecting exsolved gas contents at the tops of magma bodies that are comparable to those inferred from SO₂ emission data. Volcanic eruptions are believed to occur when pressure in a magma reservoir exceeds lithostatic pressure by an amount greater than the tensile strength of the surrounding wall rocks (Blake, 1981). Such overpressuring can be caused by an influx of new magma from below or by crystallization-induced gas exsolution (Blake, 1981, 1984; Tait et al., 1989). In the latter process, physical models suggest that the critical overpressure is achieved when the exsolved gas content of the magma reaches about 1 vol%, or if gas saturated magma only occupies a small fraction of the total reservoir volume (i.e. a gas-rich cap), as much as 10 vol% (Blake, 1984). It is important to note that the deduced maximum volume fraction of exsolved gas in these calculations is strongly dependent on the maximum degree of inflation of the reservoir that can occur by compression of the enclosing wall rocks

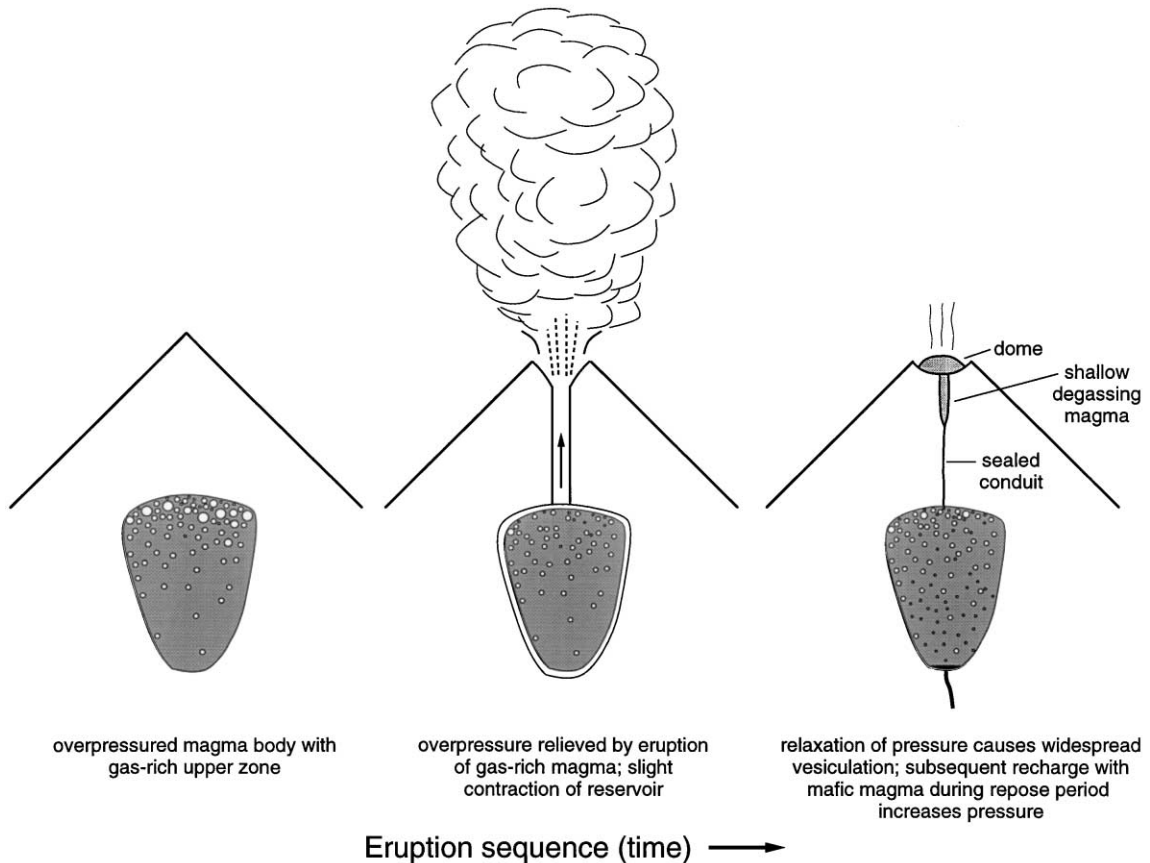


Fig. 8. Schematic of an explosive eruption cycle for a magma reservoir with a gradient in the mass fraction of exsolved gas. See text for details of model.

(Blake, 1981, 1984). The critical volume fractions of exsolved gas cited above are based on a maximum volumetric expansion ($\Delta V/V$) of the reservoir of 0.001. As an example of the effects of uncertainties in this value, if the maximum volumetric expansion ($\Delta V/V$) of the reservoir is 0.002, then the maximum gas volume fraction in a small gas saturated layer at the top of the reservoir would be 20 vol% instead of 10 vol%. Given the factor of 2–3 uncertainty inherent in estimating the maximum possible extent of volumetric expansion (Blake, 1981, 1984; Tait et al., 1989; Woods and Pyle, 1997), the maximum gas volume fraction in the upper part of a magma reservoir could be as high as 20–30 vol% exsolved gas.

The model of Blake (1984) for overpressuring due to crystallization-induced gas exsolution was extended by Tait et al. (1989) to consider the effects

of repeated eruptions from a magma body. If after an eruption, the pressure in the reservoir relaxes to its initial (pre-overpressured) value, then the volume of erupted magma will be replaced by newly exsolved gas (Fig. 8). In the closed system case (Tait et al., 1989), no new magma is injected into the reservoir during the subsequent repose period, and pressure gradually increases due to crystallization-induced gas exsolution. Alternatively, in an open system, pressure increases in the chamber through both recharge by mafic magma and crystallization-induced gas exsolution in the overlying differentiated magma (Fig. 8). Because crystallization is caused by heat loss, the extent of crystallization-induced gas exsolution in the differentiated magma will be controlled by the relative proportions of hot, mafic recharging magma and differentiated magma. Eventually the critical

overpressure in the chamber will again be reached and another explosive eruption will occur.

It is intriguing that the volume fraction of exsolved gas at the tops of many magma bodies may be about 30 vol% (~6 wt%), based on both the SO₂ emission data (Fig. 3) and melt inclusion methods (Wallace et al., 1995). As first pointed out by Candela (1991) in regard to degassing of plutons, mathematical models predict that 30 vol% porosity represents the percolation threshold at which spherical gas bubbles become sufficiently interconnected to allow permeable flow through a network of bubbles (e.g. Sur et al., 1976; Garboczi et al., 1995; Rintoul and Torquato, 1997). Thus 30 vol% may represent a physical limitation on the maximum amount of exsolved gas that can occur at the top of a magma reservoir. Once this threshold is reached, gas will be lost out of the top of the system by advection through a permeable bubble network, and will probably be transferred into an overlying hydrothermal system or leaked out to the surface.

8. Sources and fluxes of S in magmatic systems

Isotopic studies of S in intermediate and silicic magmas have demonstrated that the S is magmatic in origin and is not dominantly derived by assimilation of crustal material (Rye et al., 1984; Williams et al., 1990; McKibben et al., 1996). The ultimate source of S in these systems must therefore be from mafic magma, because it is well established that silicic magma reservoirs are created and sustained through long-term replenishment by mantle-derived basaltic magma during inter-eruption repose periods (Smith, 1979; Hildreth, 1981; Shaw, 1985). Andesitic and dacitic magma in crustal reservoirs are probably gas saturated due to recharge and underplating by basaltic magma that is saturated with multicomponent H₂O–CO₂–S gas. Vapor transfer from underplated basaltic magma into an overlying silicic magma body is probably a slow process that occurs during the long repose periods that separate eruptive episodes. If the S in crustal magmatic systems is ultimately derived from the mantle via basaltic magma, then the flux of S should be directly related to the basaltic magma flux.

Based on the relationship between eruptive volumes and repose periods for numerous intermediate to silicic magma systems spanning many orders of

magnitude in eruptive volume, it has been estimated that a basaltic magma flux of approximately 0.01 km³/year is required to sustain an individual long-lived crustal magmatic system (Smith, 1979; Shaw, 1985; Trial and Spera, 1990). If an average of 1000 ppm of S is degassed from mantle-derived basalt, then this basaltic magma flux for an individual magmatic system yields a flux of 0.052 Mt SO₂ per year. This value provides an estimate of the amount of mantle-derived S that is delivered into the base of an intermediate to silicic composition magmatic system that is periodically recharged with mafic magma. Such an estimate can be combined with the general relationship between repose time and eruptive magma volume (Smith, 1979; Trial and Spera, 1990) in order to compare the flux of SO₂ released to Earth's atmosphere from explosive eruptions with the flux of S derived from basaltic magmas that sustain crustal magma reservoirs.

Smith (1979) suggested an approximate correlation between repose time and eruptive magma volume for intermediate and silicic magmatic systems that can be expressed as:

$$\log \text{repose time (year)} = \log \text{magma volume (km}^3\text{)} + 3$$

Using a similar approach, Trial and Spera (1990) provided data (see their Fig. 1) that suggests repose periods somewhat shorter than those of Smith (1979), especially for eruptions involving 1–100 km³ of magma. Given the uncertainties involved, and the natural variability in repose times, a general relationship consistent with Trial and Spera (1990) and Smith (1979) can be expressed as:

$$\log \text{repose time (year)} = \log \text{magma volume (km}^3\text{)} \\ + 2.5(\pm 0.5)$$

Based on this volume–repose time relationship, it appears that for intermediate to silicic systems in which individual eruptions are on the order of 0.01–1 km³, the flux of SO₂ from explosive eruptions is approximately in steady state with the mantle-derived S supply rate (Fig. 9). For example, an andesitic eruption of 1 km³ will be preceded by an ~300 year repose period, during which time 3 km³ of basaltic magma is added to the system from below, contributing 16 Mt of SO₂. When the system erupts, ending

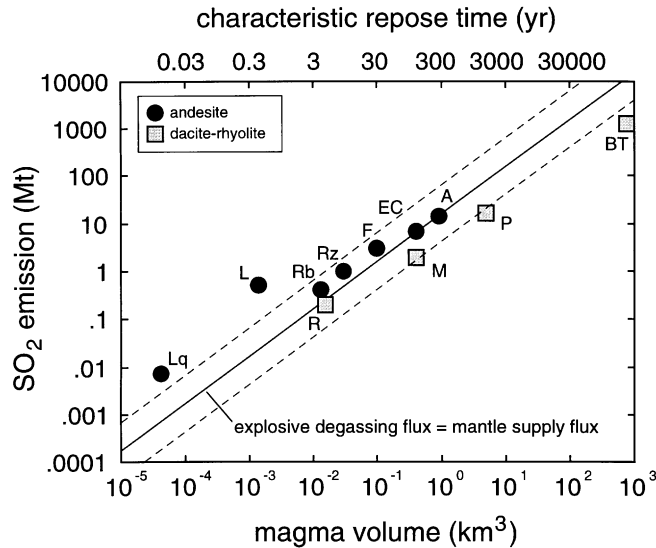


Fig. 9. Volcanic SO₂ emissions vs. total volume of erupted magma for the intermediate and silicic eruptions shown in Fig. 1. The relationship between characteristic repose period (shown on upper horizontal axis) and volume of differentiated magma erupted (shown on lower horizontal axis) is based on Trial and Spera (1990). Solid line indicates steady state balance between the amount of S introduced by prolonged degassing of basaltic magma at the base of the system during the repose period and the amount of SO₂/km³ of differentiated magma released by explosive eruptions. The solid line is calculated assuming that an individual magmatic system has a basaltic magma flux of 0.01 km³/year and 1000 ppm S degassed from basalt, yielding a S flux from the mantle of 5.2 Mt SO₂/km³ of basalt. Dashed lines correspond to an uncertainty of ± one-half order of magnitude in the relationship between repose period and eruption size.

the repose period, the systematics of Fig. 9 indicate that associated with the 1 km³ andesitic eruption is about 10–20 Mt of SO₂. Thus the mass of SO₂ released by the eruption approximately balances the mass of SO₂ added via mantle-derived basaltic magma during the repose period. The balance between eruptive SO₂ fluxes in systems characterized by 0.01–1 km³ eruptions probably reflects the efficiency with which S is transferred from basaltic magma at the base of the system to the overlying differentiated magma.

The hypothesis that long-lived crustal magmatic systems have an approximate steady state balance between input of S from basaltic magmas and loss of S from explosive eruptions can be tested by using the mantle-derived S flux to estimate a global annual SO₂ flux to the atmosphere. The number of subaerial eruptions that have occurred in the last 200 years in different size categories based on the Volcanic Explosivity Index (VEI) have been compiled by McClelland et al. (1989). These subaerial eruptions occur dominantly (≥94%; McClelland et al., 1989) from volcanoes associated with convergent plate margins. For

each of the ~20 subaerial eruptions that occur annually, the volume of magma erupted (which is related to VEI) can be used to estimate the length of the repose period preceding the eruption based on the relationship given above. The repose period time can then be used to estimate the total mass of basaltic magma that has entered each system, based on a flux of 0.01 km³/year, which in turn allows an estimate of the total mass of mantle-derived SO₂ introduced into the system. If the hypothesis of a steady state balance is correct, then the mantle-derived SO₂ that was introduced into each magmatic system during the repose period should be released during the explosive eruption that ends the repose period. The global annual flux of SO₂ from explosive eruptions can be calculated by assuming: (1) a steady state balance between mantle supply and explosive loss of SO₂; (2) the historical record of explosive volcanism for the last 200 years; (3) the relationship between eruptive volume and repose period given above; and (4) a basaltic magma flux of 0.01 km³/year. The resulting estimate for the global flux from explosive eruptions is 2.7 Mt SO₂/year, a value that agrees well with an

estimate of 0.3–3 Mt SO₂/year calculated using remote sensing data for SO₂ emissions (Pyle et al., 1996). Such agreement substantiates the hypothesis that the mantle supply flux of SO₂ is approximately in steady state with the SO₂ flux from explosive eruptions.

The two eruptions in Fig. 9 that involve less than 0.01 km³ of magma (Láscar and Lonquimay) have ratios of SO₂/km³ magma that are significantly higher than would be expected for a steady state system with a flux of 0.01 km³/year of basaltic magma. Such a pattern could be caused by shallow gas segregation, as previously discussed for Vulcanian and Strombolian eruptions. In contrast, eruptions much larger than 1 km³ (Pinatubo, Bishop Tuff) fall somewhat below the steady state S flux value. These lower values could be due to: (1) loss of S into large hydrothermal systems; (2) inefficiency in the magma withdrawal process (Spera et al., 1986); or (3) inefficiency in the transfer of S from basaltic magma in the deep roots of the system to highly differentiated magma in the upper parts of the reservoir.

9. Conclusions

Most volcanic eruptions, whether basaltic, andesitic, dacitic or rhyolitic, are characterized by emissions of SO₂ that are 10 times or more greater than the amounts that could have been derived from syneruptive exsolution of dissolved S from the erupted volume of magma. The most notable exceptions to this pattern are Hawaiian and Icelandic volcanoes; other basaltic systems (Pacaya, Etna, Stromboli) are characterized by highly variable excess SO₂ emissions. A plausible hypothesis to explain excess SO₂ emissions is that magmas in crustal reservoirs are almost universally saturated with a multicomponent gas phase consisting dominantly of H₂O, CO₂, and S-species. During sustained Plinian and pyroclastic flow-forming eruptions, significant contributions of SO₂ from syneruptive degassing of unerupted magma are unlikely given the mass balance and low pressures in the deep source reservoir that would be required for such gas loss.

Using remote sensing data for SO₂ emissions from recent explosive eruptions, it is possible to estimate the mass fractions of exsolved gas that are present in

magmas before eruption. Intermediate to silicic magmas in eruptions of 0.01–10 km³ appear to have about 1–6 wt% exsolved gas. Within this range of eruptive volume, smaller volume eruptions contain either systematically higher gas contents, higher proportions of total S in the gas phase, or both. For very small volume eruptions (<0.01 km³ of magma), apparent exsolved gas contents are highly variable, and probably largely reflect shallow segregation of gas relative to magma, such as occurs in Strombolian and Vulcanian eruptions. For eruptions >0.01 km³, the SO₂ emission vs. eruptive volume data are consistent with the hypothesis that smaller eruptions preferentially tap gas-rich upper portions of larger magma bodies. The volume fraction of exsolved gas deduced for the upper regions of many magma bodies (~30 vol%) is similar to the percolation threshold at which gas bubbles become sufficiently interconnected to allow permeable flow of gas. This value is probably the maximum exsolved gas volume fraction that can occur at the roof zone of a magma reservoir because any additional gas would be lost by advective flow through the permeable bubble network. Comparison of time–volume–eruption periodicity in individual volcanic systems, and the estimated rate at which basaltic magma supplies S into the base of such systems, suggests a relatively steady state flux of S from Earth's mantle to atmosphere through many andesitic and dacitic magmatic systems.

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