

EXCESS DEGASSING FROM VOLCANOES AND ITS ROLE ON ERUPTIVE AND INTRUSIVE ACTIVITY

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[1] Volcanoes emit larger amounts of volcanic gas than can be dissolved in the volume of erupted magma during a variety of volcanic processes, including explosive and effusive eruption and noneruptive continuous degassing. Degassing of unerupted magma with a much larger volume than that of erupted magma caused such a large degassing; erupted magma represents only a small portion of the magma that drives volcanic activity. Evaluation of the magma-gas differentiation process causing the excess degassing is necessary to understand eruption processes, magma chamber evolution, and crustal growth by magma intrusion. Three mechanisms are proposed to explain various degassing modes, including eruption of bubbleaccumulated magma, degassing of a convecting magma column, and permeable gas transportation from a deep magma chamber. Examples of large degassing in excess of the erupted magma are common in subduction zone volcanism but are rare in rift- and hot spot-associated volcanism.

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1. INTRODUCTION

[2] Volcanoes emit volcanic gas during various types of activity that range from explosive eruptions to noneruptive gas emissions. Volcanic gas is originally supplied from the mantle or lower crust to the upper crust as dissolved components in magmas. However, it is common that the amount of volcanic gases emitted from volcanoes greatly exceeds the amount of volatiles that were dissolved in the erupted magmas; this is called excess degassing of volcanoes [Andres et al., 1991; Wallace, 2001]. Excess degassing implies that the volcanic gases are derived from other sources in addition to the dissolved volatiles in the erupted magma, and a larger volume of magma that did not erupt but remains in the crust is suggested as the source of excess degassing. The excess degassing indicates that a volcano is not just a location of magma emission but is also a locus of gas emission from magmas supplied to the upper crust, including intrusive magmas. A volcano is a chimney in the crust, effectively exhausting gases supplied from deep sources (W. F. Giggenbach, personal communication, 1997). The view of larger intrusive magmas than extrusive magmas has been quantified by geological and geophysical studies of the crustal structure [e.g., Crisp, 1984] and by geochemical studies of magma chamber evolution [e.g., Hildreth, 1981]. The distribution of large intrusive magmas

(plutons) in the upper crust indicates their importance on crustal growth, but they are the results of a long history of igneous activity, and their link to the present-day volcanic activity is not clear. Excess degassing is the result of ongoing formation of intrusive magmas that can provide constraints on differentiation process of the extrusive and intrusive magmas beneath each volcano.

[3] Volcanic gas supply from a larger amount of a magma than erupted magma implies that excess degassing is caused by magma-gas differentiation in a magma chamber and conduit system. Exsolution and expansion of a volcanic gas phase (bubbles) provides the major driving force of magma ascent and explosive eruptions [Wilson and Head, 1981]. A variety of eruption styles is largely controlled by distribution of gas phase in a magma during eruption [Eichelberger et al., 1986; Jaupart and Vergniolle, 1988]. Original volatile contents in magmas commonly far exceed the amount necessary to cause explosive eruption, whereas some of those magmas erupt effusively because of gas loss from ascending magmas [Eichelberger, 1995]. Therefore, magma-gas differentiation in a magma chamber and conduit system controls not only excess degassing but also occurrence and style of eruptions. Past volcanic activity is commonly characterized by its erupted magma volume [Newhall and Self, 1982; Simkin, 1993]; however, excess degassing indicates that the erupted magma represents only a small portion of the magma that drives the eruption. Occurrence of excess degassing is different for eruptions with different styles, magma compositions, and tectonic

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TABLE 1. Glossary of Volcanological Terms

Term	Definition
Terms concerning degassing process	
Magmatic gas	A gas phase exsolved from magma, consisting of H ₂ O, CO ₂ , SO ₂ and others, which are originally dissolved in silicate melt.
Volcanic gas	A high-temperature magmatic gas emitted to the Earth's surface.
Volcanic plume	A mixture of volcanic gas and air. Volcanic plume may also contain ash and aerosols.
Degassing	Emission of a gas phase from magma (magma degassing) or a volcano (volcano degassing) as a result of volatile exsolution and bubble separation from magma.
Gas phase	In this text, this term refers to a phase of magmatic gas regardless of the exact phase, including vapor, liquid or supercritical fluid phase.
Gas species	Chemical components composing a gas phase.
Volatile (component)	Gas species contained in silicate melt or crystal.
Magma	A mixture of silicate melt, crystals and bubbles. Composition of recently erupted magma commonly ranges from basalt, andesite, dacite to rhyolite, with increasing silica content and viscosity, and decreasing temperature in this order.
Melt	A liquid of silicate.
Bubble	Magmatic gas phase distributed in magma.
Terms describing eruptions	
Plinian eruption	A continuous ejection of mixtures of highly vesiculated and fragmented magmas (volcanic ash and pumice) and volcanic gases with a high velocity ($100-400$ m/s) and large discharge rates (10^6 to $>10^8$ kg/s); the eruption continues for several hours, discharging a large volume of material (10^{10} to $>10^{13}$ kg [<i>Cioni et al.</i> , 2000; <i>Pyle</i> , 2000]).
Vulcanian eruption	An explosive eruption characterized by explosions with ballistic ejection of poorly vesiculated blocks and bombs accompanied by shock waves in the air (a cannon-like explosion), followed by continuous emission of volcanic ash for a few minutes to hours [<i>Morrissey and Mastin</i> , 2000].
Strombolian eruption	An explosive eruption characterized by the sudden ejection of gases and molten magma fragments up to a few hundreds meters above the vent, associated with the outburst of large bubbles ascending through the molten magma column [<i>Vergniolle and Mangan</i> , 2000].
Lava fountain	A mildly explosive eruption continuously ejecting a mixture of gases and molten magma fragments up to several hundreds meters height [<i>Vergniolle and Mangan</i> , 2000]. Lava fountains are caused by low-viscosity magmas and are commonly associated with lava flows.
Hawaiian eruption	Combination of lava fountainings and lava flows. Transition of lava fountaining activity to continuous quiescent lava effusion is also common.

settings [*Andres et al.*, 1991; *Wallace*, 2001; *Scaillet et al.*, 2003; *Sharma et al.*, 2004]. Quantification of excess degassing at different situation and evaluation of their mechanisms can provide an insight into eruption processes.

[4] This paper provides an overview of the nature of volcanic gas emission, in particular, from the viewpoint of excess degassing, in order to discuss the magma-gas differentiation process in a magma chamber-conduit system as a controlling mechanism of volcanic and igneous activity. The manuscript starts with brief reviews of volatile solubility and distribution in magmas and the techniques used to measure volcanic gas emissions. Next, examples of excess degassing are reviewed for a variety of magma compositions, eruption styles, and tectonic settings by comparing the amount of volcanic gas, erupted magma volume, and dissolved volatile concentrations. Excess degassing observed in different situations requires different mechanisms, and these are reviewed with their relevance to eruption styles. Finally, an estimate of global SO₂ emission rate is discussed in order to review an integrated temporal and spatial contribution of various degassing activity and its link to intrusive activity.

2. VOLATILES IN MAGMAS

[5] Volatile components dissolved in silicate melt are exsolved when their concentrations exceed their solubility, forming a magmatic gas phase (bubbles in magma). Volatile exsolution is caused either by decrease of volatile solubility due to decompression or by increase of volatile concentrations in a melt due to crystallization [*Burnham*, 1967]. Since most crystals in magma can contain little volatile components, decrease in silicate melt volume by magma crystallization increases volatile component concentrations in the residual melt, leading to saturation. Gas emission occurs as the result of physical separation of magmatic gas phase from magma. A glossary of technical terms is given in Table 1.

[6] Water is the most abundant component in volcanic gas, followed by CO_2 and SO_2 (Table 2); other components include H_2S , HCl, HF, H_2 , CO, N_2 , Ar, and He. This review is focused on behavior of H_2O , CO_2 , and SO_2 , which commonly comprise more than 95 mol % of volcanic gases [*Symonds et al.*, 1994]. Volcanic gases from subduction zone volcanoes are commonly rich in H_2O (~95 mol %), with a few exceptions of CO_2 -rich volcanic gases such as those at the Eolian arc (Vulcano and Stromboli volcanoes), Italy, and White Island, New Zealand [*Giggenbach*, 1996]. In contrast, at hot spots, volcanic gases are much more CO_2 -rich, reflecting the CO_2 -rich and H_2O -poor composition of their source magmas [*Giggenbach*, 1996; *Wallace*, 2005].

2.1. Volatile Solubility in Melts

[7] Solubility of H_2O and CO_2 is given by simple relationships between their partial pressure and concentra-

Volcano	Tectonic Volcano Setting Magma Activity		H ₂ O (mol %)	CO ₂ (mol %)	SO ₂ (mol %)	H ₂ S (mol %)	Method	References ^b	
Masaya	subduction	basalt	persistent degassing	94.2	3.4	1.4	_	FTIR	1
Miyakejima	subduction	basalt	persistent degassing	94.9	2.0	2.7	0.2	MultiGAS	2
Villarrica	subduction	basaltic andesite	mild Strombolian activity	95.0	2.0	2.1	< 0.01	MultiGAS	3
Stromboli	subduction	basalt	persistent degassing	82.9	13.6	1.7	_	FTIR	4
			Strombolian explosion	64.4	33.1	1.8	_	FTIR	4
Kilauea	hot spot	basalt	persistent degassing	89.8	3.9	5.7	0.2	FTIR	5
	1		gas pistoning ^c	61.4	31.1	1.0	5.0	FTIR	5
Pinatubo	subduction	dacite	Plinian eruption $(P_{SO2} = 11 \text{ Mpa})^d$	80.1	14.5	4.0	-	calculated	6
			Plinian eruption $(P_{SO2} = 2 \text{ Mpa})^{e}$	82.9	15.1	0.8	-	calculated	6
Erta'Ale	rift	basalt	lava lake Hornito (1130°C)	79.4	10.4	6.8	0.6	sampling	7
Kudryavy	subduction	basaltic andesite	fumarolic activity (940°C)	94.4	1.8	1.8	0.2	sampling	8
Vulcano	subduction	andesite	fumarolic activity (620°C)	86.1	11.9	0.7	0.5	sampling	9
Momotombo	subduction	andesite	fumarolic activity (844°C)	95.1	2.4	0.7	0.5	sampling	10
Satsuma-Iwojima	subduction	rhvolite	fumarolic activity (884°C)	97.5	0.4	1.0	0.04	sampling	11

TABLE 2. Molar Composition of Volcanic Gases Emitted by Various Activities^a

^aDashes indicate that values were not obtained. FTIR, Fourier transform infrared absorption spectroscopy; MultiGAS, multicomponent gas analyzer system.

^bReferences are as follows: 1, Burton et al. [2000]; 2, Shinohara et al. [2003]; 3, Shinohara and Witter [2005]; 4, Burton et al. [2007a]; 5, Edmonds and Gerlach [2007]; 6, Gerlach et al. [1996]; 7, Giggenbach and Le Guern [1976]; 8, Taran et al. [1995]; 9, Giggenbach [1996]; 10, Menyailov et al. [1986]; 11, Shinohara et al. [2002].

^cGas pistoning is an ejection of accumulated gas phase from a lava effusing vent, that causes sudden drainback and slow ascent of lava surface level in the vent [*Edmonds and Gerlach*, 2007].

^dCalculated assuming $P_{SO2} = 11$ MPa.

^eCalculated assuming $P_{SO2} = 4$ MPa.

tion in silicate melt (Figure 1 [Holloway and Blank, 1994; Zhang et al., 2007]). Solubility of H_2O is approximately a linear function of the square root of H_2O partial pressure, whereas CO_2 solubility is a linear function of CO_2 partial pressure. Water and CO_2 solubility varies with silicate melt composition and temperature; however, their controls are minor compared with pressure. Solubility of H_2O is much larger than CO_2 . Silicate melts can dissolve about 4 wt % H_2O at 100 MPa, compared with 500 ppm CO_2 (Figure 1). Volatile saturation occurs when the sum of partial pressures of the gas species exceeds the confining pressure. Because of the low solubility of CO_2 , the initial gas phase formed at the saturation pressure is CO_2 -rich, whereas the gas phase composition becomes more H₂O-rich as pressure decreases [*Holloway*, 1976].

[8] Solubility of SO₂ is not given by a simple function of SO₂ partial pressure but is given as a partition coefficient of sulfur, which is defined as a ratio of sulfur concentrations in the gas and silicate melt phases ($D_{\rm S} = C_{\rm S}^{\rm gas}/C_{\rm S}^{\rm melt}$, both in wt %), and the partition coefficient is a function of pressure, temperature, magma composition, and oxygen fugacity [*Scaillet et al.*, 1998; *Keppler*, 1999]. The complexity of sulfur solubility is due to multiple chemical forms of sulfur both in the gas phase (SO₂ and H₂S) and in the silicate melt (as sulfate and sulfide ions [*Carrol and Webster*, 1994; *Symonds et al.*, 1994]). The sulfur in silicate melts dissolves as S^{2–} (sulfide ion) under reducing conditions, as S⁶⁺



Figure 1. Solubility of (a) H₂O and (b) CO₂ in magmas. Reproduced from *Holloway and Blank* [1994].



Figure 2. Melt inclusions. (a) A photomicrograph of rhyolitic melt inclusions in a plagioclase phenocryst from pumice of Satsuma-Iwojima volcano, Japan. (b) A back-scattered electron image of basaltic melt inclusions in an olivine phenocryst of volcanic bombs from Miyakejima volcano, Japan (photographs courtesy of G. Saito).

(sulfate ion) under oxidizing conditions, and as their mixture under intermediate conditions [*Carrol and Webster*, 1994]. Experimental studies reveal that sulfur can strongly partition into the gas phase relative to rhyolitic or dacitic melt (with $D_S > 100$) under magma chamber conditions [*Keppler*, 1999; *Scaillet et al.*, 1998].

[9] The complexity of sulfur solubility also arises from the solubility of sulfur-bearing phases in a silicate melt. Sulfide (e.g., pyrrhotite, $Fe_{1-X}S$), sulfate (e.g., anhydrite, CaSO₄), and immiscible Fe-S-O liquid are not uncommon

in magmas [Luhr et al., 1984; Hattori, 1996; Larocque et al., 2000]. The dissolved sulfur concentration in silicate melt coexisting with sulfide or sulfate minerals is controlled by mineral solubility. Sulfur concentration in sulfide-saturated melts increases with temperature and cation contents, in particular of iron [O'Neill and Mavrogenes, 2002; Liu et al., 2007]. The dissolved sulfur concentration in anhydrite-saturated melts is much higher than that in sulfide-saturated melts under the same pressure-temperature condition [Carrol and Rutherford, 1985; Luhr, 1990].

2.2. Volatile Concentrations in Magmas

[10] Dissolved volatile concentrations in magmas are typically estimated by analysis of silicate melt inclusions. Melt inclusions are tiny beads of silicate melt trapped in phenocrysts during crystal growth that solidify to glass during rapid cooling after eruption (Figure 2 [Lowenstern, 1995; Wallace, 2005]). Their composition represents that of the silicate melts at the time of entrapment. Erupted magmas lose their volatiles because of degassing during eruption, but silicate melt inclusions can maintain their original dissolved volatile concentrations because their rigid host crystal serves as a pressure vessel to keep the trapped melt at high pressure even during decompression. Silicate melt inclusions are commonly small (a few to a few hundreds of μ m in diameter) and must be analyzed by microbeam analytical techniques, such as electron probe microanalyzer, secondary ion mass spectrometry, Raman spectrometry, or microbeam infrared (IR) spectroscopy for the analyses of



Figure 3. H_2O-CO_2 concentrations in melt inclusions from subduction zone basalts, modified from *Wallace* [2005], copyright 2005, with permission from Elsevier. Data shown for Cerro Negro [*Roggensack et al.*, 1997], Fuego [*Roggensack*, 2001], Guatemalan volcances behind the volcanic front (BVF [*Walker et al.*, 2003]), the Trans-Mexican Volcanic Belt [*Luhr*, 2001; *Cervantes and Wallace*, 2003a, 2003b], Stromboli [*Métrich et al.*, 2001], and Galunggung [*Sisson and Bronto*, 1998]; shown for comparison are the primary CO₂ concentrations of normal mid-ocean ridge basalt (NMORB) [*Marty and Tolstikhin*, 1998] and enriched mid-ocean ridge basalt (EMORB) [*Hekinian et al.*, 2000] magmas, Kilauea basaltic magmas [*Gerlach et al.*, 2002], and Reunion basaltic magma [*Bureau et al.*, 1999]. Gas saturation isobars are shown for 200 and 500 MPa pressure with red dashed curves, dotted curves show composition (CO₂ mole fraction) of a gas phase equilibrated with the melt, and dashed-dotted curve with arrows is shown for closed system degassing trend for magma with 5 wt % H₂O and 7000 ppm CO₂ (calculated using *Newman and Lowenstern* [2002]).



Figure 4. Variation of sulfur concentration with SiO₂ content in melt inclusions. Melt inclusions from different tectonic settings are shown by different symbols. A general trend is shown by a yellow shaded curve, which is consistent with sulfide saturation [Liu et al., 2007]. Data are taken from following references: Anderson et al. [1989], Bertagnini et al. [2003], Cervantes and Wallace [2003a, 2003b], Clague et al. [1995], Devine et al. [1984], Gerlach et al. [1994], Gurenko et al. [2005], Harris and Anderson [1984], Hauri [2002], Luhr [2001], Matthews et al. [1999], Michaud et al. [2000], Palais and Sigurdsson [1989], Roggensack et al. [1996, 1997], Roggensack [2001], Saito et al. [2001, 2005], Satoh et al. [2003], Self and King [1996], Sigurdsson et al. [1990a], Sisson and Bronto [1998], Sisson and Layne [1993], Stix et al. [2003], Thordarson et al. [1996], Wade et al. [2006], Walker et al. [2003], Westrich and Gerlach [1992], and Witter et al. [2004, 2005].

volatile components [*Ihinger et al.*, 1994; *Lowenstern*, 1995; *Di Muro et al.*, 2006].

[11] Water is the most abundant volatile component in most magma types. Subduction zone magmas are H₂O-rich with a wide range from <1 to >10 wt % but commonly ranging from 2 to 6 wt %; this is much larger than in hot spot basalts or mid-ocean ridge basalts (Figure 3 [Scaillet et al., 2003; Wallace, 2005]). Water concentrations in silicate melt of subduction zone magmas do not show any general relationship with magma compositions that range from basalt to rhyolite [Wallace, 2005]. Carbon dioxide concentrations in subduction zone magmas are much lower than H_2O , with a maximum of 2500 ppm in basaltic magmas and 500 ppm in more silicic magmas in many cases [Wallace, 2005]. Saturation pressure estimated from H₂O and CO₂ concentrations ranges 200-500 MPa for basaltic magmas (Figure 3) and 100-250 MPa for dacitic or rhyolitic magmas, and these pressure ranges are consistent with probable depth ranges of magma crystallization in the crust. The agreement of the volatile saturation pressure and actual pressure implies that the melt inclusions were trapped under gas phase saturated conditions, and these inclusions may have lost part of their original CO₂ into CO₂-rich bubbles before melt inclusion entrapment [Wallace, 2005].

[12] Sulfur concentrations in melt inclusions show large variation with decreasing sulfur concentration as silica

content increases, from >1000 ppm in basaltic magmas to <100 ppm in rhyolitic magmas (Figure 4 [Devine et al., 1984; Wallace, 2005]). Similar sulfur concentrations are observed in magmas with similar magma composition regardless of tectonic setting, indicating that the variation is not due to magma source differences but is caused by later differentiation. The sulfur concentration variation in melt inclusions is commonly consistent with sulfide solubility [Wallace and Carmichael, 1992; Wallace, 2005], suggesting that sulfur concentrations in silicate melts are controlled by sulfide solubility. Solubility of sulfide minerals in silicate melts increases with temperature and cation content, in particular of iron [Liu et al., 2007], both of which decrease during magma differentiation. Magmatic sulfides are not ubiquitous but are common although minor in volcanic rocks [Larocque et al., 2000]. Therefore the sulfur concentration variation could be caused by sulfide precipitation from magmas (Figure 4 [Devine et al., 1984; Wallace, 2005]). Another possible sink of sulfur is a gas phase. Since melt inclusions are likely to be trapped under gas phase saturated conditions (Figure 3) and a large sulfur partition coefficient can be attained under certain conditions, a significant amount of sulfur can be contained in a vapor phase under magma chamber conditions. Conditions of melt inclusions entrapment are quite variable, in particular under different tectonic settings (Figure 3), and sulfur loss to a gas phase under such variable conditions cannot create the simple relationship between sulfur content and silica content (Figure 4).

3. MEASUREMENTS OF VOLCANIC GAS EMISSION

[13] Volcanic gases are emitted during eruptions, continuous degassing from eruptive vents (persistent degassing), and fumarolic activity (Figure 5). Only the latter is easily sampled, and most volcanic gas studies have been focused on gas compositions obtained by direct sampling from fumaroles and chemical analyses [Symonds et al., 1994; Giggenbach, 1996]. However, the amount of volcanic gases emitted by fumarolic activity is commonly minor compared to that emitted by eruption and persistent degassing, and quantification of these emissions is more important than quantification of those from fumaroles. The volcanic gases emitted from eruptive vents immediately mix with the air at the exit, forming a volcanic plume, and direct sampling methods are not applicable to those situations. Measurement of volcanic plumes became possible by the recent development of remote sensing techniques [Stoiber et al., 1983; McGonigle and Oppenheimer, 2003].

[14] In addition to volcanic gas emission from summit craters, magmatic gas components are discharged by diffuse emission from the flanks of volcanoes through soil gas, hot spring water, and groundwater. Diffuse emission of magmatic CO_2 gases through soils or faults are observed at many volcanoes. Contribution of the diffuse CO_2 emission to total emission from an actively degassing volcano is variable, ranging from an equal contribution to the summit emission at Etna volcano, Italy [*Allard et al.*, 1991], to



Figure 5. Various degassing activity. (a) Plinian eruption of St. Helens volcano, Washington, on 18 May 1980 (source: U.S. Geological Survey/Cascade Volcano Observatory). The eruption column rose to more than 30 km height. (b) Aerial photo of lava dome eruption at Unzen volcano, Japan (photograph courtesy of S. Suto). Lava lobe extruded near the summit at center and flowed to the left. Volcanic gases were also emitted around the summit. The photograph was taken with a camera for geographical measurement; therefore small cross marks are printed as a scale on the original film. (c) Persistent degassing at Etna volcano, Italy (photograph courtesy of A. Aiuppa and Istituto Nazionale di Geofisica e Vulcanologia). Four craters are located in the summit area, with extensive degassing at three, Northeast, Voragine, and Bocca Nuova craters, and minor degassing at Southeast crater when photograph was taken. (d) Fumarolic degassing at Kuchinoerabu volcano, Japan.

virtually no diffuse emission at Popocatépetl volcano, Mexico [Varley and Armienta, 2001]. Although diffuse CO₂ emission is surveyed at many volcanoes, the number of emission rate data is still limited because of the nature of diffuse and heterogeneous emission from a large area [Kerrick, 2001]. Emission rate of magmatic gas components, such as halogens and CO2, as dissolved components in hot spring water and groundwater is commonly much smaller than summit gas emission rates, but their contribution to global emission rate can be significant because of their wide distribution [James et al., 1999; Hurwitz et al., 2005]. Although diffuse emission of magmatic gas components is potentially important for volatile budget in a magmatic system in a long time scale, the present review is focused on gas emission from summit craters that is directly linked to ongoing activity at a summit vent. Importance of the diffuse emission on volatile budget will be briefly discussed in section 6.2.

3.1. Measurements of SO₂ Emission Rate

[15] Volcanic gas emission rates are commonly evaluated on the basis of SO₂ emission rates measured by ultraviolet (UV) remote sensing using scattered solar radiation as the light source. Because of the low atmospheric background concentration of SO₂, high sensitivity of the UV absorption, and wide availability of the light source, the volcanic SO₂ emission rate measurements are now widely used to monitor volcanic activity [*Stoiber et al.*, 1983] and to evaluate their environmental or climatic effect [*Andres and Kasgnoc*, 1998; *Robock*, 2000]. Two techniques have been widely applied to quantify SO₂ in volcanic plumes, i.e., ground-based and satellite-based techniques.

[16] The ground-based measurement of SO₂ emission rate is performed either with a correlation spectrometer (COSPEC, Figure 6a) or with an UV spectrometer by application of differential optical absorption spectrometry. The COSPEC was originally developed to measure industrial SO₂ and NO₂ emissions in the 1960s and was applied to measure volcanic SO₂ emissions from early 1970s [*Stoiber et al.*, 1983]. In the early 2000s, compact and inexpensive instruments for the UV spectroscopy were developed using a commercially available UV spectrograph (such as Ocean Optics, USB2000) that becomes a standard



Figure 6. Instruments for SO_2 emission rate measurement. (a) Correlation spectrometer (COSPEC) during panning measurement of SO_2 emission rate at Satsuma-Iwojima volcano, Japan. (b) USB2000 (UV spectrometer) with a telescope (photographs courtesy of K. Kazahaya).

instrument for the measurements of SO₂ emission rate of volcanoes (Figure 6b [*Galle et al.*, 2002]). Both instruments quantify an integrated amount of SO₂ molecules along the light path (in units of mole/m²). The instruments are scanned to obtain an integrated SO₂ amount on a cross section of the plume (mole/m), which is multiplied by the plume velocity (m/s) to calculate an emission rate (e.g., in t/d or kg/s, Figure 7). Scanning of a plume is performed either

by traverse or panning methods. In the traverse method, the instrument is mounted on a moving platform (vehicle, boat, aircraft, or a person) vertically looking at the sky and traveling beneath and approximately perpendicular to a volcanic plume. When the traverse method is not applicable because of road inaccessibility, for example, the instrument may be placed at a fixed position and is tilted to scan a volcanic plume (panning method). The ground-based SO₂



Figure 7. A schematic diagram of ground-based SO_2 emission rate measurement techniques. The COSPEC or UV spectrometer is placed on the ground looking to the sky to measure absorption of UV light by SO_2 molecules. The absorption intensity is measured during scanning a volcanic plume either by traversing beneath the plume or by panning the instruments to obtain an integrated SO_2 amount on a cross section of the plume (mole/m). The SO_2 emission rate is calculated by multiplying the integrated concentration with plume velocity (m/s).



Figure 8. An example of the SO₂ cloud images obtained by Total Ozone Mapping Spectrometer (TOMS). The SO₂ cloud was produced by the 4-5 April 1982 eruption of El Chichón volcano, Mexico, after drifting for 4 days at 25 km altitude. This cloud contained about 7 million tons of SO₂. Cited from *Krueger et al.* [2000].

emission rate measurement is now considered to be the standard technique of volcano monitoring and has been repeatedly performed at numerous volcanoes [*Symonds et al.*, 1994].

[17] Yields of SO₂ emitted by large volcanic eruptions are measured by satellite-based UV spectrometry, such as with Total Ozone Mapping Spectrometer (TOMS) and Ozone Monitoring Instrument (OMI). The TOMS and OMI are spatially scanning UV spectrometers designed to monitor ozone structure in the Earth's atmosphere by measuring UV absorption of the reflected sunlight of the Earth's surface at several windows. Since a few reference bands for the ozone measurements overlap with absorption bands of SO₂, these instruments can also be used for mapping of SO₂ in the atmosphere (Figure 8 [Krueger et al., 1995, 2000]). The ability to measure volcanic SO₂ clouds was recognized during the eruption of El Chichón volcano, Mexico, in 1982 during operation of TOMS (Figure 8 [Krueger, 1983]); this led to development of a new algorithm to separately determine both ozone and SO₂ in volcanic clouds, resulting in the large database of SO₂ emissions from eruptions since 1978 [Krueger et al., 2000].

[18] TOMS and OMI instruments give daily snapshots of SO_2 distribution in the atmosphere, and the amount of discharged SO_2 during the previous day can be estimated from their difference. Therefore, it provides a direct estimate of SO_2 emission by a discrete explosive eruption during a short period (e.g., a few hours). The great advantage of TOMS and OMI instruments is almost continuous daily coverage of global volcanic SO_2 emissions. TOMS provided the global volcanic SO_2 emission data since 1978, except for a gap in 1994–1996 (Figure 9 [*Bluth et al.*, 1993; *Carn*

et al., 2003]). Since 2004, a new satellite sensor, OMI, measures the SO₂ emission, and TOMS ceased operation at the end of 2005 [Krotkov et al., 2006]. The OMI has a higher sensitivity and special resolution than TOMS with two orders of magnitude improvement in the detection limit (7000 tons of SO₂ by TOMS and 47 tons by OMI [Krotkov et al., 2006]). Emissions by continuous and repeated eruptions, however, need to be quantified by modeling SO₂ cloud transportation and dissipation, since the amount of SO_2 in the atmosphere decreases with time by conversion to H₂SO₄, and the conversion rates are variable, ranging from less than 10%/d in the stratosphere to 50%/d in the tropospheric clouds [Krueger et al., 1995]. The TOMS SO₂ algorithm was designed for stratospheric measurements; quantification of SO₂ in the lower troposphere is more difficult and includes larger errors [Symonds et al., 1994; Krueger et al., 1995]. Therefore TOMS could not quantify SO₂ emissions from continuously degassing volcanoes, whereas improvement of the OMI algorithm permits measurements of continuous SO₂ emissions in the lower troposphere [Krotkov et al., 2006].

[19] Hydrogen sulfide is another major sulfur species in volcanic gas, but it is not measured by the UV remote sensing techniques. Concentration of H_2S in high-temperature fumarolic gases is commonly less than that of SO₂ (Table 2). The H_2S/SO_2 ratio in a gas phase is a function of temperature, pressure, and oxygen fugacity and increases almost proportionally with pressure under a given temperature and oxygen fugacity; a gas phase derived from a high-pressure condition has a much higher H_2S/SO_2 ratio than the fumarolic gas equilibrated at atmospheric pressure [*Giggenbach*, 1987; *Burgisser and Scaillet*,



Figure 9. The SO₂ masses observed with TOMS. Red bars show eruptions at subduction zone volcanoes (Arc), and blue bars show eruptions at divergent plate boundaries or hot spot volcanoes (Non-arc). Large or well-known eruptions are labeled. Cited from web site of TOMS Volcanic Emission Groups (http://toms.umbc.edu/) with permission from S. Carn.

2007]. Volcanic gas emitted during gas-pistoning activity at Kilauea volcano has a high H₂S/SO₂ ratio (Table 2) that is attributed to the high-pressure origin of the gas [Edmonds and Gerlach, 2007]. Therefore, an eruption may discharge a significant amount of H₂S because of the higher-pressure origin of the gas phase than fumarolic gases. The H₂S gas, however, is rapidly oxidized to SO_2 in the atmosphere with a lifetime of approximately 1 day [Graedel, 1977] and can be detected as SO₂ by the satellite remote sensing. Bluth et al. [1995] observed an increase in the daily SO_2 amounts in the eruption clouds followed by eruptions of Mount Spurr, USA, and interpreted the increase as the results of gradual oxidation of H₂S discharged by the eruption. The SO₂ amount measured by TOMS and OMI includes contributions from SO₂ and H₂S, but their relative contributions could not be estimated in most cases.

[20] Large amounts of volatile compounds are commonly trapped on fresh volcanic ash as water-soluble components, such as CaSO₄, NaCl, and absorbed acid gases [Taylor and Stoiber, 1973; Rose, 1977]. Sulfur concentrations of the water-soluble components are commonly 0.1 wt % and exceed 1 wt % in some cases. Therefore, the emission of sulfur compounds as water-soluble sulfur components during eruptions is significant in comparison with the SO₂ emission detected by TOMS. Contribution of the watersoluble components to the total sulfur emission is estimated to range 30-50% for several large explosive eruptions, such as at Mount Saint Helens in 1980 [Gerlach and McGee, 1994], El Chichón in 1982 [Luhr et al., 1984], and Galunggung in 1982-1983 [de Hoog et al., 2001]. Water-soluble components will not be preserved after rains, and their analyses are not always available. Because of the scarce data set, emission of sulfur compounds trapped on volcanic ash will not be considered in the rest of this manuscript, and sulfur emissions by eruption will be evaluated on the basis of the SO_2 emission estimates by TOMS, which should be regarded as a minimum estimate.

[21] Sulfur yields emitted by large eruptions in the past can be estimated from the analysis of ice cores from Greenland and Antarctica [Delmas, 1992; Hammer et al., 1980; Zielinski, 1995; Robock, 2000]. Sulfur gases (SO₂ + H₂S) injected by large volcanic eruptions into the stratosphere will convert to sulfate aerosols that eventually fall to Earth and are deposited within the record of glacial ice. The ice provides annual to subannual resolution for more than 10,000 years and can be compared to geological or historical eruption records. The volcanic sulfate loadings can be estimated by modeling transport of volcanic aerosols in the stratosphere from the eruption locality. For example, 80 peaks of sulfate concentration were measured in core of the Greenland ice sheet over the last 2,100 years, permitting estimation of sulfur yields from a variety of identifiable eruptions [Zielinski, 1995].

3.2. Measurements of Volcanic Gas Composition

[22] Quantification of more abundant H_2O and CO_2 in volcanic plumes is as important as the SO_2 emission rate measurements. Volcanic gas composition data can provide information not only about the amount degassed but also about volatile composition of magma and its degassing conditions. Since a volcanic plume is a mixture of volcanic gas and air, the volcanic gas composition can be estimated by determining the composition of the volcanic plume and subtracting the background air composition. Volcanic plume composition is measured either by Fourier transform infrared absorption spectroscopy (FTIR) or by analytical instruments after sampling the air in the plume.

[23] Various components in volcanic gases, including H₂O, CO₂, SO₂, HCl, HF, CO, and others, have sensitive

absorption bands in the IR and can be quantified by IR absorption spectroscopy [*Mori and Notsu*, 1997]. FTIR measurements require an IR light source, such as the Sun, an IR lamp, or natural hot materials such as hot lavas [*McGonigle and Oppenheimer*, 2003]. The FTIR can quantify H₂O and CO₂ concentration in a plume, but their measurements are limited in number because of the large and noisy backgrounds of these components (in particular, H₂O) in the atmosphere. In order to estimate volcanic H₂O and CO₂, the measurements need to be conducted near the degassing vent to minimize the atmospheric H₂O and CO₂ [*Burton et al.*, 2000, 2007a; *Edmonds and Gerlach*, 2007].

[24] Volcanic plume compositions are also measured with analytical instruments after sampling the air in the plume. By flying through the eruptive plume, atmospheric studies of volcanic emissions have been conducted with various bulky instruments, such as gas chromatography, flame photometric detector, or filter samplers of acid gases and particles, to detect various trace components such as SO₂, H₂S, NO, O₃, and aerosols [Friend et al., 1982; Martin et al., 1986]. Because of the high CO2 atmospheric background, quantification of volcanic CO₂ in the plume requires precise measurements of CO₂ concentration near degassing sources prior to significant dilution. Measurement of volcanic plume CO_2 emission was realized by application of IR spectrophotometer to airborne measurement during the Mount Saint Helens eruptions [Harris et al., 1981] and was applied to other volcanoes [Gerlach et al., 1997; Gerlach and McGee, 1998; McGee et al., 2001].

[25] Another approach to measure volcanic plume composition is to bring portable gas analyzers to the rim of a degassing vent to measure concentration of volcanic gas species in a concentrated plume. Near-vent measurement is necessary to obtain volcanic gas composition including H₂O by quantifying volcanic H₂O concentrations high enough to discriminate them from the large background fluctuation. A portable multicomponent gas analyzer system (MultiGAS) was developed to facilitate the near-vent volcanic plume measurements by combining several gas analyzers into a handy package [Aiuppa et al., 2005; Shinohara, 2005]. The MultiGAS consists of several portable gas analyzers, such as a portable IR spectrometer for H₂O and CO₂, electrochemical sensors for SO2 and H2S, and a H2 semiconductor sensor, to obtain concentration ratios of these species [Shinohara, 2006]. The MultiGAS weighs less than several kg and allows easy deployment at the volcano summit and thus close to the degassing vent.

[26] Table 2 lists available volcanic gas composition data measured during eruptions and persistent degassing activity, together with calculated compositions of gases emitted during Plinian explosive eruption, plus a few representative fumarolic gas compositions. There are many other compositional data of volcanic gases emitted during eruptions and persistent degassing such as SO₂/HCl or CO₂/SO₂ ratios, but the compositional data with H₂O concentration are still limited. All data indicate that H₂O is the dominant species regardless of tectonic settings and styles of degassing activity. Compositions of the gases emitted during persistent

degassing are similar to that of fumarolic gas obtained from volcanoes in a similar tectonic setting.

4. EXCESS DEGASSING

[27] The amount of SO₂ emitted during eruptions and persistent degassing will be compared with the amount of dissolved sulfur in the erupted magma to evaluate occurrence and degree of excess degassing. The amount of volcanic gases derived from dissolved volatiles in erupted magmas is calculated as

$$M_{\rm gas} = M_{\rm magma} (C_{\rm MI} - C_{\rm MG}) F_{\rm melt}, \tag{1}$$

where $M_{\rm gas}$ and $M_{\rm magma}$ are masses of the volcanic gases and magmas, $C_{\rm MI}$ and $C_{\rm MG}$ are concentrations (in mass fraction) of the volatile component in a preeruptive melt (melt inclusion) and in a posteruptive melt (matrix glass), and F_{melt} is a silicate melt mass fraction of a magma. M_{magma} is estimated on the basis of volume measurement of lavas and tephra deposits by geological surveys, whose accuracy depends on availability of outcrops. This method is referred to as the petrological method and was developed for estimation of volcanic S and Cl discharges associated with large eruptions in the past, to evaluate the impact of volcanic eruptions on climate change [Devine et al., 1984; Palais and Sigurdsson, 1989]. The petrological method, however, often resulted in SO₂ yields lower than estimates based on measurements of the discharged sulfur, using methods such as COSPEC, TOMS, or ice core analyses (Table 3 and Figure 10 [Wallace, 2001; Scaillet et al., 2003]). Though excess degassing is estimated through the SO₂ yields, volcanic gases are commonly dominated by H₂O and CO₂ (Table 2), so that excess degassing would imply not only excess of sulfur but also of those other volcanic gas species.

4.1. SO₂ Emission by Eruptions

[28] Volcanic eruptions are always associated with gas emissions, but emission styles of gases and magmas are variable depending on eruption styles (Table 1). The SO₂ emission by eruption is commonly in excess of the dissolved sulfur amount in the erupted magma, but the degree of excess is variable depending on tectonic setting, eruption style, and magma composition (Table 3 and Figure 10). In the compilation, the explosive and effusive eruptions were distinguished on the basis of SO₂ emission data sources; eruptions measured by TOMS or ice core records are categorized as "explosive," and the others measured by ground-based UV spectroscopy are categorized as "effusive" (Table 3).

4.1.1. SO₂ Emission by Explosive Eruptions

[29] Plinian and Vulcanian eruptions are accompanied by a large degree of excess degassing (Figure 10 [*Wallace*, 2001; *Scaillet et al.*, 2003]). The degree of excess degassing is measured by the ratio of the measured SO_2 yields to the petrological estimate; this is variable depending on magma composition, ranging from 10 to 100 for dacitic and rhyolitic eruptions, 1 to 30 for andesitic eruptions, and

TABLE 3. Comparison of the Measured SO₂ Emissions With Petrological Estimates^a

Volcano	Age	Magma	S in Melt Inclusion (ppm)	S in Matrix Glass (ppm)	ΔS (ppm)	Erupted Magma Mass (Mt)	Petrological Estimate of SO ₂ Emission (Mt)	Measured SO ₂ Emission (Mt)	Method	References ^b
				Nonsubdi	uction Z	Zone Volcano	pes			
Explosive eruptions	2000	114	000	210	500	411	0.49	0.10	TOME	1
Некіа Манта Газ	2000	basalt	900	310	590 850	411	0.48	0.10	TOMS	1
Mauna Loa	1984	basalt	1,010	100	850	506	0.80	1.00	TOMS	1
Krana U-1-1-	1984	basalt	1,390	490	1,100	295	0.05	0.40	TOMS	1
Некіа	1980	basalt	910	340	5/0	322	0.37	0.50	TOMS	
Laki	1/83	basalt	1,675	205	1,470	41,525	122*	130	AI	2, 3
D11	024	1 1.	0.150	100	0.050	52 000	220*	28, 66	IC	4, 5
Eldgja	934	basalt	2,150	100	2,050	53,900	220*	110	IC	5, 6
TT 11	1104	1 .	-	10	(1	1.050	0.15	40	IC	4
Hekla	1104	dacite	71	10	61	1,250	0.15	20	IC	4, 7
Effusive eruption	1002 1007	1 1	1 000	250	750	2.070	2.1	1.0	COGDEC	0
Kilauea	1992-1997	basalt	1,000	250	/50	2,079	3.1	4.0	COSPEC	8
				Subduc	tion Zo	ne Volcanoe.	S			
Explosive eruptions										
Chikurachki	1986	basalt	2,900	350	2,550	100	0.51	0.70	TOMS	9, 10
Galunggung	1982-1983	bas-and	200	100	100	550	0.11	0.80	TOMS	9, 11
Agung	1963	bas-and	1,000	70	930	1,625	2.5*	7.0	OD	12
Redoubt	1989-1990	andesite	500	80	420	35	0.021*	0.18	TOMS	9, 13
Ruiz	1985	andesite	700	50	650	70	0.091	0.7	TOMS	9, 14, 15
El Chichón	1982	trach-and	186	156	30	2,900	0.17	7.0	TOMS	7, 16, 17
Bezymianny	1956	andesite	514	47	467	2,500	2.4	7.2	IC	4, 18, 19
Tambora	1815	phonolite	689	290	399	81,000	55*	70	IC	4, 20
Pinatubo	1991	dacite	80	60	20	12,500	0.28*	20	TOMS	9, 21
Mt. St. Helens	1980	dacite	68	25	43	1,150	0.08*	1.0	TOMS	9, 22
Katmai	1912	rhyolite	170	65	105	28,000	2.0*	26	IC	4, 23
Santa Maria	1902	dacite	198	108	90	20,400	3.7	27	IC	4, 18, 19
Krakatau	1885	rhyodacite	200	100	100	28,524	5.6*	38	IC	4, 24
Huaynaputina	1600	dacite	264	80	184	12,500	5	48	IC	25, 26
Mt. St. Helens	1480	dacite	71	38	33	2,300	0.15	15	IC	4, 18, 19
Taupo	181	rhyolite	46	38	8	80,500	1.3	16	IC	4, 18, 19
Minoan	1645 B.C.	rhyodacite	100	35	65	84,000	10.9	125	IC	27, 28
Effusive eruptions										
Arenal	1985 - 1996	bas-and	1,000	100	900	1,240	1.1*	1.3	COSPEC	29, 30
Soufriere Hills	1995 - 1998	andesite	46	70	46	690	0.063	0.70	COSPEC	31
Lascar	1989	andesite	4,400	300	4,100	3.7	0.030	0.54	COSPEC	32, 33
Unzen	1991 - 1994	dacite	220	50	170	400	0.14	0.13	COSPEC	34, 35, 36
Redoubt	1990	dacite	140	60	80	210	0.018*	0.63	COSPEC	37
St. Helens	1980 - 1986	dacite	68	25	43	180	0.015	0.50	COSPEC	22, 38

^aVolcanoes listed as nonsubduction zone volcanoes are all in Iceland except for Mauna Loa and Kilauea, which are in Hawaii. The explosive and effusive eruptions were distinguished on the basis of the SO₂ emission data sources; eruptions measured by the TOMS or ice core records are categorized as "explosive," and the others measured by the ground-based techniques are categorized as "effusive." $\Delta S = (S \text{ in melt inclusion}) - (S \text{ in matrix glass})$, and $\Delta S = S$ in melt inclusion for Soufriere Hills. Petrological estimates of SO₂ emissions were calculated with equation (1) assuming $F_{melt} = 1$, except for the data marked with asterisks, which indicate the value was calculated in the original references considering additional information. Methods are as follows: TOMS, Total Ozone Mapping Spectrometer; AT, atmospheric turbidity measurement; OD, optical depth measurement; IC, ice core analyses; COSPEC, correlation spectrometer.

^bReferences are as follows: 1, Sharma et al. [2004]; 2, Thordarson et al. [1996]; 3, Stothers [1996]; 4, Zielinski [1995]; 5, Hammer et al. [1980]; 6, Thordarson et al. [2001]; 7, Devine et al. [1984]; 8, Sutton et al. [2001]; 9, Bluth et al. [1993]; 10, Gurenko et al. [2005]; 11, de Hoog et al. [2001]; 12, Self and King [1996]; 13, Gerlach et al. [1994]; 14, Sigurdsson et al. [1990a]; 15, Krueger et al. [1990]; 16, Krueger et al. [1995]; 17, Luhr and Logan [2002]; 18, Palais and Sigurdsson [1989]; 19, Scalillet et al. [2003]; 20, Self et al. [2004]; 21, Gerlach et al. [1996]; 22, Gerlach and McGee [1994]; 23, Westrich et al. [1991]; 24, Mandeville et al. [1996]; 25, Costa et al. [2003]; 26, de Silva and Zielinski [1998]; 27, Sigurdsson et al. [1990b]; 28, Hammer et al. [1987]; 29, Williams-Jones et al. [2001]; 30, Streck and Wacaster [2006]; 31, Edmonds et al. [2001]; 32, Andres et al. [1991]; 35, Naktada et al. [1999]; 36, Satoh et al. [2003]; 37, Gerlach et al. [1994]; 38, Swanson et al. [1987].

1 to 10 for basaltic eruptions (Figure 10). Excess degassing by explosive eruption was first quantified for the eruption of El Chichón, Mexico, in 1982, that discharged 7 Mt of SO₂ and 840 Mt of magma [*Bluth et al.*, 1997; *Varekamp et al.*, 1984]; this corresponds to 0.8 wt % SO₂ in bulk magma, exceeding the SO₂ concentrations in melt inclusions (<0.1 wt % SO₂ [*Luhr et al.*, 1984]). The large excess SO₂ degassing estimated for the 1982 El Chichón eruption was first considered to be an unusual example; however, accumulation of TOMS data revealed that such excess SO_2 degassing is in fact a common feature of explosive eruptions, in particular for silicic magmas at subduction zones [*Wallace*, 2001; *Scaillet et al.*, 2003].

[30] Basaltic explosive eruptions at rifts and hot spots do not show significant excess degassing (Figure 10 [*Wallace*, 2001; *Scaillet et al.*, 2003; *Sharma et al.*, 2004]). Basaltic



Figure 10. Comparison of measured and petrological estimates of SO_2 emissions by various eruptions. Data and their sources are listed in Table 3. The solid and dashed lines indicate 1:1 and 10:1 correlation line of the measured versus the petrologically estimated SO_2 emissions.

explosive eruptions at rifts and hot spots are dominated by lava fountain and lava effusion eruptions and are much less explosive than the explosive eruptions at subduction zones, which are Plinian or Vulcanian eruptions. In contrast, an explosive eruption of rhyolitic magma in the rift environment (A.D. 1104 Hekla eruption at Iceland) shows evidence for large excess degassing (Figure 10), suggesting that the absence of excess degassing in basaltic eruptions at rifts and hot spots is not simply due to tectonic setting but caused by the eruption style or the magma composition [*Scaillet et al.*, 2003].

4.1.2. SO₂ Emission by Effusive Eruptions

[31] Effusive eruptions have lower magma and gas emission rates but longer duration than explosive eruptions. Changes in emission rates as well as eruption styles, such as sporadic explosive eruptions, often occur during the long duration of an eruption, and excess degassing during effusive eruptions needs to be evaluated considering these variations. Since volcanic plumes of low-activity effusive eruptions likely remain in the lower troposphere, TOMS does not provide precise emission rates of a small and continuous plume; thus, variations in SO₂ emission rates during effusive eruptions are monitored commonly by repeated ground-based measurements.

[32] Kilauea volcano, Hawaii, is the only quantified example of an effusive eruption at a hot spot, and this example does not indicate excess degassing (Figure 10). Kilauea volcano has erupted effusively for more than 20 years and was monitored for SO₂ and magma emission in detail [*Andres et al.*, 1989; *Sutton et al.*, 2001]. Eruption rates and styles are variable on short time scale, with

activity including lava fountains and continuous low-activity lava effusions, but the annual magma effusion rate and SO_2 emission rate has been almost constant at about 0.1 km³/a and 0.5 Mt/a, respectively. The constant ratio between magma and SO_2 emission rates suggests the absence of excess degassing at Kilauea volcano.

[33] Effusive eruptions at subduction zones show a variable degree of excess degassing but are also associated with different eruption sequences. The eruption of dacitic magma at Unzen volcano was a simple example of a lava dome eruption without major explosive activity and was not associated with excess degassing [Hirabayashi et al., 1995; Nakada et al., 1999; Satoh et al., 2003]. In contrast, significant excess degassing was observed during lava dome eruptions at Mount Saint Helens and Reboubt volcanoes, for example (Table 3). Lava dome eruptions at Mount Saint Helens volcano occurred immediately after the Plinian eruption on 18 May 1980, with the Plinian and lava dome eruptions both showing large excess degassing (Figure 10 [Swanson et al., 1987; Gerlach and McGee, 1994]). A large degree of excess degassing was also observed during Plinian and lava dome eruptions at Redoubt volcano (Table 3), but degassing continued even after the end of lava dome extrusion, discharging an additional 0.18 Mt of SO₂ [Gerlach et al., 1994].

4.2. SO₂ Emission by Persistent Degassing

[34] Intense volcanic gas emission occurs even without magma extrusion, known as persistent degassing (also called passive, quiescent, or noneruptive degassing). Since persistent degassing is associated with little magma discharge, definition of excess degassing is not applicable to this activity in a strict sense. Persistent degassing commonly continues many years, yielding gas emission comparable to large eruptions and evidently requiring degassing of a large amount of magma. Such degassing is also considered as excess degassing of a volcano in a broad sense. Andres and Kasgnoc [1998] listed 49 volcanoes which continuously emit SO₂ with relatively constant activity over the last 25 years (Table 4). These volcanoes exhibit various eruptive activity including Vulcanian, Strombolian, lava dome, and lava flow eruptions as well as persistent degassing without eruption; persistent degassing commonly contributes a majority of the gas emission from these volcanoes. The top 15 volcanoes in Table 4 continuously emit >0.2 Mt/a of SO2, and 10 years of degassing at these volcanoes yields 2 Mt of SO₂, larger than the yield of the 1980 Plinian eruption at Mount Saint Helens (Table 3).

[35] The simplest examples of persistent degassing are continuous and long-term gas emission activity without any eruption, such as at Masaya volcano, Nicaragua, and Satsuma-Iwojima, Japan (Table 4). Masaya volcano is a basaltic volcano that continued to degas since 1993 with only a few minor explosions [*Duffell et al.*, 2003; *Rymer et al.*, 1998]. The constant volcanic gas emission at the rhyolitic dome of Satsuma-Iwojima volcano has been monitored for about 30 years but may have continued for hundreds of years without any magmatic eruption [*Shinohara et al.*, 2002].

Volcano Name Country		Tectonic Setting ^b	Magma Type ^c	Eruptive Activities ^d	SO ₂ Flux (t/d)	
Etna	Italy	?	В	LF, ST, FO	4000	
Bagana	Papua New Guinea	S	А	LD, VU	3300	
Lascar	Chile	S	А	LD, VU	2400	
Ruiz	Colombia	S	А	LD, VU	1900	
Sakurajima	Japan	S	А	VÚ	1900	
Manam	Papua New Guinea	S	В	ST, VU	920	
Yasur	Vanuatu	S	В	ST	900	
Klauea-ERZ	Hawaii	Н	В	LF, FO	800	
Masaya	Nicaragua	S	В	absent	790	
Stromboli	Italy	S	В	ST	730	
Langila	Papua New Guinea	S	BA	ST. VU	690	
Galeras	Colombia	S	А	LD.VU	650	
Fuego	Guatemala	S	В	LF. ST. VU	640	
San Cristobal	Nicaragua	S	D	LD. VU	590	
Satsuma-Iwojima	Japan	S	R	absent	570	
Total	1.				26,200	

TABLE 4. Examples of Continuously Degassing Volcanoes^a

^aModified after Andres and Kasgnoc [1998].

^bTectonic settings are as follows: S, subduction; H, hot spot; ?, tectonic setting of Etna volcano is still a matter of debate [*Doglioni et al.*, 2001]. ^cMagma types are as follows: B, basalt; BA, basaltic andesite; A, andesite; D, dacite; R, rhyolite.

^dEruptive activities are as follows: LF, lava flow; LD, lava dome; FO, lava fountain; ST, Strombolian explosion; VU, Vulcanian explosions.

The largest example of persistent degassing without magma discharge is the gas discharge at Miyakejima volcano, Japan, which discharged 17 Mt of SO₂ during 2000–2003 [*Kazahaya et al.*, 2004] and continues today. Since the intense gas emissions started after major eruptive events in 2000, this example was not included in the compilation by *Andres and Kasgnoc* [1998] (Table 4). The SO₂ emission of 17 Mt requires degassing of 5000 Mt (\sim 2 km³) of magma with 0.17 wt % sulfur concentration in the basaltic melt inclusion [*Saito et al.*, 2005].

[36] Strombolian eruptions are often observed at persistent degassing basaltic volcanoes (Table 4). Each Strombolian eruption is a discrete explosion lasting less than a few minutes, but explosions repeat with regular intervals, and persistent degassing occurs during the intervening periods. At Stromboli volcano, Italy, the typical duration of each explosion was 15 s with a typical frequency of about 13 explosions per hour. The amount of volcanic gases emitted by the explosions is estimated to range from 2 to 45% of total gas emission from the volcano, and the balance (55-98%) is emitted by the persistent degassing [Harris and Ripepe, 2007; Patrick et al., 2007]. Comparison of the total magma and gas emissions during Strombolian activity, including explosions and persistent degassing, indicates a large excess degassing from the volcano. At Stromboli volcano, magma discharge rates during normal Strombolian activity are from 15 to 150 t/d, whereas SO₂ emission rates are about 800 t/d. If the volcanic gases were derived from a magma with 0.3 wt % S (the maximum value measured for primitive basaltic magmas in Italy), the measured volcanic gas emission corresponds to a magma degassing rate of $1.3 \times$ 10^{5} t/d, i.e., degassing of 50–100 km³ of basalt during 5000 years activity of the volcano [Allard et al., 1994].

[37] Lava lake activity is another form of persistent degassing of basaltic volcanoes. Lava lakes are long-lasting surficial reservoirs of molten magmas without an outflow, but they continuously discharge a large amount of heat and gases. Lava lake examples are not listed in Table 4 because their SO₂ emission rates are relatively small, but these are still significant, such as 100 t/d at Erta'Ale volcano, Ethiopia [*Oppenheimer et al.*, 2004], and 50 t/d at Erebus volcano, Antarctica [*Kyle et al.*, 1990], with years to decades of stability. The surfaces of lava lakes are continuously renewed by convective motion, and the magma renewal needs to originate from a large source to maintain the heat and gas discharge at the surface [*Francis et al.*, 1993; *Tazieff*, 1994; *Harris et al.*, 1999].

[38] Vulcanian eruption and lava dome extrusion are commonly observed during persistent degassing at andesitic volcanoes (Table 4). Contribution of persistent degassing to the total gas emission is commonly large compared to emissions by eruptive activity but is also variable depending on the size and frequency of eruptions. Popocatépetl volcano, Mexico, is the largest example of persistent degassing by an andesitic volcano, with repeated lava dome growth and Vulcanian eruptions. The discharge of andesitic magma was estimated to be 3×10^7 m³ (~70 Mt) in 1996–2000, whereas the SO₂ discharge totaled 15 Mt in the same period [Delgado-Granados et al., 2001; Witter et al., 2004]. With an assumption of 0.05 wt % S concentration in the magma, a common concentration in andesitic melt inclusions (Figure 4), the total SO_2 emission requires a magma degassing of 15,000 Mt (~6 km3), i.e., two orders of magnitude larger than the magma output by eruption.

[39] Soufrière Hills volcano, West Indies, showed large excess degassing regardless of eruption style, including lava dome extrusion, Vulcanian eruptions, and persistent degassing (Figure 11 [*Scientific Advisory Committee*, 2007]). The eruption of andesite magma continued since 1995 with three periods of lava dome extrusion interrupted by repose periods of a few years. Emission rate of SO_2 has been nearly constant during all stages, as shown by the good



Figure 11. Cumulative amount of SO_2 and lava emitted from Soufrière Hills volcano, Montserrat (modified after Scientific Advisory Committee [2007]). The thick black curve and red dashed curve are variation of cumulative mount of SO₂ and magma emitted from the volcano since 25 July 1995, respectively. The thin blue dotted line and pink dashed line are averaged SO₂ and magma emission rates, which are 7.3 kg/s (630 t/d) and 2.2 m³/s (450 kt/d), respectively. There were three major lava extrusion periods shown by yellow shaded boxes. Major Vulcanian eruptions are shown also by vertical arrows, associated with a jump in the cumulative SO₂ amount. The Soufrière Hills eruption began on 18 July 1995 and was phreatic until the first appearance of lava on 15 November 1995. SO₂ emission measurements began on 28 July 1995. So strictly speaking, the origins of the two averaged data lines for lava and SO₂ should not be the same. It will make very small difference to the overall picture.

agreement of the cumulative SO_2 curve with the average SO_2 emission rate (Figure 11). Appreciable jumps in the cumulative SO_2 curve were caused by large Vulcanian eruptions, as indicated by vertical arrows on Figure 11, but these jumps are relatively minor in the total SO_2 emission from the volcano. An order of magnitude of excess degassing was estimated for the lava extrusion period (an example is given in Table 3 [*Edmonds et al.*, 2001]), and additional degassing during the persistent degassing period implies that even larger excess degassing occurred during the complete period of activity of the volcano.

5. EXCESS DEGASSING MECHANISMS

[40] Two sources are generally considered to cause excess degassing of a volcano: one is bubbles in erupted magma, and the other is volatile components in unerupted magma. Excess degassing occurs during a variety of eruptive activity, including Plinian, Strombolian, Vulcanian, and lava dome eruptions, as well as by persistent degassing. The excess degassing mechanisms might similarly be variable. For example, Plinian eruptions discharging magmas and gases in a high-speed column cannot be associated with a syneruptive gas supply from unerupted magma [*Wallace*, 2001], whereas volcanic gases emitted with little magma extrusion cannot be derived from erupted magma [*Kazahaya et al.*, 1994; *Edmonds et al.*, 2003]. Two extreme cases of Plinian eruption and persistent degassing will be discussed, then extended to other types of eruption.

5.1. Preeruptive Bubbles in Erupted Magma

[41] A preeruptive gas phase (bubbles) in a magma chamber is considered to be the major source of excess degassing during Plinian eruptions [Wallace, 2001; Scaillet et al., 2003]. The petrological method assumes that all the volcanic gases are derived from volatiles dissolved in the melt, implying that the magma was undersaturated with volatiles at the time of melt inclusion entrapment. However, volatile saturation may occur prior to the melt inclusion entrapment. Melt inclusions then provide a record of volatile concentration in the presence of bubbles and do not represent total concentration of the volatile components in the bubble-bearing magma. Contribution of the preeruptive gas phase (bubbles) to excess degassing was examined in detail for the 1991 Plinian eruption of Mount Pinatubo [Westrich and Gerlach, 1992; Wallace and Gerlach, 1994; Gerlach et al., 1996]. Melt inclusions of this eruption had high H₂O (6.1-6.6 wt %) and CO₂ (280-415 ppm) concentrations, with a corresponding saturation pressure of 250-290 MPa. Since the saturation pressure overlaps with the geophysically and petrologically estimated magma chamber depth of 6-11 km, the melt was saturated with the H₂O-CO₂ gas phase in the magma chamber. Such evidence suggests coexistence with a gas phase (bubbles), and thus the large excess degassing by the Plinian eruption was attributed to contribution of the preeruptive gas phase. On the basis of experimental solubility data, the compositions of the preeruptive gas phase were estimated to be $1-4 \mod \% SO_2$, 80-83 mol % H₂O, and 15 mol % CO₂, with the preeruptive gas contents of 1.3-6.6 wt % relative to magma (Table 2 [Gerlach et al., 1996]).

[42] Various other sources have been examined for the cause of excess degassing by the 1991 eruption of Pinatubo, including evaporation of hydrothermal fluids containing sulfate and breakdown of sulfur-bearing minerals in the magma. Hydrothermal systems and mineral deposits can store a significant amount of sulfur in the form of sulfur, sulfide, and sulfate [Oppenheimer, 1996]. However, conversion of these sulfur species to SO₂ requires specific temperatures and oxygen fugacities that are difficult to achieve during eruptions [Gerlach et al., 1996]. Anhydrite (calcium sulfate) and pyrrhotite (iron sulfide) are relatively common in magmas, and decomposition of these minerals during eruption could potentially contribute to excess sulfur degassing [Devine et al., 1984]. In particular, anhydrite was abundant in dacitic magma of Pinatubo erupted in 1991, corresponding to 0.13-0.48 wt % SO₃ concentration in the whole rock [Bernard et al., 1991]. Andesitic magma of El

Chichón, erupted in 1982, was also associated with large excess degassing; the magma contained abundant anhydrite, corresponding to 1.3 wt % SO₃ concentration in the whole rock [*Luhr et al.*, 1984]. These minerals in the erupted magmas, however, are commonly euhedral (perfect crystals), without a significant reaction rim; therefore, syner-uptive decomposition is unlikely [*Luhr et al.*, 1984; *Bernard et al.*, 1991].

[43] Concentrations of H₂O and CO₂ in melt inclusions indicate that melt inclusions are trapped under gas phase saturated conditions at many volcanoes (Figure 3 [Wallace, 2005]). Experimental studies demonstrate strong sulfur partitioning into the gas phase relative to silicate melt [Scaillet et al., 1998; Keppler, 1999]. On the basis of the experimental data and volatile concentrations measured in melt inclusions, sulfur concentrations in the preeruptive gas phase were calculated for various eruptions to range up to 10 wt %. In order to account for the observed SO₂ emissions, bubble contents in the preeruptive magma were estimated as 5 and 1 wt % for silicic and mafic magmas, respectively [Scaillet et al., 2003; Wallace, 2003]. These estimates indicate that more than 90% of sulfur species in the magma occurs in bubbles prior to eruption of intermediate to silicic magma at subduction zone [Scaillet et al., 2003].

[44] Bubbles are formed either by decompression or crystallization of magma, but vesiculation (bubble formation) itself does not change the bulk volatile content of the magma. Large content of sulfur-rich bubbles in a magma requires either very sulfur-rich original magma or bubble supply from other sources. Since most silicate melt is sulfide saturated (Figure 4), sulfur concentration in a silicate melt supplied to a magma chamber is similar to that in melt inclusions unless the magma experienced significant evolution in composition, temperature, or oxygen fugacity. Therefore, an order of magnitude larger sulfur content in bubbles than in melt inclusions cannot be caused by simple vesiculation (bubble formation) of a magma and requires accumulation of bubbles. Magmas may originally have been bubble bearing when they ascended to the chamber (Figures 12a and 12b). Magma crystallization will increase dissolved volatile concentration in residual melt, eventually causing bubble formation (Figures 12c-12e). Crystallization-induced volatile saturation is likely a common process in a magma chamber as evidenced by variation of H₂O-CO₂ concentration in melt inclusions (Figure 3 [Anderson et al., 1989; Wallace, 2005]). Wallace et al. [1995] compared the concentrations of volatile components, trace elements, and crystals in different eruption units of the Bishop tuff, eastern California, and revealed that the Plinian eruptions occurred from a magma chamber with preeruptive bubble content gradient from less than 2 wt % of the magma in the deeper region to 6 wt % near the magma chamber top. However, magma crystallization itself cannot increase volatile concentration in the bulk magma, and an additional process is necessary to concentrate volatiles in the erupted magmas.

[45] Ascending bubbles in a magma chamber may accumulate to the top to form bubble-rich magma and may cause

Plinian eruptions with excess degassing (Figure 12). In order to accumulate a ten times larger amount of sulfur than originally dissolved in a silicic magma, the exsolved gas phase needs to be supplied either from at least a ten times larger magma body or from a separate sulfur-rich source, such as a basaltic magma (Figure 12). Basaltic magmas typically have a high sulfur concentration (Figure 4) and thus can effectively supply SO₂-rich bubbles. Traces of basaltic magmas are commonly found in the eruption products from silicic magmas, indicating a coexistence of or mingling with basaltic magma in the silicic magma chamber [Bacon, 1986; Eichelberger, 1980; Saito et al., 2001]. Erupted magmas at Pinatubo were mostly dacite; however, traces of basaltic magmas are also present, and this mafic component is considered to have acted as the excess sulfur source as well as provided the eruption trigger [Pallister et al., 1992, 1996].

[46] Supply of SO₂-rich gases from basaltic to dacitic magma is inferred from the occurrence of sulfide and sulfate minerals in 1991 eruption products from Mount Pinatubo [Hattori, 1993, 1996]. Partially decomposed sulfide minerals found in the Pinatubo dacitic and basaltic magmas indicate that the sulfide minerals had been stable in both magmas during an early, reduced stage. Later formation of anhydrite in dacitic magma required subsequent addition of sulfur and oxidation of the magma. The addition of sulfur as well as magma oxidation is likely caused by an influx of SO₂ from the basalt, which also caused accumulation of SO2-rich bubbles in the dacitic magma. Absence of anhydrite in the basalt also suggests that the SO₂ influx to dacitic magma was derived from the basaltic magma. Similar occurrences of sulfide and sulfate minerals in the 1980 El Chichón magmas [Luhr et al., 1984] and 1985 Nevado del Ruiz magmas [Fournelle, 1990] suggest that SO₂ influx is commonly associated with Plinian eruptions and large excess degassing [Hattori, 1993]. Larger excess sulfur degassing was observed for eruptions of more silicic magmas (Figure 10), and this correlation is reasonable if the excess amount of SO₂ was supplied from an underplated basaltic magma.

5.2. Gas Transport From Unerupted Magma

[47] Persistent degassing occurs without magma eruption; therefore, a model for this kind of degassing must explain the mechanism of gas transport from unerupted magma. The large-rate and long-term volcanic gas emission must be derived from a large magma chamber. For example, Sakurajima volcano, Japan, has continued SO2 emission of 2 kt/d for 50 years with total SO₂ emissions corresponding to the degassing of 15 km³ magma with an initial 0.05 wt % S. Estimated depth of a large magma chamber commonly ranges from 5 to 10 km, such as at Sakurajima [Kriswati and Iguchi, 2003], Miyakejima [Ueda et al., 2005], and Soufrière Hills volcanoes [Aspinall et al., 1998; Barclay et al., 1998]. A model of persistent degassing must explain continuous gas transport from a km³-size magma chamber at 5-10 km depth to a degassing vent at the surface. Two models have been proposed: one is based on convecting



Figure 12. Schematic diagrams of bubble accumulation processes in a magma chamber. (a) Magmas supplied from a deep source may be volatile supersaturated at the magma chamber pressure. The bubble-bearing magma, however, will not cause significant excess degassing because volatile concentration in the bulk magma is the same as that in the supplied magma. (b) Bubbles in a chamber will ascend by their buoyancy and be accumulated at the top of the chamber. Eruption of the bubble-accumulated magma will result in significant excess degassing and will leave a large amount of bubble-lost but volatile-saturated magma in the chamber. (c) Crystallization of magmas will concentrate volatile components in the melt, causing volatile saturation (bubble formation). (d) Increase in the volatile concentration by crystallization will be proportional to degree of crystallization. For example, 50 vol % crystallization will double the concentration of the volatile components. (e) Accumulation of bubbles to chamber top will create a bubble-rich magma and volatile-saturated magma will remain in the chamber. (f) Sulfur-rich basaltic magma underplated beneath silicic magmas in a chamber could be a source of SO₂-rich bubbles. (g) Silicic magma with SO₂-rich bubbles transferred from basaltic magma will cause eruptions with excess degassing leaving volatile-saturated basaltic magma in the chamber.

magma column [*Kazahaya et al.*, 1994; *Stevenson and Blake*, 1998], and the other is permeable gas flow though volcanic conduit [*Edmonds et al.*, 2003].

5.2.1. Degassing of a Convecting Magma Column

[48] In convecting magma column model, magma convects through a narrow conduit between a deep magma chamber and a shallow level, where gases escape from the convecting magma (Figure 13). Magma convection occurs because degassing at the top of the magma column increases

the density of the magma, resulting in gravitational instability. Since the gas phase-magma separation occurs at a shallow depth and hence low pressure, most of the volatile components in the magma will escape. The density of degassed magma is larger than nondegassed magma because of the loss of bubbles at low pressure and because of the density increase due to the decrease in dissolved water concentration at high pressure (Figure 13c). The dense degassed magma will sink through a magma column filled



Figure 13. Schematic diagrams of degassing model in a convecting magma column. (a) A cylindrical magma filled conduit with 1-50 m radius connects a deep magma chamber at several km depth to shallow depths. Counterflows of ascending nondegassing magma and descending degassed magma coexist in a narrow conduit, causing continuous supply of nondegassed magma from the chamber and return of degassed magma to the chamber. (b) Ascending magma is water-rich and also bubble bearing above volatile saturation level (green dashed line) and has much less density than water-poor and bubblepoor descending magma. Bubble-rich ascending magma will lose gas phase by permeable gas flow through the bubbly magma at the magma column top and become a degassed magma with increased density; this will sink through a column filled with less dense nondegassed magma. (c) Convection is driven by density difference between nondegassed and degassed magmas. Above the volatile saturation level, large density difference will be created by vesiculation (bubble formation) of nondegassed magma and bubble separation to create degassed magma. The degassed magma has larger density than nondegassed magma even below the volatile saturation level because silicate melt density decreases with water dissolution; therefore the degassed magma will continue to descend until it reaches a physical barrier, likely at the bottom of a magma chamber. Dehydration-induced crystallization will cause solidification of the descending magma, which will slow the magma descent, whereas magma density will increase with solidification, resulting in acceleration of the magma descent.

with less dense nondegassed magma until it reaches a base, likely the bottom of a deep magma chamber. Nondegassed magmas in a chamber ascend, compensating for the descending degassed magmas, creating a nonstop link of degassing and convective transport of magmas between a deep magma chamber and the near-surface top of the magma column. The convecting magma column model assumes insignificant mixing of descending and ascending magmas; significant mixing causes loss of the driving force of the convection. The convecting magma column model can explain the essential features of persistent degassing, long-term continuous discharge of large amounts of volcanic gases without magma discharges. Convective magma flow allows volatile components to travel with the magma from a deep and large chamber for near-surface extraction through a narrow and long magma column. Since convection is driven by degassing near the surface, such convection is a stable process and can continue as long as the magma chamber contains buoyant, nondegassed magmas.

^[49] Lava lakes are direct examples of the convecting magma column degassing. Large amounts of gases and heat are continuously emitted from the lava lake, whose surface is continuously renewed by convective movement of magma [*Tazieff*, 1994]. Thermal energy budgets of lava lakes require the continuous renewal of the lava lake to maintain its molten state, suggesting a convective exchange of magmas between the lava lake and a deeper magma chamber [*Francis et al.*, 1993; *Harris and Stevenson*, 1997].

[50] The composition of volcanic gases emitted during persistent degassing of basaltic volcano indicates that degassing occurs at low pressure, supporting the idea of degassing from a convecting magma column. Volcanic gases emitted during persistent degassing at Villarrica volcanoes have compositions similar to that expected from the difference of the dissolved volatile contents in melt inclusions and matrix glasses, and low-pressure degassing was interpreted to be the source of the volcanic gas [Shinohara and Witter, 2005]. Contrasting gas compositions were measured by FTIR at Stromboli during persistent degassing and intermittent Strombolian eruptions. Gases emitted during eruptions are CO₂-rich, that is, equilibrated at high pressure (70-80 MPa), whereas gases emitted during persistent degassing are CO₂-poor with equilibrium pressure of $\leq 0.3-4$ MPa (Table 2 [Burton et al., 2007a]).

Similar contrast in gas compositions was observed also during persistent degassing and gas-pistoning activity at Kilauea volcano [*Edmonds and Gerlach*, 2007]. Those examples indicate that bubble rise from a deep source may cause Strombolian or gas-pistoning activity but persistent degassing needs to be caused by gases that escaped from magma at low pressure.

[51] The rate of volcanic gas discharge from a convecting magma column can be calculated on the basis of a fluid dynamic model of volumetric magma flow through a conduit [*Kazahaya et al.*, 1994; *Stevenson and Blake*, 1998]. On the basis of laboratory observations of overturning fluids, the magma upflow rate (=downflow rate, *Q*) of concentric counterflows with an inside upflow and an outside downflow through a pipe (conduit) is expressed as follows [*Stevenson and Blake*, 1998]:

$$Q = \pi (R^*)^2 \operatorname{Ps}(g\Delta\rho R^4/\mu_d), \qquad (2)$$

where *R* is the conduit radius, Ps is a Poiseulle number, *R** is a ratio of the upflow radius to the conduit radius, *g* is the acceleration due to gravity, $\Delta \rho$ is density difference between nondegassed and degassed magmas, and μ_d is viscosity of the descending degassed magma. The Poiseulle number (Ps) is a parameterize terminal velocity of the ascending flow (*v*) given by the following equation as a function of a viscosity ratio of descending and ascending flows (μ_d/μ_c) and *R**:

$$\mathbf{Ps} = v\mu_d / (g\Delta\rho R^2) = f(\mu_d / \mu_c, R^*).$$
(3)

[52] The Ps and R^* were determined by laboratory experiments as 0.064 and 0.6, respectively, at $\mu_d/\mu_c > 12$. This fluid dynamic model reveals that magmas can flow rapidly enough to cause volcanic gas discharges with the observed rate. If we assume a basaltic magma with μ_c = 10 Pa s, $\mu_d/\mu_c = 100$, and $\Delta \rho = 50$ kg/m³, we can calculate that a 3 m radius conduit can allow counterflows with a flow rate of 5×10^3 kg/s (1.5×10^5 m/d); this can cause the observed discharge of 800 t/d SO₂ at Stromboli volcano by degassing of magmas with an initial concentration of 0.1 wt % sulfur. Magma viscosities and density difference used in this calculation are obtained for bubble-free magmas; therefore it is applicable to magma flow below the vesiculation level (Figure 13c). Above the vesiculation level, magma density difference will become larger at lower pressure because of larger bubble content in nondegassed magma than in degassed magma, and that will accelerate magma convection. Magma viscosity, however, increases with magma ascent because of water content decrease, bubble content increase, and dehydration-driven crystallization, causing slowdown of magma flow. Magma density and viscosity also vary with crystallization kinetics, bubble deformation, or bubble separation from magma [Blundy and Cashman, 2005; Llewellin and Manga, 2005; Burton et al., 2007b], and their effects on the magma convection are not yet quantified.

[53] Persistent degassing commonly occurs at volcanoes with low-viscosity basaltic magmas but is also common with more viscous andesitic magmas. Persistent degassing is observed even at dacitic and rhyolitic volcanoes with much more viscous magmas, but the number of examples is small (Table 4). Conduit convection of silicic magmas is controversial because their large viscosities, up to several orders of magnitude larger than basaltic magmas, will slow the magma flow. The small number of examples of persistent degassing at dacitic and rhyolitic volcanoes can be due to the difficulty of magma convection with viscous silicic magmas. Conduit of silicic magmas, however, is commonly considered to have a larger radius than that of basaltic magma [Stevenson and Blake, 1998]. A larger conduit radius may compensate for the larger viscosities because magma flow rate is proportional to the fourth power of the conduit radius (equation (2)). However, conduit geometry is not yet well quantified for each volcano, and validity of conduit magma convection at silicic volcanoes must be examined also considering other constraints such as magma degassing pressure estimated from compositions of volcanic gases and dissolved volatiles.

[54] Satsuma-Iwojima volcano is a unique example of persistent degassing from rhyolitic magma and is also unique for its low volatile content in melt inclusions $(H_2O = 1.4 \text{ wt }\%, CO_2 = 140 \text{ ppm})$ and high temperature of the rhyolitic magma (~1000°C) estimated by petrological study [Saito et al., 2001]. Gas saturation pressure of the melt is 50 MPa, implying that gas phase forms only at a shallow depth (<2 km). The H₂O/CO₂ mole ratio of volcanic gas (~250, Table 2 [Shinohara et al., 2002]) is almost identical to the ratio of dissolved volatiles (~250 [Saito et al., 2001]), and the good agreement requires almost complete discharge of the dissolved H₂O and CO₂ at near-atmospheric pressure to account for the observed volcanic gas composition. The low-pressure degassing is consistent with the idea that it occurs at the top of a convecting magma column [Kazahaya et al., 2002]. To account for 600 t/d of SO2 emitted from the volcano, the necessary conduit radius is estimated with equation (2) to be 25 m for the high-temperature rhyolite with $\mu_d = 10^6$ Pa s, $\Delta \rho = 50$ kg/m³, and 0.01 wt % of sulfur. The high temperature and low water content of the Satsuma-Iwojima rhyolite provide a favorable condition for conduit magma convection because of lower magma viscosity and lower degree of dehydration-driven crystallization than common rhyolites. These conditions might be the cause of the unique occurrence of persistent degassing from rhyolitic magma at Satsuma-Iwojima volcano. Comparison of volcanic gas composition and dissolved volatiles in melt inclusion provide a constraint of degassing conditions; however, such quantitative comparisons are not yet performed at other persistently degassing silicic volcanoes, and validity of the conduit magma convection model at other andesitic or dacitic volcanoes must be examined with future studies of volcanic gases and melt inclusions.

5.2.2. Permeable Gas Flow Model

[55] A gas phase may ascend by permeable flow through a volcanic conduit connecting a deep magma chamber to the

surface. Volcanic conduits may have a higher permeability than the surroundings because of high concentrations of bubbles and fractures and may provide the permeable gas flow path connecting a deep magma chamber to the surface. Permeable gas flow is considered for a variety of volcanic processes, including gas loss from ascending magma [Melnik and Sparks, 1999; Gonnermann and Manga, 2007], gas phase migration in a magma chamber [Candela, 1994; Bachmann and Bergantz, 2006], and hydrothermal fluid circulation caused by a cooling magma chamber [Cathles, 1977; Shinohara and Kazahaya, 1995]. Such flow through a volcanic conduit has been implicitly assumed in physical models of volcanic gas emissions [e.g., Chiodini et al., 1993; Fischer et al., 1996]; however, an explicit model of gas transport from a deep magma chamber to a vent has only recently been proposed for Soufrière Hills volcano [Edmonds et al., 2003].

[56] At Soufrière Hills volcano, excess degassing is thought to be caused by transport of a SO₂-rich gas from a basaltic magma chamber by permeable gas flow through a volcanic conduit (Figure 14 [*Edmonds et al.*, 2003]). The large amount of SO₂-rich gases cannot be supplied by the erupted andesitic magma with low-S content and was attributed to an unerupted basaltic magma at a 5-7 km depth. Since large excess SO₂ degassing was observed both during lava dome eruption and the eruption repose period (Figures 7 and 8), permeability of the volcanic conduit and the SO₂-rich gas supply from the basaltic magma is assumed to be similar whether or not it was erupting [*Edmonds et al.*, 2003].

[57] The permeability necessary to cause the observed gas emission rates at Soufrière Hills volcano was calculated to be on the order of 10^{-9} to 10^{-12} m² for a gas flow through a conduit of 1000 m² cross-sectional area driven by lithostatic pressure gradient [Edmonds et al., 2003]. The calculated permeability range overlaps with the upper end of measured values for volcanic rocks $(10^{-11} \text{ to } 10^{-14} \text{ m}^2)$ [Melnik and Sparks, 2002; Gonnermann and Manga, 2007]), and the agreement indicates validity of the permeable gas flow model at a shallow region. The volcanic rocks, however, are surface samples which do not necessarily represent permeability at depth. Permeability of volcanic conduit likely decreases with depth because porosity, and therefore permeability, of ascending molten magma decreases with depth [Melnik and Sparks, 1999], and permeability of geological formation commonly increases with depth, in particular at depth larger than 1 km [Saar and Manga, 2004]. The permeable gas flow model must be tested for its efficiency at a deep region (5-10 km) with quantitative estimates of volcanic conduit permeability at the depth.

[58] The gas phase supplied to the permeable conduit consists of the exsolved gas species at a magma chamber depth (5–10 km). Therefore, composition of volcanic gas supplied by the permeable gas flow must be distinct from the gases emitted at low pressure from the convecting magma column, in particular for the CO_2/H_2O ratio because of their contrasting solubility (Figures 1 and 2). The

comparison of compositions of the volcanic gases and melt inclusions at Stromboli, Villarrica, and Satsuma-Iwojima volcanoes indicate low-pressure source for the persistent degassing, consistent with the conduit magma convection model (Table 2 [Kazahaya et al., 2004; Shinohara and Witter, 2005; Burton et al., 2007a]). However, data on volcanic gas and melt inclusion compositions are not yet available at persistently degassing andesitic volcanoes, such as at Soufrière Hills volcano, and we need comparison of those data to confirm the high-pressure degassing inferred from the permeable gas flow model.

5.3. Excess Degassing Mechanisms During Various Eruptive Styles

[59] Three mechanisms have been proposed as the source of excess degassing for the two extreme cases, Plinian eruption and persistent degassing. These mechanisms are not necessarily exclusive of each other, and multiple mechanisms may contribute in some cases. Persistent degassing occurs in close association with Strombolian, Vulcanian, and lava dome eruptions; here the interplay of the degassing mechanisms with these eruption processes is discussed.

[60] Bubbles accumulated in a magma chamber, that is, responsible for excess degassing during Plinian eruptions, can also contribute to excess degassing during other type of eruptions. Lava dome eruptions immediately after Plinian eruptions, such as at Mount Saint Helens and Redoubt volcanoes, were accompanied by large excess degassing, similar to that observed during the earlier Plinian activity (Table 3 [Gerlach and McGee, 1994; Gerlach et al., 1994]). Magmas emitted by lava dome eruptions are derived from a magma chamber remnant from the explosive activity, which may yet contain accumulated bubbles responsible for the excess degassing during subsequent lava dome eruptions. However, additional sources of degassing are also required at Redoubt volcano, where persistent degassing continued long after the end of lava dome extrusions [Gerlach et al., 1994]. Persistent degassing after eruption indicates either degassing of a convecting magma column or permeable gas flow from a magma chamber occurred simultaneously with or subsequent to the lava dome eruption.

[61] Vulcanian eruption commonly occurs at persistently degassing andesitic or dacitic volcanoes, where transition between these activity and lava dome eruption is also common, such as at Soufrière Hills [Edmonds et al., 2003], Galeras [Zapata et al., 1997], Sakurajima [Hirabayashi et al., 1986], Lascar [Matthews et al., 1997], and Popocatépetl [Witter et al., 2005] volcanoes. In the permeable gas flow model, the SO₂ emission during repetition of persistent degassing and lava dome extrusions is attributed to a continuous SO₂-rich gas supply from deep-seated basalt magma though a permeable conduit (Figure 14a [Edmonds et al., 2003]). The long-term near-constant SO₂ emission rate implies that permeability of the volcanic conduit is nearly constant during dome extrusion and persistent degassing (Figure 11). In contrast, permeability change due to hydrothermal mineral precipitation and opening/ closure of fracture and bubble networks is proposed to



Figure 14. Schematic diagrams of excess degassing mechanisms during lava dome extrusions. (a) Permeable gas flow model [*Edmonds et al.*, 2003]. The SO₂-rich gases derived from a mafic magma at depth ascend through a permeable volcanic conduit to the surface. Variation of SO₂ emission rate is controlled by changes in volcanic conduit permeability through magma cooling, sealing by hydrothermal mineral precipitation, and closure of fractures and bubble networks. (b) Convecting magma column model. Volcanic gases are continuously supplied by the magma convection in a volcanic conduit, and the SO₂ emission rate is controlled by the convection rate. When the top of the convecting magma reaches the surface, the degassed magma flows out from the conduit resulting in lava extrusion.

cause short-term variation of SO₂ emission rate and pressure accumulation at the upper part of the volcanic conduit causing Vulcanian explosions [*Edmonds et al.*, 2003].

[62] The repetition of persistent degassing and lava dome extrusions with excess degassing can be explained also on the basis of a convective magma column degassing model (Figure 14b). The convecting magma column model assumes that all the degassed magma produced at the top of the magma column descends back to the magma chamber (Figure 13). When the top of the convecting magma column reaches the surface, part of the degassed magma can flow out from the conduit to form lava domes or flows (Figure 14b). In this model, the near-constant SO₂ emission rate implies a near-constant magma convection rate, whereas the variable lava extrusion rates reflect changes in magma column height, likely controlled by a magma chamber overpressure. At the top of the convecting magma column, blockade of continuous overturn of degassed and nondegassed magmas will cause pressure accumulation beneath degassed magma because of the ascending bubble-rich magma and may result in Vulcanian explosions. Further tests of the two models are necessary to draw conclusions about the persistent degassing mechanism at andesitic and dacitic volcanoes; it is also important to understand eruption processes of the lava dome and Vulcanian eruptions.

[63] Strombolian eruptions commonly occur during persistent degassing at basaltic volcanoes. For example, at Stromboli volcano, Strombolian explosions occur almost every 5 minutes with typical durations of 15 s, and continuous degassing occurs during rest of the time [Harris and Ripepe, 2007; Patrick et al., 2007]. The rapid transition from persistent degassing to Strombolian explosions implies that the large bubbles ascend through the convecting magma column. The origin of the large bubbles, their behavior and ability to activate seismic signals, and diversity of petrological features of erupted magmas have been studied assuming a stagnant magma column [Jaupart and Vergniolle, 1988; Ripepe et al., 2001; Lautze and Houghton, 2005] or an ascending magma [Parfitt, 2004]. A magma column accommodating Strombolian eruptions, however, is convecting in many cases, and consideration of counterflows in the convecting magma column may alter the implications of the previous studies.

5.4. Degassed Magma Chamber

[64] Excess degassing produces a large amount of degassed magmas, which have less potential for future eruptions and likely solidify in the crust to form intrusive magma bodies (plutons). Degassed magmas produced by degassing of a convecting magma column will solidify as intrusive magma bodies soon after their return to a deep magma chamber because their low water concentration causes dehydration-driven crystallization [Blundy and Cashman, 2005], and they have little potential to cause future eruptions. Degassing of a convecting magma column is not only a mechanism of continuous volcanic gas discharge but also of continuous creation of large intrusive magma bodies beneath volcanoes (i.e., endogenous or cryptic growth of volcanoes [Francis et al., 1993]). The density increase caused by degassing results in a measurable gravity increase over scales of tens of kilometers, as observed at Sakurajima and possibly at Etna volcanoes [Locke et al., 2003]. Accumulation of the crystallized magma beneath volcanoes will result in a dense body with high seismic velocity, consistent with high-velocity zones indicated by seismic tomography or dense bodies suggested by gravity studies [De Luca et al., 1997].

[65] An eruption of bubble-accumulated magma removes only the exsolved volatiles from the unerupted magma (Figure 12), and the unerupted magma in a chamber still maintains its dissolved volatiles at their saturation concentrations as a driving force for future eruptions. The unerupted magma, however, cannot cause excess degassing by future eruption without additional volatile sources. Volatile addition to the unerupted degassed magma is a possible process, but it produced an even larger amount of unerupted degassed magma. Therefore, in average, unerupted degassed magma is solidified as intrusive magma bodies; thus, excess degassing should be accompanied by formation of large intrusive magma bodies.

[66] Solidification and degassing processes of magma chambers control the petrological diversity of plutonic rocks and the evolution of magmatic hydrothermal systems [*Candela*, 1994; *Shinohara and Kazahaya*, 1995; *Marsh*, 2000]. Magmas degassed by convective magma column degassing contain low concentrations of volatiles and cannot be the volatile source of a magmatic hydrothermal system. The degassed magma is still hot and can drive a hydrothermal system dominated by meteoric water [*Cathles*, 1977]. In contrast, magmas degassed by bubble removal in a chamber still contain most of their original H₂O concentration and can create magmatic water-dominated hydrothermal systems, closely related to ore mineralization [*Hedenquist and Lowenstern*, 1994].

[67] The amount of the intrusive magma must be larger than the erupted magma at subduction zone volcanoes, as their eruption commonly results in excess degassing. Comparison of the erupted and intruded magma volumes estimated from geological and geophysical evaluation of crustal structures indicates that only 10-20% of the magmas supplied to the upper crust have erupted, with the balance of the magmas solidified in the crust [*Crisp*, 1984; *Fisher*]

and Schmincke, 1984; White et al., 2006]. The intrusive/ extrusive volume ratio varies depending on tectonic setting: about 10:1 at subduction zones, 5:1 at oceanic hot spots, and 6:1 at ocean ridges [*Crisp*, 1984]. Since the geologically estimated ratio represents the results of a long history, integration of the gas emission data in time and space is necessary to compare with the geological estimate, as discussed in section 6.

6. GLOBAL DEGASSING RATE

[68] The global emission rate of volcanic gases is important to evaluate their time and space-integrated effect not only on the crustal evolution but also on the global environment [Berresheim and Jaeschke, 1983; Graf et al., 1997]. Volcanic gas emissions, in particular SO₂, have significant effects on climate and atmospheric chemistry [Robock, 2000]. Sulfur dioxide injected into stratosphere by Plinian eruptions has a long residence time and will be converted to sulfate aerosols, which scatter solar radiation and cause cooling at the Earth's surface [Bluth et al., 1997]. Volcanic eruptions are by far the largest contributor to stratospheric sulfate aerosols [Pyle et al., 1996]. In contrast, less violent eruptions, such as Hawaiian, lava flows, or lava dome, as well as persistent degassing, cause a continuous addition to the troposphere, resulting in near-surface environmental effects [Andres and Kasgnoc, 1998]. In order to evaluate these two effects separately, we must distinguish the global emission rates of explosive eruptions and continuous degassing.

6.1. Global SO₂ Emissions by Explosive Eruptions

[69] The TOMS instruments have provided almost continuous daily coverage of global volcanic activity since 1978 (Figure 9). During 1978–2001, TOMS detected 141 eruptive events with SO₂ emissions, which include 100% of volcanic explosivity index (VEI) > 4 eruptions and 60% of VEI = 3 eruptions [*Carn et al.*, 2003]. VEI is a logarithmic scale of explosive eruptions based on both magnitude (erupted volume) and intensity (eruption column height) information [*Newhall and Self*, 1982]. The magnitude portion of VEI (*k*) is described as follows [*Pyle et al.*, 1996]:

$$k = (\log_{10} M) - 4, \tag{4}$$

where *M* is erupted magma volume (m^3) and *k* is equal to VEI for explosive eruptions with a large eruption column. This index has been adopted by the Smithsonian Institute in their compilations of past volcanic eruptions and is widely used [*Simkin and Siebert*, 1994]. This index is practical for explosive eruptions but is not useful for effusive eruptions whose eruption column height is small, resulting in a small VEI even for a large eruption volume.

[70] Bluth et al. [1993] estimated an annual rate of global SO_2 emission from explosive eruptions as 3.7 Mt/a, with a 70% contribution from subduction zone volcanoes, on the basis of a compilation of TOMS data during 1978–1992. In contrast, the average annual SO_2 emissions detected by

TABLE 5. Annual Flux of Volcan	ic SO_2^a
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Activity	Method	Year	Arc Volcanoes	Nonarc Volcanoes	References ^b
Global flux					
Explosive eruptions	TOMS	1974 - 1994	2.6	1.1	1
A A	TOMS	1996-2001	0.1	0.7	2
	VEI-SO ₂ relation	(4 < VEI < 6)	0.9°		3
Continuous degassing	COSPEC	· /	9.2	0.5	4
Continuous degassing activities					
Popocatépetl volcano, Mexico		1994 - 2005	2.0		5
Miyakejima volcano, Japan		2000 - 2007	2.8		6, 7

^aUnit is Mt/a. TOMS, Total Zone Mapping Spectrometer; VEI, volcanic explosivity index; COSPEC, correlation spectrometer.

^bReferences are as follows: 1, *Bluth et al.* [1993, 1997]; 2, *Carn* [2003]; 3, *Pyle et al.* [1996]; 4, *Andres and Kasgnoc* [1998]; 5, *Witter et al.* [2005]; 6, *Kazahaya et al.* [2004]; 7, Japan Meteorology Agency Web site (http://www.seisvol.kishou.go.jp/tokyo/320_Miyakejima/320_So2emission.htm).

^cSum of the fluxes from arc and nonarc volcanoes.

TOMS in 1996–2001 was 0.8 Mt/a, with a contribution by subduction zone volcanoes of only 15% (Table 5 [*Carn et al.*, 2003]). The large difference between these two estimates is caused by the heterogeneous occurrence of eruptions over time. During 1978–1992, the total SO₂ emission was 52 Mt, of which more than half was emitted by two eruptions: Pinatubo volcano in 1991 (20 Mt) and El Chichón in 1982 (7 Mt). Since the frequency of larger eruptions is smaller, we need to estimate a time-averaged SO₂ emission rate, considering contributions from large but less frequent eruptions.

[71] The time-averaged frequency of past eruptions was estimated on the basis of a comprehensive survey of past volcanic eruptions with an eruption-size scale of VEI [*Simkin and Siebert*, 1994]. Frequency of explosive eruptions is known to follow a power law distribution with the following relationship (Figure 15a [*Simkin*, 1993; *Pyle et al.*, 1996]):

$$\log_{10} \lambda = 2.83 - 0.79k, \tag{5}$$

where λ is the number of eruptions with a magnitude between *k* and *k* + 1 per year (equation (4)). The intercept and slope of the regression line vary about ±10% depending on duration of the data set (Figure 15a [*Pyle et al.*, 1996]). On the basis of this relationship, a Pinatubo-class eruption (VEI = 6) is expected to occur only once in every 100 years; therefore, including the 1991 Pinatubo eruption in the 14 year sum of SO₂ emissions caused an overestimate of the average value.



Figure 15. Correlation between (a) frequency and magnitude of eruptions over the past 200 years and (b) average SO₂ yields and magnitude of eruptions, reprinted from *Pyle et al.* [1996] with kind permission of Springer Science and Business Media. In Figure 15a, eruption rates of volcanic explosivity index (VEI) = 2 and 3 for the decade 1975–1985 [*McClelland et al.*, 1989] are assumed to be representative of volcanic activity over the past 200 years; 50- and 200-year averaged rates were adopted for VEI = 4 and 5 eruptions [cf. *Simkin*, 1993]. Recurrence rates of VEI = 6 eruptions (200- and 500-year average) [*Simkin and Siebert*, 1994] are shown for reference but were not included in the regression. Figure 15b shows data from the TOMS database [*Bluth et al.*, 1993]. Because TOMS cannot sample all eruptions of VEI = 3 [*Bluth et al.*, 1993; *Krueger et al.*, 1995], only eruptions of VEI = 4–6 were included. However, extrapolation to VEI = 3 does not significantly underestimate the SO₂ yields per event. Small dots are raw data from the TOMS database, and large dots show averaged value at a given eruption magnitude. Error bars show ± 0.5 log unit error, which covers 70% of spread of the data.

[72] The SO₂ yields by eruptions increase with eruption magnitude (Figure 15b [*Pyle et al.*, 1996]):

$$\log_{10} F_{\rm SO2} = 0.75k - 0.21,\tag{6}$$

where F_{SO2} is the SO₂ yield (kt). The SO₂ yields span a wide range for eruptions of a given magnitude. If we allow a ±0.5 log unit error for SO₂ yields for a given magnitude of eruption, this accounts for 70% of spread of the data as shown by the error bars on Figure 15b. On the basis of equations (5) and (6), the annual SO₂ emission for each eruption size can be obtained. *Pyle et al.* [1996] estimated an annual SO₂ loading to stratosphere as 0.9 Mt by considering all eruptions of $4 \le \text{VEI} \le 6$ and 25% of VEI = 3 eruptions. If we also include all VEI = 3 and VEI = 7 eruptions in order to estimate an average SO₂ emission, the annual SO₂ emission amounts to 1.3 Mt. Both estimates are in the middle of the two averages of TOMS data from 1978 to 1992 (3.7 Mt/a) and 1996 to 2001 (0.8 Mt/a).

[73] Equation (6) implies that the average SO₂ concentration in erupted magmas is smaller for eruptions with larger magnitude. Assuming magma density of 2500 kg/m³, we can estimate that the average SO₂ concentrations in magmas are 800, 1400, and 2500 ppm for eruptions of VEI = 6, 5, and 4, respectively. This dependence is consistent with the trend showing that smaller eruptions appear to have a greater excess of SO₂ than larger eruptions [*Wallace*, 2001]. Greater excess of SO₂ might imply a larger contribution of preeruptive gas phase accumulated in the upper part of a magma chamber, either due to a relatively fixed amount of bubble-rich magmas or due to a larger degree of bubble accumulation necessary to initiate a smaller eruption [*Wallace*, 2001].

[74] The regression lines given by equations (5) and (6) were obtained for subaerial eruptions in all types of tectonic settings, including subduction zones, rifts, and hot spots (Figure 12), although this compilation is dominated by subduction zone volcanoes; therefore the average SO_2 emission rate obtained from equations (5) and (6) likely underestimates the contribution from nonsubduction zone volcanoes. Out of 122 VEI \geq 4 eruptions between 1500 and 1980, only 16 eruptions were reported for nonsubduction zone volcanoes, including 12 eruptions in Iceland [Newhall and Self, 1982, Table 4]. Therefore, the frequency magnitude relationship expressed by equation (5) is dominated by that of subduction zone volcanoes. The dominance of explosive eruptions at subduction zones is not due to the difference in magma production rate because magma output rates at subduction zone volcanoes and oceanic intraplate volcanoes are comparable, at 0.4–0.6 and 0.3–0.4 km³/a, respectively [Crisp, 1984]. Since the VEI is an index of explosivity but not eruption volume, the VEI undervalues the contribution of eruptions at divergent plate boundaries and hot spots, which are dominated by effusive eruptions.

[75] The relationship between the eruption magnitude and SO₂ yield was also obtained with TOMS data for eruptions only of subduction zone volcanoes (Figure 15b). *Pyle et al.*

[1996] compiled TOMS data of VEI \geq 4 eruptions during 1979-1993; all eruptions occurred at subduction zone volcanoes. Eruptions at rift or hot spot volcanoes yield larger amounts of SO₂ than from similar magnitude eruptions at subduction zone volcanoes [Bluth et al., 1993], but the eruption magnitudes and SO₂ yields are poorly correlated [Stoiber et al., 1987; Schnetzler et al., 1997]. The TOMS data indicate that annual SO₂ emission rates of large eruptions at nonsubduction zone volcanoes are 1.1 and 0.7 Mt/a in 1974-1994 and 1996-2001, respectively [Bluth et al., 1993; Carn et al., 2003]. The average values are based on a short-period data set but indicate that SO₂ emissions by large eruptions at divergent plate boundaries and hot spots are comparable to the emissions from subduction zones (Table 5). Degassing activity of nonsubduction zone volcanoes is quite localized. The SO₂ emissions are recorded only from volcanoes in Hawaii, Nyamuragira, Iceland, and Galapagos (Figure 9).

6.2. Global SO₂ Emission by Continuous Degassing

[76] Estimates of SO₂ emission rates by continuous degassing are obtained by repeated ground-based measurements at individual volcanoes. Ideally, the global SO₂ emission rate is based on a time-averaged compilation of SO₂ emission data from all degassing volcanoes; however, this is limited by existing data, which are biased to volcanoes in more populated regions. In order to include all existing SO₂ data, published references and personal communication was used [*Andres and Kasgnoc*, 1998; *Stoiber et al.*, 1987]. *Andres and Kasgnoc* [1998] compiled 49 continuously degassing volcanoes and 25 sporadically degassing volcanoes, with a global SO₂ emission rate of 9.7 Mt/a (Table 5).

[77] The compiled data indicate that continuous emissions of SO₂ are dominated by subduction zone volcanoes (Table 5), with 9.2 Mt/a of SO₂ out of the total of 9.7 Mt/a. In contrast, SO_2 emission from rifts and hot spots listed by Andres and Kasgnoc [1998] was almost completely due to emissions from Kilauea volcano, which emits 0.5 Mt/a of SO₂. Other listed volcanoes were Erebus volcano, Antarctica (0.03 Mt/a), Erta'Ale volcano, Ethiopia (0.008 Mt/a), and Ol Donyo Lengai carbonatite volcano, Kenya (0.006 Mt/a). Lava lake activity are also common at Nyamuragira and Nyiragongo volcanoes [Tazieff, 1994], which emit large amounts of SO₂ during large eruptions as well as by continuous degassing from the lava lake and effusive lavas; however, their emission rates were not measured in sufficient detail to allow a quantitative evaluation [Carn and Bluth, 2003]. Other volcanoes at nonsubduction zones with large magma eruption rates, such as at Iceland, Galapagos, and Reunion, do not show intense continuous degassing activity.

[78] In subduction zones, SO₂ emission by continuous degassing (9.2 Mt/a) is ten times larger than by explosive eruptions (\sim 1 Mt/a; Table 5). The larger SO₂ emission associated with continuous degassing but with little magma eruption implies a large production rate of intrusive magmas; this is consistent with a large intrusive/extrusive

magma volume ratio of about 10:1 [Crisp, 1984; White et al., 2006]. Although the ratio of explosive/continuous SO_2 emission rates apparently agrees with the geologically estimated intrusive/extrusive magma volume ratio, direct comparison of these ratios is too simplistic because explosive eruptions at subduction zone volcanoes are accompanied by a large degree of excess degassing, in particular of silicic volcanoes (Figures 10 and 12). If the excess SO_2 is supplied from unerupted silicic magma, the excess degassing during explosive eruptions also causes a large intrusive/ extrusive magma volume ratio that results in a much larger ratio than the geologically estimated ratio that is suggested from the SO₂ emission data. In contrast, SO₂-rich gas supply from S-rich basaltic magma does not require a large intrusive/extrusive magma volume ratio for explosive eruptions, and a total intrusive/extrusive magma volume ratio including contribution of continuous degassing may result in a similar number with the geologically estimated ratio. In this case, unerupted magma is dominated by basalt and andesite, as continuous degassing is dominated by basaltic and andesitic volcanoes (Table 4). This estimate, however, does not agree with the view that an averaged chemical composition of the upper crust at young subduction zones is andesitic to dacitic [Taylor and McLennan, 1995; Togashi et al., 2000]. Quantification of the contribution of magmas with different composition to excess degassing is necessary not only to understand the origin of excess degassing but also to understand the crustal growth process.

[79] Volcanoes at rift and hot spots do not show excess degassing, either during large eruptions or due to continuous degassing; the lack of excess degassing appears to indicate little degassing from unerupted magma, implying the absence of intrusive activity. Intrusive to extrusive volume ratios at Iceland and Hawaii are estimated as 1:1 to 8:1, on the basis of a geological and geophysical evaluation of crustal structure [Crisp, 1984; White et al., 2006]. The small but still significant ratios contradict the observed lack of excess degassing. The lack of excess degassing could be due to a lack of SO₂ measurements during excess degassing periods. On the basis of ground deformation study, magma supply rate to Kilauea volcano was estimated to be constant for 1961-1992 at 0.18 km³/a, whereas eruption rates were variable from almost zero in 1976-1982 to 0.1 km³/a in 1983-1997, implying that intrusive activity was minor in 1983-1997 but was significant in 1976–1982; the lack of excess degassing was estimated on the basis of systematic SO₂ measurements starting from 1979 [Cayol et al., 2000; Sutton et al., 2001]. In order to evaluate the excess degassing of a volcano, we may require a data set for a longer period of time to cover the long-term variation of activity.

[80] The global estimate for continuously degassing volcances is limited by the existing data set, and the present compilation provides only a minimum estimate. In contrast to localized activity at rifts and hot spots, there are many more volcances associated with subduction zones. The global emission rate is controlled mainly by contributions from a few volcances. The top five volcances listed in Table 4 yield more than half of the global emissions. Therefore, lack of data for a few large degassing volcanoes will result in a large underestimate. For example, two large emissions were reported after publication of the compilation by Andres and Kasgnoc [1998]: Popocatépetl volcano, Mexico, discharged 20 Mt SO₂ during 1994–2005 [Witter et al., 2005], and Miyakejima volcano, Japan, discharged 20 Mt SO₂ in 2000-2007 [Kazahaya et al., 2004; Japan Meteorology Agency Web site, http://www.seisvol.kishou. go.jp/tokyo/320_Miyakejima/320_So2emission.htm]. Considering a few other possibly large contributions from Ambrym volcano, Vanuatu [Bani et al., 2008], and Nyamuragira and Nyiragongo volcanoes, Congo [Carn et al., 2003; Carn, 2003], global SO₂ emissions by continuously degassing may be double the present estimate. A new satellite sensor, OMI, can quantify SO₂ emission from continuously degassing volcanoes to the lower troposphere [Krotkov et al., 2006], and its daily and global coverage of degassing activity will largely improve the global estimate in the near future.

[81] The present evaluation of global emission rate is based only on SO₂ emission rate from summit craters, but magmatic gas components are also discharged by diffuse emission of soil gas, hot spring, and groundwater. Waters in volcanic edifice dissolve magmatic gases, resulting in reduction of emission rate from summit craters [Symonds et al., 2001]. But magmatic gas entrapment by waters effectively occurs at low gas emission rate [Symonds et al., 2001]; the large SO₂ emission rates from summit crater, as listed in Table 4, are less likely be affected by the entrapment process. Diffuse emission of magmatic gas components is also observed at apparently dormant volcanoes such as at central Oregon Cascades, United States, with emission rate of 32 t/d of CO₂ (from a 75-km-long segment [James et al., 1999]) and 14 t/d of Cl (from a 260-km-long segment [Hurwitz et al., 2005]). A significant amount of diffuse emission of magmatic CO_2 gas through soil is observed both at actively degassing volcanoes and apparently dormant volcanoes, such as at Mammoth Mountain, United States [Allard et al., 1991; Farrar et al., 1995]. Although a range of diffuse CO_2 emission rate is estimated at actively degassing volcanoes from negligible emission to equal contribution to summit emission, the contribution may not exceed 10% of the summit emission in many cases [Kerrick, 2001]. Although the rate of diffuse emission is commonly small, it may contribute to volatile budget of a magmatic system because of its long-lived activity and also to global emission rates because of its wide distribution. Incorporation of diffuse emission data is necessary for better evaluation of volatile budget in a magmatic system as well as in a global scale; however, the number of diffuse emission rate data is still limited, and a better database is necessary to integrate them in a time and space-averaged estimate.

7. SUMMARY AND PROBLEMS

[82] Large excess degassing is associated with various volcanic activities, including explosive and effusive erup-

tions and during persistent degassing with and without eruptive activity. On average, an order of magnitude larger amount of magma in a crustal magma chamber supplies gases to cause the excess degassing, and the degassed chamber solidifies to form a pluton. Excess degassing during explosive eruption is caused by magmas that accumulate bubbles, either from a large silicic magma body or via a S-rich basaltic magma that provides excess gas to the silicic magma before eruption. Large excess degassing is caused by persistent degassing without magma discharge and is caused by transport volatile components from a large magma chamber, either through convecting magma column degassing or by gas phase flow through a permeable volcanic conduit. Excess degassing is an important concept to understand the volatile budget, eruption mechanisms, and differentiation of magmas in the crust, but major questions, such as mechanism, source, and causes of excess degassing, are not yet well understood.

[83] Three different models have been proposed to explain excess degassing under different conditions. These models are based largely on the sulfur budget, and they have yet to be confirmed by independent evidence. Volcanic gas is dominated by H₂O and CO₂, and this composition can provide constraints to the origin of the volatiles, such as source magma composition or degassing pressure. For example, contrasting degassing pressures are estimated on the basis of volcanic gas compositions emitted during Strombolian eruptions and persistent degassing [Burton et al., 2007a; Edmonds and Gerlach, 2007]. The volcanic gas composition data, however, are still quite limited, in particular for volatiles emitted during eruptions. Accumulation of volcanic gas composition data is necessary to constrain the mechanisms and conditions of degassing as well as to evaluate the relative contribution of different excess degassing mechanisms.

[84] Excess degassing mechanisms are coupled to eruption processes. Examples of excess degassing and their models revealed magma-gas phase differentiation processes in a magma chamber and conduit system, and the differentiation processes control degassing and eruption styles. Degree of excess degassing during Plinian eruption is larger with smaller eruption, suggesting that the eruption triggering is controlled by the content of accumulated bubbles, although the quantified examples are still limited. Strombolian, Vulcanian, and lava dome eruptions are commonly associated with persistent degassing, implying occurrence of these eruptions either through a convecting magma column or through a gas-permeable volcanic conduit. Eruption models commonly consider a stagnant or rising magma column, but these excess degassing mechanism models need to be incorporated to the eruption models that will also provide, in turn, a test of the excess degassing mechanism models.

[85] The original source of excess degassing is not yet clear, in particular for silicic volcanism. Excess amounts of volatiles emitted from silicic volcanoes are derived either from a unerupted magma of the same composition as the erupted magmas or from an unerupted S-rich basaltic magma. The former model is simple and possible, at least to some degree, in all cases, but contribution of basaltic magmas is commonly observed in eruption products of silicic magma eruption, and there is also evidence of SO₂rich gas supply from basaltic magma in some cases, such as for the 1991 Pinatubo eruption. The relative importance of these two magma sources, however, has not been studied for many other eruptions, and it is necessary to evaluate it not only for excess degassing mechanisms but also to understand evolution of magmas in a chamber and the present crustal growth through solidification of degassed magma.

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REFERENCES

- Aiuppa, A., C. Federico, G. Giudice, and S. Gurrieri (2005), Chemical mapping of a fumarolic field: La Fossa Crater, Vulcano Island (Aeolian Islands, Italy), *Geophys. Res. Lett.*, 32, L13309, doi:10.1029/2005GL023207.
- Allard, P., et al. (1991), Eruptive and diffuse emissions of CO_2 from Mount Etna, *Nature*, 351, 387–391, doi:10.1038/351387a0.
- Allard, P., J. Carbonnelle, N. Métrich, H. Loyer, and P. Zettwoog (1994), Sulphur output and magma degassing budget of Stromboli volcano, *Nature*, 368, 326–330, doi:10.1038/368326a0.
- Anderson, A. T., Jr., S. Newman, S. N. Williams, T. H. Druitt, C. Skirius, and E. Stolper (1989), H₂O, CO₂, Cl and gas in Plinian and ash-flow Bishop rhyolite, *Geology*, *17*, 221–225, doi:10.1130/0091-7613(1989)017<0221:HOCCAG>2.3.CO;2.
- Andres, R. J., and A. D. Kasgnoc (1998), A time-averaged inventory of subaerial volcanic sulfur emissions, J. Geophys. Res., 103, 25,251–25,261, doi:10.1029/98JD02091.
- Andres, R. J., P. R. Kyle, J. B. Stokes, and W. I. Rose (1989), SO₂ from the episode 48A East Rift Zone eruption of Kilauea volcano, Hawaii, *Bull. Volcanol.*, 52, 113–117, doi:10.1007/ BF00301550.
- Andres, R. J., W. I. Rose, P. R. Kyle, S. de Silva, P. Francis, M. Gardeweg, and H. Moreno Roa (1991), Excessive sulfur dioxide emissions from Chilean volcanoes, *J. Volcanol. Geotherm. Res.*, 46, 323–329, doi:10.1016/0377-0273(91)90091-D.
- Aspinall, W. P., A. D. Miller, L. L. Lych, J. L. Latchman, R. C. Stewart, R. A. White, and J. A. Power (1998), Soufrière Hills eruption, Montserrat, 1995–1997: Volcanic earthquake locations and fault plane solutions, *Geophys. Res. Lett.*, 25, 3397–3400, doi:10.1029/98GL00858.
- Bachmann, O., and G. W. Bergantz (2006), Gas percolation in upper-crustal silicic crystal mushes as a mechanism for upward heat advection and rejuvenation of near-solidus magma bodies, *J. Volcanol. Geotherm. Res.*, *149*, 85–102, doi:10.1016/j.jvolgeores.2005.06.002.
- Bacon, C. R. (1986), Magmatic inclusions in silicic and intermediate volcanic rocks, J. Geophys. Res., 91, 6091–6112, doi:10.1029/ JB091iB06p06091.

- Bani, P., C. Oppenheimer, V. I. Tsanev, S. A. Carn, S. J. Cronin, R. Crimp, J. A. Calkins, D. Charley, and M. Lardy (2008), First measurements of sulphur and bromine degassing from Ambrym volcano, Vanuatu, *Bull. Volcanol.*, in press.
- Barclay, J., M. J. Rutherford, M. R. Carrol, M. D. Murphy, J. D. Devine, J. Gardner, and R. S. J. Sparks (1998), Experimental phase equilibria constraints on pre-eruptive storage conditions of the Soufrière Hills magma, *Geophys. Res. Lett.*, 25, 3437–3440, doi:10.1029/98GL00856.
- Bernard, A., D. Demaiffe, N. Mattielli, and R. S. Punongbayan (1991), Anhydrite-bearing pumices from Mount Pinatubo: Further evidence for the existence of sulfur-rich silicic magmas, *Nature*, *354*, 139–140, doi:10.1038/354139a0.
- Berresheim, H., and W. Jaeschke (1983), The contribution of volcanoes to the global atmospheric sulfur budget, *J. Geophys. Res.*, *88*, 3732–3740, doi:10.1029/JC088iC06p03732.
- Bertagnini, A., N. Métrich, P. Landi, and M. Rosi (2003), Stromboli volcano (Aeolian Archipelago, Italy): An open window on the deep-feeding system of a steady state basaltic volcano, *J. Geophys. Res.*, 108(B7), 2336, doi:10.1029/2002JB002146.
- Blundy, J., and K. Cashman (2005), Rapid decompression-driven crystallization recorded by melt inclusions from Mount St. Helens, *Geology*, *33*, 793–796, doi:10.1130/G21668.1.
- Bluth, G. J. S., C. C. Schnetzler, A. J. Krueger, and L. S. Walter (1993), The contribution of explosive volcanism to global atmospheric sulphur dioxide concentrations, *Nature*, *366*, 327–329, doi:10.1038/366327a0.
- Bluth, G. J., C. J. Scott, I. E. Sprod, C. C. Schnetzler, A. J. Krueger, and L. S. Walter (1995), Explosive emissions of sulfur dioxide from the 1992 Crater Peak eruptions, in *The 1992 Eruptions of Crater Peak Vent, Mount Spurr, Volcano, Alaska*, edited by T. E. C. Keith, U.S. Geol. Surv. Bull., 3139, 37–45.
- Bluth, G. J. S., I. William, I. E. Sprod, C. C. Schnetzler, A. J. Krueger, and A. J. Krueger (1997), Stratospheric loading of sulfur from explosive volcanic eruptions, J. Geol., 105, 671–683.
- Bureau, H., N. Metrich, and M. P. Semet (1999), Fluid-magma decoupling in a hot-spot volcano, *Geophys. Res. Lett.*, 26, 3501–3504, doi:10.1029/1999GL005422.
- Burgisser, A., and B. Scaillet (2007), Redox evolution of a degassing magma rising to the surface, *Nature*, 445, 194–197, doi:10.1038/nature05509.
- Burnham, C. W. (1967), Hydrothermal fluids at the magmatic stage, in *Geochemistry of Hydrothermal Ore Deposits*, edited by H. L. Barnes, pp. 34–76, Holt, Rinehart, and Winston, New York.
- Burton, M. R., C. Oppenheimer, L. A. Horrocks, and P. W. Francis (2000), Remote sensing of CO₂ and H₂O emission rates from Masaya volcano, Nicaragua, *Geology*, 28, 915–918, doi:10.1130/0091-7613(2000)28<915:RSOCAH>2.0.CO;2.
- Burton, M. R., P. Allard, F. Muré, and A. La Spina (2007a), Magmatic gas composition reveals the source depth of slug-driven Strombolian explosive activity, *Science*, *317*, 227–230, doi:10.1126/science.1141900.
- Burton, M. R., H. M. Mader, and M. Polacci (2007b), The role of gas percolation in quiescent degassing of persistently active basaltic volcanoes, *Earth Planet. Sci. Lett.*, 264, 46–60, doi:10.1016/j.epsl.2007.08.028.
- Candela, P. A. (1994), Combined chemical and physical model for plutonic devolatilization: A non-Rayleigh fractionation algorithm, *Geochim. Cosmochim. Acta*, 58, 2157–2167, doi:10.1016/0016-7037(94)90002-7.
- Carn, S. A. (2003), Eruptive and passive degassing of sulphur dioxide at Nyiragongo volcano (D.R. Congo): The 17 January 2002 eruption and its aftermath, *Acta Vulcanol.*, *14*, 75–86.
- Carn, S. A., and G. J. S. Bluth (2003), Prodigious sulfur dioxide emissions from Nyamuragira volcano, D.R. Congo, *Geophys. Res. Lett.*, *30*(23), 2211, doi:10.1029/2003GL018465.
- Carn, S. A., A. J. Krueger, G. J. S. Bluth, S. J. Schaefer, N. A. Krotkov, I. M. Watson, and S. Darra (2003), Volcanic eruption detection by the Total Ozone Mapping Spectrometer (TOMS)

instruments: A 22-year record of sulphur dioxide and ash emissions, in *Volcanic Degassing*, edited by C. Oppenheimer, D. M. Pyle, and J. Barclay, *Geol. Soc. Spec. Publ.*, *212*, 177–202.

- Carrol, M. R., and M. J. Rutherford (1985), Sulfide and sulfate saturation in hydrous silicate melts, *J. Geophys. Res.*, 90, 601–612.
- Carrol, M. R., and J. D. Webster (1994), Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 231–279, Mineral. Soc. of Am., Washington, D. C.
- Cathles, L. M. (1977), An analysis of the cooling of intrusives by ground-water convection which includes boiling, *Econ. Geol.*, 72, 804–826.
- Cayol, V., J. H. Dieterich, A. T. Okamura, and A. Miklius (2000), High magma storage rates before the 1983 eruption of Kilauea, Hawaii, *Science*, 288, 2343–2345, doi:10.1126/science. 288.5475.2343.
- Cervantes, P., and P. J. Wallace (2003a), Role of H₂O in subduction-zone magmatism: New insights from melt inclusions in high-Mg basalts from central Mexico, *Geology*, *31*, 235–238, doi:10.1130/0091-7613(2003)031<0235:ROHOIS>2.0.CO;2.
- Cervantes, P., and P. J. Wallace (2003b), Magma degassing and basaltic eruption styles: A case study of the 2000 yr B.P. eruption of Xitle volcano, central Mexico, *J. Volcanol. Geotherm. Res.*, *120*, 249–270, doi:10.1016/S0377-0273(02)00401-8.
- Chiodini, G., R. Cioni, and L. Marini (1993), Reactions governing the chemistry of crater fumaroles of Volcano Island, Italy and implications for volcanic surveillance, *Appl. Geochem.*, *8*, 357– 371, doi:10.1016/0883-2927(93)90004-Z.
- Cioni, R., P. Marianelli, R. Santacroce, and A. Sbrana (2000), Plinian and Subplinian eruptions, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 477–494, Academic, San Diego, Calif.
- Clague, D. A., J. G. Moore, J. E. Dixon, and W. B. Friesen (1995), Petrology of submarine lavas from Kilauea's Puna Ridge, Hawaii, *J. Petrol.*, *36*, 299–349.
- Costa, F., B. Scaillet, and A. Gourgaud (2003), Massive atmospheric sulfur loading of the AD 1600 Huaynaputina eruption, *Geophys. Res. Lett.*, 30(2), 1068, doi:10.1029/2002GL016402.
- Crisp, J. A. (1984), Rates of magma emplacement and volcanic output, *J. Volcanol. Geotherm. Res.*, 20, 177–211, doi:10.1016/0377-0273(84)90039-8.
- de Hoog, J. C. M., G. W. Koetsier, S. Bronto, T. Sriwana, and M. J. van Bergen (2001), Sulfur and chlorine degassing from primitive arc magmas: Temporal changes during the 1982–1983 eruptions of Galunggung (west Java, Indonesia), *J. Volcanol. Geotherm. Res.*, *108*, 55–83, doi:10.1016/S0377-0273(00)00278-X.
- Delgado-Granados, H., L. Cárdenas González, and N. Piedad Sánchez (2001), Sulfur dioxide emissions from Popocatépetl volcano (Mexico): Case study of a high-emission rate, passively degassing erupting volcano, *J. Volcanol. Geotherm. Res.*, *108*, 107–120, doi:10.1016/S0377-0273(00)00280-8.
- Delmas, R. J. (1992), Environmental information from ice cores, *Rev. Geophys.*, *30*, 1–21, doi:10.1029/91RG02725.
- De Luca, G., L. Filippi, G. Patane, R. Scarpa, and S. Vinciguerra (1997), Three-dimensional velocity structure and seismicity of Mt. Etna volcano, Italy, *J. Volcanol. Geotherm. Res.*, 79, 123–138, doi:10.1016/S0377-0273(97)00026-7.
- de Silva, S., and G. Zielinski (1998), Global influence of the AD 1600 eruption of Huaynaputina, Peru, *Nature*, *393*, 455–457, doi:10.1038/30948.
- Devine, J. D., H. Sigurdsson, A. N. Davis, and S. Self (1984), Estimates of sulfur and chlorine yield to the atmosphere from volcanic eruptions and potential climatic effects, *J. Geophys. Res.*, 89, 6309–6325.
- Di Muro, A., B. Villemant, G. Montgnac, B. Scaillet, and B. Reynard (2006), Quantification of water content and speciation in natural silicic glasses (phonolite, dacite, rhyolite) by confocal microRaman spectrometry, *Geochim. Cosmochim. Acta*, 70, 2868–2884, doi:10.1016/j.gca.2006.02.016.

- Doglioni, C., F. Innocenti, and G. Mariotti (2001), Why Mt. Etna?, *Terra Nova*, *13*, 25–31, doi:10.1046/j.1365-3121.2001.00301.x.
- Duffell, H. J., C. Oppenheimer, D. M. Pyle, B. Galle, A. J. S. McGonigle, and M. R. Burton (2003), Changes in gas composition prior to a minor explosive eruption at Masaya volcano, Nicaragua, *J. Volcanol. Geotherm. Res.*, 126, 327–339, doi:10.1016/S0377-0273(03)00156-2.
- Edmonds, M., and T. M. Gerlach (2007), Vapor segregation and loss in basaltic melts, *Geology*, 35, 751–754, doi:10.1130/G23464A.1.
- Edmonds, M., D. Pyle, and C. Oppenheimer (2001), A model for degassing at the Soufrière Hills Volcano, Montserrat, West Indies, based on geochemical data, *Earth Planet. Sci. Lett.*, *186*, 159–173, doi:10.1016/S0012-821X(01)00242-4.
- Edmonds, M., C. Oppenheimer, D. M. Pyle, R. A. Herd, and G. Thompson (2003), SO₂ emissions from Soufrière Hills volcano and their relationship to conduit permeability, hydrothermal interaction and degassing regime, *J. Volcanol. Geotherm. Res.*, *124*, 23–43, doi:10.1016/S0377-0273(03)00041-6.
- Eichelberger, J. C. (1980), Vesiculation of mafic magma during replenishment of silicic magma reservoirs, *Nature*, 288, 446–450, doi:10.1038/288446a0.
- Eichelberger, J. C. (1995), Ascent of viscous magmas from crustal reservoirs, *Annu. Rev. Earth. Planet. Sci.*, 23, 41–63, doi:10.1146/annurev.ea.23.050195.000353.
- Eichelberger, J. C., C. R. Carrigan, H. R. Westrich, and J. R. Shannon (1986), Non-explosive volcanism, *Nature*, *323*, 598–602, doi:10.1038/323598a0.
- Farrar, C. D., M. L. Sorey, W. C. Evans, J. F. Howele, B. D. Kerr, B. M. Kennedy, C.-Y. King, and J. R. Southon (1995), Forestkilling diffuse CO₂ emission at Mammoth Mountain as a sign of magmatic unrest, *Nature*, 376, 675–678, doi:10.1038/376675a0.
- Fischer, T. P., G. B. Arehart, N. C. Sturchio, and S. N. Williams (1996), The relationship between fumarole gas composition and eruptive activity at Galeras volcano, Colombia, *Geology*, 24, 531–534, doi:10.1130/0091-7613(1996)024<0531:TRBFGC>2.3.CO;2.
- Fisher, R. V., and H.-U. Schmincke (1984), *Pyroclastic Rocks*, Springer, Berlin.
- Fournelle, J. (1990), Anhydrite in Nevado del Ruiz November 1985 pumice: Relevance to the sulfur problem, *J. Volcanol. Geotherm. Res.*, 42, 189–210, doi:10.1016/0377-0273(90)90076-R.
- Francis, P. W., C. Oppenheimer, and D. Stevenson (1993), Endogenous growth of persistently active volcanoes, *Nature*, 366, 554–557, doi:10.1038/366554a0.
- Friend, J. P., A. R. Bandy, J. L. Moyers, W. H. Zoller, R. E. Stoiber, A. L. Torres, W. I. Rose Jr., M. P. McCormick, and D. C. Woods (1982), Research on atmospheric volcanic emissions: An overview, *Geophys. Res. Lett.*, 9, 1101–1104, doi:10.1029/GL009i009p01101.
- Galle, B., C. Oppenheimer, A. Geyer, A. J. S. McGonigle, M. Edmonds, and L. Horrocks (2002), A miniaturized ultraviolet spectrometer for remote sensing of SO₂ fluxes: A new tool for volcano surveillance, *J. Volcanol. Geotherm. Res.*, *119*, 241–254, doi:10.1016/S0377-0273(02)00356-6.
- Gerlach, T. M., and K. A. McGee (1994), Total sulfur dioxide emissions and pre-eruption vapor-saturated magma at Mount St. Helens, 1980–88, *Geophys. Res. Lett.*, 21, 2833–2836, doi:10.1029/94GL02761.
- Gerlach, T. M., and K. A. McGee (1998), Rates of volcanic CO₂ degassing from airborne determinations of SO₂ emission rates and plume CO₂/SO₂: Test study at Puù Òò cone, Kilauea volcano, Hawaii, *Geophys. Res. Lett.*, 25, 2675–2678, doi:10.1029/98GL02030.
- Gerlach, T. M., H. R. Westrich, T. J. Casadevall, and D. L. Finnegan (1994), Vapor saturation and accumulation in magmas of the 1989–1990 eruption of Redoubt volcano, Alaska, *J. Volcanol. Geotherm. Res.*, *62*, 317–337, doi:10.1016/0377-0273(94)90039-6.

- Gerlach, T. M., H. R. Westrich, and R. B. Symonds (1996), Preeruption vapor in magma of the climactic Mount Pinatubo eruption: Source of the giant stratospheric sulfur dioxide cloud, in *Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines*, edited by C. G. Newhall and R. S. Punongbayan, pp. 415–433, Univ. of Wash. Press, Seattle.
- Gerlach, T. M., H. Delgado, K. A. McGee, M. P. Doukas, J. J. Venegas, and L. Cárdnas (1997), Application of the LI–COR CO₂ analyzer to volcanic plumes: A case study, Volcán Popocatépetl, Mexico, June 7 and 10, 1995, *J. Geophys. Res.*, 102, 8005–8019, doi:10.1029/96JB03887.
- Gerlach, T. M., K. A. McGee, T. Elias, A. J. Sutton, and M. P. Doukas (2002), Carbon dioxide emission rate of Kilauea Volcano: Implications for primary magma and the summit reservoir, *J. Geophys. Res.*, 107(B9), 2189, doi:10.1029/2001JB000407.
- Giggenbach, W. F. (1987), Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand, *Appl. Geochem.*, 2, 143–161, doi:10.1016/0883-2927(87)90030-8.
- Giggenbach, W. F. (1996), Chemical composition of volcanic gases, in *Monitoring and Mitigation of Volcanic Hazards*, edited by R. Scarpa and R. I. Tilling, pp. 221–256, Springer, Berlin.
- Giggenbach, W. F., and F. Le Guern (1976), The chemistry of magmatic gases from Erta'Ale, Ethiopia, *Geochim. Cosmochim. Acta*, 40, 25–30, doi:10.1016/0016-7037(76)90190-3.
- Gonnermann, H. M., and M. Manga (2007), The fluid mechanics inside a volcano, *Annu. Rev. Fluid Mech.*, *39*, 321–356, doi:10.1146/annurev.fluid.39.050905.110207.
- Graedel, T. (1977), The homogeneous chemistry of atmospheric sulfur, *Rev. Geophys.*, *15*, 421–428, doi:10.1029/RG015i004p00421.
- Graf, H.-F., J. Feichter, and B. Langmann (1997), Volcanic sulfur emission: Estimates of source strength and its contribution to the global sulfate distribution, *J. Geophys. Res.*, *102*, 10,727–10,738, doi:10.1029/96JD03265.
- Gurenko, A. A., A. B. Belousov, R. B. Trumbull, and A. V. Sobolev (2005), Explosive basaltic volcanism of the Chikurachki volcano (Kurile arc, Russia): Insights on pre-eruptive magmatic conditions and volatile budget revealed from phenocryst-hosted melt inclusions and groundmass glasses, *J. Volcanol. Geotherm. Res.*, 147, 203–232, doi:10.1016/j.jvolgeores.2005.04.002.
- Hammer, C. U., H. B. Clausen, and W. Dansgaard (1980), Greenland ice sheet evidence of post-glacial volcanism and its climatic impact, *Nature*, 288, 230–235, doi:10.1038/288230a0.
- Hammer, C. U., H. B. Clausen, W. L. Friedrich, and H. Tauber (1987), The Minoan eruption of Santorini in Greece dated to 1645 BC?, *Nature*, *328*, 517–519, doi:10.1038/328517a0.
- Harris, A., and M. Ripepe (2007), Temperature and dynamics of degassing at Stromboli, *J. Geophys. Res.*, *112*, B03205, doi:10.1029/2006JB004393.
- Harris, A. J. L., and D. S. Stevenson (1997), Thermal observations of degassing open conduits and fumaroles at Stromboli and Vulcano using remotely sensed data, *J. Volcanol. Geotherm. Res.*, 76, 175–198, doi:10.1016/S0377-0273(96)00097-2.
- Harris, A. J. L., L. P. Flynn, D. A. Rothery, C. Oppenheimer, and S. B. Sherman (1999), Mass flux measurements at active lava lakes: Implications for magma recycling, *J. Geophys. Res.*, 104, 7117–7136, doi:10.1029/98JB02731.
- Harris, D. M., and A. T. Anderson Jr. (1984), Volatiles H₂O, CO₂, and Cl in a subduction related basalt, *Contrib. Mineral. Petrol.*, 87, 120–128, doi:10.1007/BF00376218.
- Harris, D. M., M. Sato, T. J. Casadevall, W. I. Rose, and T. J. Bornhorst (1981), Emission rate of CO₂ from plume measurements, in *The 1980 Eruptions of Mount St. Helens, Washington*, U.S. Geol. Surv. Prof. Pap., 1250, 201–207.
- Hattori, K. (1993), High-sulfur magma, a product of fluid discharge from underlying mafic magma: Evidence from Mount Pinatubo, Philippines, *Geology*, *21*, 1083–1086, doi:10.1130/ 0091-7613(1993)021<1083:HSMAPO>2.3.CO;2.

- Hattori, K. (1996), Occurrence and origin of sulfide and sulfate in the 1991 Mount Pinatubo eruption products, in *Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines*, edited by C. G. Newhall and R. S. Punongbayan, pp. 807–824, Univ. of Wash. Press, Seattle.
- Hauri, E. (2002), SIMS analysis of volatiles in silicate glasses, 2: Isotopes and abundances in Hawaiian melt inclusions, *Chem. Geol.*, *183*, 115–141, doi:10.1016/S0009-2541(01)00374-6.
- Hedenquist, J. W., and J. B. Lowenstern (1994), The role of magmas in the formation of hydrothermal ore deposits, *Nature*, *370*, 519–527, doi:10.1038/370519a0.
- Hekinian, R., F. Pineau, S. Shilobreeva, D. Bideau, E. Gracia, and M. Javoy (2000), Deep sea explosive activity on the Mid-Atlantic Ridge near 34°50'N: Magma composition, vesicularity, and volatile content, J. Volcanol. Geotherm. Res., 98, 49–77, doi:10.1016/S0377-0273(99)00190-0.
- Hildreth, W. (1981), Gradients in silicic magma chambers: Implications for lithospheric magmatism, *J. Geophys. Res.*, 86(B11), 10,153–10,192.
- Hirabayashi, J., J. Ossaka, and T. Ozawa (1986), Geochemical study on volcanic gases at Sakurajima volcano, Japan, J. Geophys. Res., 91, 12,167–12,176, doi:10.1029/JB091iB12p12167.
- Hirabayashi, J., T. Ohba, K. Nogami, and M. Yoshida (1995), Discharge rate of SO₂ from Unzen volcano, Kyushu, Japan, *Geophys. Res. Lett.*, 22, 1709–1712, doi:10.1029/95GL01319.
- Holloway, J. R. (1976), Fluid in the evolution of granitic magmas: Consequences of finite CO₂ solubility, *Geol. Soc. Am. Bull.*, *87*, 1513–1518, doi:10.1130/0016-7606(1976)87<1513: FITEOG>2.0.CO;2.
- Holloway, J. R., and J. G. Blank (1994), Application of experimental results to C-O-H species in natural melts, in *Volatiles in Magmas, Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 187–230, Mineral. Soc. of Am., Washington, D. C.
- Hurwitz, S., R. H. Mariner, U. Fehn, and G. T. Snyder (2005), Systematics of halogen elements and their radioisotopes in thermal springs of the Cascade Range, central Oregon, western USA, *Earth Planet. Sci. Lett.*, 235, 700–714, doi:10.1016/ j.epsl.2005.04.029.
- Ihinger, P. D., R. L. Hervig, and P. F. McMillan (1994), Analytical methods for volatiles in glasses, in *Volatiles in Magmas*, *Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 67–129, Mineral. Soc. of Am., Washington, D. C.
- James, E. R., M. Manga, and T. P. Rose (1999), CO₂ degassing in the Oregon Cascades, *Geology*, *27*, 823–826, doi:10.1130/0091-7613(1999)027<0823:CDITOC>2.3.CO;2.
- Jaupart, C., and S. Vergniolle (1988), Laboratory models of Hawaiian and Strombolian eruptions, *Nature*, *331*, 58–60, doi:10.1038/331058a0.
- Kazahaya, K., H. Shinohara, and G. Saito (1994), Excessive degassing of Izu-Oshima volcano: Magma convection in a conduit, *Bull. Volcanol.*, 56, 207–216, doi:10.1007/BF00279605.
- Kazahaya, K., H. Shinohara, and G. Saito (2002), Degassing process of Satsuma-Iwojima volcano, Japan: Supply of volatile components from a deep magma chamber, *Earth Planets Space*, *54*, 327–335.
- Kazahaya, K., H. Shinohara, K. Uto, M. Odai, Y. Nakahori, H. Mori, H. Iino, M. Miyashita, and J. Hirabayashi (2004), Gigantic SO₂ emission from Miyakejima volcano, Japan, caused by caldera collapse, *Geology*, 32, 425–428, doi:10.1130/G20399.1.
- Keppler, H. (1999), Experimental evidence for the source of excess sulfur in explosive volcanic eruptions, *Science*, *284*, 1652–1654, doi:10.1126/science.284.5420.1652.
- Kerrick, D. M. (2001), Present and past nonanthropogenic CO₂ degassing from the solid earth, *Rev. Geophys.*, *39*, 565–585, doi:10.1029/2001RG000105.
- Kriswati, E., and M. Iguchi (2003), Inflation of the Aira caldera prior to the 1999 eruptive activity at Sakurajima volcano detected by GPS network in south Kyushu, *Ann. Disast. Prev. Res. Inst. Kyoto Univ.*, 46B, 817–826.

- Krotkov, N. A., S. A. Carn, A. J. Krueger, P. K. Bhartia, and K. Yang (2006), Band residual difference algorithm for retrieval of SO₂ from the Aura Ozone Monitoring Instrument (OMI), *IEEE Trans. Geosci. Remote Sens.*, 44, 1259–1266, doi:10.1109/TGRS.2005.861932.
- Krueger, A. J. (1983), Sighting of El Chichón sulfur dioxide clouds with the Nimbus 7 total ozone mapping spectrometer, *Science*, 220, 1377–1379, doi:10.1126/science.220.4604.1377.
- Krueger, A. J., C. C. Schnetzler, L. S. Walter, and S. D. Doiron (1990), TOMS measurement of the sulfur dioxide emitted during the 1985 Nevado del Ruiz eruptions, *J. Volcanol. Geotherm. Res.*, *41*, 7–15, doi:10.1016/0377-0273(90)90081-P.
- Krueger, A. J., L. S. Walter, P. K. Bhartia, C. C. Schnetzler, N. S. Krotko, I. Sprod, and G. J. S. Bluth (1995), Volcanic sulfur dioxide measurements from the total ozone mapping spectrometer instruments, *J. Geophys. Res.*, 100, 14,057–14,076, doi:10.1029/95JD01222.
- Krueger, A. J., S. J. Schaefer, N. Krotkov, G. Bluth, and S. Barker (2000), Ultraviolet remote sensing of volcanic emissions, in *Remote Sensing of Active Volcanism, Geophys. Monogr. Ser.*, vol. 116, edited by P. J. Mouginis-Mark, J. A. Crisp, and J. H. Fink, pp. 25–43, AGU, Washington, D. C.
- Kyle, P. R., K. Meeker, and D. Finnegan (1990), Emissions rates of sulfur dioxide, trace gases and metals from Mount Erebus, Antarctica, *Geophys. Res. Lett.*, 17, 2125–2128, doi:10.1029/ GL017i012p02125.
- Larocque, A. C. L., J. A. Stimac, J. D. Keith, and M. A. E. Huminicki (2000), Evidence for open-system behavior in immiscible Fe-S-O liquids in silicate magmas: Implications for contributions of metals and sulfur to ore-forming fluids, *Can. Mineral.*, *38*, 1233–1249, doi:10.2113/gscanmin.38.5.1233.
- Lautze, N. C., and B. F. Houghton (2005), Physical mingling of magma and complex eruption dynamics in the shallow conduit at Stromboli volcano, Italy, *Geology*, *33*, 425–428, doi:10.1130/G21325.1.
- Liu, Y., N.-T. Samara, and D. R. Baker (2007), Sulfur concentration at sulfide saturation (SCSS) in magmatic silicate melts, *Geochim. Cosmochim. Acta*, 71, 1783–1799, doi:10.1016/ j.gca.2007.01.004.
- Llewellin, E. W., and M. Manga (2005), Bubble suspension rheology and implications for conduit flow, *J. Volcanol. Geotherm. Res.*, *143*, 205–217, doi:10.1016/j.jvolgeores.2004.09.018.
- Locke, A. C., H. Rymer, and J. Cassidy (2003), Magmas transfer processes at persistently active volcanoes: Insights from gravity observations, *J. Volcanol. Geotherm. Res.*, 127, 73–86, doi:10.1016/S0377-0273(03)00179-3.
- Lowenstern, J. B. (1995), Application of silicate-melt inclusions to the study of magmatic volatiles, in *Magmas, Fluids, and Ore Deposits, Short Course Ser.*, vol. 23, edited by J. F. H. Thompson, pp. 71–99, Mineral. Assoc. of Can., Quebec, Que., Canada.
- Luhr, J. F. (1990), Experimental phase relations of water- and sulfur- saturated arc magmas and the 1982 eruptions of El Chichón volcano, *J. Petrol.*, *31*, 1071–1114.
- Luhr, J. F. (2001), Glass inclusions and melt volatile contents at Paricutin volcano, Mexico, *Contrib. Mineral. Petrol.*, *142*, 261–283.
- Luhr, J. F., and M. A. V. Logan (2002), Sulfur isotope systematics of the 1982 El Chichón trachyandesite: An ion microprobe study, *Geochim. Cosmochim. Acta*, 66, 3303–3316, doi:10.1016/ S0016-7037(02)00931-6.
- Luhr, J. F., I. S. E. Carmichael, and J. C. Varekamp (1984), The 1982 eruptions of El Chichón volcano, Chiapas, Mexico: Mineralogy and petrology of the anhydrite-bearing pumices, *J. Volcanol. Geotherm. Res.*, 23, 69–108, doi:10.1016/0377-0273(84)90057-X.
- Mandeville, C. W., S. Carey, and H. Sigurdsson (1996), Magma mixing, fractional crystallization and volatile degassing during the 1883 eruption of Krakatau volcano, Indonesia, *J. Volcanol.*

Geotherm. Res., 74, 243-274, doi:10.1016/S0377-0273(96)00060-1.

- Marsh, B. D. (2000), Magma chambers, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 191–206, Academic, San Diego, Calif.
- Martin, D., B. Ardouin, G. Bergametti, J. Carboneelle, R. Faivre-Pierret, G. Lambert, M. F. Le Cloarec, and G. Sennequier (1986), Geochemistry of sulfur in Mount Etna plume, *J. Geophys. Res.*, 91, 12,249–12,254, doi:10.1029/JB091iB12p12249.
- Marty, B., and I. N. Tolstikhin (1998), CO₂ fluxes from mid-ocean ridges, arcs and plumes, *Chem. Geol.*, *145*, 233–248, doi:10.1016/S0009-2541(97)00145-9.
- Matthews, S. J., M. C. Gardeweg, and R. S. J. Sparks (1997), The 1984 to 1996 cyclic activity of Lascar volcano, northern Chile: Cycles of dome growth, dome subsidence, degassing and explosive eruptions, *Bull. Volcanol.*, *59*, 72–82, doi:10.1007/ s004450050176.
- Matthews, S. J., R. S. J. Sparks, and M. C. Gardeweg (1999), The Piedras Grandes-Soncor eruptions, Lascar volcano, Chile; Evolution of a zoned magma chamber in the central Andean upper crust, *J. Petrol.*, 40, 1891–1919, doi:10.1093/petrology/ 40.12.1891.
- McClelland, L., T. Simkin, M. Summers, E. Nielsen, and T. C. Stein (Eds.) (1989), *Global Volcanism 1975–1985*, 657 pp., Prentice-Hall, Englewood Cliffs, N. J.
- McGee, A. K., M. P. Doukas, and T. M. Gerlach (2001), Quiescent hydrogen sulfide and carbon dioxide degassing from Mount Baker, Washington, *Geophys. Res. Lett.*, *28*, 4479–4482, doi:10.1029/2001GL013250.
- McGonigle, A. J. S., and C. Oppenheimer (2003), Optical sensing of volcanic gas and aerosol emissions, in *Volcanic Degassing*, edited by C. Oppenheimer, D. M. Pyle, and J. Barclay, *Geol. Soc. Spec. Publ.*, 213, 149–168.
- Melnik, O., and R. S. J. Sparks (1999), Non-linear dynamics of lava dome extrusion, *Nature*, 402, 37–41, doi:10.1038/46950.
- Melnik, O., and R. S. J. Sparks (2002), Dynamics of magma ascent and lava extrusion at Soufrière Hills volcano, in *The Eruptions of Soufrière Hills Volcano, Montserrat, From 1995 to 1999*, edited by T. H. Druitt and B. P. Kokelaar, *Mem. Geol. Soc. London*, 21, 153–171.
- Menyailov, I. A. A., L. P. Nikitina, V. N. Shaper, and V. P. Pilipenko (1986), Temperature increase and chemical change of fumarolic gases at Momotombo volcano, Nicaragua, in 1982–1985: Are these indicators of a possible eruption?, J. Geophys. Res., 91, 12,199–12,214, doi:10.1029/JB091iB12p12199.
- Métrich, N., A. Bertagnini, P. Landi, and M. Rosi (2001), Crystallization driven by decompression and water loss at Stromboli volcano (Aeolian Islands, Italy), *J. Petrol.*, *42*, 1471–1490, doi:10.1093/petrology/42.8.1471.
- Michaud, V., R. Clocchiatti, and S. Sbrana (2000), The Minoan and post-Minoan eruptions, Santorini (Greece), in the light of melt inclusions: Chlorine and sulphur behaviors, *J. Volcanol. Geotherm. Res.*, 99, 195–214, doi:10.1016/S0377-0273(00)00173-6.
- Mori, T., and K. Notsu (1997), Remote CO, COS, CO₂, SO₂, HCl detection and temperature estimation of volcanic gas, *Geophys. Res. Lett.*, 24, 2047–2050, doi:10.1029/97GL52058.
- Morrissey, M. M., and L. G. Mastin (2000), Vulcanian eruptions, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 463– 476, Academic, San Diego, Calif.
- Nakada, S., H. Shimizu, and K. Ohta (1999), Overview of the 1990–1995 eruption at Unzen Volcano, *J. Volcanol. Geotherm. Res.*, *89*, 1–22, doi:10.1016/S0377-0273(98)00118-8.
- Newhall, C. G., and S. Self (1982), The volcanic explosivity index (VEI): An estimate of explosive magnitude for Historical volcanism, *J. Geophys. Res.*, 87, 1231–1238.
- Newman, S., and J. B. Lowenstern (2002), VOLATILECALC: A silicate melt-H₂O-CO₂ solution model written in Visual Basic Excel, *Comput. Geosci.*, 28, 597–604, doi:10.1016/S0098-3004(01)00081-4.

- O'Neill, H. S. C., and J. A. Mavrogenes (2002), The sulfide capacity and the sulfur content at sulfide saturation of silicate melts at 1400°C and 1 bar, *J. Petrol.*, *43*, 1049–1087, doi:10.1093/petrology/43.6.1049.
- Oppenheimer, C. (1996), On the role of hydrothermal systems in the transfer of volcanic sulfur to the atmosphere, *Geophys. Res. Lett.*, 23, 2057–2060, doi:10.1029/96GL02061.
- Oppenheimer, C., A. J. S. McGonigle, P. Allard, M. J. Wooster, and V. Tsanev (2004), Sulfur, heat, and magma budget of Erta'Ale lava lake, Ethiopia, *Geology*, *32*, 509–512, doi:10.1130/ G20281.1.
- Palais, J. M., and H. Sigurdsson (1989), Petrologic evidence of volatile emissions from major historic and pre-historic volcanic eruptions, in *Understanding Climate Change, Geophys. Monogr. Ser.*, vol. 52, edited by A. L. Berger, R. E. Dickinson, and J. Kidson, pp. 31–53, AGU, Washington, D. C.
- Pallister, J. S., R. P. Hoblitt, and A. G. Reyes (1992), A basalt trigger for the 1991 eruptions of Pinatubo volcano?, *Nature*, *356*, 426–428, doi:10.1038/356426a0.
- Pallister, J. S., R. P. Hobitt, G. P. Meeker, R. J. Knight, and D. F. Siems (1996), Magma mixing at Mount Pinatubo: Petrographic and chemical evidence from the 1991 deposits, in *Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines*, edited by C. G. Newhall and R. S. Punongbayan, pp. 687–731, Univ. of Wash. Press, Seattle.
- Parfitt, E. A. (2004), A discussion of the mechanisms of explosive basaltic eruptions, J. Volcanol. Geotherm. Res., 134, 77–107, doi:10.1016/j.jvolgeores.2004.01.002.
- Patrick, M. R., A. J. L. Harris, M. Ripepe, J. Dehn, D. A. Rothery, and S. Calvari (2007), Strombolian explosive styles and source conditions: Insights from thermal (FLIR) video, *Bull. Volcanol.*, 69, 769–784, doi:10.1007/s00445-006-0107-0.
- Pyle, D. M. (2000), Size of volcanic eruptions, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 263–269, Academic, San Diego, Calif.
- Pyle, D. M., P. D. Beattie, and G. J. S. Bluth (1996), Sulphur emissions to the stratosphere from explosive volcanic eruptions, *Bull. Volcanol.*, *57*, 663–671, doi:10.1007/s004450050119.
- Ripepe, M., S. Ciliberto, and M. D. Schiava (2001), Time constraints for modeling source dynamics of volcanic explosions at Stromboli, J. Geophys. Res., 106, 8713–8727, doi:10.1029/ 2000JB900374.
- Robock, A. (2000), Volcanic eruptions and climate, *Rev. Geophys.*, 38, 191–219, doi:10.1029/1998RG000054.
- Roggensack, K. (2001), Unraveling the 1974 eruption of Fuego volcano (Guatemala) with small crystals and their young melt inclusions, *Geology*, *29*, 911–914, doi:10.1130/0091-7613(2001)029<0911:UTEOFV>2.0.CO;2.
- Roggensack, K., S. N. Williams, S. J. Schaefer, and R. A. Parnell Jr. (1996), Volatiles from the 1994 eruptions of Rabaul: Understanding large caldera systems, *Science*, *273*, 490–493, doi:10.1126/science.273.5274.490.
- Roggensack, K., R. L. Hervig, S. B. McKnight, and S. N. Williams (1997), Explosive basaltic volcanism from Cerro Negro volcano: Influence of volatiles on eruptive style, *Science*, 277, 1639–1642, doi:10.1126/science.277.5332.1639.
- Rose, W. I. (1977), Scavenging of volcanic aerosol by ash: Atmospheric and volcanologic implications, *Geology*, *5*, 621–624, doi:10.1130/0091-7613(1977)5<621:SOVABA>2.0.CO;2.
- Rymer, H., B. van Wyk de Vries, J. Stix, and G. Williams-Jones (1998), Pit crater structure and processes governing persistent activity at Masaya volcano, Nicaragua, *Bull. Volcanol.*, *59*, 345–355, doi:10.1007/s004450050196.
- Saar, M. O., and M. Manga (2004), Depth dependence of permeability in the Oregon Cascades inferred from hydrogeologic, thermal, seismic, and magmatic modeling constraints, *J. Geophys. Res.*, 109, B04204, doi:10.1029/2003JB002855.
- Saito, G., K. Kazahaya, H. Shinohara, J. Stimac, and Y. Kawanabe (2001), Variation of volatile concentration in a magma system of Satsuma-Iwojima volcano deduced from melt inclusion analyses,

J. Volcanol. Geotherm. Res., *108*, 11–31, doi:10.1016/S0377-0273(00)00276-6.

- Saito, G., K. Uto, K. Kazahaya, H. Shinohara, Y. Kawanabe, and H. Satoh (2005), Petrological characteristics and volatile content of magma from the 2000 eruption of Miyakejima volcano, Japan, *Bull. Volcanol.*, 67, 268–280, doi:10.1007/s00445-004-0409-z.
- Satoh, H., G. Saito, H. Shinohara, and Y. Yamaguchi (2003), Sulfur source for the 1991–1995 Unzen eruption: Evidence from melt inclusions in pyroxenes, *Geophys. Res. Lett.*, 30(23), 2220, doi:10.1029/2003GL017629.
- Scaillet, B., B. Clement, B. W. Evans, and M. Pichavant (1998), Redox control of sulfur degassing in silicic magmas, *J. Geophys. Res.*, 103, 23,937–23,949, doi:10.1029/98JB02301.
- Scaillet, B. J., F. Luhr, and M. R. Carrol (2003), Petrological and volcanological constraints on volcanic sulfur emissions to the atmosphere, in *Volcanism and the Earth's Atmosphere, Geophys. Monogr. Ser.*, vol. 139, edited by A. Robock and C. Oppenheimer, pp. 11–40, AGU, Washington, D. C.
- Schnetzler, C. C., G. J. S. Bluth, A. J. Krueger, and L. S. Walter (1997), A proposed volcanic sulfur dioxide index (VSI), *J. Geophys. Res.*, 102, 20,087–20,091, doi:10.1029/97JB01142.
- Scientific Advisory Committee (2007), Assessment of the hazards and risks associated with the Soufrière Hills Volcano, Eighth Report of the Scientific Advisory Committee on Montserrat Volcanic Activity, 31 pp., Foreign and Commonw. Off., London.
- Self, S., and A. J. King (1996), Petrology and sulfur and chlorine emissions of the 1963 eruption of Gunung Agung, Bali, Indonesia, *Bull. Volcanol.*, 58, 263–285, doi:10.1007/s004450050139.
- Self, S., R. Gertisser, T. Thordarson, M. R. Rampino, and J. A. Wolff (2004), Magma volume, volatile emissions, and stratospheric aerosols from the 1815 eruption Tambora, *Geophys. Res. Lett.*, 31, L20608, doi:10.1029/2004GL020925.
- Sharma, K., S. Blake, S. Self, and A. J. Krueger (2004), SO₂ emissions from basaltic eruptions, and the excess sulfur issue, *Geophys. Res. Lett.*, 31, L13612, doi:10.1029/2004GL019688.
- Shinohara, H. (2005), A new technique to estimate volcanic gas composition: Plume measurements with a portable multi-sensor system, *J. Volcanol. Geotherm. Res.*, *143*, 319–333, doi:10.1016/j.jvolgeores.2004.12.004.
- Shinohara, H. (2006), Near vent volcanic plume measurement by a portable multi-gas-sensor system to estimate volcanic gas composition, *Eos Trans. AGU*, *87*(52), Fall Meet. Suppl., Abstract V43E-01.
- Shinohara, H., and K. Kazahaya (1995), Degassing processes related to magma-chamber crystallization, in *Magmas, Fluids, and Ore Deposits, Short Course Ser.*, vol. 23, edited by J. F. H. Thompson, pp. 47–70, Mineral. Assoc. of Can., Quebec, Que., Canada.
- Shinohara, H., and J. Witter (2005), Volcanic gases emitted during mild Strombolian activity of Villarrica volcano, Chile, *Geophys. Res. Lett.*, 32, L20308, doi:10.1029/2005GL024131.
- Shinohara, H., K. Kazahaya, G. Saito, N. Matsushima, and Y. Kawanabe (2002), Degassing activity from Iwodake rhyolitic cone, Satsuma-Iwojima volcano, Japan: Formation of a new degassing vent, 1990–1999, *Earth Planets Space*, 54, 175–185.
- Shinohara, H., K. Fukui, K. Kazahaya, and G. Saito (2003), Degassing process of Miyakejima volcano: Implications of gas emission rate and melt inclusion data, in *Melt Inclusions in Volcanic Systems Advances in Volcanology*, vol. 4, edited by B. De Vivo and R. Bodnar, pp. 147–161, Elsevier, Amsterdam.
- Sigurdsson, H., S. Carey, J. M. Palais, and J. Devin (1990a), Preeruption compositional gradients and mixing of andesite and dacite erupted from Nevado del Ruiz volcano, Colombia in 1985, *J. Volcanol. Geotherm. Res.*, 41, 127–151, doi:10.1016/ 0377-0273(90)90086-U.
- Sigurdsson, H., S. Carey, and J. Devine (1990b), Assessment of the mass, dynamics, and environmental effects of the Minoan eruption of Santorini volcano, in *Thera and the Aegean World 2*, edited by D. A. Hardy, pp. 101–108, Thera Found., London.

- Simkin, T. (1993), Terrestrial volcanism in space and time, *Annu. Rev. Earth Planet. Sci.*, *21*, 427–452, doi:10.1146/annurev.ea. 21.050193.002235.
- Simkin, T., and L. Siebert (1994), *Volcanoes of the World*, 2nd ed., 349 pp., Geoscience, Tucson, Ariz.
- Sisson, T. W., and S. Bronto (1998), Evidence for pressure-release melting beneath magmatic arcs from basalt at Galunggung, Indonesia, *Nature*, 391, 883–886, doi:10.1038/36087.
- Sisson, T. W., and G. D. Layne (1993), H₂O in basalt and basaltic andesite glass inclusions from four subduction-related volcanoes, *Earth Planet. Sci. Lett.*, *117*, 619–635, doi:10.1016/0012-821X(93)90107-K.
- Stevenson, D. S., and S. Blake (1998), Modeling the dynamics and thermodynamics of volcanic degassing, *Bull. Volcanol.*, *60*, 307–317, doi:10.1007/s004450050234.
- Stix, J., G. D. Layne, and S. N. Williams (2003), Mechanisms of degassing at Nevado del Ruiz volcano, Colombia, J. Geol. Soc., 160, 507–521, doi:10.1144/0016-764902-028.
- Stoiber, R. E., L. L. Malinconico, and S. N. Williams (1983), Use of the correlation spectrometer at volcanoes, in *Forecasting Volcanic Events, Dev. Volcanol.*, vol. 1, edited by H. Tazieff and J.-C. Sabroux, pp. 425–444, Elsevier, Amsterdam.
- Stoiber, R. E., S. N. Williams, and B. Huebert (1987), Annual contribution of sulfur dioxide to the atmosphere by volcanoes, *J. Volcanol. Geotherm. Res.*, 33, 1–8, doi:10.1016/0377-0273(87)90051-5.
- Stothers, R. B. (1996), The great dry fog of 1783, *Clim. Change*, *32*, 79–89, doi:10.1007/BF00141279.
- Streck, M. L., and S. Wacaster (2006), Plagioclase and pyroxene hosted melt inclusions in basaltic andesites of the current eruption of Arenal volcano, Costa Rica, *J. Volcanol. Geotherm. Res.*, 157, 236–253, doi:10.1016/j.jvolgeores.2006.03.040.
- Sutton, A. J., T. Elias, T. M. Gerlach, and J. B. Stokes (2001), Implications for eruptive processes as indicated by sulfur dioxide emissions from Kilauea volcano, Hawaii, 1979–1997, *J. Volcanol. Geotherm. Res.*, 108, 283–302, doi:10.1016/S0377-0273(00)00291-2.
- Swanson, D. A., D. Dzurisin, R. I. Holcomb, E. Y. Iwatsubo, W. W. Chadwick Jr., T. J. Casadevall, J. W. Ewert, and C. C. Heliker (1987), Growth of the lava dome at Mount St. Helens, Washington, (USA), 1981–1983, Spec. Pap. Geol. Soc. Am., 212, 1–16.
- Symonds, R. B., W. I. Rose, G. J. S. Bluth, and T. M. Gerlach (1994), Volcanic-gas studies: Methods, results, and applications, in *Volatiles in Magmas, Rev. Mineral.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 1–66, Mineral. Soc. of Am., Washington, D. C.
- Symonds, R. B., T. M. Gerlach, and M. H. Reed (2001), Magmatic gas scrubbing: Implications for volcano monitoring, *J. Volcanol. Geotherm. Res.*, *108*, 303–341, doi:10.1016/S0377-0273(00)00292-4.
- Taran, Y. A., J. W. Hedenquist, M. A. Korzhinsky, S. I. Tkachenko, and K. I. Shumulovich (1995), Geochemistry of magmatic gases from Kudryavy volcano, Itrup, Kurile Islands, *Geochim. Cosmochim. Acta*, 59, 1749–1761, doi:10.1016/0016-7037(95)00079-F.
- Taylor, P. A., and R. E. Stoiber (1973), Soluble material on ash from active central American volcanoes, *Geol. Soc. Am. Bull.*, *84*, 1031–1042, doi:10.1130/0016-7606(1973)84<1031:SMOA-FA>2.0.CO;2.
- Taylor, S. R., and S. M. McLennan (1995), The geochemical evolution of the continental crust, *Rev. Geophys.*, *33*, 241–265, doi:10.1029/95RG00262.
- Tazieff, A. (1994), Permanent lava lakes: Observed facts and induced mechanisms, J. Volcanol. Geotherm. Res., 63, 3–11, doi:10.1016/0377-0273(94)90015-9.
- Thordarson, T., S. Self, N. Oskarsson, and T. Hulsebosch (1996), Sulfur chlorine, and fluorine degassing and atmospheric loading by the 1783–1784 AD Laki (Skaftar) eruption in Iceland, *Bull. Volcanol.*, *58*, 205–225, doi:10.1007/s004450050136.

- Thordarson, T., D. J. Miller, G. Larsen, S. Self, and H. Sigurdsson (2001), New estimates of sulfur degassing and atmospheric mass-loading by the 934 AD Eldgja eruption, Iceland, *J. Volcanol. Geotherm. Res.*, 108, 33–54, doi:10.1016/S0377-0273(00)00277-8.
- Togashi, S., N. Imai, Y. Okuyama-Kusunose, T. Tanaka, T. Okai, T. Koma, and Y. Murata (2000), Young upper crustal chemical composition of the orogenic Japan Arc, *Geochem. Geophys. Geosyst.*, 1(11), 1049, doi:10.1029/2000GC000083.
- Ueda, H., E. Fujita, M. Ukawa, E. Yamamoto, M. Irwan, and F. Kimata (2005), Magma intrusion and discharge process at the initial stage of the 2000 activity of Miyakejima, central Japan, inferred from tilt and GPS data, *Geophys. J. Int.*, *161*, 891–906, doi:10.1111/j.1365-246X.2005.02602.x.
- Varekamp, J. C., J. F. Luhr, and K. Prestegaard (1984), The 1982 eruption of El Chichón volcano (Chiapas, Mexico): Character of the eruptions, ash-fall deposits, and gas phase, *J. Volcanol. Geotherm. Res.*, 23, 39–68, doi:10.1016/0377-0273(84)90056-8.
- Varley, N. R., and M. A. Armienta (2001), The absence of diffuse degassing at Popocatépetl volcano, Mexico, *Chem. Geol.*, 177, 157–173, doi:10.1016/S0009-2541(00)00389-2.
- Vergniolle, S., and M. Mangan (2000), Hawaiian and Strombolian eruptions, in *Encyclopedia of Volcanoes*, edited by H. Sigurdsson, pp. 447–461, Academic, San Diego, Calif.
- Wade, J. A., T. Plank, W. G. Melson, G. J. Soto, and E. H. Hauri (2006), The volatile content of magmas from Arenal volcano, Costa Rica, J. Volcanol. Geotherm. Res., 157, 94–120, doi:10.1016/j.jvolgeores.2006.03.045.
- Walker, J. A., K. Roggensack, L. C. Patino, B. I. Cameron, and O. Matías (2003), The water and element contents of melt inclusions across an active subduction zone, *Contrib. Mineral. Petrol.*, *146*, 62–77, doi:10.1007/s00410-003-0482-x.
- Wallace, P. J. (2001), Volcanic SO₂ emissions and the abundance and distribution of exsolved gas in magma bodies, *J. Volcanol. Geotherm. Res.*, *108*, 85–106, doi:10.1016/S0377-0273(00)00279-1.
- Wallace, P. J. (2003), From mantle to atmosphere: Magma degassing, explosive eruptions, and volcanic volatile budgets, in *Melt Inclusions in Volcanic Systems, Dev. Volcanol.*, vol. 4, edited by B. De Vivo and R. Bodnar, pp. 147–161, Elsevier, Amsterdam.
- Wallace, P. J. (2005), Volatiles in subduction zone magmas: Concentrations and fluxes based on melt inclusion and volcanic gas data, J. Volcanol. Geotherm. Res., 140, 217–240, doi:10.1016/ j.jvolgeores.2004.07.023.
- Wallace, P., and I. S. E. Carmichael (1992), Sulfur in basaltic magmas, *Geochim. Cosmochim. Acta*, 56, 1863–1874, doi:10.1016/0016-7037(92)90316-B.

- Wallace, P. J., and T. M. Gerlach (1994), Magmatic vapor source for sulfur dioxide released during volcanic eruptions: Evidence from Mount Pinatubo, *Science*, 265, 497–499, doi:10.1126/ science.265.5171.497.
- Wallace, P. J., A. T. Anderson Jr., and A. M. Davis (1995), Quantification of pre-eruptive exsolved gas contents in silicic magmas, *Nature*, *377*, 612–616, doi:10.1038/377612a0.
- Westrich, H. R., and T. M. Gerlach (1992), Magmatic gas source for the stratospheric SO₂ cloud from the June 15, 1991, eruption of Mount Pinatubo, *Geology*, 20, 867–870, doi:10.1130/0091-7613(1992)020<0867:MGSFTS>2.3.CO;2.
- Westrich, H. R., J. C. Eichelberger, and R. L. Hervig (1991), Degassing of the 1912 Katmai magmas, *Geophys. Res. Lett.*, *18*, 1561–1564, doi:10.1029/91GL01667.
- White, S. M., J. A. Crisp, and F. J. Spera (2006), Long-term volumetric eruption rates and magma budgets, *Geochem. Geophys. Geosyst.*, 7, Q03010, doi:10.1029/2005GC001002.
- Williams-Jones, G., J. Stix, M. Heiligmann, J. Barquero, E. Fernandez, and E. D. Gonzalez (2001), A model of degassing and seismicity at Arenal volcano, Costa Rica, *J. Volcanol. Geotherm. Res.*, 108, 121– 139, doi:10.1016/S0377-0273(00)00281-X.
- Wilson, L., and J. W. Head (1981), Ascent and eruption of basaltic magma on the Earth and Moon, J. Geophys. Res., 86, 2971– 3001, doi:10.1029/JB086iB04p02971.
- Witter, J. B., V. C. Kress, P. Delmelle, and J. Stix (2004), Volatile degassing, petrology, and magma dynamics of the Villarrica Lava Lake, Southern Chile, *J. Volcanol. Geotherm. Res.*, 134, 303–337, doi:10.1016/j.jvolgeores.2004.03.002.
- Witter, J. B., V. G. Kress, and C. G. Newhall (2005), Volcán Popocatépetl, Mexico. Petrology, magma mixing, and immediate sources of volatiles for the 1994-present eruption, *J. Petrol.*, 46, 2337–2366, doi:10.1093/petrology/egi058.
- Zapata, G. J. A., et al. (1997), SO₂ fluxes from Galeras volcano, Colombia, 1989–1995: Progressive degassing and conduit obstruction of a Decade Volcano, *J. Volcanol. Geotherm. Res.*, 77, 195–208, doi:10.1016/S0377-0273(96)00094-7.
- Zhang, Y., X. Zhengjiu, Z. Mengfan, and W. Haoyue (2007), Silicate melt properties and volcanic eruptions, *Rev. Geophys.*, 45, RG4004, doi:10.1029/2006RG000216.
- Zielinski, G. A. (1995), Stratospheric loading and optical depth estimates of explosive volcanism over the last 2100 years derived from the Greenland Ice Sheet Project 2 ice core, *J. Geophys. Res.*, *100*, 20,937–20,955, doi:10.1029/95JD01751.

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