Integrating Petrologic and Remote Sensing Perspectives on Magmatic Volatiles and Volcanic Degassing

The volatile constituents—H₂O, CO₂, and S—and Cl—play an important role in the generation, evolution, and eruption of magma. Knowledge of the abundance and flux of these volatiles is important for understanding the hazard implications of volcanic activity, explosive eruptive behavior of volcanoes, recycling of volatiles in subduction zones, formation of magmatic-hydrothermal ore deposits, additions of volcanic gases to Earth’s atmosphere, and potential climatic impacts of large volcanic eruptions.

Over the past 25 years, new developments in technology have led to major advances in our ability to measure the fluxes of volatiles released from erupting volcanoes. At the same time, new micro-analytical techniques have made it possible to measure the pre-eruptive concentrations of magmatic volatiles through the use of tiny melt inclusions trapped in phenocrysts in volcanic rocks. Comparison of the data acquired from these different perspectives has highlighted some major gaps in our understanding of both the abundance of the different volatiles, and the ways in which they are transported through magmatic systems and released to the atmosphere by degassing.

Remote Sensing Approaches

Sulfur dioxide (SO₂) is the easiest of the main magmatic volatiles to measure in volcanic plumes, because its concentration is relatively high compared to ambient atmospheric values. However, CO₂ and H₂S can also be analyzed using aircraft-based gas analyzers and sensors [e.g., McGee et al., 2001], and H₂O, HCl, HF, CO₂, and several other species can be measured using Fourier-Transform Infrared (FTIR) spectroscopy [e.g., Burton et al., 2000]. Remote sensing of SO₂ is achieved using absorption bands of SO₂ gas in the ultraviolet (UV) and infrared (IR) regions of the electromagnetic spectrum. Numerous remote measurements of SO₂ fluxes from active volcanoes have been made, including both ground-based and airborne use of the UV correlation spectrometer (COSPEC) since the early 1970s, and the satellite-based Total Ozone Mapping Spectrometer (TOMS; Figure 1) since 1978 [Kneebone et al., 2000; see: http://skye.gsfc.nasa.gov].

Building on the measurements of volcanic SO₂ from space pioneered by the UV TOMS instruments, recent years have seen launches of IR sensors that have augmented the SO₂ mapping capabilities available to volcanologists [Reaño et al., 1997]. The Moderate Resolution Imaging Spectroradiometer (MODIS) carried by NASA’s Earth Observing System (EOS) Terra and Aqua satellites, and the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) on EOS/Terra offer the potential to quantitatively measure SO₂ plumes emitted by many quiescent volcanoes. Measurements of larger SO₂ clouds in the upper troposphere and stratosphere, traditionally the domain of TOMS, can also now be accomplished several times daily using data from the High Resolution Infrared Sounder (HIRS) on NOAA’s polar-orbiting satellites [Prata et al., 2003]. Moreover, further developments are anticipated in 2004 with the launch of the Ozone Monitoring Instrument (OMI) on EOS/Aura. OMI will be the successor to TOMS and is expected to be able to routinely measure volcanic SO₂ including passive plumes in the atmospheric boundary layer.

An advanced multispectral IR sensor (SEVIRI; http://www.esa.int/msg/pag1.html) on the European Space Agency’s new Meteosat Second Generation (MSG) satellite, expected to be operational very soon, will provide geostationary coverage of volcanic clouds over Europe and Africa. Geostationary platforms stare at the same places and allow for very frequent coverage, which will result in sensing of short-lived eruptions, and the IR bands are ideal for SO₂ and ash sensing. Despite having greater volcanic activity, North and South America have no comparable IR coverage, and from 2004 to −2012, will lose important geostationary ash detection capability on the GOES satellite. After 2012, a new sensor called ABI (Advanced Baseline Imager), which is currently being developed, will fly over the Americas and provide robust coverage of volcanic clouds.

Measurement of volcanic clouds by multispectral techniques has demonstrated the utility of examining clouds from different perspectives. There is really no one method or spectral range that is universally appropriate for evaluating SO₂ in volcanic plumes. Each sensor is limited by its spatial, temporal, or spectral resolution, and thus, observes only a portion of a plume, or is best suited for evaluating a plume for a short period of time or under a restricted range of meteorological and volcanological conditions. Interference by co-emitted ash, meteorological clouds, background reflectivity, and the presence or generation of aerosols, ice, and other gases in the plumes all affect retrievals to varying degrees, and are unique to each setting and event.

Knowledge of meteorological conditions (relative humidity, temperature, wind vectors) also plays a vital role in evaluating gas fluxes, particularly for effusive emissions. The scientific utility of remotely sensed data is often dependent on the ability to measure or model surrounding environmental conditions. A multispectral approach is vital because volcanic clouds evolve, sometimes rapidly, both in physical and chemical character during the first few days of emission into the atmosphere. With the addition of new tools and techniques has come the discovery of many new complexities and processes affecting the fate of volcanic emissions.

Recent Developments in Ground-based and Airborne Methods

Ground-based and airborne techniques for monitoring volcanic emissions are also advancing. One important development is the application of miniature UV spectrometers to SO₂ retrieval [Galle et al., 2002]. These low-cost, lightweight devices will probably supplement the COSPEC as the instrument of choice for proximal surveillance of degassing volcanoes.

Another development is an airborne system devised by the U.S. Geological Survey that directly measures concentrations of CO₂, SO₂, and H₂S by extraction sampling of plumes. The system includes an infrared gas analyzer, chemical sensors, a closed-path FTIR instrument, a COSPEC, a high-precision barometer, a temperature probe, and a GPS receiver. Measurements sample a range of altitudes along traverses orthogonal to plume (wind) direction or along orbits circling a volcano (Figure 2A).
Data for all gases are recorded at 1-s intervals and tagged with latitude, longitude, altitude, temperature, and pressure. Gas concentrations in plume cross-sections are contoured with mapping software (Figures 2B, 2C) and used with in-flight wind data to calculate emission rates.

The system is modular and can be deployed on fixed-wing aircraft and helicopters, or mounted on vehicles for ground-level measurements, making it suitable for a wide range of volcanic environments. It is applicable to volcanoes of the western United States and Alaska, where locations are remote, ground access is difficult, and wet climates, snowpack, and glaciers foster hydrothermal and ground waters that can scrub acid magmatic volatiles (SO₂, HCl, HF), masking degassing at depth during critical early stages of unrest. Campaigns to date have constrained CO₂ emission rates from as low as 200–300 tons/day at Mammoth Mountain and Mount Baker, to as high as 8000–9000 tons/day at Popocatépetl and Kilauea [McGee et al., 2001; Gerlach et al., 2002, and references therein].

Except in rare cases, the gas emission monitoring techniques covered in this article are not likely to measure effectively the diffuse degassing flux of volcanoes. Although tending to be smaller in magnitude than vent degassing, diffuse degassing is an important component of the total gas emission at many volcanoes, and in some instances—Mammoth Mountain being a notable example—it can be the dominant mode of degassing. Eddy covariance methods and soil gas efflux surveys offer alternative monitoring techniques for diffuse degassing.

Petrologic Studies of Magmatic Volatiles

With the techniques summarized above, volcanologists now have at their disposal a toolkit of instruments capable of quantifying emissions of SO₂ and other volatiles at a range of temporal and spatial scales. Used in concert, these techniques have the potential to produce a vastly improved and expanded volcanic degassing data set. Complementary to these developments in remote sensing, new sampling and micro-analytical techniques have made it increasingly possible to get information on magmatic volatiles directly from samples of volcanic material. Because the solubility of most volatile components is strongly pressure-dependent, magmas exsolve gas during ascent to the surface.

To understand eruptive behavior, it is important to know the total volatile content of magma during its pre-eruptive storage within the Earth’s crust. An important source of information on dissolved volatiles in magmas is through the analysis of glass inclusions trapped inside of crystals. When melts crystallize, the crystals grow imperfectly, causing small blebs of melt to be trapped inside of the crystals. If the magma erupts and cools rapidly, then these trapped melt inclusions quench to glass. Because the crystalline host for the inclusions is relatively rigid, they act as tiny pressure vessels and prevent the trapped melt from degassing, even though the bulk magma decompresses to surface pressure during eruption. For this reason, trapped melt (glass) inclusions commonly retain their original dissolved volatiles. Melt inclusions are now routinely analyzed for many volatile species (H₂O, CO₂, S, Cl, F) using infrared and Raman spectroscopy, electron microprobe, and secondary ion mass spectrometry (SIMS).

Comparison of Remote Sensing and Petrologic Perspectives–The Excess Sulfur Problem

It is possible to use data for S in melt inclusions to make an estimate of how much S would
be released in a volcanic eruption based on knowledge of the total volume of erupted magma. However, such estimates assume that the only S released during an eruption is S that was originally dissolved in the silicate liquid (melt) portion of the magma. Comparison of such “petrologic” estimates based on melt inclusion data with \( \text{SO}_2 \) emissions measured for recent eruptions by remote sensing techniques has led to a conundrum, known as the “excess” sulfur problem, concerning S mass balance during volcanic eruptions [Andres et al., 1991]. Concentrations of dissolved S in magmas before eruption, as estimated from melt inclusion data, are commonly far too low (by 1 to 2 orders of magnitude) to account for the total mass of \( \text{SO}_2 \) released during the eruption, as measured by remote sensing techniques (Figure 3). Excess S is observed in most eruptions for which remote sensing and melt inclusion data are available, and in particular, is characteristic of explosive eruptions of intermediate and silicic magma in subduction zone settings [Andres et al., 1991]. In contrast, basaltic eruptions from divergent plate boundaries and hot spots, such as Hawaiian and Icelandic volcanoes, often do not show evidence of excess S emissions (Figure 3).

It has commonly been assumed that magmas of intermediate-to-silicic composition only become vapor-saturated during shallow ascent and emplacement, during eruptive decompression, or during advanced (pegmatitic) stages of plutonic crystallization. However, numerous lines of evidence from petrologic, remote sensing, and volcanic gas data suggest that the “excess” S problem is caused by the presence of an exsolved C-O-H-S vapor phase in the magma before eruption [Luhr et al., 1984; Andres et al., 1991; Westrich and Gerlach, 1992; Wallace, 2003]. That is, the concentrations of dissolved volatiles are sufficient to cause saturation of the magma with a multi-component vapor phase, which would presumably be present as bubbles dispersed throughout magma in crustal storage reservoirs. As a result, eruptions of silicic magma can release large amounts of \( \text{SO}_2 \) derived from pre-eruptive exsolved vapor, despite the fact that such magmas generally have very low concentrations of dissolved S. Techniques for quantifying the mass fraction of exsolved vapor in magma before eruption are thus important for understanding \( \text{SO}_2 \) flux data used for forecasting and monitoring eruptions, and for assessing the potential climatic impacts of volcanic eruptions.

The large amounts of volatiles implied by these estimates suggest that exsolved vapor accumulates in the apical regions of magma bodies during repose periods between eruptions, or may get trapped below hydrothermal caps above the body. The presence of an exsolved vapor phase in crystallizing magma bodies may also play an important role in triggering volcanic eruptions. Remote sensing data frequently observe spatial separation of \( \text{SO}_2 \) and ash in explosive eruptions, and improved frequency of IR satellite data is likely to clarify whether a gas-rich phase is released early in explosive events, an idea consistent with observations [Rose et al., 2003].

**Sources of Volatiles in Crustal Magmatic Systems**

Isotopic studies of S and CO\(_2\) in intermediate-to-silicic magmas have demonstrated that a large component of these volatiles is...
mantle-derived. The ultimate source of S and CO$_2$ must therefore be from mafic magma, because it is well established that silicic magma reservoirs are created and sustained through long-term intrusion of mantle-derived basaltic magma into the crust. It should be noted, however, that in the case of subduction zones, some portion of the mantle S and C (and almost all H$_2$O) may ultimately have been recycled from subducted sediments and altered oceanic crust.

Andesitic, dacitic, and rhyolitic magmas in crustal reservoirs are probably vapor-saturated due to recharge and underplating by basaltic magma that is saturated with multi-component CO-HS vapor. In this regard, vapor saturation of intermediate to silicic magmas can be viewed as the inevitable consequence of the relatively high CO$_2$ concentration of basaltic magmas coupled with relatively low CO$_2$ solubility in silicate melts at crustal pressures.

Vapor transfer from underplated basaltic magma into an overlying silicic magma body is probably a slow process that occurs during the long repose periods that separate eruptive episodes. In systems where intrusion of basaltic magma into the lower crust generates silicic magma by partial melting and/or fractional crystallization, transfer of volatiles into mid-to-upper-crustal silicic magma chambers may be a very complex process compared to systems in which basaltic magma intrudes directly into a silicic magma reservoir. However, in either case, if the S and CO$_2$ in crustal magmatic systems are largely derived from the mantle via basaltic magma, then the flux of these volatiles should be directly related to the basaltic magma flux.

The importance of mantle-derived basalt as a source of volatiles is exemplified by mafic cinder cones surrounding Popocatépetl (“Popo”) volcano in central Mexico. Mafic-andesite eruptions explosively from Popo during the current eruption (December 1994 to 2002) have phenocryst assemblages and major- and trace-element systematics that indicate mixing of mafic and silicic magma, and SO$_2$ and CO$_2$ emissions have both been very high [see references in Wallace, 2003]. Quaternary mafic cinder cones in the region surrounding Popo provide samples of possible mafic end members involved in mixing. Olivine-hosted melt inclusions from these cones contain 1000–6000 ppm S, 250–2100 ppm CO$_2$, and 1.3–5.2 wt% H$_2$O [Cervantes and Wallace, 2003]. The high S contents suggest that mafic magma recharging into the Popo system provides an abundant source of S that may explain the very large SO$_2$ emissions from the current eruption. The H$_2$O and CO$_2$ contents are sufficiently high that these mafic magmas would be vapor-saturated at the depths of a shallow crustal magma chamber beneath the volcano, so recharging mafic magmas could transfer significant volatiles during recharge events.

**Future Directions**

Future directions in remote sensing of volcanic clouds feature multispectral retrievals to examine the interactions and removal rates of different species in the clouds, and to provide more comprehensive evaluations of emission fluxes throughout various phases (e.g., explosive versus effusive) of volcanic activity. Progress in understanding budgets of the major magmatic volatiles requires integration of remote sensing and volcanic gas data on fluxes of CO$_2$, SO$_2$, H$_2$S, H$_2$O, and HCl with petrologic data on temperature, pressure, oxygen fugacity, and dissolved volatiles in both differentiated magma stored in crustal reservoirs and mafic magma recharging these systems.

Experimental studies of vapor-melt partitioning of volatiles are also needed, particularly for S. Such studies are crucial for developing and calibrating thermodynamic models for predicting vapor saturation and degassing of a multi-component vapor phase over a wide range of conditions. Seismic studies of sub-volcanic magma bodies can also potentially play an important role in the problem of determining volatile budgets, by providing evidence for the presence and abundance of exsolved vapor in magma stored within the Earth’s crust.

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Coastal Observatory Investigates Energetic Current Oscillations on Southeast Florida Shelf

Coastal circulation along the southeast Florida shelf is strongly related to the dynamics of the Florida Current. The current follows the steep bottom terrain along the shelf break separating the deep ocean from the coastal zone (Figure 1a, b). Energetic and complex flow regimes arise along the current’s western edge, causing transient features such as sub-meso-scale eddies [Lee and Mayer, 1977; Shay et al., 2000] and energetic internal oscillations [Mooers, 1975; Soloviev et al., 2003], which affect mixing between the shelf and deeper ocean waters. Understanding of these regimes is important for modeling and prediction of the coastal circulation on the southeast Florida shelf and description of western boundary current/continental shelf interactions.

A striking feature of the circulation on the shelf off southeast Florida is the energetic baroclinic supertidal oscillation, which produces 10-hr period current velocity oscillations with a 0.5- m s⁻¹ amplitude. At the same time, current velocity oscillations induced by the barotropic tide usually do not exceed about 0.05-m s⁻¹ amplitude. Spectral analysis of the sea level signal reveals the expected semi-diurnal tidal peak close to the 12-hr time period (Figure 1c). The corresponding peak, however, is not seen in the velocity spectrum; instead, a 10-hr peak close to the 12-hr time period (Figure 1c). The magnitude at which the squared current velocity magnitudes within the 8- to 12.5-hour band for each summer from 1999–2002 are shown.

Variability of the baroclinic currents affects societally relevant issues such as navigation, acoustics, search and rescue operations, beach erosion, and coastal pollution from sewage plants, harmful algal blooms, and oil spills [Peters et al., 2002]. These important practical issues could require that the baroclinic current oscillation on the southeast Florida shelf be more fully understood and its frequency and importance in nature be assessed.

Project Background

The South Florida Ocean Measurement Center (SFOMC) was established in 1998 through a partnership involving government and academia. A congressional grant, along with a