

and a capping (8-12 m) hyaloclastite. Contacts between lithologic layers are gradual, mostly marked by changes in modal mineralogy, although there is also a distinct change in plagioclase morphology concurrent with its modal increase. From pyroxenite to gabbro, plagioclase shifts from fine, interstitial sprays to large laths in a subophitic intergrowth with pyroxene. Whole rock and pyroxene compositions display typical fractionation trends (e.g. Fe/Mg, Ti, Zr, Nb increase up-section). Furthermore, a weighted sum of 22 whole rock compositions from the internal layers match the hyaloclastite composition well for most non-mobile elements. All these factors suggest formation of the three internal layers by fractional crystallization and evolution of a magma whose composition is represented by the hyaloclastite. Any proposed differentiation process must address some specific observations. Cluster and CSD analysis reveal that pyroxene grains grew in clusters under steady-state conditions of nucleation and growth. Pyroxene grain size is nearly uniform throughout the pyroxenite, suggesting thermal conditions were maintained over a long crystallization interval. Progression of a typical solidification front would produce a fine-grained roof crust beneath the quenched top, but there is no evidence of such a layer in Theo's. Unlike magmas for which solidification fronts are invoked, Theo's parent magma was highly mafic and Al-poor, yielding a low viscosity magma (4 Pa-s) that crystallized only pyroxene over a long temperature interval. We will consider two formation models in which differentiation was driven by crystallization at flow top and bottom, but accumulation only occurred at the base. One model addresses the possible role of convection.

V12E MCC: 3008 Monday 1340h

Volcanic Emissions to the Troposphere: Origins, Processes and Monitoring (joint with A, B)

Presiding: M Herzog, University of Michigan; S A Carn, Joint Center for Earth Systems Technology, University of Maryland, Baltimore County

V12E-01 1340h

The Chemistry of Tropospheric Volcanic Plumes

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Persistently degassing volcanoes contribute substantial amounts of many different chemical species to the troposphere, including acidic gases (sulfur dioxide, HF and HCl), toxic trace metals (including mercury, cadmium and lead) and aerosols of different types. The continuous release of such species from active volcanoes may lead to significant short- and medium-range environmental impacts as well as constituting an important contribution to global natural emissions inventories. However, the emissions from many important volcanic centers remain poorly characterized meaning that the global volcanic emissions of many species are not reliably constrained. Further, the chemical evolution of volcanic plumes from emission source (magma) to the point of deposition remains poorly understood. Our work seeks to build upon and extend previous efforts in this field. We have deployed a range of field instruments at active volcanoes (including those in Nicaragua, Italy and Chile) in order to study different aspects of volcanic plume chemistry. These studies have included the use of an impactor (particles), sun photometry (particles), filter packs (particles and gases) and UV spectrometry (gases). Our primary aims are to look for trends in emission composition with style of degassing (e.g. open-vent vs fumarolic) and to consider how the emittants are processed during transport under different atmospheric conditions. As well as contributing to the understanding of local and regional scale impacts of volcanic plumes, this work will enable us to improve global flux estimates of volcanic emissions, such as trace metals and aerosols (particularly important given the ongoing efforts of climate modelers to include particles in their models). We are also working to identify previously unconsidered components in volcanic plumes. We have recently identified

nitric acid emissions from volcanoes, suggesting that volcanoes are not only important atmospheric sources of chemicals exsolved from magma, but may also be important as high temperature reaction environments for plume-air mixtures.

V12E-02 1355h

Aerosol Evolution Within a Low-Temperature Volcanic Plume

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In order to investigate the early evolution of aerosols within a volcanic plume, atmospheric samples were collected at Poas, a persistently degassing volcano in Costa Rica. Chemical bulk compositions and morphologies of the collected aerosols were examined using transmission electron microscopy. Aerosol morphologies correlate with distinctions in composition and with sampling location. A bimodal size distribution of aerosols is observed at all sampling locations. The small aerosols exist in clusters of semi-spherical bodies averaging 35nm across, characteristic of homogeneously nucleated aerosols. The large aerosols are solid and/or liquid, with the solid aerosols averaging 150nm across, characteristic of primary aerosols. The large liquid aerosols have more complex bulk chemistry than the small homogeneously nucleated aerosols, both size and composition suggesting they condensed on already existing aerosols. Both size modes of aerosols are 300nm larger 280m distant from source, indicating that coagulation commences immediately and occurs uniformly for both modes of aerosols. Aerosol compositions were compared with predictions of an equilibrium model assuming homogeneous nucleation of aerosols generated by mixing the 92°C volcanic gases with ambient temperature air. The collected aerosols have different and more complex compositions than the model predicts to be stable in the plume. We suggest that heterogeneous nucleation and coagulation are important processes in the first seconds of plume travel and these processes, as well as the inclusion of airborne, locally-produced mineral dust must be considered in an accurate model of plume evolution.

V12E-03 1410h

The Critical Role of UV Satellite Data in Monitoring Volcanic Sulfur Dioxide Emissions in the Troposphere

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From the Congo to the Galápagos Islands to Iceland, effusive eruptions of sulfur-rich basaltic magma often liberate prodigious quantities of SO₂ (~0.05-5 Tg) over days or weeks of continuous emissions. Much of this SO₂ (and hence derived sulfate aerosol) resides in the troposphere, although there is evidence that small amounts reach the stratosphere following larger eruptions. Measurements by the Total Ozone Mapping Spectrometer (TOMS) instruments since 1978 indicate that such emissions represent an important and persistent source of tropospheric SO₂, contributing >30% of the total volcanic SO₂ measured by TOMS to date. Continued monitoring of this SO₂ source is therefore critical to any assessment of global volcanic degassing and its potential environmental or climatic impacts. Detection of SO₂ emissions from space also acts as an important signature of eruptive activity in the absence of other observations, allowing eruptions from remote volcanoes to be monitored. The ultraviolet wavelengths used by TOMS are comparatively insensitive to the effects of atmospheric water vapor, which perturbs retrievals of SO₂ in the infrared. Since the most prolific sources of tropospheric SO₂, such as Nyamuragira (D.R. Congo) and the Galápagos volcanoes, are located in the tropics, TOMS has been the most suitable tool for measuring these emissions, which are also very difficult and hazardous to study using ground-based or airborne techniques. UV measurements at higher spatial and spectral resolution than TOMS will be continued

in 2004 by the Ozone Monitoring Instrument (OMI) on the EOS/Aura satellite. The increased sensitivity of OMI will permit detection of smaller volcanic clouds, along with lower tropospheric and boundary layer SO₂ plumes and hence expand the capabilities of UV satellite data. Temporal resolution is the major constraint on polar-orbiting UV satellite data, with only one image per day available at low latitudes. This complicates attempts to estimate the mass of SO₂ produced by continuously-emitting effusive eruptions, and will also apply to observations of passive degassing using OMI. We are exploring several techniques to combat this, including derivation of SO₂ fluxes and loss rates from TOMS data and use of contemporaneous geostationary satellite imagery to constrain eruption timing. Several examples will be presented, including eruptions of Nyamuragira and Cerro Azul (Galápagos Is).

URL: <http://skye.gsfc.nasa.gov>

V12E-04 1425h

Forward modeling of volcanic aerosols transmissions at different latitudes; quantifying the effects of varying tropospheric water vapor on ash detection.

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Current algorithms for volcanic ash cloud detection by satellite, based upon a difference in transmissivity of silicate ash at 11 and 12 microns, are subject to significant and yet poorly quantified modulation by atmospheric water vapor. In order to investigate these effects we have written an aerosol forward model, based upon Mie-scattering code, and embedded it in a MODTRAN-based atmospheric radiative transfer model. This facilitates investigation of errors associated with inverse solutions derived from satellite data, and more importantly for this study, can be used to vary the atmosphere within which a hypothetical volcanic ash cloud is contained. We have taken images of the most well parameterized ash clouds of the satellite age, the sequence of eruptions of Mt. Spurr in mid to late 1992, and applied the forward model to predict transmission spectra of the ash clouds. Calculations were performed for the ash clouds both within the cloud's original atmosphere and within that of a sequence of eruptions of Soufriere Hills Volcano, Montserrat, in the British West Indies in the late 1990s. Preliminary results indicate a +1-3.5 K brightness temperature difference (BTD) effect associated with increasing the temperature and water vapor content of the atmosphere. This translates to a significant loss of detectability in terms of cloud area; up to half the area of the clouds no longer have a negative brightness temperature difference, and an effect on reducing the optical depth and mass of the cloud. In most cases there was very good agreement between the 'clear ocean' BTD and the modeled effect, suggesting a potential source of in-image calibration for detection algorithms. In terms of mass and optical depth retrievals however, it is obvious that both 11 and 12 micron channel radiances are affected by the presence of water vapor, clearly indicating the need for atmospheric correction before quantifying the size or concentration of ash in clouds from satellite data.

V12E-05 1440h

Investigation Of Volcanic Gas Emission By MAX-DOAS And I-DOAS

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Simultaneously measurements of BrO, SO₂ and other trace gases in volcanic plumes were made. With a Mini - MAX-DOAS (Multi Axis Differential Optical Absorption Spectroscopy) an image of the BrO and SO₂

distribution in a volcanic plume was determined. Reactive bromine in the form of BrO was found to be present in volcanic plumes and mixing ratios up to 1 ppb were determined at Soufriere Hills Volcano on Montserrat. These give volcanoes the potential to be a BrO source that is at least locally important and may be even relevant on a global scale. BrO plays an important role in the tropospheric and stratospheric ozone cycle. BrO is - in comparison to HBr - not water-soluble and can therefore reach the stratosphere during large eruptions or otherwise is dispersed in the troposphere. MAX-DOAS and I-DOAS (Imaging-DOAS) are optical remote-sensing methods using scattered sunlight. They allow highly sensitive and specific detection of many trace gases simultaneously (specific molecules not just elements) and can measure the temporal and spatial variation of these gases. The Mini-MAX-DOAS is lightweight, robust and has a very low power consumption, which permits measurements of atmospheric trace gases in remote locations, such as volcanoes often are. The I-DOAS allows taking two-dimensional pictures from a volcanic plume with very high spatial resolution. Therefore it provides useful information about the chemical composition and its variability in a volcanic plume and the possibility to study plume dispersal and chemical transformations. An introduction in these techniques that are newly applied in volcanic gas research will be given as well as several measurement results from different volcanic sites.

V12E-06 1455h

Mixing Ratios of Br, BrO, Cl, and ClO in High-Temperature Volcanic Gases

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Bobrowski et al. recently reported 1-ppb levels of BrO gas in plume 4-7 km downwind of the summit of Soufriere Hills volcano, Montserrat (Nature, 15 May 2003, v. 423, p. 273-276). This first detection of BrO in volcanic plume is potentially important evidence of halogen-catalyzed tropospheric ozone destruction. Bobrowski et al. conclude that volcanoes either directly emit BrO or emit bromine species that are rapidly converted to reactive bromine in volcanic plume. Thermodynamic speciation models show that HBr, HCl, and HF are by far the dominant halogen species emitted at 900 - 1200°C by degassing magma of arc, divergent plate, and hot spot volcanoes; they have molar mixing ratios exceeding those of BrO, ClO, and FO by factors $>10^8$; the predicted mixing ratios of BrO, ClO, and FO are generally $<10^{-13}$. Direct magma degassing is therefore not the source of the observed 1-ppb levels of BrO in the Soufriere Hills plume, nor is it likely to be a significant source of ClO. Furthermore, attempts to enhance BrO by high-temperature mixing of volcanic gas and air, as can occur in close proximity to erupting magma and by advection of air through hot volcanic domes, failed to boost BrO levels above 1 ppb in the speciation models. Thus it does not appear that the volcano is in any way the direct source of BrO observed in the Soufriere Hills plume, and alternatives for its origin need to be considered. For example, volcanoes may emit bromine and chlorine species that can be converted rapidly to reactive Br and Cl by gas phase and/or heterogeneous reactions in the volcanic plume. The conversion rates of HBr and HCl, which clearly are emitted by degassing magma, to reactive Br and Cl may be enhanced by relatively high mixing ratios for OH in volcanic plumes; speciation models give OH mixing ratios for degassing magma in the range 10^{-8} to 10^{-5} , compared to typical background atmospheric values of 10^{-14} . Speciation models also indicate that direct magma degassing of reactive Br and Cl as atomic Br and Cl at mixing ratios of 10 to 300 ppb is plausible; atomic Br and Cl mixing ratios increase dramatically to levels of 2500 to 6500 ppb in high-temperature volcanic gas/air mixtures containing ~10% air; the models predict no significant reactive F species. Direct volcano degassing of atomic Br and Cl could give rise to BrO and ClO downwind by reaction with O₃; this may account for the observed 1-ppm levels of BrO in the Soufriere Hills plume. Although the mixing ratios of reactive Br and Cl are several orders of magnitude lower than those of HBr and HCl in magma degassing, they can be greatly increased by oxidation from mixing with air, and unlike HBr and HCl, they are not susceptible to scrubbing. Their role in the destruction of tropospheric and stratospheric ozone during volcanism may therefore merit further consideration.

V12E-07 1510h

Organics and Halocarbons in Volcanic Gas Emissions: Sampling, Analysis, and Estimates of Source Strengths for Diffuse and Fumarolic Gas Emissions

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The well-established interest in organic compounds in volcanic emissions, emerging in the early 1800's and continuing through modern times, has led to a long history of method development for the analysis of trace organics in volcanic gases. Both the sampling and analysis techniques have often been hampered by strong matrix effects, such as interferences by aerosol and ash scattering in spectroscopy, or the adverse impact of sulfur, acids and water on chromatographic and wet chemical techniques. Established methods exist for the ground-based sampling of fumaroles and diffuse degassing structures, whereas remote OP-FTIR spectroscopy appears promising for the detection and quantification of organic compounds during dangerous eruptive phases. The most successful collection techniques are based on a multiple-fold enrichment of the analytes during sampling, either by the absorption flask technique ("Giggenbach bottle"), or by in-line separation of water and sulfur from the analytes with subsequent trapping onto solid adsorbents. For organic analytes present at relatively high concentrations (e.g., C₁-C₆ hydrocarbons), the first technique has been used extensively. For labile and trace compounds (pptv to ppbv abundance), the latter technique has proven more reliable provided that the gas is dried sufficiently during sampling and that suitable dry gas volumes are sampled. A poor choice of sampling technique, or its incorrect application, may lead to erroneous results. These are often obvious by the finding of near-air concentrations, since volcanic gases are strongly enriched with respect to ambient air for a large range of compounds. Quantitative and independent testing of the air fraction possibly entrained during sampling must be performed in order to achieve reliable results. By using gas chromatography coupled with mass spectrometric detection (GC-MS), unambiguous simultaneous identification of compounds can be achieved by two independent analytical techniques. Unlike with ion trap MS, relatively soft electron impact ionization with either sector scanning or quadrupole MS instruments yields characteristic mass fragment spectra for a large range of compound types, from saturated and cyclic hydrocarbons to more labile iodocarbons. Detection limits of 10 to 50 pptv can be achieved routinely. Data are available from several volcanoes around the world, ranging in emission temperatures from 100 to 900°C. Global fumarolic fluxes (volcanic source strengths) for certain halocarbons are estimated to be on the order of up to 10^{-5} Tgy⁻¹. Although this represents only a small fraction of the total releases including anthropogenic sources, the global fumarolic fluxes for some halocarbons account for a comparatively more significant fraction of natural sources. For example, CCl₃F (CFC-11) has been detected in volcanic gases with an estimated flux of 1.3×10^{-5} Tgy⁻¹, making subaerial volcanism the sole natural source currently known for this compound. Diffuse degassing appears to emit amounts similar to those of high-temperature fumarolic discharges, whereas the output by explosive emissions is not known. During pre-industrial times, volcanic emissions would have represented a larger fraction of global emissions, since the anthropogenic burden at the time was negligible.

URL: <http://www.geochem.ethz.ch>

V12E-08 1525h INVITED

Quantifying Volcanic Emissions of Trace Elements to the Atmosphere: Ideas Based on Past Studies

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Extensive data exist from volcanological and geochemical studies about exotic elemental enrichments in volcanic emissions to the atmosphere but quantitative data are quite rare. Advanced, highly sensitive techniques of analysis are needed to detect low concentrations of some minor elements, especially during major eruptions. I will present data from studies done during low levels of activity (incrustations and silica tube sublimates at high temperature fumaroles, from SEM studies of particle samples collected in volcanic plumes and volcanic clouds, from geochemical analysis of volcanic gas condensates, from analysis of treated particle and gas filter packs) and a much smaller number that could reflect explosive activity (from fresh ashfall leachate geochemistry, and from thermodynamic codes modeling volatile emissions from magma). This data describes a highly variable pattern of elemental enrichments which are difficult to quantify, generalize and

understand. Sampling in a routine way is difficult, and work in active craters has heightened our awareness of danger, which appropriately inhibits some sampling. There are numerous localized enrichments of minor elements that can be documented and others can be expected or inferred. There is a lack of systematic tools to measure minor element abundances in volcanic emissions. The careful combination of several methodologies listed above for the same volcanic vents can provide redundant data on multiple elements which could lead to overall quantification of minor element fluxes but there are challenging issues about detection. For quiescent plumes we can design combinations of measurements to quantify minor element emission rates. Doing a comparable methodology to succeed in measuring minor element fluxes for significant eruptions will require new strategies and/or ideas.

V12F MCC: 3010 Monday 1340h

Many Facets of Garnet: Recorders of Crust and Mantle Dynamics I (joint with T)

Presiding: D L Whitney, University of Minnesota; D Hirsch, Western Washington University

V12F-01 1340h INVITED

Computer Simulation of Thermodynamic Mixing Properties and Trace Element Incorporation in Garnet Solid Solutions

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Garnet solid solutions are present in many igneous and metamorphic environments. Thermodynamic mixing properties of these solid solutions must be known accurately in order to retrieve the pressure-temperature ($P - T$) conditions of garnet growth, and hence constrain part of a rock's $P - T$ evolution. Over the past 25+ years, many experimental determinations of garnet thermodynamic mixing properties have been made, but doubts remain about the accuracy of our knowledge of garnet thermodynamics. Recently developed techniques (e.g., Lavrentiev et al., J. Phys. Chem. B, 2001) allow computational studies of mixing properties in geologically relevant solid solutions to be made for the first time. We present results of simultaneous high- P , high- T computer experiments, aimed at determining garnet mixing properties, using modified Monte Carlo and quantum mechanical methods. We derive excess volume and enthalpy data for garnets with compositions along the pyrope-almandine and pyrope-grossular joins at P up to 20 GPa and T exceeding 2273 K. These are compared with existing laboratory experiments and commonly used thermodynamic data bases. As seen in the experimental data, simulations show virtually ideal mixing behaviour in garnets on the pyrope-almandine join, while large excess volumes and enthalpies of mixing are predicted for garnets along the pyrope-grossular join. Simulations shed additional light on the link between microscopic structural behaviour and macroscopic thermodynamic properties: the avoidance of certain Ca-Mg contacts in the solid solutions (see Bosenick et al., Phys. Chem. Min., 2000) at high temperature and pressure manifests itself in dips in the excess enthalpies, which disappear at higher temperatures and lower pressures. Computer simulation of trace element incorporation into garnet solid solutions shows this avoidance may also be responsible for some remarkable features of rare earth element garnet-melt partitioning behaviour (e.g., van Westrenen et al., Phys. Chem. Min., 2003).

V12F-02 1400h INVITED

REE and Trace-Element Diffusivities in Garnet Determined From Resorption-Induced Stranded Diffusion Profiles

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