

framework. It is dynamically disordered and its internal vibrations are similar in energy to those of H₂O vapor, with an O-H bond energy of about 45 kJ/mole. External librational modes are located around 200 cm⁻¹ and translational around 10 cm⁻¹. In contrast, class II H₂O bonds to an alkali cation located in the six-membered tetrahedral ring through the lone-pair of the O atom. At about 5 K the H-bonding with the framework is roughly 1 kJ/mole.

In the zeolite bikaite, the H₂O molecules occur in infinite channel ways parallel to [010] and they build a hydrogen-bonded H₂O chain that has been termed 'one-dimensional ice'. The molecules in the chains are ordered, whereby one H atom per molecule is not bonded and the second is hydrogen-bonded to a neighboring H₂O molecule. The hydrogen-bonded O-H stretching bands in the Raman spectra show little line broadening, which is untypical for many hydrogen-bonded systems. With increasing temperature, hydrogen bonding between the H₂O molecules weakens and H₂O ultimately diffuses out of the channels by 620 K.

V72B-1327 1330h POSTER

Experimental determination of the solubility of natural wollastonite in pure water up to pressures of 5.0 GPa

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The solubility of natural, near-end-member wollastonite (>99.5% Ca₃Si₃O₉) has been determined at temperatures from 400 to 800°C and pressures between 0.8 and 5.0 GPa in piston-cylinder apparatus with the weight-loss method. The reproducibility was monitored by performing several experiments under constant conditions. Run durations needed to reach constant weight loss were determined by varying run times at constant pressure and temperature conditions. To allow experiments above pressures of 3.5 GPa we have developed a new type of gold capsules, which also minimizes the water lost during the sealing and initial pressurization.

Chemical analysis of quench products and the fact that no additional solid phases formed during dissolution indicate that wollastonite dissolves congruently in the above pressure-temperature range. Additional experiments in a hydrothermal diamond anvil cell confirm these results on the basis of optical and raman characterization. Traces of iron in the natural wollastonite starting material leads to the formation of minor amounts of 10 µm sized andradite crystals. We also observed that the oriented growth of wollastonite-II from the wollastonite-I crystal. The phase transition from wollastonite-I to wollastonite-II requires no more than a few minutes at 3.5 GPa and 700°C.

The molality of dissolved CaSiO₃ equivalent varies between 0.015 and 1.344 and increases systematically with both temperature and pressure up to 3.0 GPa. Above 3.0 GPa the starting material reacts to the high-pressure modification wollastonite-II. The solubility of wollastonite-II appears to be lower and relatively pressure-independent in the given temperature range. For pressures above 0.5 GPa, the solubility of wollastonite can be fitted to the following equation (T in Kelvin) $\log m_{\text{woll(aq)}} = 8.10 + (-13594.92)/T + 4492411.90/T^2 + 10.31 \log r_{\text{H}_2\text{O}}$.

From this it follows that, for a given pressure and temperature, the molality of dissolved CaSiO₃ equivalent is up to an order of magnitude lower than that for pure SiO₂ (1). The solubility of calcite (2) is similar to wollastonite at 500°C but is two times less at 800°C.

(1) Manning, Geochim. Cosmochim. Acta 58, 1994; (2) Caciagli & Manning, Eos. Trans. AGU, 82(47), 2001.

V72B-1328 1330h POSTER

Zircon: Free Energy of Formation of Aqueous Solubility Measurements at High T and P

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We measured the silica solubility at 800 °C, 12 kbar, of small (~0.5 mg) limpid euhedral zircon crystals grown by a flux-melt method (Hanchar et al., Am.

Min., 86, 667, 2001). Incongruent solution occurs according to $\text{ZrSiO}_4 = \text{ZrO}_2 + \text{SiO}_2, \text{aq}$. Zircon lost ~0.1 mg after exposure of 1-2 mg of zircon to ~32 mg H₂O in welded Pt envelopes for 90-120 hr in piston-cylinder apparatus using NaCl-graphite furnaces. The average solubility was 0.0645±0.007 molal (m), or a mole fraction (X_G) of 0.00116. Reversibility was established by rerunning the baddeleyite-coated zircons with a fluid initially slightly SiO₂-oversaturated, as determined by the forward experiments, resulting in weight gains of the composite crystals. Similar runs on sintered ZrO₂ compacts yielded spontaneous surface nucleation and growth of zircons up to 1 mm. Concentrations were corrected for a small, measured solubility of ZrO₂ (0.001 m). Nonideality of aqueous silica was calculated assuming that SiO_{2, aq} consists of a mixture of monomers and dimers (Zotov and Keppler (Chem. Geol., 184, 71, 2002; Newton and Manning, GCA, in press). Our zircon solubility and that of quartz at the same conditions (X_G=0.02634, Manning, GCA, 58, 4831, 1994) give activity coefficients at the two concentrations of 0.730 and 0.255, respectively. The activity coefficients and concentrations yield the free energy of formation of zircon from the oxides at 800 °C, 12 kbar of -18.46±0.96 kJ/mol, which translates to -11.91±0.96 kJ/mol at 800 °C, 1 bar. Our value is compatible with previous estimates based on experiment (Schulring et al., Am. Min., 61, 166, 1976) and high-T oxide-melt calorimetry (Ehlison and Navrotsky, J. Am. Ceram. Soc., 75, 1430, 1992), but is four times more precise than these estimates.

V72C MCC: 270 Sunday 1330h

Lessons Learned From Santa Maria/Santiaguito, Guatemala: Implications of Long-Lived Silicic Eruptions I (joint with S)

Presiding: B Cameron, University of Wisconsin, Milwaukee; A Harris, University of Hawaii

V72C-01 1330h

Santa Maria and Santiaguito: a Superb Field Volcanological Laboratory

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One of three actively erupting volcanoes in Guatemala, Santa Maria/Santiaguito has been the site of geological work for more than 100 years and is still a magnet for scientists. Santa Maria's 1902 crater offers unusual access to its gradually changing sequential eruptive products over the past 25 ka. Preservation of composite cone lavas and fragmental deposits is excellent. The mixed magma plinian 1902 eruption has well preserved fall deposits over much of western Guatemala and Southern Mexico and spans a compositional gap from basaltic andesite to dacite. The Santiaguito dome activity has been continual since 1922 with an oscillating eruption rate. A variety of eruption styles have been observed, including endogenous dome extrusion, exogenous block lava flows, block and ash flows, lahars and floods and frequent (several times a day) small vertical ash eruptions. The volcano is accessible by ground routes which are no more than a few hours walk at relatively low altitudes from good roads, and including an unusual summit perspective. There is a long context of field observations there, enabling long term studies of dome phenomena to be placed in a context. There is a volcano observatory and an active observer who provides daily observations. Monitoring efforts are planned to improve. The morning weather is usually clear, in spite of a climate that has frequent fog, and this aids in both ground and satellite remote sensing observations. The volcano has active fumaroles and a gas plume with unusual chemistry. A geothermal drill site near Zunil, a few km NE of Santa Maria offers insight into the subsurface geology. The volcano is located upslope from the Boca Costa, an extraordinarily productive area of commercial agriculture which has a growing population and provides important foreign exchange income for Guatemala. So the volcano's future activity and the associated ever changing volcanic hazards of the area are a priority for government agencies. URL: <http://www.geo.mtu.edu/volcanoes/santamaria/>

V72C-02 1345h INVITED

The Soufriere Hills Volcano, Montserrat, is log logistic

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The Soufriere Hills Volcano, Montserrat, experienced a remarkable episode of activity in September-October, 1997. During this period, 75 vulcanian explosions generated plumes that commonly rose between 5 to 15 km a.s.l. accompanied by pyroclastic flows. Repose intervals between vulcanian explosions varied from 2.77 to 33.7 hrs, with a median repose interval of 9.0 hr and mean of 9.6 hr. During the eruption, this narrow range of repose intervals was used in a practical way to provide qualitative forecasts of volcanic hazard. We analyzed repose intervals for these 75 vulcanian explosions and discovered they fit a log logistic distribution with > 99% confidence. This comparatively simple, two parameter model accounts for departures from a classical material failure model (Weibull distribution) at long repose intervals, and serves as the basis for improved hazard forecasts. The crucial differences between Weibull, and log logistic probability models for volcano repose interval are illustrated by comparing their hazard functions. For Weibull distributions the hazard increases indefinitely; the volcano must erupt explosively eventually and as time increases the probability of an eruption in the next time interval becomes much greater. In contrast the log logistic hazard function goes through a simple maximum. We note that largest magnitude eruptions in the time series, deduced from column height estimates and seismic explosion amplitudes, correlate with the peak in the log logistic hazard function. The excellent model fit is explained in terms of two competing processes operating in the upper conduit on different time scales. Gas bubble pressure increases with time due to exsolution and due to rheological stiffening of magma of magma following an abrupt decompression caused by a previous explosion. Once bubble gas pressure exceeds the tensile strength of the magma an explosion occurs a material failure model that should follow a Weibull distribution. However, this process is inhibited by depressurization of gas bubbles due to development of permeability and gas escape. Under these conditions, the timing of vulcanian explosions is expected to follow a log logistic distribution, with the exact timing of individual explosions governed by random variation in the material strength of the magma. Because key parameters in the probability density function have bases in the physical properties of the magma, we suspect that the log logistic survivor function should be applicable to hazard forecasts for vulcanian explosions at other silicic domes.

V72C-03 1400h INVITED

Observations of Santiaguito's Eruptive and Passive Emissions

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In January of 2002, geoscientists from the U.S. and Guatemala made a series of geophysical measurements and observations of Santiaguito volcano, Guatemala. The current activity includes low-level degassing from summit fumaroles, pyroclastic eruptions approximately every 1-2 hours with plume heights typically less than 2km, numerous rockfalls, and a slowly advancing lava flow. Our studies are focusing on providing baseline information and constraints for modeling conduit and eruption processes.

On January 11, digital video of the Santiaguito summit was taken continuously for six hours, during which time 6 explosive eruptions of varying sizes occurred. From Santa Maria's summit, we were able to observe the dome surface within Santiaguito's summit crater.

The crater is approximately 300 m in diameter, enclosing a smaller, 150 m diameter ring of vents. Erupted gases and pyroclastic materials often occurred through the ring-shaped arrangement of vents. The largest observed eruption exited through vents spread over nearly the whole dome, while smaller events were emitted through the inner ring vents only. The ring structure is thought to represent the surface expression of a funnel-shaped series of fractures generated from a much narrower conduit at depth. Santiaguito's eruption characteristics are consistent with slug, or intermittent, flow, that is the release of gas pockets from depth. The dome cap appears to be fairly rigid, with no observed flexure during eruptions. Summit fumaroles include two types: those unaffected by and apparently isolated from the main eruptive conduit, and those which are alternately opened and sealed by the eruptive activity. These physical characteristics of Santiaguito's eruptive and passive activity may provide clues to help decipher SO₂ degassing trends.

V72C-04 1415h INVITED

Sedimentation from wind-advected strong volcanic plumes

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Volcanic plumes are classified as strong and weak plumes, when the characteristic plume velocity is much greater or much smaller than the wind speed respectively. Eruptions like the 1902 Santa Maria Plinian event are characterized by strong plumes, which are less common in nature than weak plumes, but they are typically more hazardous due to the larger volume released and the wider area affected. They are characterized by a sub-vertical convective column that, at the neutral-buoyancy level typically 15 to 35 km (Santa Maria c. 20 km), spreads out as a lateral current that sediments particles of various sizes. Numerical modeling helps understand plume dynamics and is an important tool for hazard assessment. We develop descriptions of key processes influencing tephra dispersal from strong volcanic plumes and describe the propagation of the spreading current due to both gravity and wind advection using scaling arguments and a simplified geometry. New parameterizations are used to describe the wind field below the spreading current, particle aggregation and particle-density variations. We conducted a broad study to investigate the effects of these processes and made comparisons with field observations. The greatest variations resulted from wind advection below the spreading current, which shifts downwind the plume-corner mass accumulation and the position of transitions in fallout regimes. Aggregation makes the deposit thin more rapidly and distal segments, representing fine-particle fallout, can be suppressed. Particle aggregation strongly depends on the initial grainsize distribution. Variations of particle density and lithic content do not significantly affect sedimentation patterns represented on semi-log plots. The model provides acceptable reproduction of observations of the propagation of the spreading current and tephra-fallout deposits.

V72C-05 1430h INVITED

Three types of crust: Inferred emplacement rates and styles of a megablocky flow field surrounding Sabancaya volcano, Peru

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Sabancaya volcano is a complex edifice located ~70 km NW of Arequipa, Peru. It is surrounded by a large (~64 km²) andesitic/trachyandesitic lava flow field comprising 39 identifiable lobes that were emplaced during the Holocene. Flow morphology is distinct from that observed on evolved lavas in North America, providing an important foil to these well studied examples. The Sabancaya flows are channeled, and are characterized by steep, thick (>120 m) margins. Underlying slopes range from 10° near the vent to <1°

distally. Surface folding, with multiple fold generations, is common. Fold wavelengths and amplitudes are on the order of 25 m and 5 m, respectively. The flows are covered with angular blocks ranging in size from 40 cm to several meters. Preliminary data suggest that block-size distribution within a single lobe is more dependent on the proximity of fold crests than on distance from the vent. Fold amplitude (~5 m) suggests a minimum thickness for a ductile surface crust during emplacement; in contrast, the largest block size on the surface (>3 m) reveals the thickness of the brittle deforming surface crust.

Hand-sample analyses reveal large (>>0.5 cm) plagioclase phenocrysts in a glassy, a vesicular matrix with occasional cm-sized inclusions of basaltic andesite. Crystal-size distributions in the groundmass determined from samples collected along the flow length are essentially constant, suggesting that the lavas experienced little cooling during emplacement, consistent with a well insulated lava flow. Model results indicate that the flow lobe interior could have remained hot, and possibly molten, for thousands of years. Thus, the Sabancaya flows display 3 types of surface crust: a brittle, thin (3-5 m) surface layer that generated the large, angular blocks observed on the surface; a ductile, thicker (>5 m) layer that deformed during emplacement to generate the observed folds; and the thermal crust, which may have been several tens of meters thick. Morphologic, petrologic and geochemical evidence suggest that these flows were erupted at high temperatures and emplaced relatively rapidly; these characteristics can be better understood in light of recent observations of active flows at the Santiaguito dome.

V72C-06 1445h

Modelling the Effusive Eruption of Volcan de Colima, Mexico 2001-02

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Volcan de Colima has produced frequent eruptions during historic times; both effusive, with dome growth and blocky lava flows, and explosive, e.g. the plinian event of 1913. In general, the mechanisms that influence an eruption to change from effusive to explosive or vice versa remain poorly understood. Field measurements and monitoring at Volcan de Colima have allowed the development of a model of its most recent effusive eruption, which started with the formation of a lava dome on 8 May 2001 and continues to the present. Based on physical characteristics, the eruption has been divided into seven phases. Digital models of the different stages of dome growth were used to calculate the volume and the associated extrusion rates. The initial stages included the filling of the large crater, which had been formed by the three major explosions that occurred in 1999, and the smaller inner crater formed by the 22 February 2001 explosion. Later stages followed the over-spilling of the crater rim and the development of several short blocky lava flows with associated rockfalls.

The 2001/2 eruption has been characterised by a low rate of effusion (maximum 0.62 m³ s⁻¹). The rate of degassing has been variable, with the flux of SO₂ varying from 50 to 900 t d⁻¹. The location and temperature of the summit fumaroles have undergone migration associated with the development of different lobes of the dome. In addition, the seismicity has varied from extremely low levels at the beginning of the eruption, to extended periods of harmonic tremor in May 2002. These parameters, along with temporal geochemical variations within the local spring waters and monitoring of diffuse degassing of CO₂ at several locations, have been combined to form a model of this eruption.

V72D MCC: 270 Sunday 1515h

From Magma to Tephra: Crystallization, Fragmentation, and Flow I

Presiding: M J Davis, Schott Glass Technologies

V72D-01 1515h

Short Timescales for Crustal Residence, Transport and Contamination of Flood Basalt Magma: Crystal Isotope Stratigraphy of the Columbia River Basalt Group.

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Geochemical studies of continental flood basalt magmas provide evidence for contributions from one or more enriched reservoirs. There is, however, no consensus on the role of continental crust as a major source of enriched signatures. With its stratigraphy defined and mapped at the scale of individual flows, the Columbia River Basalt Group (CRBG) is the most thoroughly studied continental flood basalt province in the world. Its tectonic position (overlying both thin accreted Mesozoic crust and thick ancient cratonic crust) makes the CRBG ideal for isolating the contribution of crust in the petrogenesis of continental flood basalts. Many flows are plagioclase-phyric. Because plagioclase in basaltic magmas can be assumed to have grown at crustal pressures, growth layers in plagioclase phenocrysts record changes in the chemical and isotopic composition of the magma occurring at crustal depths.

We have initiated a micro-sampling study utilizing laser ablation multicollector ICP-MS (ThermoFinnigan Neptune) to analyze ⁸⁷Sr/⁸⁶Sr variability in plagioclase and clinopyroxene phenocrysts (where present) and associated groundmass. Initial results are: 1) plagioclase and clinopyroxene phenocrysts within CRBG lavas are overall less radiogenic than host groundmass and 2) plagioclase phenocrysts are commonly zoned from less radiogenic cores to more radiogenic rims. The rims may have similar compositions to, or be less radiogenic than, host groundmass. One-dimensional diffusion modeling applied to observed ⁸⁷Sr/⁸⁶Sr zoning and crystal/groundmass gradients constrains phenocryst residence times, and the timescale of crustal-level petrogenetic events that modified CRBG magmas. Residence times for phenocrysts in their final host liquid may be as little as 10 years prior to quenching.

These results require that the ⁸⁷Sr/⁸⁶Sr composition of the CRBG magmas increased rapidly with time at crustal pressures during and after phenocryst growth. This could result from mixing between magmas from isotopically distinct mantle reservoirs. If so, some involvement of the isotopically more enriched magma must always occur after the initiation of crystallization in the less enriched magma, in order to generate the monotonic crystal-groundmass variations observed. More likely, our results indicate crustal contamination is occurring during and after phenocryst growth in crustal magma chambers, and/or during transport to the surface as the magma is erupted.

V72D-02 1530h

Apparent Viscosity of Andesites Links Eruption Style to Crystallinity

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Magmatic viscosity varies in function of pressure, temperature, silica content, and volatile content, whereas apparent viscosity depends also on size, shape and concentration of its crystals and vesicles.

The primary effect of high crystallinity is to physically increase the apparent viscosity depending on the packing type, size distribution, and aspect ratio of its crystals. Although a crystal concentration of <5% has virtually no effect on apparent viscosity, the high crystal concentrations found in the common arc-type andesite, can play a very significant role, for they not only act as chemical and physical buffers but also as movement inhibitors.

The Einstein-Roscoe equation $\eta = \eta_0(1 - \Phi/\Phi_m)^{-2.5}$ can be used to determine the apparent viscosity η of a liquid with an initial viscosity η_0 that contains a known