the lake between 1995 and 2001, an annual budget of approximately 11x103 tonnes of magmatic S entering the lake is required. COSPEC measurements for March 2001give minimum SO2 flux of 40 t/d. This flux is of the same magnitude as the flux measured by Andres et al. in 1991. Assuming that this flux was relatively constant during the last 6 years (consistent with visual observations), it implies a mean annual S output of 7200 tonnes as SO2(g). As it is extremely difficult to remove SO2 from a hydrothermal system (Symonds et al., 2001), the total SO2 budget must come from the magma. The corresponding volume of degassed magma is 3.9x10-3 km3 per year. The negligible volume of degassed magma, required to insure a balance of the sulphur budget, can be either recycled at depth by convection in the conduit or accreted within the edifice (consistent with low micro-gravity variations due to magma movement since 1995; Rymer et al., 2000). Therefore, the magma feeding at Pos volcano appears to be in low steady state regime.

V22E-13 1650h

Proximal Ignimbrite Geometry on Santorini, Greece Using Ground Penetrating Radar

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Ground penetrating radar (GPR) surveys on Santorini, Greece, are used to constrain the 3-dimensional geometry of the near-surface pyroclastic deposits produced by the 3.6 ka caldera-forming Minoan eruption. Specifically, the results elucidate deposit structures at the south end of the island. More than 2.4 km of radar survey data were collected at a measurement spacing of 0.5-1.0 m, using the common offset reflection method (3 m offset) and radar frequencies of 50 and 100 MHz. Imaging depths of the raw data were typically small (<10 m) due to noise introduced by a local aviation radar facility which was in line-of-sight of most of the field survey. Most noise was removed by the application of standard radar signal processing techniques, allowing imaging to depths of 20-30 m, greater than the typical thickness of the Minoan eruption package. Survey lines were run between deposit exposures to ensure direct correlation between the observed depositional units and the geophysical data. This approach allows characterization of the radar signature of each deposit and facilitates subsurface mapping where exposures are absent. The phase 1 Plinian pumice is defined in the radar profiles as a unit with near constant thickness and little internal structure. The phase 2 surge and phase 3 massive tuff have similar radar propogation properties so the contact is poorly-defined by GPR, but the data reveal the cross-bedded internal structure of the surge allowing it to be mapped. The radar characterizations of the units and their contacts are continuous over the survey area, creating a well-defined image of the eruption package geometry over a 2-km-wide proximal segment of the volcano slope. The results show that the depositional package of airfall, surge deposits, massive tuff and ignimbrite is surprisingly uniform in thickness, except in minor paleo-lows where it thickens. In addition, each unit in the survey area is approximately uniform in thickness. The geometrical uniformity changes near the paleo-coast location, where the depositional package dramatically thickens as it crosses a line of low, coast-parallel paleo-sea cliffs. Observations of the deposits at the current coastline, outboard of the paleocliffs, suggest that the increase in thickness is due dominantly to a sudden thickening of the phase 4 pyroclastic flow deposit. This geometry contrasts with previous models, based on interpolation between outcrops. These proposed that the deposits of phases 2 and 3 thin gradually with distance from the caldera rim while phase 4 gradually thickens. The GPR results suggest that the flows were more energetic than the previous model implied, and too energetic to bulk deposit in the subaerial, proximal area. Most of the mass of pyroclastics swept down the slope and into the sea, leaving behind only thin veneers. The velocity reduction caused by a combination of the phase 4 flow thickening as it passed over the ancient sea cliffs, and by entering the sea, caused the flow to switch to a strongly depositional mode resulting in a thickened deposit. An implication of these results is that most of the Minoan pyroclastic flow deposits on Santorini, apart from those near and on the outer coast, were emplaced aggradationally.

V31A MC: Hall D Wednesday 0830h

Understanding Volcanoes Through Multiparameter Measurements and Their Interpretation: Martinelli Memorial III

Presiding: **P Hellweg,** UC Berkeley**; N M Perez,** Inst Technol Renewable Energies

V31A-0928 0830h INVITED POSTER

The Evolution of the State of Mt. Etna Volcano in the last ten Years Inferred Through Multidisciplinary Investigations

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In the last 30 years the eruptive activity of Mt. Etna has occurred near annually. After the 1991-1993 eruption, the most important lateral eruption in the last three centuries both in terms of duration (473 days) and lava erupted (ca. 235.106 m3), the volcano has not shown its activity through lateral eruptions but, since 1995, through frequent summit eruptive phenomena as vigorous strombolian activity, more than one hundred spectacular lava fountains, and lava flows from the summit craters. The last lateral July-August 2001 eruption occurred after this intense summit activity about ten years later the previous 1991-1993 lateral eruption. In this work we present multidisciplinary investigations conducted during these ten years preceding the 2001 eruption. The different disciplines and monitoring techniques (volcanological observations, seismology, ground deformation, petrology, gravimetry, geochemistry, geomagnetism) allowed us to obtain a knowledge of the state of the volcano and to evaluate its evolution. The positive gravity anomaly, the ground deformation inflation, the seismicity pattern and the SO2 flux indicate that from 1994 an intrusive process interested a crust volume at 2-5 km b.s.l. under the summit crater area. This volume probably represents an intermediate storage zone. From the second half of 1996 to 1997 the recharge process of the volcanic system was particularly intense, as evidenced by the maximum value of the gravity anomaly, the continuous increasing of the areal dilatation, the increasing of the cumulative seismic strain release pattern, the increasing of the SO2 mean flux. The chronology of these phenomena, together with a strong seismic swarm occurred in the western flank on January 1998, suggested magma migration towards the upper part of the plumbing system. This is confirmed by the composition of the erupted products from the summit craters that became progressively more primitive. Also previous eruptions, such as the 1989 and 1991-1993, showed analogous phenomenal pattern culminating with the eruptive phases. From 1998 the intensification of the summit craters activity, which indicated re-alimentation and strong tension accumulation, has been preceded by a decrease of the gravity anomaly and accompanied by a decrease of the SO2 mean flux, and by a partial attenuation of the areal dilatation and of the cumulative seismic strain release trends. Moreover, a slow and continuous increase in the total geomagnetic field observed on the north flank of the volcano and the absence of significant anomalies at the south supported a possible demagnetisation in the summit area. Different observations indicated that the tension accumulation did not appear equilibrated by the energy discharge occurred through the lava flow summit eruptions (February-November 1999; January-June 2001) and through the several tens of strong explosive events which took place at the summit craters during the 1998-2001 before the July 2001 eruption.

V31A-0929 0830h POSTER

Intrusive Mechanisms Evidence Occurred During January-April 2001 at Mt. Etna and Preceding the July 2001 Eruption

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In this work we show seismological and ground deformation evidence for the intrusive phase which prepared the July 17- August 10, 2001 lateral eruption at Etna. The analysis performed on the seismicity and ground deformation measurements, during the eight months preceding the eruption, highlighted a strict relationship between seismic strain release at depth and surface deformation. This joint analysis provided strong constraints on the magma rising mechanisms. The axes of maximum compression, obtained by the analysis of fault plane solutions, showed an orientation predominantly orthogonal to the N-S direction which is in agreement with the surface displacements measured by the permanent GPS network. The inferred orientation of the compressive axis of focal mechanisms and the deformation pattern suggested that both the seismicity and the deformation were caused by the same stress source due to the initial magma intrusion of a near-vertical dyke oriented about N-S. The source appears to be shifted by a few kilometres south of the summit region. The analysed period, which preceded the July 2001 eruption, was mainly marked by the occurrence of a strong seismic swarm on April 20-24, 2001, composed by more than 250 events (Mmax = 3.6) with prevalent dextral shear mechanisms in the western flank. The swarm showed a ca. NE-SW earthquake alignment which, in agreement with previous cases, can be interpreted as the response of the medium to an intrusive process along the ca. N-S volcano-genetic trend. These mechanisms, leading to the July 17- August 10, 2001 lateral eruption, are analogous to the ones observed some months before the 1991-93 lateral eruption and, more recently, in January 1998 before the February-November 1999 summit eruption.

V31A-0930 0830h POSTER

Seismic Evidences of Magma Intrusion at Intermediate Depth Before the July-August 2001 Mt. Etna (Italy) Eruption.

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Several authors investigated the seismic behavior before Mt. Etna eruptions and some models were proposed in order to explain peculiar features of seismicity before flank eruptions. In particular, stress and strain fields seem to modify their orientation due to the action of magma overpressure. Recently, about 40 seismic stations boosted the Mt. Etna permanent network and permitted to study with great detail seismicity occurred before July-August 2001 eruption. More than 2600 earthquake occurred in about 8 months prior the seismic swarm that heralded the lateral eruption and pointed out a change of the dynamic condition acting on the volcano, starting from November 5, 2000. Seismicity in the period November 2000 June 2001 was characterised by the occurrence of several relevant seismic swarms. The epicentres of events spread in a wide area covering mostly of the southern and eastern part of the volcano and delineate two main alignments. A NNW-SSE epicentres alignment builds up gradually and was composed by earthquakes occurred clustered and sparsely in time. A clear NE-SW alignment was also defined mainly by the occurrence of a 4 days swarm. A peculiar feature of the earthquakes spatial pattern is the depth distribution. Under the eastern part of the volcano the seismicity is confined in the depth range 1 6 km b.s.l., in the western part hypocentres are distributed in two volumes under 5 km and upper 2 km b.s.l., respectively. This pattern defines two volumes affected by few earthquakes. These volumes correspond to crust portions where magma reservoirs were located by previous works. On the basis of a fault plane solutions analysis, we observe relevant rotation of maximum compressive axis at very short distance, indicating a local stress source elongated in NNW-SSE direction at about 5 - 6 km depth under the summit craters. Analyses on the space distribution of b value outline that the NNW-SSE epicentres alignment shows the higher value. We suggest that in the investigated period a migration of a magmatic mass occurred through out a major geological barrier located in coincidence of the local stress source detected. Furthermore the NNW-SSE earthquakes alignment is interpreted as the fragile response of the medium to the eruptive dyke early intrusion phases.

V31A-0931 0830h POSTER

Visual Evidence of Seismo-Acoustic Wave Propagation at Mount Etna

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Mount Etna commenced eruptive activity in the spring of 2001 with several vents exploding and lava flows extruding from the southeast crater. In May 2001 we recorded several days of broad band seismic data in conjunction with infrasonic acoustic wave monitors. During this deployment we noted that infrasonic acoustic waves were observable visually in gasses and clouds above volcanic vents where activity was the strongest. Digital video recordings show sudden changes in light near the active vents. The visual observations represent pressure waves passing through the mouth of the vent, subsequently deforming cloud particles such that the index of refraction is significantly modified, producing a visually apparent disturbance. Infrasonic waves are further observed as pressure pulses exciting remote fumaroles where normally continuous flow is disturbed by atmospheric pressure waves. Infrasonic activity on Etna was substantial, occurring every few seconds, although all three active vents each contributed to the background acoustic noise. Acoustic noise couples into the ground, interfering with the broad band seismic signals used to establish source mechanics and explosion physics. We present cross-correlation cluster analysis used to discriminate between explosions at numerous vents during the eruptive phases of multi-crater systems such as Etna and Stromboli and compare these to mono-vent explosive activity at Karymsky Volcano, Russia.

V31A-0932 0830h POSTER

Monitoring Monitoring Evolving Activity at Popocatepetl Volcano, Mexico, 2000-2001

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After 6 years of small eruptions, activity at Mexico's 5,452m high Popocatepetl Volcano in central Mexico, peaked in the December 2000-January 2001 eruptions. Precursors included an important increase in seismicity as well as in magmatic components of spring water and small scale deformation which resulted in growth of a new crater dome from January 16 on.

Evacuation of the towns nearest the volcano over Christmas was decided because of the possibility of pyroclastic flows. During the previous years, crater dome growth, contraction and explosive clearing has dominated the activity.

The January 22 eruption produced an eruption column approximately 17km high with associated pyroclastic flows. Ejecta was composed of both basic and evolved scoria and pumice and dome lithics. A large proportion of the juvenile material was intermediate between these 2 endmenbers (59-63percent SiO2 and 3.5 to 5.5 MgO) consistent with a small basic pulse entering a more evolved larger batch of magma.

The January eruption left a large pit which has been partially infilled by another crater dome this August 2001.

V31A-0933 0830h POSTER

Unrest at Iliamna Volcano, Alaska in 1996 - Evidence for a Magmatic Intrusion?

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Iliamna Volcano is a 3-km high, glacially-scoured, ice-covered stratovolcano in the Cook Inlet region of south-central Alaska. It has a prominent fumarolic field on its southeast face, and frequently produces large steam clouds that have occasionally been mistaken for ash clouds. Iliamna has not erupted historically - its most recent eruptive activity occurred approximately 300 ybp. Iliamna Volcano has been monitored by a four (1993-1996) to six (1996-present) station local seismic net, as well as a larger network that spans the Cook Inlet region. In 1996 an increase in volcano-tectonic earthquakes was detected. A relatively small swarm of 90 located earthquakes occurred in May 1996. A larger swarm began with 328 located earthquakes in August 1996, peaked with 493 located earthquakes in September 1996, then gradually declined through mid-1997. An increase in SO_2 emissions was also observed during the fall of 1996, roughly coincident with the larger seismic swarm. No other physical changes were observed in or around the volcano in 1996-97.

Relocation of hypocenters for 1995-1999 using a new velocity model and station corrections indicates that the 1996-1997 events form a north-south trend at depths of 0-4 km below sea level that extends 7 km to the south of the volcano under several Pleistocene-aged vents. This trend is not coincident with any changes in the configuration of the seismic network. In contrast, hypocenters of events occurring before and after the 1996-1997 swarm are located within the Iliamna edifice at depths of 1-3 km above sea level. The average background seismicity rate at Iliamna prior to mid-1996 and after 1997 was 2-4 located events per month.

Fault-plane solutions for larger Iliamna events between 1995 and 2000 indicate strike-slip, normal, and reverse faulting mechanisms. Most events have an oblique component of slip. An inversion of 17 fault-plane solutions for the principal stress direction within 10 km of the volcano using the program FMSI yields an average misfit of 7.28°, indicating a heterogeneous stress field. An inversion of 10 fault plane solutions for events occurring to the south of Iliamna in 1996-1997 yields an average misfit of 2.67° and indicates that primarily oblique strike slip faulting (p-axis oriented SSW and plunging 30°) took place in this cluster.

Increased seismicity and SO_2 flux at Iliamna in 1996-1997 can be explained by a two-part intrusion of magma, involving a small volume of material in May 1996 and a larger volume of material in August 1996. This intrusion may have reactivated existing faults beneath the Pleistocene vents south of Iliamna Volcano, resulting in the observed pattern of seismicity.

V31A-0934 0830h POSTER

Bulk Viscosity of Bubbly Magmas and the Amplification of Pressure Waves

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The bulk viscosity of magma is needed in order to describe the dynamics of a compressible bubbly magma flowing in conduits and to follow the attenuation of pressure waves travelling through a compressible magma. We developed a model for the bulk viscosity of a suspension of gas bubbles in an incompressible Newtonian liquid that exsolves volatiles (e.g. magma). The suspension is modeled as a close pack of spherical cells, consisting of gas bubbles centered in spherical shells of a volatile-bearing liquid. Following a drop in the ambient pressure the resulting dilatational motion and driving pressure are obtained in terms of the two-phase cell parameters, i.e. bubble radius and gas pressure. By definition, the bulk viscosity of a fluid is the relation between changes of the driving pressure with respect to changes in the resulted expansion strain-rate. Thus, we can use the two-phase solution to define the bulk viscosity of a hypothetical cell, composed of a homogeneously compressible, one-phase, continuous fluid. The resulted bulk viscosity is highly non-linear. At the beginning of the expansion process, when gas exsolution is efficient, the expansion rate grows exponentially while the driving pressure decreases slightly. That means that bulk viscosity is formally negative. The negative value reflects the release of the energy stored in the supersaturated liquid (melt) and its conversion to mechanical work during exsolution. Later, when bubbles are large enough and the gas influx decreases significantly, the strain rate decelerates and the bulk viscosity becomes positive as expected in a dissipative system. We demonstrate that amplification of seismic wave travelling through a volcanic conduit filled with a volatile saturated magma may be attributed to the negative bulk viscosity of the compressible magma. Amplification of an expansion wave may, at some level in the conduit, damage the conduit walls and initiate opening of new pathways for magma to erupt.

V31A-0935 0830h POSTER

Tornillos: Pieces of a Puzzle

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In the past decade several of the ash eruptions at Galeras volcano (Colombia) have been preceded by tornillos. These unusual seismic events of unknown origin have screw-like profiles on seismograms and can last up to several minutes. Since 1997, a joint project between the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) and the Instituto de Investigación e Información Geocientífica, Minero-Ambiental y Nuclear (INGEOMINAS) has supplemented the short-period network of the Observatorio Vulcanológico de Pasto with four broadband, three-component seismometer stations, continuous fumarole gas chemistry measurments, electromagnetic sensors, an infrasound sensor and weather observations in the hopes to learn more about the physical or chemical process which generates tornillos and their significance in the sequence leading to ash explosions. The events of a suite of tornillos which occurred at Galeras Volcano between 08 December 1999 and 11 February 2000 were recorded well at the crater rim broadband stations, ANG and ACH. They appear to be more complex than many of the tornillos recorded previously. They are multichromatic, having narrow spectral peaks at up to 9 frequencies. Some peaks last throughout the entire tornillo, others only contribute to the turn-on transient. We compare polarization, frequency, amplitudes and decay measured from this suite of tornillos in each frequency band at the stations ANG and ACH. They indicate a single source location for all these tornillos. While other parameters correlate well at both stations, the amplitude of the 1.9 Hz peak is nearly twice as large at ACH than at ANG. This may indicate a distinct radiation pattern at this frequency. While none of these observations gives us a clear picture of the source process of tornillos, they provide additional puzzle pieces we can add those collected from other measurements.

V31A-0936 0830h POSTER

Caldera Deflation: Constraining Magma Chamber Physics and Predicting Hazards From Gravity and Elevation Changes

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Caldera forming eruptions are environmentally and economically the most devastating volcanic events. Inflation is usually considered to be an important precursor to activity. Here, we show that during caldera deflation a volcanic system may also enter a hazardous stage.

We have evaluated published gravity-height ($\Delta g/\Delta h$) data on Krafla, Askja, Kilauea and Campi Flegrei in order to discriminate between subsurface processes during caldera subsidence. With respect to end-member gravity-height correlations such as the free air gradient (FAG) and the Bouguer corrected free air (BCFAG), $\Delta g/\Delta h$ gradients may be interpreted in terms of subsurface mass redistribution or density changes. $\Delta g/\Delta h$ gradients during subsidence will either plot along the FAG or the BCFAG or fall above, below or between these predicted lines. Within Δg vs Δh diagrams, we have discriminated between three regions, each of which is evaluated in terms of subsurface processes occurring during volcano subsidence. These processes include either mass and density

V

decrease, mass and density increase or mass decrease and density increase within the magma chamber.

We have interpreted $\Delta g/\Delta h$ gradients as possible indicators of precursors of volcanic activity and propose that gravity - height surveys may help to detect precursors of caldera collapse due to magma drainage. The case of the Askja 1875 eruption in Iceland has been evaluated in terms of the beginning of the eruptive episode being induced by roof collapse of an evacuating magma chamber.

Based on other examples of recent volcanic roof collapse, we evaluate the contribution of gravity-height surveys in assessing volcanic risks during caldera subsidence including the trigger mechanism for caldera-forming explosive eruptions.

V31A-0937 0830h POSTER

Magma intrusion system and 3D structure of Iwate volcano, Japan revealed from active seismic survey

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The three-dimensional P-wave velocity structure of the Iwate volcano, northeastern Japan, is obtained through an active seismic survey. The survey was conducted by 70 scientists from 11 Japanese universities and other national organizations in October 2000. Nine artificial explosions using dynamite charge of 200-250 kg were detonated at the bottom of 50 m borehole. We deployed vertical 330 seismometers in a 40 x 40 km^2 area, and obtained approximately 2700 travel-time data. We take 22 x 28 horizontal grid nodes with a grid interval of 0.02^o for latitudinal and longitudinal directions, and 16 vertical grid nodes at 1-km intervals. After inverting the data by TOMG3D [Zhao et al., 1992] , the weighted RMS residual is reduced from 0.36 s to 0.17 after 10 iterations. The rigorously solved region confirmed by the checkerboard test is limited to the region around the volcanic edifice in a 20 x 13 km^2 horizontal area and 5 km vertically.

The most prominent feature is a column-like high-velocity body (Vp > 5.6 km/s) that extends vertically for 2 km beneath the caldera, of which the horizontal location coincides with the high-Bouguer anomaly. Therefore this body is interpreted as a magmatic body that has intruded from a deeper region and accumulated over a long time. A moderate-velocity region (4.6 < Vp < 5.4 km/s) extends eastward from this high-velocity column, and coincides with the sites of the last flank eruption, so called the Yakebashiri lava flow. As the vents of the lava flow are oriented ENE, the magma considered to be moving approximately eastward from the caldera region along the path of the moderate-velocity body. The western part of the volcano extending from the caldera is also characterized by a moderate-velocity region, coinciding with the locations of many geophysical and geodetic phenomena in the 1998 volcanic unrest. This suggests the moderate-velocity in the western region represents a region of dike intrusion from the conduit beneath caldera.

V31A-0938 0830h POSTER

Present State of the Long Valley Caldera/California Derived From DC-Resistivity Imaging and Self-Potential Measurements

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The geoelectrical methods make sense to apply in volcanic areas since porosity, permeability, ionic mobility, ionic concentration in rock fluids, and cation exchange capability are modified by volcanic - magmatic activity directly and processes generated by volcanism (geothermal systems). Resistivity of volcanic rocks is a meaningful indicator for changes in porosity and ionic mobility, ionic concentrations in fluids, mobility of fluids caused by changes in temperature.

A large-scale Direct-Current (DC) imaging investigation of the Long Valley system included both an active 21 km DC-survey line across the caldera and the mapping of natural self-potential (SP) anomalies in the western and central part. The deep sounding Electrical Resistivity Tomography (ERT) was applied successfully. The 21 km long dipole-dipole profile in east-west direction according to Wannamaker et al. (1991) was selected deliberately in order to compare the results.

For the detection of the potential differences special stand alone transient recorders were applied. This kind of signal recording offers the possibility of statistical methods for signal enhancement. The recorded time series yield information not only about the DC-resistivity than special effects like induced polarization events and self-potentials.

The first application of tomographic resistivity sounding in Long Valley is resulting in a recent 2-D model of resistivity distribution in subsurface after the resurgence of volcanic activity in the 80ies. The inversion result reveals numerous resistivity structures which are in very good correlation with known geologic and tectonic structures. The tomographical inversion of DC-data was carried out with the goal to study the geological structures of the Long Valley Caldera down to 3-4 km, especially in the part affected by the resurgent dome and the hydrothermal system by use of geoelectrical parameters. The important structural components include low-resistivity regions beneath the western half of caldera, which are originated by the shallow hydrothermal system. A large conductive segment under the Medial Graben, already described by Wannamaker et al. (1991), can also be seen, whereas the majority of resurgent dome appears highly resistive. The interpretation of the resistivity model is sustained by self-potential anomalies, measured in the western part of caldera, by the comparison with known fault zones and by implications for fluid flow inferred from geothermal data, whereupon the resurgent dome is not influenced by the present hydrothermal fluid flow.

URL: http://www.geo.uni-leipzig.de/∼lvc

V31A-0939 0830h POSTER

New Perspectives on Explosive Paroxysmal Phenomena at Stromboli Volcano (Italy)

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Continuous seismic monitoring and periodic, visual observations of volcanic activity for surveillance purposes started on Stromboli volcano, Italy, in the 1980s. From 1985 on, two eruptions occurred in December 1985 - April 1986 and May 1993, along with two small overflows in 1990 and 1994, respectively. Apart from these few episodes of lava effusion, the persistent Strombolian activity of the volcano throughout these years had several fluctuations, with some episodic climax which yielded powerful explosions. According to seismic records, typical paroxysmal phases consisted of a variable number of explosion quakes in fast succession (i.e., from tens of seconds to a few minutes), associated with an outstanding increment in the amplitude of volcanic tremor. Throughout these phases - which are called explosive sequences (Falsaperla et al., 1989) - the sudden ejection of lapilli, fragments of old rock, and bombs of variable dimensions can easily affect an area larger than the crater terrace where the active craters are located. This can yield serious consequences for tourists who climb up to the top of the volcano.

In this note, we study the explosive sequences of Stromboli between 1985 and 1999, providing a characterization in energy and duration. In the time span aforementioned, the occurrence frequency of similar phases was two per year on average. We propose analyses of their frequency content, comparing records obtained from two three-component, short-period (1 s) and broadband (10 - 0.01 s) seismic stations. We also investigate the time span preceding some sequences to highlight possible common features from the seismic and volcanic viewpoints.

Petrological analysis indicates a different composition of the volcanic products ejected during these explosive sequences with respect to the ejecta associated with the usual Strombolian activity (Bertagnini et al., 1999). Such a finding is in agreement with seismic data, which lead us to surmise that these paroxysmal phases are the result of partial obstruction of the volcanic conduit during periods of descending magma column. The onset of the sequence, causing the sudden removal of the material which forms the obstruction, would trigger the sudden depressurization of the conduit and the fast rising of magma from depth.

V31A-0940 0830h POSTER

Insights Into Vulcanian Fountain Collapse Mechanisms Revealed by Multiphase Numerical Simulations, and the Influence of Volatile Leakage on Eruptive Style

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Numerical models of short-duration Vulcanian explosions with time-varying vent flux have received little attention, and no previous eruption model has tried to combine highly unsteady vent dynamics with the explosive dispersal of pyroclastics. Testing the validity of these numerical models by comparison with the 1997 explosions at the Soufrire Hills volcano in Montserrat have revealed two important characteristics of Vulcanian fountain collapse and associated pyroclastic currents. First, our results suggest that leakage of exsolved gas through surrounding country rock or through the overlying magma/bubble mixture over a short period (10-12 hours) can greatly affect the energy of the explosion and can dramatically change the character of fountain collapse. Model input parameters estimated by field observations of the Soufrire Hills eruption resulted in a simulated explosion (SimA) which matched the qualitative character of several observed events, but whose plume ascent was more energetic than that which was observed. By 20 s, SimA developed an overhanging plume, which created a veil of falling pyroclastic material a few hundred m from the vent. Pyroclastic currents then originated from an intra-plume region ventward of this veil. Another simulation (SimC), with initial conditions determined from those of SimA after 12 hours of gas leakage, resulted in a less energetic plume and a fountain collapse qualitatively very different from SimA. SimC formed no veil of falling material, but instead resulted in a narrow region of collapsing material, shaped like an inverted cone and centered above the vent. These results suggest that the gas content in a pre-explosion conduit not only affects the energy of the resulting explosion, but also dictates the style of fountain collapse, with two end-member types illustrated by our simulations. A simulation with an intermediate level of gas leakage reasonably matched the observed events. The second revelation of our study is the internal dynamics of the overhang type of fountain collapse. The overhang itself was not the main source of the pyroclastic currents, but rather their source was an annular region of downward directed particles closer to the central axis of the explosion, resulting in pyroclastic currents that pierced the overhanging veil. The simulations illustrated interesting differences in behavior of coarse and fine particles.

V31A-0941 0830h POSTER

Determination of 3D Sub-structure at Somma-Vesuvius Volcano: the Effect of Magma Quenching due to gas Exolution.

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We present new results on the velocity structure of the Somma-Vesuvius volcano, obtained by a joint inversion of P and S-wave arrival times from both shots, collected during the TOMOVES experiments, and local earthquakes. The inclusion of a large set of earthquake data in the inversion, recorded by both temporary and permanent seismic stations allowed to extend the well

resolved volume beneath the Somma-Vesuvius down to about 5 km of depth. The obtained results show the presence of a high Vp and Vs anomaly at the crater axis, and define the transition from the limestones in the Apennines to the local structure of the Somma-Vesuvius. We interpret the central high Vp and Vs anomaly as due to a high rigidity body, within which most of the seismicity concentrates. Laboratory experiments at high temperatures and pressures on the 1944 eruption lava samples support the interpretation of this anomaly in terms of magma quenched in the main shallow conduits, because of gas exolution with moderate decrease of temperature. The volatile exolution from the melt caused by depressurisation of magma body at the eruption onset and through its explosive phases is able to rise the temperature of the melt solidus within the magma well above the eruptive temperature, causing the immediate quenching of the system. This paper shows a good example of how seismological, tomographic images and petrological laboratory experiments constrain magmatic models with important implications for the hazard assessment at Somma-Vesuvius, and at other volcanoes World-wide, where similar seismological evidences have been recently observed.

V31A-0942 0830h POSTER

Diffuse Degassing Rate of Carbon Dioxide and Volcanic Activity

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Volcanoes release to the atmosphere significant amount of gases through visible and non-visible manifestations. Monitoring diffuse degassing rate from volcanoes is becoming a potential geochemical tool for volcanic surveillance. During the last 15 years, ground efflux studies had been mainly focused on CO_2 because it is the most abundant volatile component in magma after the H_2O and the first major specie that exsolves from magma as it rises up from depth (Symonds et al., 1994; Giggenbach, 1996). Thus, diffuse CO_2 emission studies is considered to be very useful for monitoring volcanic activity. This is quite evident when diffuse CO_2 degassing surveys are applied on the same volcanic system following similar sampling distribution. Therefore, significant secular and spatial variations of CO_2 ground efflux will imply magma movement and/or changes of seismic activity. On the contrary, this relationship between volcanic activity and diffuse CO_2 degassing rate is difficult to visualize when we try to compare the total output of diffuse CO_2 degassing from different volcanic systems. Major problems are mainly related with covered area, sampling distribution, sampling density, CO_2 multiple origin, etc. One way to solve this difficulty is to quantify the magmatic fraction of the diffuse CO_2 degassing rate, but it is a hard task since it will imply to perform hundreds of helium and carbon isotopic measurements for each survey. Statistical-graphical analysis of diffuse CO_2 degassing surveys is a simple and useful tool to detect overlapping geochemical populations: background, peak and intermediate populations. Peak values of diffuse CO_2 degassing are mainly due to deep perturbations of the magmatic-hydrothermal system on the surface environment. Therefore, mean values of CO_2 ground efflux peak population could be a useful geochemical parameter to compare diffuse CO_2 degassing rate among different volcanic systems. Mean values of peak populations related to diffuse CO_2 degassing surveys from different volcanoes seem to show a strong relationship with volcanic activity.

V31A-0943 0830h POSTER

Surface Degassing Rates of Carbon Dioxide, Helium and Hydrogen at Tenerife, Canary Islands

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Tenerife is the largest island of the Canarian archipelago (2,034 Km^2), and its most recent eruption took place along the NW rift-zone in 1909, Chinyero volcano. Water supply is mainly obtained from its ground water reservoir which is reached by thousands of well and galleries. Some galleries showed an enriched-CO_2 inner atmosphere because of a continuous magmatic degassing process, which is also affecting the ground water chemistry. Gas emission studies through galleries could provide a 3-D picture of the degassing model for Tenerife. An in situ method was applied for measuring CO_2, He and H_2 fluxes from a horizontal drilling "gallery" by means of a tracer gas method. Methane (99.995%) was applied as a tracer and injected into the gallery "Fuente del Valle" at known flow, 38 mL/min. Well mixed gas and tracer were regularly analyzed, every 5 minutes, by means of a VARIAN 2002P microGC from April 27 to May 2, 2000.

CO_2 and CH_4 measurements were performed by means of a 10 m Poraplot Q column at 40°C, a TCD, and He as gas carrier. He, Ne and H_2 measurements were analyzed by means of a 20 m high resolution Molecular Sieve 5Å column at 60°C, a TCD, and Ar as gas carrier. (CH_4)gas/(CH_4)air ratio was >1000 during this experiment. CO_2 concentrations seem to be affected by short-term meteorological fluctuations and showed a range from 23 to 30%. An strong correlation is observed between CO_2 content and He/Ne ratios, which ranged from 0.320 to 0.390. CO_2 flux ranged from 1.5 to 5.5 Kg/d showing an average of 2.9 ± 0.7 Kg/d. Secular variations of CO_2 flux showed regularly peak levels almost every 12 hours. Assuming that a number of 100 galleries at Tenerife might release this level of CO_2, the island subsurface degassing rate of CO_2 could account for 300 Kg/d. Observed He flux ranged 2.8 to 9.0 mg/d showing an average of 5.0 ± 1.2 mg/d. In the case of H_2, flux levels ranged from 2.5 to 7.0 mg/d showing an average of 4.5 ± 0.9 mg/d. Subsurface degassing rate monitoring could be a potential geochemical tool for seismic-volcanic surveillance at Tenerife.

V31A-0944 0830h POSTER

Diffuse Degassing of CO_2 and H_2 in and Around the NE Volcanic Rift-Zone of Tenerife, Canary Islands

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The NE volcanic rift-zone of Tenerife is one of the three major volcanic rift-zones of this island. The most recent eruptive activity along the NE volcanic rift-zone took place in 1704/05, Siete Fuentes, Fasnia and Arafo volcanoes. On the contrary, the NW volcanic rift-zone has been the scenario for the most recent eruptions at Tenerife: Chinyero (1909) and Chahorra (1798) volcanoes. The purpose of this study is to evaluate the spatial distribution of the diffuse CO_2 and H_2 degassing rates as well as the total CO_2 and H_2 efflux from the NE volcanic rift-zone.

A soil gas efflux survey of 557 sampling sites was carried out in and around the NE volcanic rift-zone (210 Km^2) in summer 2001. Soil CO_2 efflux values ranged from non-detectable levels up to 40.6 $gm^{-2}d^{-1}$. Statistical-graphical analysis of the data showed that the background population accounts for 92% of total data with a mean of 1.8 $gm^{-2}d^{-1}$. The peak group showed a mean of 25.9 $gm^{-2}d^{-1}$ and represents 1.1% of total data. Soil gas samples were collected at a 40 cm depth to estimate soil H_2 efflux by means of multiplying H_2/CO_2 ratio times soil CO_2 efflux for each sampling site. Soil H_2 efflux values ranged from non-detectable levels up to 42.5 $mgm^{-2}d^{-1}$, and showed also three overlapping geochemical populations. Anomalous soil CO_2 and H_2 efflux levels are not spatially correlated. Carbon isotopic measurements suggest clearly that CO_2 efflux along the NE volcanic rift-zone has an strong biogenic component. Total surface degassing rates from the study area is 681 td^{-1} for CO_2 and 65 Kgd^{-1} for H_2.

V31A-0945 0830h POSTER

Dissolved gas ^{222}Rn, ^{220}Rn and $^{220}Rn/^{222}Rn$ in the Ground Water System of Las *Cañadas*, Tenerife, Canary Islands

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Tenerife (2,034 Km^2) could be considered as an unique natural-scale laboratory for hydrological studies at oceanic volcanic islands. Thousands of well and galleries have been drilled (1,650 Km) reaching the island volcanic aquifer at different depth and elevations. *Cañadas*' aquifer is located in the central part of Tenerife and is affected by Teide volcanic-hydrothermal system. The purpose of this study is to evaluate the concentration levels of dissolved gas ^{222}Rn and ^{220}Rn as well as their spatial distribution at *Cañadas*' aquifer.

Dissolved gas ^{222}Rn and ^{220}Rn were measured at 13 observation sites "galleries" on July and August, 2001. Concentration of these dissolved gases were performed by means of a gas-water exchange membrane and an electrostatic-type alfa detector SARAD RTM2010-2 during 24 hours, allowing to measure alfa particles from its radioactive progeny, ^{214}Po, ^{216}Po and ^{218}Po in hourly basis. Dissolved gas ^{222}Rn concentrations ranged from 0.12 to 67.3 BqL^{-1}, and ^{220}Rn content ranged from 0.06 to 24.5 BqL^{-1}. Median values for dissolved gas ^{222}Rn and ^{220}Rn are 1.7 and 0.64 BqL^{-1}, respectively. Most of the ground waters showed dissolved gas ^{222}Rn concentrations lower than 10 BqL^{-1}, and relatively high levels up to 67.3 y 24.7 BqL^{-1} where observed at two galleries on the eastern side of *Cañadas*' aquifer. $^{220}Rn/^{222}Rn$ ratio ranged from 0.1 to 0.6. A wide range of ^{222}Rn and $^{220}Rn/^{222}Rn$ ratios were just detected at the recharge zone of *Cañadas*' aquifer and a more limited range was observed at lower elevations. Teide volcanic-hydrothermal system might be playing a role on this spatial distribution. These results could be useful for hydrological modelling of *Cañadas*' aquifer and the geochemical monitoring for the seismic-volcanic surveillance of Tenerife.

V31A-0946 0830h POSTER

Dynamics of Carbon Diffuse Degassing Species (CO_2, CO & CH_4) From the Summit Cone of Teide Volcano, Tenerife, Canary Islands

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CO_2 is the predominant carbon component in volcanic gases, and it is the least soluble of the major species in magmatic melts. The two remaining carbon components are CO and CH_4. Most of the diffuse emission studies on volcanoes are related to CO_2 but significant amounts of other C species in volcanic gases could be emited through the surface environment of volcanoes in a diffuse form. To understand the dynamics of diffuse CO_2, CH_4 and CO degassing from Teide volcano (3,716 m), soil flux surveys had been performed to evaluate spatial and temporal variations.

Diffuse CO_2 degassing surveys were yearly performed by means of a portable NDIR sensor since 1999 during the summer term. The observed highest diffuse CO_2 emission rates were 3,0 (1999), 12,0 (2000) and 12,6 (2001) $Kgm^{-2}d^{-1}$. Soil gas samples were also collected at 40 cm depth using a metallic a metallic probe and analyzed within 24 hours by means of VARIAN 2002P and 2003P microGCs. Diffuse CH_4 and CO degassing rates were estimated by multiplying CO_2 efflux times CH_4/CO_2 and CO/CO_2 ratios at each sampling site, respectively. CH_4 efflux showed values of 23 (1999), 123 (2000) and 3,761 (2001) $gm^{-2}d^{-1}$. For CO efflux, the observed highest values were 1.3 (2000) and 31.4 (2001) $gm^{-2}d^{-1}$. Diffuse CO_2, CH_4 and CO degassing spatial distribution seem to be afected by deep processes as well as meteorological fluctuations, specially wind speed. The total output of diffuse CO_2 emission for the 2001 survey was 399 td^{-1} which is relatively higher than previous surveys: 100 (1997), 168 (1999), and 43 (2000) td^{-1}. In the case of CO, diffuse degassing rates from the study area were 7.2 and 136 Kg/d for the 2000 and 2001 surveys, respectively. Diffuse CO/CO_2 degassing ratio were similar for both recent surveys: $1.6x10^{-4}$ (2000) and $3.4x10^{-4}$ (2001). These results are useful for Teide volcano monitoring program.

V

V31A-0947 0830h POSTER

Continuous Monitoring of Diffuse CO_2 Degassing From Cumbre Vieja Volcano, La Palma, Canary Islands, Spain

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La Palma (730 Km^2) is the northwesternmost island of the Canarian archipelago. Cumbre Vieja (<1 Ma) is situated in the southern part of La Palma, and is the most active basaltic volcano in The Canaries (7 eruptions in 500 yrs). The main geostructural features of Cumbre Vieja volcano are three volcanic rift-zones of N-S, NE, and NW orientation. The most recent eruption in the archipelago occurred in the southern part of the N-S rift-zone, *Teneguia* volcano, in 1971. To date fumarolic activity is absent and relative low diffuse CO_2 efflux values (<65 $gm^{-2}d^{-1}$) are found around this volcano. Diffuse degassing of CO_2 is continuously measured according to the accumulation chamber method at Pico Birigoyo (1,900 m elevation), a cincer cone located at the intersection of the three volcanic-rift zones. Meteorological and soil physical variables are also measured in an hourly basis and GSM-transmitted to ITER facilities about 150 Km far away.

Medium-term diffuse CO_2 efflux values ranged from non-detectable levels to 7.9 $gm^{-2}d^{-1}$, with a median value of 3.4 $gm^{-2}d^{-1}$. The sample efflux distribution could be described as a normal distribution N (3.40, 1.22). Secular variations of diffuse CO_2 efflux show a strong linear dependence with the regression coeficient (R^2=+0.79) due to the IR sensor's capability to discriminate these low CO_2 emission rates. Wind speed ranged from 0 to 28.8 Km/h, with an upper quartile of 12.9 Km/h. Wind speed (R^2=+0.01) and wind direction (R^2=+0.03) do not show a correlation with the observed diffuse CO_2 efflux. On the contrary, barometric pressure fluctuations (range 9.43 HPa) at diurnal and semi-diurnal frequencies are inversely correlated with diffuse CO_2 efflux (R^2=-0.22). CO_2 efflux lags the barometric pressure variations by 4-6 hours. These results suggest a combination of viscous flow (driven by pressure gradients) and diffusion (driven by concentration gradients) as the main transport components to explain the observed diffuse CO_2 efflux temporal variations at Cumbre Vieja volcano.

V31A-0948 0830h POSTER

Secular and Spatial Variations of Diffuse CO_2 Degassing From Cumbre Vieja Volcano, La Palma, Canary Islands, Spain

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La Palma (730 Km^2) is the northwestmost island of the Canarian archipielago and rises 6.5 Km from the oceanic basement. Constructive and destructive geological processes are responsible for the actual geomorphology of La Palma (Navarro, 1992; Ancochea et al., 1994). Recent volcanic activity is mainly concentrated at Cumbre Vieja volcano, in the southern part of La Palma. The most recent eruption occurred in the southernmost part of Cumbre Vieja volcano along its N-S rift zone in October 1971, and lasted for 32 days. Since fumarolic degassing is not present at Cumbre Vieja volcano, diffuse degassing studies are useful geochemical tools for monitoring magma movement and seismicity changes. The purpose of this study is to evaluate the spatial and temporal variations of diffuse CO_2 degassing rates at Cumbre Vieja volcano.

Soil CO_2 efflux surveys of approximately 600 observation sites were carried out during the 2000 and 2001 summer periods. Soil CO_2 efflux measurements were performed with the accumulation chamber method by using a portable NDIR sensor and a PC. Statistical-graphical analysis showed three overlapping geochemical populations for both surveys. CO_2 efflux peak populations, the geometric means were 271 and 58.6 $gm^{-2}d^{-1}$ for the 2000 and 2001 surveys, respectively. Most of Cumbre Vieja volcano showed background diffuse CO_2 degassing rates. Anomalous CO_2 efflux values are spatially related to the volcanic rift-zones. Carbon isotopic signatures showed a mixing of deep and shallow seated CO_2. Diffuse CO_2 emission rates from Cumbre Vieja volcano were 2,925 and 1,165 td^{-1} for the 2000 and 2001 surveys, respectively. These results are useful for Cumbre Vieja seismic-volcanic monitoring.

V31A-0949 0830h POSTER

Diffuse Carbon Dioxide Degassing Monitoring at Santa Ana-Izalco-Coatepeque Volcanic System, El Salvador, Central America

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Santa Ana volcanic complex (0.22 Ma), located 40 Km west of San Salvador, comprises Santa Ana, Izalco, and Cerro Verde stratovolcanoes, the Coatepeque collapse caldera, as well as several cinder cones and explosion craters. Most recent activity has occurred at Izalco (1966) and Santa Ana which shows a permanent acidic crater lake with an intense fumarolic activity. In addition, Santa Ana exhibits a SO_2-rich rising plume though no local seismicity has been reported. Weak fumarolic activity is also present at two locations within the Santa Ana volcanic complex: the summit crater of Izalco and Cerro Pacho at Coatepeque caldera. Other important structural features of this volcanic complex are two fault/fissure systems running NNW-SSE that can be identified by the alignment of the stratovolcanoes and numerous cinder cones and explosion craters.

In January 2001, a 7.6 magnitude earthquake occurred about 150 Km SE of Santa Ana volcano. A soil gas and CO_2 efflux survey was performed to evaluate the impact of this seismic event upon the diffuse degassing rates in Santa Ana volcanic complex in March 2001. A total of 450 soil gas and diffuse CO_2 efflux measurements were carried out covering an area of 209.5 Km^2. CO_2 efflux ranged from non-detectable values to 293 $gm^{-2}d^{-1}$, with a median of 8.9 $gm^{-2}d^{-1}$ and an upper quartile of 5.2 $gm^{-2}d^{-1}$. The CO_2 efflux spatial distribution reveals the existence of areas with CO_2 efflux higher than 60 $gm^{-2}d^{-1}$ associated to the fault/fissure systems of NNW-SSE orientation. One of these areas, Cerro Pacho, was selected for the continuous monitoring of diffuse CO_2 efflux in late May 2001. Secular variations of diffuse CO_2 efflux ranged from 27.4 to 329 $gm^{-2}d^{-1}$ with a median of 130 $gm^{-2}d^{-1}$ and a quartile range of 59.3 $gm^{-2}d^{-1}$. An increasing trend of 43 $gm^{-2}d^{-1}$ was observed between May and August 2001 overlapped to high-frequency minor fluctuations related to meteorological variables' changes. However, a larger observation time-span is needed to understand the influence of the rainy-season and meteorological parameters in the observed CO_2 efflux time series.

V31A-0950 0830h POSTER

Diffuse Emission of Carbon Dioxide From *Irazú* Volcano, Costa Rica, Central America

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Irazú (3,432 m) is a stratovolcano situated 50 Km east of San *José*, the capital of Costa Rica. Major geomorphological features at *Irazú* are five craters (Main Crater, Diego de La Haya, Playa Hermosa, La Laguna and El *Piroclástico*), and at least 10 satellitic cones which are located on its southern flank. Its eruptive history is known from 1723. Since then, have ocurred at least 23 eruptions. All known Holocene eruptions have been explosive. The focus of eruptions at the summit crater complex has migrated to the west towards the historically active crater from 1963 to 1965. Diffuse degassing studies are becoming an additional geochemical tool for volcanic surveillance. The purpose of this study is to evaluate the spatial distribution of diffuse CO_2 emission as well as CO_2 efflux from *Irazú* volcano.

A soil CO_2 flux survey of 201 sampling sites was carried out at the summit of *Irazú* volcano in March 2001. Sampling site distribution covered an area of 3.5 Km^2. Soil CO_2 efflux measurements were performed by means of a portable NDIR sensor LICOR-800. Soil CO_2 efflux values ranged from non-detectable values to 316.1 $gm^{-2}d^{-1}$ Statistical-graphical analysis of the data showed three overlapping geochemical populations. The background mean is 3 $gm^{-2}d^{-1}$ and represents 91.3 % of the total data. Peak group showed a mean of 18 $gm^{-2}d^{-1}$ and represented 1.2 % of the data. Anomalous CO_2 flux values are mainly detected in the South sector of the main crater, where landslides have previously occurred. Diffuse CO_2 degassing rate of the study area yields 44.2 td^{-1}.

V31A-0951 0830h POSTER

Spatial and Secular Variations of Diffuse CO_2 Degassing From *Poás* Volcano, Costa Rica, Central America

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Poás volcano is a large basaltic-andesite stratovolcano with a hot, acidic crater lake and shallow hydrothermal system confined within the active crater. It is one of four historically active volcanoes in the Cordillera Central of Costa Rica. Diffuse CO_2 degassing studies are becoming a useful geochemical tool for volcano monitoring. The purpose of this study is to evaluate secular and spatial variations of diffuse CO_2 emission rates from *Poás* volcano.

Diffuse CO_2 efflux surveys covering an area of 2.2 Km^2 at *Poás* were carried out from April 14 to May 4, 2000, and February 1 to 28, 2001, respectively. Diffuse CO_2 efflux measurements were performed according to the accumulation chamber method by using a NDIR sensor. Diffuse CO_2 degassing rates up to 1,841 and 2,263 $gm^{-2}d^{-1}$ were observed for the 2000 and 2001 surveys, respectively. Both studies showed three overlapping populations. Most of the study area showed background diffuse CO_2 degassing rates in both surveys. Peak population's geometric mean were 101 and 1,768 $gm^{-2}d^{-1}$ for the 2000 and 2001 surveys, respectively. Peak CO_2 efflux values were mainly identified inside the crater, but spatial variations within the crater were observed. These changes might be related with new fumarolic activity within the crater. Fumarole geochemical data showed $CO_2/^3He$ ratio of 3.6x10^{10} and $\delta^{13}C(CO_2)$=-4.46 $^o/_{oo}$. The total output of diffuse CO_2 emission from the study area were 93 and 139 td^{-1} for 2000 and 2001 surveys, respectively. Monitoring these spatial and secular variations could be useful for the volcano monitoring program at *Poás*.

V31A-0952 0830h POSTER

Simulation of 3D Seismic Wave Propagation with Volcano Topography

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We investigate the possibilities of using three-dimensional finite difference (FD) methods for numerical simulation of the seismic wave field at active volcanoes. We put special emphasis on the implementation of the boundary conditions for free surface topography.

We compare two different approaches to solve the free surface boundary conditions. The algorithms are implemented on parallel hardware and have been tested for correctness and stability. We apply them to smooth artificial topographies and to the real topography of Mount Merapi, Indonesia. We conclude, that grid stretching type methods (e.g. Hestholm & Ruud, 1994) are not well suited for realistic volcano topography as they tend to become unstable for large topographic gradients. The representation of topography through staircase shaped grids (Ohminato & Chouet, 1997) results in stable calculations, while demanding very fine gridding.

The simulations show the effects of a three-dimensional surface topography on elastic wave propagation. Ground motion at the surface is severely affected by topography. If neglected, this may jeopardize attempts to determine source location by analyzing particle motion. Numerical studies like this can help to understand wave propagation phenomena observed on field recordings in volcano seismology. Future studies will aim at separating the wave effects of internal scattering, topography and sources (tremors, tectonic events, pyroclastic flows).

V31B MC: 305 Wednesday 0830h

Nanoparticles in the Environment I

(joint with A, H, OS, P, MR)

Presiding: **A Navrotsky,** Univ of California-Davis**; J Banfield,** UC Berkeley

V31B-01 0830h

Characterization of Colloidal Nanoparticles Released from Hg-bearing Mine Wastes

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The release of mercury from mine waste tailings at historic mining sites in the California coastal ranges is a significant pollution threat to local water sources and fish populations. The transport of mercury associated with nanometer-scale (50-400 nm) colloidal particles is one of the major pathways for mercury release from these mine sites. This study has used laboratory column ex-periments to generate colloids from calcines and unprocessed waste rock from the New Idria (NI) and Sulphur Bank (SB) mines. Colloid generation was initiated by flowing two solutions of vary-ing ionic strength through the columns in the presence of malonic acid. The colloidal material generated was characterized by ATEM, Extend X-ray absorption fine structure (EXAFS) analysis, and chemical sequential extraction techniques.

ATEM analysis indicates that the colloids generated from the NI calcines consist of crystalline alunite-jarosite and hematite, a poorly ordered Si-Al gel and HgS. This mixture is very similar to that present in the bulk calcine material and suggests that these colloids are formed by detach-ment/breakup of the bulk material. Hg-LIII-EXAFS and sequential extractions indicate that 90% of the mercury present in these colloids is in the HgS form. The column experiments on the SB calcines produced only a small amount of colloidal material when the first few pore volumes of solution were flowed through. These consist of quartz, poorly ordered Si-Al-Fe gel and HgS. Hg-LIII-EXAFS spectra confirms that HgS is the dominant mercury species in these colloids. Raising the pH of the colloid-free column effluent from the SB calcines experiment results in the precipita-tion of a poorly ordered Si-Al-Fe rich gel, which is similar to that observed at the waste pile/lake interface next to the SB mine (Clear lake, CA). EXAFS and ATEM results indicate that mercury can be associated with this precipitated colloidal material. Colloids generated using unprocessed waste rock from the SB mine site consist of Cr-oxide, hematite, mackinawite (FeS0.9), and HgS formed via the detachment/breakup mechanism. As for the two previous systems Hg-EXAFS re-sults indicates that HgS is the dominant mercury-bearing phase in these colloids.

This study shows that the colloidal transport of mercury from these particular mine sites occurs predominantly as HgS and not as Hg sorbed to minerals phase as previously thought. Also the mechanisms of colloid generation (i.e. detachment/breakup or dissolution/reprecipitation) varies according to the composition of the starting material.

V31B-02 0845h

Grain Boundary Carbon in Synthetic Quartzite: Implications for Electrical Conduction in the Crust

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Despite the repeated implication that grain boundary graphite forms electrically connected networks in the earth's deep crust, little is known about the equilibrium microstructure of graphite at high pressures and temperatures. To evaluate this, we conducted several piston cylinder experiments designed to equilibrate carbon with crystalline SiO_2. In one set of experiments, stacked single crystal (SC) disks of polished quartz were coated with 0 to 150 nm of carbon film in 50 nm increments. The stacks were positioned horizontally in graphite capsules and were heated at 1.4 GPa to 1150°C for 48 hours in one experiment, and to 1500°C for 0.05 and 5 hours in two others. In another set of experiments, we produced two polycrystalline (PC) quartzites in textural equilibrium with small amounts of carbon. A powder consisting of 75-150 μm grains of natural crystals was fired for three days at atmospheric P and 1000°C and coated with a 30-50 nm carbon film. In one experiment, the powder was encased in a graphite capsule; in the other, a Pt capsule was used. Both were equilibrated for 120 hours at 1300°C, 1 GPa.

Polished sections of the products revealed that the low-T SC run contained a thin, dark film on all interfaces including the uncoated face; the short duration, high-T SC run contained a dark film on all of the coated interfaces, but not on the uncoated interface; and the longer duration, high-T SC run contained isolated opaque blebs that increased in density with increasing thickness of the initial film. Additionally, these SC products contained a small number of fractures with thin, dark films, blebs, or dendrites. Both PC experiments produced similar products, largely composed of polygonal quartz grains and apparently unconnected small dark grains located along grain boundaries. Most of these dark grains exhibited a rounded or globular morphology, but a few showed rational faces.

The results suggest that carbon films are not stable along quartz grain boundaries. Instead, carbon appears as rounded shapes that are likely to be interconnected only at elevated volume fractions. However, the presence of films in the lower T and short duration experiments may point to relatively sluggish kinetics for carbon textural equilibrium, and therefore to the possibility that carbon films may be present as transient features in the crust.

URL: http://www.rpi.edu/~pricej/work/C/

V31B-03 0900h

Adsorption of Water on the TiO_2 (Rutile) [110] Surface: A DFT Study

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Periodic DFT calculations (CASTEP) using slabs separated by vacuum gaps were carried out to model the H_2O-TiO_2 (rutile) [110] interface. Positions of all atoms were allowed to relax except atoms in the central layer of the slab. Both associative (i.e., Ti-OH_2) and dissociative (i.e., 2 TiOH) adsorption mechanisms were considered for 1/2 monolayer and monolayer coverages. Five different orientations of H_2O molecules on the TiO_2 surface were studied to determine the most energetically favorable water positions. Two slab thicknesses (3 Ti layers and 5 Ti layers) were chosen to test the effect of slab depth on calculated surface structures. Results indicate that associative adsorption is favorable by 8 to 15 kJ/mole/H_2O depending on the slab thickness for full monolayer coverage, whereas the opposite was calculated for 1/2 monolayer coverage. The associative adsorption mechanism is consistent with experiment. The role of H-bond formation on the adsorption energies and structures will be discussed.

V31B-04 0915h INVITED

Surface Charge and Ion Sorption Properties of Titanium Dioxide

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The interaction of submicron metal oxide particles with natural aqueous solutions results in the hydroxylation of surface sites, which impart a pH-dependent surface charge. The charged submicron particles influence processes such as nanoparticle assembly and alteration, crystal growth rates and morphologies, colloid flocculation, and contaminant transport.

The surface charge and ion sorption properties of metal-oxide particles may be studied by potentiometric titrations, using hydrogen-electrode concentration-cells or traditional glass electrodes and an autotitrator. These techniques have been used to quantify the adsorption of various ions (Na^+, Rb^+, Ca^{2+}, Sr^{2+}, Cl^-) on rutile, at ionic strengths up to 1.0 molality and temperatures to 250°C. The crystalline rutile used in these studies is less than 400 nm in diameter, has a BET surface area of 17 m^2/g, and the 110 and 100 faces predominate. The negative surface charge of the rutile was enhanced by increasing temperature, increasing ionic strength, and decreasing the ionic radii of the electrolyte cation. Moreover, the addition of a divalent cation significantly enhances the negative charge of the rutile surface. These data have been rationalized with the MUSIC model of Hiemestra and van Riemsdijk, and a Basic Stern layer description of the electric double layer (EDL). Model fitting of the experimental data provides binding constants for the adsorbed counterions and divalent cations, and capacitance values as well as corresponding electrical potential values of the binding planes.

Recently, new studies have been initiated to determine particle size affects on the proton induced surface charge and ion sorption properties of titanium dioxide. In these studies, anatase with a BET surface area of 40 and 100 m^2/g (primary particle sizes of 40 and 10 nm, respectively) is being investigated. The complexity of both the experimental and modeling procedures increases with decreasing particle size. For example, the fine-grained powders must be adequately dispersed, and agglomeration must be minimized during titration. Moreover, when rationalizing the experimental data, curvature of the nanoparticles must be accounted for in the description of the EDL. Preliminary experiments suggest that the proton induced surface charge of 10nm anatase is similar to that of rutile at 25°C in 0.03m RbCl media.

V31B-05 0930h INVITED

Nanoscale Structure at Mineral-Fluid Interfaces

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The nature of nanoparticles and their role in the natural environment is currently a subject of renewed interest. The high surface area (and surface area-to-volume ratio) of nanoparticles exerts a widespread influence on geochemical reactions and transport processes. A thorough understanding of the nanoscale world remains largely hypothetical, however, because of

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