

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 >10⁸; 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 x 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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Resorption of garnet at very high temperatures may produce stranded diffusion profiles for trace elements; these can be exploited by measurement and modeling to yield quantitative estimates of diffusion coefficients for species that often defy definitive experimental determination of diffusion rates. Knowledge of intracrystalline diffusion rates in garnet for major and trace components provides vital constraints on the rates and mechanisms of diverse processes in the crust and mantle, providing information on time-temperature relationships across the broad P-T range of garnet stability. Trace-component diffusivities in particular are needed for proper application of garnet-based geochronometers, and the relatively slow diffusion of trace components also makes their diffusion rates especially crucial for the determination of uplift and cooling histories in the deep crust and mantle. Unfortunately, experimental determination of diffusion rates for trace elements in garnet (e.g., Y, REE) has proven extremely difficult, because sluggish diffusion yields transport only over micron or submicron distances for laboratory time scales. As a result, few experimental data exist. A promising complementary approach is to measure and model the stranded diffusion profiles produced by garnet resorption in nature, as has been done recently for the major divalent cations (Carlson, 2002, *Am Min* 87:185). A special requirement is to find rocks in which original garnet crystallization took place at temperatures high enough to homogenize the internal distribution of trace components, and in which later resorption occurred at temperatures high enough and times long enough to produce measurable diffusion profiles. The contact aureole of the Makhavinekh Lake Pluton (Nain Plutonic Suite, Labrador) provides rocks suitable for such a study. LA-ICP-MS analyses of Y and REE profiles in garnets, combined with thermal models for the contact aureole (McFarlane et al., 2003, *JMG* 21:405) allow extraction of diffusivities using the coupled resorption-diffusion model of Carlson (2002). Preliminary results expand the available database for Y and REE diffusion in garnet, yielding values generally consistent with the sparse experimental data.

V12F-03 1420h

REE Zoning in Garnet as a Record of Pressure Changes During Growth

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Radial variations in the concentrations of rare-earth elements (REE) in garnets from metamorphic rocks of the Llano Uplift of central Texas display systematic patterns that indicate that the REE may be sensitive recorders of changes in pressure during growth. LA-ICP-MS analysis of REE concentrations was performed at interior and rim positions of centered sections through garnets from garnet-clinopyroxenites at Whitt Ranch (WR) and from garnet-clinopyroxenites (PHM) and pelitic gneisses (PHP) at Purdy Hill. REE-abundance curves are flatter for PHM garnets than for WR garnets. Curves for WR garnets flatten towards rims; curves for PHM garnets steepen towards rims; and curves for PHP garnets first steepen in HREE towards rims, and then flatten, with negative slopes in HREE for some rim analyses. WR garnets contain negative Eu anomalies in interiors that disappear towards rims; PHM garnets contain small positive Eu anomalies throughout; and PHP garnets contain small negative Eu anomalies in both interiors and rims. Garnet-inclusion suites document that PH garnets formed at higher pressures than WR garnets, which suggests that flatter REE-abundance curves reflect higher pressures, corroborating the observations of Bea et al. (1997, *Geostds News* 21:253). Flattening of curves from interiors to rims suggests that WR garnets grew as pressure increased, which is supported by the distribution of inclusions in garnet: interiors contain plagioclase inclusions but rims do not, accounting for the rimward loss of negative Eu anomalies. Conversely, steepening of curves in PHM garnets may imply that they grew during decompression, although positive Eu anomalies suggest breakdown of plagioclase during garnet growth. Relative depletion of HREE in the rims of PHP garnets may record the growth of xenotime. Application of the Gd/Dy-in-garnet barometer of Bea et al. to PHP samples yielded pressures of 0.4-0.5 GPa, inconsistent with their eclogite-facies origin and with prior grt-opx barometry at PH of 1.5-2.1 GPa. Thus, although the shapes of the REE-abundance curves for the Llano garnets change systematically with pressure in a manner similar to the pattern described by Bea et al., the ratio of Gd/Dy alone fails to capture the complex behavior of the REE over the full range of pressure commonly experienced by crustal metamorphic rocks.

V12F-04 1435h

Application of Garnet-Accessory Phase Thermometry: a Combined EMP and SIMS Study

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Fe-Mg exchange thermometry involving garnet and other phases requires appropriate bulk compositions, and is often compromised by bulk diffusion within garnet and retrograde net-transfer reactions that dissolve garnet or shift biotite compositions. Application of garnet-accessory phase thermometry provides a robust, multi-faceted alternative. Garnet-accessory phase pairs are resistant to diffusive reequilibration of Y and HREE, display evidence for an approach to compositional equilibrium, record metamorphic events in detail with yttrium distribution, and provide temporal constraints for such events via correlated monazite or xenotime age estimates. Precise garnet-accessory phase thermometry is extendible to low-Y garnets using secondary-ion mass spectrometry (SIMS), which furnishes additional information on trace element residence in major phases. Empirical garnet-xenotime thermometry requires only measurement of the yttrium concentration in the garnet of interest; garnet-monzite thermometry requires calculation of molar components in garnet, plagioclase, apatite, and monazite, plus a fluid fugacity estimate. Establishing criteria for selection of appropriate mineral pairs is crucial. Electron Microprobe (EMP) garnet-accessory phase thermometry is applied to three samples from the Mesoproterozoic of New Mexico (Grt-Bt-St schist, Grt-Bt-Sil migmatite, Grt-Ms-St (biotite-absent) schist). In the former samples, Grt-Bt thermometry estimates are compromised by garnet resorption and diffusive reequilibration, and the latter sample is unsuitable for Grt-Bt thermometry. Correlation of appropriate garnet-monzite pairs yields peak T estimates of 550 to 590°C for the Grt-Bt-St schist, compared to 525-535°C for Grt-Bt thermometry, and T estimates of 610-650°C for pre-melting garnet-monzite pairs in the migmatite, compared to Grt-Bt peak T estimates of 580-620°C. Additionally, T estimates for earlier-formed garnet-monzite pairs (490-525°C, Grt-St-Bt schist; 465-530°C, migmatite) are recovered. Apatite and plagioclase are absent from the Grt-Ms-St rock, precluding application of the garnet-monzite thermometer, but garnet-xenotime thermometry yields T estimates of ca. 530°C for garnet cores, and 550-620°C for post staurolite-in garnet. All temperature estimates are linked to monazite ages, as determined by EMP chemical methods, ranging from 1440 to 1300 Ma. Garnet-monzite thermometry is extended to selected migmatites (British Columbia (BC), New England (NE)) via SIMS analysis of low-Y garnet. Garnet rim (152±0.5 ppm Y) - high Y monazite pairs from the BC migmatite yield T estimates of ca. 660°C, considerably lower than the peak T estimate of 820°C; this mineral pair is interpreted as pre-melting garnet and monazite. In the NE migmatite, very low Y (3.4±0.12 ppm) anatectic garnet correlated with 350 Ma high grade monazite domains yields a T range of 720-755°C, consistent with previous peak T estimates of 740°C, and formation of monazite on melt crystallization.

V12F-05 1450h INVITED

Quantitative Prograde P-T Paths From Inclusion Assemblages in Eclogitic Garnets

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Many workers have used garnet inclusions as qualitative indicators of the early history of tectonically exposed eclogites. Assemblages indicative of crustal facies combined with standard P-T conditions of those facies and thermobarometry on the matrix eclogite constrain the prograde path. However, now that conditions of some blueschist, amphibolite and granulite facies rocks have been extended to much higher pressures, in the range of 10-20 kbar, those assignments

are in need of review. While undertaking studies on eclogites from the Blue Ridge of North Carolina and the Franciscan in northern California, the authors have identified key inclusion assemblages of sphene-rutile-epidote-quartz and phengite-omphacite together with garnet that constrain the prograde P-T path based on univariant assemblages corrected for observed solid solutions. Equilibria that have proved most useful are those bounding epidote stability and two key reactions, one involving sphene/rutile: (1) clinozoisite + sphene = grossular + rutile + H₂O, and the second being the phengite barometer: garnet + Mg-celadonite = clinopyroxene + muscovite. Reactions (1) and (2) have negative slopes, intersecting with the Mg/Fe K_D garnet-clinopyroxene thermometer and providing a reasonable estimate of pre- to syn-eclogite facies P-T. In the case of the Bakersville eclogite samples from North Carolina, the inclusion assemblage yields 10 ± 2 kbar and 500 ± 50°C with reaction (1) compared to the peak assemblage at P > 15 ± 2 kbar and 700 ± 50°C. These data combined with evidence for a granulite facies overprint indicate a clockwise P-T path for those eclogites. A similar study on the Healdsburg eclogite samples from California yields about 500°C and 12 ± 1 kbar for the garnet cores, 14 ± 2 kbar for mantles and 16 ± 2 kbar for rim-matrix assemblages. The introduction of late glaucophane, epidote and chlorite partially replacing omphacite and garnet implies a retrograde return to the blueschist facies and a counterclockwise P-T path. The inclusion thermobarometry indicates that both eclogite bodies were continuously buried during prograde metamorphism. The geological evidence suggests that both eclogite bodies formed in subducted oceanic plates. The mechanism for a sudden pressure increase could be related to a change in the subduction angle or to oceanward underthrusting by another cold oceanic plate.

V12F-06 1510h

Garnet from diamondiferous metamorphic rocks of Kokchetav massif, Kazakhstan as a peak pressure recorder

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Garnet is a key mineral coexisting with diamond both in kimberlite (as xenocrysts, in diamondiferous garnet peridotites and eclogites, as inclusions in diamond) and in UHP metamorphic rocks of Kokchetav massif (diamondiferous gneisses, garnet-pyroxene rocks, dolomitic marbles and diamond facies eclogites). In UHPM rocks garnets are of particular importance as inclusions in zircons protected from retrograde metamorphism. Diamond formation conditions in eclogitic (E-type) upper mantle environment are estimated based upon Grt-Cpx thermometry and coesite barometry (e.g. Sobolev et al., *PNAS*, 2000, 97:11875) at P=5.5-6.0 GPa and T=1000-1300°C. These data are supported by diamond synthesis in carbonate-silicate fluid (e.g. Palyanov et al., *Nature*, 1999, 400: 417). E-type garnet may dissolve up to 0.3 wt.% Na₂O (Sobolev, Lavrentyev, *Contr. Min. Petr.*, 1971, 31:1) depending on pressure and Na₂O contents in coexisting pyroxene and melts (fluids). Majorite component (pyroxene solid solution) was reported in rare garnets from diamonds (e.g. Moore, Gurney, *Nature*, 1985, 318:553) and UHP conditions were experimentally confirmed for such garnets (Irfine, *Phys. Earth. Pl. Int.*, 1987, 45:324; Gasparik, *Phys. Chem. Min.*, 2002, 29:170; Luth, *Am. Miner.*, 1997, 82:1198). Garnets from Kokchetav diamondiferous metamorphic rocks demonstrate considerably lower Na₂O solubility (up to 0.2 wt.% in rare samples) and absence of majorite component. However, coexisting pyroxenes may contain up to 50 mol.% jadeite. Several UHP experiments performed with Kokchetav eclogites and dolomitic marbles using a split-sphere apparatus resulted in detection of up to 0.3-0.4 wt.% Na₂O in newly formed eclogitic garnets at P=5.7 and 7.0 GPa, T=1400 and 1700°C respectively. Majorite component was also determined in newly formed garnets reaching about 5% with Si (pfu)=3.05-3.06. Similar garnets without Na₂O were also obtained in UHP experiments with diamondiferous dolomitic marbles (e.g. Palyanov et al., *Dokl. Earth. Sci.*, 2001, 380:671). Based on the difference in Na₂O and majorite contents in natural Kokchetav garnets, and those coexisting with diamonds in kimberlite and obtained in UHP experiments, we conclude that the peak of metamorphism at Kokchetav massif occurred at P about 4.5-5.0 GPa and T=900-1000°C (Sobolev, Shatsky, *Nature*, 1990, 343:742; Shatsky et al., *Contr. Min. Petr.*, 1999, 137:185; Sobolev et al., *Dokl. Earth. Sci.*, 2001, 380:237) but not exceeding 6.0 GPa (e.g. Ogasawara et al., *Island Arc*, 2000, 9:400).

The Origin of Garnet Megacrysts in Sulu UHP Clinopyroxenite, East China

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Abundant garnet megacrysts occur in one garnet clinopyroxenite layer from Rizhao of the Sulu UHP terrane, east China. The clinopyroxenite layers with various contents of garnet (trace to > 40%), ilmenite (< 5 %) and minor olivine form part of a strongly serpentinized peridotite body. Megacrystic Grt-bearing clinopyroxenite consists of variable amounts of megacrystic and porphyroblastic Grt, fine-grained matrix of Grt + Di + Ilm ± Ol (Fo₈₂₋₈₅), and secondary Amp, Chl and Spl. The megacrystic Grt with ellipsoidal and spherical shapes ranges from 2.5 to 12 cm, are coated with Chl + Amp ± Cpx ± Ep ± Mt/Spl and develops distinct pressure shadow. Megacrystic Grt (Prp₄₄₋₅₆Gr_{s21-41}Alm₁₈₋₂₆) has similar compositions to porphyroblastic Grt (Prp₄₀₋₄₃Gr_{s37-40}Alm₂₀₋₂₁) but differs from matrix Grt (Prp₂₅₋₃₂Gr_{s46-56}Alm₁₈₋₂₂). At some interfaces between Grt and Cpx, Grt contains Ca-rich and Mg-poor compositions (Prp₂₃₋₂₅Gr_{s58-60}Alm₁₇₋₁₉). At least 6 types of inclusions occur: (a) trace spinel ± magnetite lamellae, (b) trace dolomite, (c) trace amphibole (3.0-3.4 wt% Na₂O; 0.3-0.4 wt% K₂O; 0.4-0.5 wt% TiO₂), (d) ilmenite with magnetite lamellae and rare spinel, (e) abundant coarse-grained Cpx (0.5-1.0 wt% Na₂O) with characteristic exsolution lamellae of Amp (0.4-1.3 wt% Na₂O; 0.7-1.0 wt% K₂O; Mg ~ 0.9; 0.1 - 0.2wt% TiO₂) + Ilm ± Grt described by Zhang and Liou (2003), and (f) composite phases of Cpx (e) + Ilm + Amp with ilmenite exsolution lamellae. The Grt megacrysts are fractured and veined with amphibolite facies assemblage Amp + Spl + Cpx ± Pl and do not contain exsolved rutile needles. Available experimental data (4-15 GPa, 1000-1400°C) of an Ilm-rich garnet clinopyroxenite composition indicate that Grt coexisting with Cpx contains considerable amount of TiO₂ (> 1 wt%) only at P > 5 GPa; the results constrain the maximum depth for the formation of Grt megacryst. Parageneses and compositions of inclusion phases in megacrystic Grt and matrix minerals suggest the protolith of the megacrystic Grt-bearing clinopyroxenite probably was a high-Al clinopyroxenite formed at mantle wedge with an initial assemblage Cpx + Ilm + Spl ± Ol ± Dol at P < 3 GPa and T ~ 1200°C. Subsequent increase in P and decrease in T as the mantle fragment involved in a continental subduction zone, spinel reacted to form Grt whereas the Al-Ti bearing Cpx exsolved Amp + Grt + Ilm lamellae at subduction depths < 150 km. During exhumation and hydration, Grt coalesced to form megacrysts that engulfed relict lamellae-rich Cpx, Ilm, Spl, Amp and dolomite as inclusions. Porphyroblastic garnet formed subsequently and lamellae-rich Cpx recrystallized to matrix assemblage of Cpx + Grt + Ilm at ~800°C, ~3 GPa. Deformation at crustal depths fractured megacrysts and amphibolite facies recrystallization occurred.

V12G MCC: 3006 Monday 1340h

Rift Zones on Volcanic Islands: Structure, Evolution, and Magmatic Processes I (joint with S, T)

Presiding: T R Walter, Rosenstiel

School of Marine and Atmospheric Science, University of Miami; A KLGEL, University of Bremen

V12G-01 1340h INVITED

Effects of Mechanical Layering on Dike Emplacement, Faulting, and Surface Deformation in Rift Zones

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All rift zones in volcanic islands contain normal faults and dikes as their main structural elements. During rifting episodes there is normally fault slip, graben development and dike emplacement. Field and geodetic studies, however, show that most dikes emplaced in rift zones do not reach the surface but rather become arrested at certain crustal depths. Geodetic measurements of the surface deformation during rifting episodes are routinely used to model the depth to the tips, as well as the geometries, of arrested dikes. Most inverse models to infer the geometries of arrested dikes assume the rift zone to be a homogeneous, isotropic, elastic half space. All rift zones in volcanic islands, however, contain normal faults and other discontinuities, and consist of rock layers that often have contrasting mechanical properties, such as soft pyroclastic rocks and stiff basaltic lava flows. To explore the effects of mechanical layering on fault slip and dike emplacement during a rifting episode, many boundary-element models were run. In these models, the rift zone already has a graben, represented by two (boundary) normal faults, dipping at 70° toward the center of the rift zone. The rift zone is taken to be 10 km thick. In all the models the lower tips of the boundary faults are at the depth of 4 km below the surface; in some models the upper fault tips extend to a depth of 1.5 km below the surface, in others all the way to the surface. The rift zone is composed of alternating stiff (high Young's modulus) and soft (low Young's modulus) layers. In most models, the only loading is the internal magmatic overpressure that drives the dike. The first models indicate that the stresses generated by a dike propagating vertically up toward the bottom part of a graben tend to open up the boundary faults of the graben. However, when the upper tip of the dyke reaches the same crustal level as the bottom tips of the boundary faults, the magmatic overpressure associated with the dike forces the faults to close and subsequently, as the dike tip continues its propagation up into the graben, encourages reverse slip on these normal faults. The faults remain closed until the magmatic overpressure is relaxed. For the faults extending to the surface, the reverse slip generates a hoist. The second models show that soft layers and a weak contact at shallow depths suppress dike-tip tensile stresses and encourage dike arrest. Soft layers and a weak contact also suppress the surface stresses and deformation induced by arrested dikes and encourage transfer of the surface tensile stresses to the regions above the lateral ends of the weak contact. In these models, the tensile stress at the rift-zone surface in a large area above the arrested dike itself is very small, but rises above the lateral ends of the weak contact, many kilometers from the dike tip. Thus, for a dike arrested in a layered rift zone, straightforward inversion of surface-deformation data may yield geometric results that have little relation to the actual geometry of the arrested dike. The predictions of the numerical models are generally supported by field results from the volcanic rift zones of Tenerife (Canary Islands) and Iceland.

V12G-02 1355h INVITED

Stresses Associated to the Onset of the Pu'u 'Ō'ō Kūpaianaha Eruption

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Ground deformation and seismicity are used in a complementary way in order to determine stressing processes before and at the onset of the Pu'u 'Ō'ō Kūpaianaha eruption. After the magnitude 7.2 Kalaupana earthquake and before the start of the ongoing eruption in 1983, deformation of Kilauea volcano was the most rapid ever recorded. Modeling shows that this deformation was characterized by the dilation of a dike-like magma system within Kilauea's rift-zones, coupled with aseismic creep over a narrow zone of a low-angle fault located beneath the volcano's south flank. For the 1976-1983 period, rates of rift zone opening averaged 40 centimeters a year resulting in a magma supply of 0.19 cubic-kilometer per year. The onset of the Pu'u 'Ō'ō Kūpaianaha eruption was associated with a 2.1 meter fissure opening in the east rift-zone and a significant change of the south-flank seismicity pattern and rates. Coulomb stresses associated to the fissure opening are computed using a three-dimensional boundary element method for two different models that fit the deformation data equally well - a model in which the inflating rift dike propagated from a depth of 3 km to the free surface, and a model of an isolated intrusion of a shallow dike. Then, Coulomb stresses are computed independently from earthquake rates using a newly developed method [Dieterich *et al.*, 2000]. We find that the Coulomb stresses determined from seismicity agree with the model corresponding to the propagation of the rift dike to the surface. Moreover this model is mechanically consistent with our model for the 1976-1983 period.

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Simultaneous Submarine and Subaerial Volcanic Activity on the Flanks of the Western Canary Islands La Palma and El Hierro

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The westernmost and youngest Canary Islands La Palma (2.0 Ma) and El Hierro (1.1 Ma) are presently in their shield stages. The subaerial and submarine morphology of both islands is characterized by one or three elongated ridges, respectively, commonly interpreted as volcanic rift zones. Our investigations indicate that young submarine volcanic activity off the islands is not confined to the extensions of these rift zones, but is also dispersed along the island flanks. Fresh basaltic rocks dredged along these flanks (RV "Poseidon" cruise 270 in 2001, and RV "Meteor" cruise M43 in 1998) comprise basanites to tephrites and alkali basalts. Remarkably, the dredged lavas are geochemically more diverse than those of the Holocene subaerial ridges. Fresh basalts have been recovered from 21 young volcanoes on the submarine flanks of El Hierro at depths from 800 to 2300 m. Another 25 volcanic cones can be tentatively identified from morphologies similar to the dredged ones. These submarine volcanoes off El Hierro occur in a dispersed manner on the blunt noses representing the extensions of the postulated subaerial northeast and northwest rift zones but also off the rift axes. Young volcanoes also occur within the Las Playas and El Julian landslide scars, testifying to renewed volcanic activity following large landslides. On the east flank of La Palma, we recovered basaltic rocks from 8 volcanic cones at depths between 850 and 2200 m and at a distance of up to 30 km off the rift axis, recognizing another 20 possible volcanoes in the same area from high-resolution bathymetric data. Remarkably, young submarine volcanoes are comparatively rare on the western flank and the submarine extension of the Cumbre Vieja rift zone. The high density of apparently young volcanoes on the NE and NW slopes of El Hierro suggests that submarine volcanism is volumetrically important during subaerial growth stages of the Canary Islands. Our results indicate that a broad melting anomaly involving distinct sources must occur in the mantle beneath La Palma and El Hierro.