eastern sector of the main crater. These observed spatial variations of soil Hg^0 anomalies are temporarily correlated with an increase of fumarolic activity in the eastern part of the crater. In addition, spatial distribution of peak values of Hg^0 in the eastern sector of the crater follows a N-S trending parallel to local faulting. Soil Hg^0 distribution were spatially well correlated with CO_2 efflux data for the period 2000-2003 (Melián et al., 2001). These results suggest that a deep perturbation of the Poás volcanic-hydrothermal system has been responsible for the observed spatial distribution pattern of soil volatiles.

URL: http://www.iter.es

V21C-0540 0830h POSTER

Dynamics of diffuse helium degassing from Cumbre Vieja volcano, La Palma, Canary Islands

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La Palma island (730 km^2) is the northwestern most island of the Canarian archipelago. Cumbre Vieja volcano (220 km^2) is the result of the volcanic activity in the southern part of the island during the last 1 Ma. Six historical eruptions had occurred at Cumbre Vieja, and the most recent one took place at the extreme south of this volcano in 1971. Three major volcanic rift-zones trending N-S, NW-SE and NE-SW constitute Cumbre Vieja´s major structural features. The aim of this study is evaluate the use of diffuse helium degassing for monitoring Cumbre Vieja volcano since (1) diffuse degassing studies seems to become a powerful geochemical tool for volcano surveillance (Hernández et al., 2001), and (2) helium is an ideal geochemical gas tracer because it is chemically inert, physically stable, sparingly soluble in water under ambient conditions. Since 1997 diffuse degassing surveys are regularly performed at Cumbre Vieja. During the last 2 years these surveys have investigated helium in the soil atmosphere. Soil gas samples were collected at 40 cm deep using a metallic probe and stored in vacutainers by means of water displacement technique. Soil gas samples were analyzed for ^4He and CO_2 contents by means of a QMS within 24 hours. CO_2 efflux measurements were also performed by means of a portable NDIR sensor according to the accumulation chamber method. ΔHe contour maps ($\Delta He = He_{soilatmosphere}$-$He_{air}$) were constructed using kriging as interpolation method. Both surveys showed a good spatial agreement for ΔHe, and their peak values (> 1,800 ppbV) were mainly observed at the summit area of Cumbre Vieja along the N-S rift-zone, suggesting a deep origin for the degassing through this major structure. The total output for diffuse ^4He emission rate at Cumbre Vieja was estimated by multiplying CO2 efflux times ΔHe /ΔCO_2 ratio at each sampling site. The results showed an increase on the diffuse ^4He emission rate from 67 to 167 kg d^{-1}. Monitoring these results could be useful for the volcanic surveillance.

URL: http://www.iter.es

V21C-0541 0830h POSTER

Monitoring Diffuse Carbon Dioxide Degassing and Surface Pressure Gradient at Cerro Negro Volcano, Nicaragua

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Diffuse CO_2 emission studies are becoming a useful geochemical tool for volcano monitoring. Significant temporal variations of diffuse CO_2 degassing rate seem to be directy related to changes of activity volcanic. Since 1999 a research collaboration program between INETER and ITER has been established for monitoring diffuse CO_2 emission from Cerro Negro, the most active volcano from the western hemisphere.
Surface pressure gradient and diffuse CO_2 degassing surveys were carried out on March 2002 and 2003 at Cerro Negro. An additional survey of CO_2 efflux was performed on December 1999. Sampling site distributions were similar for the 1999, 2002 and 2003 surveys covering an area of 0.6 km^2. Pressure gradient measurements were performed by means of a Setra 239 pressure transducer, and soil CO_2 efflux measurements were performed by means of a portable NDIR sensor according to the accumulation chamber method. Surface pressure gradient values ranged from -11.7 to 232.8 Pam^{-1} and -24.2 to 102.0 Pam^{-1} for 2002 and 2003 surveys, respectively. Soil CO_2 efflux ranged from 0.5 to 35,000 $gm^{-2}d^{-1}$ for 1999, 0.3 to 26,500 $gm^{-2}d^{-1}$ for 2002, and 0.3 to 3,002 $gm^{-2}d^{-1}$ for 2003 surveys. The total diffuse CO_2 output for the 2003 survey was estimated about 34 td^{-1}, which is one and two orders of magnitude lower than the estimated for the 1999 survey, 2,800 td^{-1}, (Salazar et al., 2001) and the 2002 survey, 280 td^{-1}, (Galindo et al., 2002). These surveys took place 3 (1999), 17 (2002) and 29 (2003) months after the most recent eruption of Cerro Negro, August 1999. The observed decreasing trend on the diffuse CO_2 emission is temporarily correlated with a reducing tendency on the surface pressure gradient suggesting a lower advective component for the diffuse degassing mechanism on the surface environment at Cerro Negro. These results show a clear relationship between diffuse CO_2 emission and the eruptive cycle of Cerro Negro; therefore, the potential of this geochemical tool for its volcanic surveillance.

URL: http://www.iter.es

V21C-0542 0830h POSTER

Dinamic of Diffuse CO2 Degassing at the NW Volcanic Rift-Zone of Tenerfe, Canary Island

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Tenerife is one of the most active volcanic island of the Canarian archipelago with six historical eruptions. The most recent volcanic activity took place along the NW rift-zone in 1909, Chinyero volcano. Fumarolic activity is absent along the NW rift-zone; therefore, diffuse CO_2 degassing studies constitute a major geochemical program for the volcanic surveillance of the area. The first survey was carried out in 2000, and 446 observation sites were well distributed along the study area of (72 Km^2). The most recent survey of diffuse CO_2 degassing and surface pressure gradient measurements was carried out from July 17 to August 6, 2003 with 441 observation sites covering the same area. Soil CO_2 efflux measurements were performed by means of a portable NDIR sensor according to the accumulation chamber method, while pressure gradient measurements were performed by means of a Setra 239 Model pressure transducer. Statistical-graphical analysis of the soil CO_2 efflux data showed two overlapping populations. The background geometric mean was 1.7 $gm^{-2}d^{-1}$ and represents 97.5% of the total data. The highest observed CO_2 efflux value for this 2003 survey was 13 $gm^{-2}d^{-1}$, and it is very similar to the observed highest value for the 2000 survey, 15 $gm^{-2}d^{-1}$. These peak measurements are 7-9 times background values. Most of the study area showed background values of diffuse CO_2 emission rate for both surveys. Peak CO_2 efflux values are spatially correlated to volcanic alignments with a WNW-ESE trend suggesting a clear structural control on the mechanism of diffuse degassing. Surface pressure gradient distribution did not show a clear relationship with CO_2 efflux distribution. For the 2000 and 2003 survey, the estimated total output for de diffusee CO2 emissioon were 79 and 146 td-1, respectively.

URL: http://www.iter.es

V21C-0543 0830h POSTER

Structurally controlled diffuse ^{222}Rn degassing along the NW volcanic rift-zone of Tenerife, Canary Islands

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Three major volcanic rift-zones trending NW-SE, NE-SW and N-S are identified at Tenerife island. Most of the volcanic activity have occurred along these three major structures. The most recent eruption, Chinyero (1909), occurred along the NW rift-zone. The aim of this research is to evaluate the relationship between structural characteristics of the study area with diffuse ^{222}Rn degassing rates. Nearly fifty cinder cones have been analysed in detail to infer the eruptive fissures trend. The strike values of the 26 eruptive fissures identified ranged from 95 to 176°E, showing a mean value of 116°E. These results suggest that most of the eruptions took place along preferential pathways of WNW-ESE trended fissures and that these eruptions were effectively true fissure type eruptions. Parallel to the structural study a soil gas ^{222}Rn survey of 424 sampling sites was carried out along the NW rift-zone from July 17 to August 6, 2003. Soil gas ^{222}Rn was analyzed in situ by means of a portable radiation monitor Pylon AB-5. The highest observed soil gas ^{222}Rn was 136 pCiL^{-1}. Statistical-graphical analysis showed two overlapping populations. Soil gas ^{222}Rn concentration background geometric mean was 23 pCiL^{-1} and represents 98% of the total data. Most of the study area showed background levels of soil ^{222}Rn concentration, while peak levels were aligned along the NW rift-zone. The good spatial correlation of the soil gas ^{222}Rn concentration with the WNW-ESE trend of the rift-zone suggest that the ^{222}Rn diffuse emission is structurally controlled in the study area.

URL: http://www.iter.es

V21D MCC: Level 1 Tuesday 0830h

Crustal and Mantle Processes in Ophiolites and Ocean Crust Generation III Posters *(joint with GP, OS, T)*

Presiding: **A Davis,** Cambridge University

V21D-0544 0830h POSTER

Preliminary Results on the Structure of Ocean Crust from new Holes Drilled in Fast-Spread Crust During ODP Leg 206

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ODP Leg 206 successfully accomplished the initial phase of a multi-leg drilling program that aims to sample a complete section of upper oceanic crust through the extrusive lavas, the sheeted dike complex, and into the gabbros. Drilling was conducted at Site 1256 (6.7N, 91.9W), which resides on 15-Ma oceanic lithosphere of the Cocos plate that was created by superfast seafloor spreading (220 mm/yr). Two holes, 1256C and 1256D were drilled into the basement to a depth of 340.3 mbsf (89.6 m sub-basement) and 752 mbsf (502 m sub-basement) respectively. The main stratigraphy of upper oceanic crust at Site 1256 consists of a sequence of massive flows and thin sheet flows with minor amounts of pillow basalts and breccias. The sequence is slightly altered and has N-MORB composition. Structural analysis carried out on board on the recovered cores from both Holes 1256C and 1256D revealed the occurrence of primary igneous as well as post-magmatic structures. Primary igneous features include magmatic fabrics, laminations and flattened vesicles, folds and shear-related structures, late magmatic veins, and fracturing. Postmagmatic structures include veins, shear veins, microfaults, joints, and breccia. Veins are the most prominent structural features and show a variety of morphologies ranging from planar and curviliear to anastomosing. In many cases veins are oriented in en echelon, and Riedel-shear arrays, giving in such case useful shear indications. Shear veins are mostly present in massive coarser-grained lithologic units and are filled with fibrous clay minerals. Shear veins and microfaults indicate both strike-slip and oblique apparent senses of shear. In Hole 1256D shear veins show a change in the sense of shear, from reverse to normal, from 645 mbsf to the bottom of the hole. More than 600 veins and joints from the basement units of Hole C and more than 1700 features from Hole D were measured in the archive half relative to the core barrel reference frame. True dip data show that structures inHole 1256D are mostly gently dipping, having most common frequency dip angles of 15°. Other dip angles are represented nearly by the same frequency throughout the hole. In Hole 1256C, true dip angles show a maximum in frequency between 10° and 20°; however, dip values around 50°-55° and 90° are common as well. Late magmatic veins are mostly gently dipping in the two holes, showing the highest frequency at 15° and 5°. By contrast, shear veins are moderately to steeply dipping in the two holes (maximum frequency ranges from 45° to 75°). In Hole

1256C, the distribution of true dips per lithologic unit (i.e., massive flows and sheet flows vs. pillowed, brecciated or glassy units) shows that, in the upper units (sheet flows), the dip values are bimodally distributed in sets making an angle of 50°-60°. This is linked to the presence of conjugate systems of veins in the upper part of the hole, whereas in the middle and lower parts, true dips are mostly clustered in one group. In the lower three igneous units (sheet flows), structures mainly have gentle dips. In Hole 1256D, the distribution of true dip angles with depth does not show any systematic variation. The variation in dips of the veins and in their density seem to be related mainly to the physical properties and morphology of the lithologic units rather than to the depth of their occurrence. Further investigations and elaboration of our results are in progress, with the aim of understanding the link between structural features and local vs. regional stress field.

V21D-0545 0830h POSTER

Condition of Development of Channeled Flow in Analogue Partially Molten Medium

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Melt migration in partially molten medium is conceptually classified into two contrasting models; homogeneous permeable flow and localized channeled flow. The transition from homogeneous flow to localized one is promoted with advance of melting and deformation of the medium, but the physics behind this transition is not yet clarified well. Here we show two kinds of experimental results which are mutually related. One is a development of the channeled flow in a so-called Rayleigh-Taylor Instability experiments. Dense viscous fluid is poured at the top of the matrix fluid; homogeneous mixture of soft transparent gel and viscous fluid having equal density. Liquid fraction is varied for this matrix fluid to see how the fraction controls the development. At the intermediate gel fraction (between70% to about 40%) the dense fluid at first migrates through the grain boundary as permeable flow. But local heterogeneity in the gel fraction induces relative movement of solid phase, which in turns enhances the localization of the flow and deformation. We measured the motion of fluid phase and solid phase separately by PIV/PTV methods. Estimated relative motion and divergence of velocity field of the solid phase show that the state in the relative movement of the solid phase could cause heterogeneous distribution of the solid fraction. The deformation-induced compaction plays an important role. The second experimental result is rheology of the dense suspension of soft gel and viscous fluid. Deformation experiment with concentric cylinders shows that the mixture system has yield strength at the intermediate gel fraction. In the stress state above the yield strength the region where deformation rate is large has low viscosity and its internal structure evolves to the state in heterogeneous distribution of viscosity. We would like to show that this nature is critical in the development of flow from homogeneous one to localized one.

V21D-0546 0830h POSTER

Lava-seawater vapor interaction at the mid-ocean ridge crest: an important volcanic process to explain lava transport and flow morphology on the deep sea floor

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Eruption of lava from seafloor vents at the mid-ocean ridge (MOR) crest remains a poorly understood phenomena, despite the fact that it is the dominant volcanic process on earth. During the last decade only a handful of MOR eruptions have been documented using either NOAA-PMEL hydrophone detected events or serendipity, and observations of seafloor manifestations of those effusive events did not capture the actual interaction between erupted lava and near-freezing ambient seawater. Because of the great physical and technological obstacles to actually observing volcanic eruption processes in the deep sea, we must rely on the physical and chemical evidence left behind in the cooled seafloor lava flows to deduce the likely processes that occurred. Based on observations and sampling of numerous lava flows from slow to fast-spreading MORs we find a plethora of delicate macroscopic features preserved on the crusts of lava flows and in lava pillars that suggest intense and extensive interactions between hot magma and seawater during seafloor eruptions resulting in a briny vapor phase. Undersides of many lobate and sheet lava crusts have glassy drips (lava stalactites) and flanges (relict bubble walls) that could only have formed in cavities initially filled with a hot vapor at magmatic temperatures as lava was transported across the seafloor. Detailed petrologic observations of the surfaces of drips and flanges, including the presence of molten salt, exotic Cl- and S-bearing secondary silicates, secondary sulfates and almost pure forsterite, suggest that the vapor phase was flashed seawater. This vapor phase is a key to understanding delicate drip structures formed on lava crusts and the mechanisms by which lava is distributed far from eruptive fissures on the deep sea floor. We suggest that vaporized seawater is incorporated at the flow front as lava moves over the seafloor. The vapor rises as streams of bubbles through the lava behind the flow front and then collects beneath the rapidly chilled, insulating upper crust. The vapor exists at near magmatic temperatures beneath the crust and facilitates the formation of delicate drip structures and complex surface morphologies of the flow, especially when the effusion rate is fast and a variety of sheet and lobate flow surfaces form. Subsequent, cooling of the vapor and cracking of the crust leads to collapse of the crust into the underlying void. Entrapment of vapor beneath submarine lava flows may also have significant impact on the ability of flows to travel long distances (km to 10s of km) across pre-eruption seafloor by reducing the effective friction between the flow and the water-saturated seafloor. Recent results of SEM and a variety of microscopic analytical techniques on drip structures in seafloor lavas will be presented.

V21D-0547 0830h POSTER

Morphologic Comparison of Submarine Lava Channels on the East Pacific Rise and Simulated Channel Flows

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Submarine lava channels observed on the East Pacific Rise (EPR) between $9-10^{\circ}$ N exhibit five prominent surface textures: lobate, jumbled, lineated, folded, and smooth. These textures are similar in appearance and distribution to final morphologies observed in polyethylene glycol (PEG) channel flows produced in laboratory simulations. Maps of the surface textures for both submarine and simulated flows were made to compare the distribution of the various textural types. Photomosaics of tow-camera images taken near the axial summit collapse trough of the EPR were used to analyze the submarine lava channels. The mosaics are made from swaths of images that have a 6-m field of view, and cross channels that are as wide as 115 m. PEG channel flows were produced on slopes of $<10^{\circ}$. The final flow morphologies formed by solidified PEG after extrusion had ceased were mapped and compared to the submarine cross-channel mosaics. Levees of both submarine and PEG channels are lobate. The outer margins of PEG levees are easy to see, but flow margins are not as obvious in the submarine images, making it difficult to determine submarine flow and levee widths. After effusion of PEG has ceased in simulated flows, the solidified crust on the wax within the channel subsides, leaving a high-standing levee and a low-lying channel crust. Similarly, images of the channel-levee margin in submarine flows show the crust in the channel at a lower level than the top of the levees, indicating subsidence of channel crust after the eruption had ceased. The channel-levee transitions in submarine flows are characterized by a zone of jumbled lava. Jumbled pieces of solidified PEG are not present at the channel-levee margin after drain-out, but a shear zone is observed at this location during emplacement. The observed jumbled region in submarine channels may be generated by a similar shear zone at the channel-levee margin, combined with pieces of crust broken during channel subsidence. Crust textures in submarine channels are various combinations of jumbled, lineated, and smooth, while PEG channel crusts are typically smooth or folded. Analysis of flow textures, as well as channel and levee dimensions in submarine flows, will contribute to a better understanding of the emplacement and evolution of lava flows at mid-ocean ridges.

URL: http://www.whoi.edu/atlantis74

V21D-0548 0830h POSTER

Hydrothermal Alteration of the Lower Oceanic Crust: Sr Isotopic Constraints from the CCSP CY-4 Drill Hole, Troodos Ophiolite, Cyprus

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Our understanding of the structure and geometry of mid-ocean ridge hydrothermal systems is severely hindered by a dearth of continuous samples into the plutonic complexes of the ocean crust as it is this region that provides the power to drive hydrothermal circulation and preserves a record of magma chamber processes. Although the Troodos ophiolite most probably formed in a supra-subduction zone environment, its well-preserved outcrops have made an invaluable contribution to our understanding of ocean ridge processes. CY-4 drilled as part of the Cyprus Crustal Study Project provides a unique continuous sample of 2263 m of the lower Troodos crust. The hole was initiated in sheeted dikes before grading into isotropic gabbros around 675 m. An intrusive transition is evident at 1330 m between the isotropic gabbros and lower layered gabbros, pyroxenites and crustal peridotites. Petrographic observations and strontium isotopic analyses presented here investigate the incursion of seawater derived hydrothermal fluids into the lower oceanic crust. Previous studies of the Troodos ophiolite have determined the primary igneous composition of the magmas ($^{87}Sr/^{86}Sr$ =0.7032-0.7040) and the range of hydrothermal fluids ($^{87}Sr/^{86}Sr$ =0.7047-0.7059). Samples from the sheeted dike complex are variably altered with strontium isotopic compositions elevated above the primary igneous signatures of the Troodos magmas but generally lower than the restricted hydrothermal range observed for dikes throughout the rest of the ophiolite. Samples proximal to the sheeted dike - gabbro boundary do yield strontium isotope ratios within the hydrothermal fluid range. Within a few hundred metres below the dike-gabbro transition most samples yield near primary strontium isotopic ratios suggesting only limited pervasive penetration of seawater-derived Sr. Most samples down to the bottom of the hole show little increase in Sr ratios. Rare hydrothermally altered samples with associated veins and secondary halos have $^{87}Sr/^{86}Sr$ elevated towards hydrothermal values indicating significant channelling of hydrothermal fluids at deeper levels in the Troodos crust.

V21D-0549 0830h POSTER

Sub-seafloor hydrothermal alteration of oceanic crust of the Oman ophiolite - Interaction with global environmental change -

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The chemical change of rocks during hydrothermal alteration was investigated in a complete section through the Wadi Fizh oceanic crust in the Oman ophiolite was investigated in order to evaluate seawater-rock interaction through the oceanic crust. 20 elements analyzed in this study are classified into 6 groups: Group 1 (Ca, P, Al), Group 2 (Mg, Ni, Co, Cr), Group 3 (Fe, Ti, Na, Mn, Zn, Y), Group 4 (K, Rb, Ba), Group 5 (Li, Cd) and Group 6 (other elements such as Sr, Cu). The degree of alteration is assessed by 87Sr/86Sr ratios of rocks and the abundance of secondary minerals. Heavy metals (Cu, Zn, Ni, Cr, Co and Cd) and phosphorus were leached from the lower oceanic crust during amphibolite facies ($> 450u^{C}$) alteration. Even if the scavenging and/or removal by hydrous Fe and Mn oxides is taken into consideration, the alteration of ophiolite complex, as a whole, works as a source of phosphorus to the ocean during the mid-Cretaceous. This period is characterized by deposition of black shales and oil generation caused by superplume activity. Although such

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carbon should have been supplied directly by mantle outgassing, nutrients such as phosphorus and silica required for the production of marine organic matter would have been supplied from enhanced hydrothermal activity.

V21D-0550 0830h POSTER

Constraining Hydrothermal Fluxes: Insights From the Northern Oman Ophiolite

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Hydrothermal circulation is an intrinsic process at all oceanic spreading centres and makes an important contribution to global geochemical cycles. However, large uncertainties remain in the magnitude of hydrothermal fluxes and the hydrothermal contribution to global geochemical budgets. A multi-phase hydrothermal system in the northern Oman ophiolite is investigated as an analogue for understanding modern oceanic process and the magnitude of hydrothermal fluxes in arc-related environments. Field mapping of the Wadi Rajmi area combined with trace element discrimination methods are used to identify three hydrothermal regimes which correlate with the complex magmatic-tectonic evolution of the area. The first hydrothermal regime is associated with formation and cooling of the crustal (V1) sequence within an oceanic spreading environment. The second and third regimes are associated with later (V2) localised magmatic intrusions in an off-axis environment. Strontium isotope geochemistry is used to investigate the character of each regime and predict a time-integrated high-temperature fluid flux of $\sim 4.5 \pm 1.1 \times 10^7$ kgm^{-2} for the initial spreading related hydrothermal event and lower estimates for the later regimes. The flux calculated is comparable to a similar prediction made for the Troodos ophiolite (Bickle & Teagle, 1992), but is significantly higher than that calculated for mid-ocean ridge systems (Teagle et al, 2003). This supports previous suggestion that oceanic spreading systems in supra-subduction settings maintain greater hydrothermal fluxes than normal oceanic environments, and this has important implications for the hydrothermal contribution to global geochemical budgets

V21D-0551 0830h POSTER

High Temperature Hydrothermal Circulation in the Deep Oceanic Crust - Sr Isotopes and Trace Elements Modelisation Constraints on the Origin of the Fluids

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Previous field, petrological and geochemical works have identified high temperature hydrous alteration traces throughout the gabbros of the Samail ophiolite. Temperatures have been calibrated for the successive stages of alteration, starting with orthopyroxene-pargasite coronas (above 975 °C) and ending with the low temperature (LT) lizardite serpentinisation (below 500 °C). Sr isotopic analyses performed on massive gabbros, dikes and veins and associated minerals depart from typical mantle signatures and are characterized by radiogenic Sr isotopic ratios suggesting seawater as the most likely hydrothermal contaminant. The main water channels may be submillimetric microcracks with a dominantly vertical attitude and constituting the recharge hydrothermal system, whereas dikes and veins represent the discharge part. This model requires that these dikes have been generated by hydration of the crystallizing gabbros via seawater penetration, near the internal wall of the LVZ-magma chamber, i.e. at temperatures well above the near 1000 °C temperature recorded so far. We used the numerical plate model of Vernières et al. (1997) to simulate the chemical evolution of Sr isotopes and some trace elements in fluids through the gabbro column. This approach takes into account mineralogical and porosity variations due to dissolution-precipitation processes, as well as variations of partition coefficients as a function of distance from the fluid source. The aim of modelling was twofold: (1) to provide estimates of the chemical evolution of fluids as a result of high-temperature interaction with gabbros, and (2) to constrain the fluid-rock ratios throughout the gabbros sequence. Such an approach sheds new lights on the importance of high temperature hydrothermal processes and on the geochemical modifications they induced during oceanic crust formation at fast spreading ridge. Vernières J., Godard M., Bodinier J.-L., 1997. A plate model for the simulation of trace element fractionation during partial melting and reactive magma transport in the Earth's upper mantle. J. Geophys. Res. 102, 24771-24784.

V21D-0552 0830h POSTER

Linking Basement Vein Compositions to Porewater Geochemistry Across the Eastern Flank of the Juan de Fuca Ridge, ODP Leg 168

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Leg 168 of the Ocean Drilling Program (ODP) investigated the heat flow, fluid chemistry and crustal alteration associated with ridge flank hydrothermal systems. 10 sites were drilled on the eastern flank of the Juan de Fuca Ridge, along an 80 km transect, between 20 and 100 km east of the spreading centre. Recovered cores consisted of 100-500 m of sediment with shallow penetration (1.7-48.1 m) into the underlying igneous basement (0.8 to 3.6 Ma). Here we use the composition of calcium carbonate minerals, from veins within the upper basement, to reconstruct the evolving chemistry of hydrothermal fluids with increasing crustal age and sediment cover thickness. We show for the first time, a clear link between the alteration of the basement rocks as recorded by secondary minerals, and the near basement sedimentary pore fluids which are often assumed to be representative of the basement fluids responsible for low temperature alteration of the upper crust. Our results show that the carbonates precipitated from basement fluids that ranged in strontium isotopic composition from near modern seawater ($^{87}Sr/^{86}Sr \sim 0.70918$) to the near-basement pore fluid values at any one site. $^{87}Sr/^{86}Sr$ ratios are independent of mineralogy with both aragonite and calcite precipitating from variably evolved fluids with the range in carbonate $^{87}Sr/^{86}Sr$ increasing with crustal age. A parallel geochemical evolution of basement fluids and sediment pore-waters is shown since $^{87}Sr/^{86}Sr$ ratios of near-basement pore fluids decrease from 0.709013 to 0.707108 away from the ridge axis. A correlation exists between $^{87}Sr/^{86}Sr$ ratios and $\delta^{18}O$-calculated fluid temperatures, with more geochemically evolved carbonates having precipitated from warmer fluids. Given an observed increase in basement temperature with age, from 16°C to 64°C along the transect, a progressive chemical development of basement fluid is demonstrated.

V21D-0553 0830h POSTER

En echelon knolls in the Nosappu Fracture Zone, NW Pacific: A possible leaky transform fault zone

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During JAMSTEC R/V KAIREI cruise KR03-07, we mapped significant en echelon arrays of knolls and ridges on the NNW-trending Nosappu Fracture Zone between Hokkaido and Shatsky Rise, NW Pacific. This fracture zone has been known to be irregular, including a deep-sea channel, the Nakwe Channel, enigmatic for inside the wide oceanic plate. Considering the previously recognized magnetic lineament dislocation, the fracture zone has long (more than 150 km) left-lateral strike-slip component as a ridge-ridge transform fault zone between the Izanagi and Pacific plates during Early Cretaceous. Detail multi-narrowbeam mapping around 37 N latitude, 150 E longitude (covering 78 km x 137 km), indicated many small knolls and ridges that form en echelon arrangement. Some are boomerang, sock or E-letter in shape. The two dominant directions of ridges are recognized, one is parallel to the fracture zone and the other is in left-handed en echelon fashion. Besides these ridges, there are other types of ridges or conical knolls lower than 500 m in relief; one is a group of rather large knolls extending to NE, roughly perpendicular to the fracture zone direction, and the other is independent small knolls, summing up to five or six in number. Another expression of a depression zone was recognized with a moderate angle to the fracture zone in a crank fashion. This may correspond to the so-called Nakwe Channel which has been wrongly mistaken. Such en echelon arrays are involved in a 50 km wide NNW-SSE zone, which is sharply demarcated by fault scarps. These characteristics in the fracture zone area and associated knolls suggest that this part of the Nosappu Fracture Zone might have developed in a fault interaction area which has a left-lateral component of leaky transform faulting close to the spreading ridge.

URL: http://www.press.first.tsukuba.ac.jp

V21D-0554 0830h POSTER

Drilling the Largest Oceanic Detachment in the World: the Godzilla Mullion in the Parece Vela Rift

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Recently discovered megamullions at slow-spreading ridges have been interpreted as exhumed footwalls of oceanic detachment faults in magma-starved ridge environments. These features are believed to result from extreme tectonic extension, and thus they are ideal to study processes of tectonic extension in oceanic lithosphere. In addition to tectonic issues, these features provide excellent tectonic windows to the lower crust and uppermost mantle. Drilling megamullion structures allows us to study tectonic processes, serpentinization and magnetization at shallow depth and mantle composition and fabrics at a deeper level. The largest megamullion structure in the world is the Godzilla Mullion in the extinct Parece Vela backarc basin, Philippine Sea. Recent reconnaissance studies by our group have revealed the following unique characteristics of this structure: (1) The Godzilla Mullion is huge, $\sim$ 10 times larger in area than megamullions identified so far on the Mid-Atlantic Ridge (MAR). (2) The latest KR03-01 cruise dredged mantle peridotites (see Snow et al., this session) from entire length of the Godzilla Mullion (over 125 km), suggesting that an ultramafic exposure of some $\sim$ 7000 km2. (3) The Godzilla Mullion develops along the full along-strike length of the spreading segment. In the MAR, the megamullions normally develop at inside corners of ridge-transform intersections. (4) Peridotites from the Parece Vela Basin include very fertile lherzolites with spinel Cr# [Cr/(Cr+Al)] = $\sim$ 0.17. (5) The Godzilla Mullion was formed in a relatively fast intermediate-spreading environment with 7.0 cm/y full-rate. We may expect a relatively high magmatic budget in the fast/intermediate-spreading Parece Vela Basin, since a high magmatic budget is generally expected for a fast-spreading ridge. However, the characteristics noted above instead indicate a small degree of mantle melting. We suggest that these features may result from the characteristic ridge-transform geometry of short first-order segments sandwiched by closely-spaced fracture zones. We propose to drill the Godzilla Mullion using the IODP's non-riser platform, employing an offset drilling strategy. Although there may be uniqueness inherited from the characteristic ridge-transform geometry, we value the following two major merits of drilling the Godzilla Mullion: (1) The Godzilla Mullion is the nominally fastest megamullion in the world, providing a

necessary bridge in observations of oceanic lithospheric processes between the existing and planned fast (i.e., Hess Deep) and slow spreading (i.e., MARK and 15-20 FZ) drill holes. (2) The length of the Godzilla Mullion ($\sim$ 125 km) suggests that an unusually deep oceanic as yet unsampled mantle section may be exposed.

V21D-0555 0830h POSTER

Oceanic Core Complex Development Within the Ductile and Brittle Regimes, Atlantis Bank, Southwest Indian Ridge

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In slow-spreading mid-ocean ridge environments, both magmatic and tectonic processes accommodate spreading, where the latter can be manifested as detachment fault systems. Atlantis Bank, an oceanic core complex formed $\sim$12 Ma at the intersection of the ultra-slow-spreading Southwest Indian Ridge and the Atlantis II transform, is dissected by transform-parallel normal faults that provide unique cross-sections through all levels of the detachment fault system. Gabbro collected in ODP Hole 735B and with the manned submersible *Shinkai 6500* from the footwall, hanging wall, and detachment fault surface provide details of the extensional fault system exposed over 36 km normal to the ridge axis, (>3.5 m.y. of crustal accretion). Together the sample suite provides an ideal basis for interpreting the process of strain localization and fabric development associated with formation of long-lived oceanic detachment faults. Continuous core from ODP Hole 735B demonstrates that the main shear zone associated with denudation of the core complex is 200 m thick. The core samples exhibit magmatic fabrics and metamorphic fabrics of submagmatic, granulite (650° - 900°C), amphibolite (450° - 650°C), greenschist (300° - 450°C) and subgreenschist grades. Analysis of the *in situ* dive samples indicates that the structurally deepest samples collected from the footwall are characterized by a zone of granulite-grade crystal-plastic deformation with varying fabric intensity. Structurally above the granulites lies a zone of amphibolite-grade protomylonitic to mylonitic fabrics overprinted by semi-brittle to brittle greenschist-grade deformation. The amphibolites contain 20 - 30 mm-thick zones of high-strain mylonite that increase in number and decrease in thickness upward toward the detachment fault surface. Samples from the localized slip plane or detachment fault surface are highly altered and deformed in both the ductile and brittle regimes. Thermometry and microstructural analysis of *in situ* dive samples demonstrates that ductile deformation initiated at 950°C and continued through 600°C. Folded pyroxene porphyroclasts show that ductile deformation began after exsolution. Two-pyroxene thermometry based on mineral composition data from orthopyroxene and clinopyroxene porphyroclast hosts and their exsolution lamellae in gabbro mylonite yield temperatures of 950°C. Equivalent analysis of adjacent recrystallized ortho- and clinopyroxene neoblasts yield temperatures 850° - 950°C, demonstrating that ductile deformation continued through 850°C. Amphibole-plagioclase thermometry based on mineral composition data from recrystallized amphibole and the associated plagioclase porphyroclasts and neoblasts in oxide gabbro mylonite indicates that ductile deformation began around 890°C and continued through 600°C. The greenschist-grade overprint of granulite gabbro mylonite, manifested by the foliation-parallel growth of green amphibole, chlorite and serpentine around plagioclase neoblasts, preserves a subsequent lower-temperature history. The microstructures of the granulite-grade footwall rocks and those of the detachment fault surface breccias suggest that deformation initiated at high temperatures in the ductile regime, and continued to lower temperatures through the semi-brittle and brittle regimes as fault rocks were denuded along the detachment fault system. Models for the development of oceanic core complexes developed purely within the brittle regime clearly do not apply to the well-exposed and sampled Atlantis Bank region of the Southwest Indian Ridge.

V21D-0556 0830h POSTER

Pre-Obduction, Syn-Magmatic Extensional Deformation and Unroofing of a Fore-Arc Ophiolite, the Thetford-Mines Complex of Southern Quebec.

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The Ordovician Thetford Mines Ophiolite Complex (TMOC) is a peri-continental supra-subduction zone fore-arc terrane obducted onto the Laurentian margin during the Taconic Orogeny. Stratigraphic correlations suggest that the Mont-Orford and Asbestos Ophiolites are correlative, which implies obduction of a 100 km long oceanic slab. The TMOC is affected by syn-obduction (syn-emplacement) deformation, and two post-obduction events: (i) Silurian backthrusting and normal faulting, and (ii) Acadian folding and reverse faulting. The post-obduction deformation tilted the southern part of the TMOC to the vertical, exposing from base to top: cumulate Dunitic, Pyroxenitic and Gabbroic Zones, a hypabyssal unit (either sheeted dykes or a subvolcanic breccia), and an ophiolitic extrusive/sedimentary sequence, upon which were deposited (unconformably) a forearc basin. Our mapping has revealed the presence of numerous pre-obduction faults, spaced c.1 km apart on average. In the plutonic part of the crust, the faults are manifested as sheared or mylonitic dunites and syn-magmatic breccias, and may correspond to along-strike breaks in lithology. Fault breccias are cut by undeformed, 10-m scale, websteritic to lherzolitic intrusions, demonstrating the pre- to syn-magmatic nature of the faulting, and suggesting a role in transfer of melt to the surface. Assuming that rhythmic cumulate layering was originally paleo-horizontal, then kinematic analysis implies that these were originally normal faults separating a series of tilted (30-90 degrees) blocks. Swarms of dykes are oriented parallel to the major faults and locally constitute a sheeted complex, locally removed by syn-volcanic unroofing and erosion. In the upper part of the crust, the faults correspond to marked lateral changes in the thickness and facies assemblages seen in supracrustal rocks, are locally marked by prominent subvolcanic breccias, and have upwardly decreasing throws, which together suggest that they are growth faults. In most places, the base of the exposed volcano-sedimentary sequence is a major erosional surface, which can penetrate down to the Pyroxenitic Zone. The evidence for coeval extension and magmatism, and the presence of a sheeted dyke complex, imply that the TMOC formed by seafloor spreading. The dominance of a boninitic signature in cumulate and volcanics rocks suggests that spreading occurred in a subduction zone environment, possibly in a fore-arc setting.

V21D-0557 0830h POSTER

Structure, metamorphism and timing of an exhumed Cretaceous subduction zone beneath the Oman Ophiolite

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The Semail ophiolite in Oman was emplaced from NE to SW at least 200 km over the Arabian passive margin, probably over 450 km in total, during the late Cretaceous (95-70 Ma). The first phase of obduction involved NE-directed subduction of Triassic-Jurassic basalt at least 45-50 km beneath the ophiolite, whilst the crustal sequence was forming (U-Pb zircons from plagiogranites, ca. 95 Ma). Amphibolites accreted beneath the mantle sequence peridotites have P-T conditions of 840-870°C and 10-12 kbar with 40Ar/39Ar hornblende cooling ages of 95-92 Ma. During the later stages of obduction the leading edge of the continental margin was subducted to depths where carpholite-bearing rocks (6-8 kbar), blueschist (12-15 kbar) and eclogite (ca. 20 kbar) facies metamorphism formed in a ductile deforming NE-dipping subduction zone. Five concordant U-Pb ages from the As Sifah eclogites constrain the HP metamorphic peak at 79.1±0.3 Ma. Detailed structural mapping and restoration of the continental margin, combined with P-T and U-Pb geochronology confirms the model of one protracted phase of ophiolite obduction along a NE-dipping subduction zone, at convergence rates of ca. 17 mm/a-1. NE-directed extensional crenulation schistosity and NNE oriented stretching lineations in the eclogite and blueschist facies rocks are consistent with SW-directed exhumation of footwall HP rocks. NE facing folds and spectacular sheath folds with greatly attenuated limbs in the upper plate sediments are interpreted as antithetic backfolds, with shortening in the upper plate balanced by the subduction of the lower plate, consistent with a NE-directed subduction of the continental margin rocks beneath the SW-obducting ophiolite, Haybi and Hawasina thrust sheets. Recent suggestions of a nascent SW-directed subduction beneath the Oman margin are not consistent with the sedimentary evolution of the shelf and slope carbonates, the geological structure of Saih Hatat, or the U-Pb geochronology of the ophiolite and eclogites.

V21D-0558 0830h POSTER

Tectonic Implications of Ultra-High Pressure Minerals in the Loubusa Ophiolite, Tibet

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An unusual collection of ultrahigh pressure (UHP) and associated minerals has been recovered from podiform chromitites of the Luobusa ophiolite, southern Tibet. The minerals were hand picked from mineral separates but many of the minerals are enclosed in, or attached to, chromite grains leaving now doubt as to their provenance. The mineral collection includes diamond, graphite, moissonite, coesite, CrC, SiFe, silicates, wüstite, PGE and base metal alloys, and a wide variety of native elements (Si, Fe, Ti, Ni, Cr, W, Au, Ag, Zn, Cu, Pb, Sn). Diamonds from Luobusa are clear, colorless octahedra with high Ni aggregation states confirming their natural origin and indicating a long residence time in the mantle. A few have dark inclusions of a Mg-Fe silicate, probably enstatite. Graphite occurs as grey, tabular prisms and irregular grains, many of which preserve a hexagonal morphology. Abundant moissonite forms small, euhedral or broken crystals ranging from dark blue to green to colorless. Some grains of moissonite and Fe-silicides contain inclusions of native Si. Coesite occurs with kyanite as rims on native Ti. Primary Os-Ir and Pt-Fe alloys, interpreted to be of UHP origin, are intergrown with chromite grains, whereas secondary PGE minerals and alloys occur along cracks where they are associated with a variety of sulfide minerals. Numerous octahedral Mg-Fe silicate grains have been pseudomorphed by serpentine. There is no evidence that the Luobusa ophiolite itself was formed at great depth, thus the UHP minerals are interpreted as xenocrysts incorporated into the chromitites during crystallization. Their preservation in this high-temperature, relatively oxidizing environment is difficult to explain. Our preferred model calls for rapid rise of deep mantle rocks to relatively shallow levels where they were picked up by boninitic melts and incorporated into the chromitites upon cooling and crystallization. Preservation of the UHP minerals in this environment may have been facilitated by inclusion in xenolithic blocks and by relatively rapid crystallization and cooling of the host chromitites.

V21D-0559 0830h POSTER

Interesting Inclusions From Podiform Chromitites in Luobusa Ophiolite, Tibet

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For the past decade, diamonds and unusual mineral asemblages were reported in podiform chromitites of the Luobusa ophiolite, southern Tibet, China (Bai 1993, Bai 2000, Yan 2001). These minerals were found from heavy mineral separation of chromitites. These minerals include (1) native elements, (2) alloys, (3) carbide (SiC, CrC), (4) platinium group elements (PGE) and arsenides, (5) silicates (Ol, Opx, Cpx, Amp, Srp, Chl, Uv, Prp, Alm, Wo, Zrn, Ap, Bt, Spn, Rt, Pl, Kfs, Phl, Sil, Qz and octahedral serpentine (possible pseduomorph after ringwoodite?), (5) oxide (corundum and chromite), (6) carbonates. Despite many questions as to these minerals above still remain open, these

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mineral inclusions would provide us the important infomation on the formation of the podiform chromitites. In this study, octahedral serpentine was discovered both on a thin section and from the heavy mineral separation. These octahedral inclusions exist within chromites, forming a line. These minerals are approximately 5-15μm in diameter and have well octahedral morphology. EPMA, laser raman spectrometer and transmission electron microscopy (TEM) were used to determine the structure and chemical composition of this crystal. For the present, there are several interpretations of this octahedral silicate. One possibility is that if the octahedral structuer is euhedral so this octahedral serpentine may be pseudomorph after ringwoodite because of its chemical composition and octahedral crystal shape. Another is that ocahedral minerals are melt inclusions. Linear occurrence of octahedral minerals is similar to that of fuluid inclusions. If the octahedral structuer is negative crystal shape reflecting octahedral crystal of cromian spinel, then octahedral inclusions may be melt inclusions judging from linear occurrence. At the same time, zircons were obtained from the mineral separation from chromitites. U-Pb dating of these zircons by LA-ICP-MS yielded two different ages. One group has relatively younger age 107-534 Ma, which nearly plots on a concordia line. Another group has older age 1460-1822 Ma, which plots off the concordia line. Cathode luminescence images of these zircons indicate that some zircons have clear oscillatory zoning whereas other zircons show apparent homogeneous overgrowth. But any correlation between CL image and the U-Pb age was not identified in particular. Luobusa ophiolite has been recognized as fragment of Tethys oceanic crust formed in Cretaceous at 100-120 Ma (Allegre et al. 1984). The minimum age 107 Ma corresponds to the age of the formation of Luobusa ophiolite and all other age of zircons in chromitites is much older than that of ophiolite. In addition, the inclusions in the zircons were analyzed by EPMA and laser raman spectrometer. Several zircons contain some inclusions, which are quartz, feldsper, mica, apatite, titanite and others. These inclusions are the minerals composed of crustal material, which means that these zircons were crystalized in the low pressuer crustal condition. On the other hand, Yu et al. (2001) reported that zircons from chromitites in Luobusa ophiolite have shorter inter-atomic distances for Zr-O and Si-O bonds. They concluded that Tibetan-zircons were derived from the high-pressure mantle environment. Judging from the line of evidence mentioned avobe, it is highly possible that these zircons captured by chromitites were originated from recycled crustal materials convecting through upper mantle.

V21D-0560 0830h POSTER

Sr and Nd isotopic constraints on the protoliths of the Chinese Tianshan UHP metamorphic complex, West China

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The Chinese Tianshan high- to ultrahigh-pressure metamorphic belts resulted from multiple Paleozoic collisional events. Recent discovery of coesite pseudomorphs within garnets in eclogites extends the metamorphic conditions into the ultrahigh-pressure field up to pressures of 26 kb and temperatures in the range of $\sim$490 to 590^{o}C. Unlike most of the UHP metamorphic belts in the world which are thought to result from continent-continent collisions, the Chinese Tianshan UHP metamorphic belts developed during the subduction of. oceanic lithosphere. We present new Sr and Nd isotopic composition data on a suite of metabasites (including eclogite and blueschist, and their retrograde counterparts) and metagraywackes to better constraint the protoliths of the metamorphic assemblage. The metabasites have initial $^{87}Sr/^{86}Sr$ and ϵ_{Nd} ranging from 0.70248 to 0.70890, and -3.03 to +8.51, respectively. The metagraywackes have initial $^{87}Sr/^{86}Sr$ and ϵ_{Nd} ranging from 0.70658 to 0.71091, and -5.53 to -9.41, respectively. A t = 350 Ma, the age of peak metamorphism, is assigned to calculate the initial Sr and Nd isotopic compositions, and thus it is a minimum age correction. Sr-Nd isotopic systematics as well as published major and trace element data suggest that: (1) the metabasites were derived from protoliths similar to the ocean island basalts which extend the depleted mantle array into the relatively enriched E-MORB domain; (2) they bear an Sr isotopic signature suggesting various degrees of seawater alteration; and (3) the metagraywackes may represent recycled sediments from nearby continental basements. It has been shown that the pillow basalts in nearby ophiolite zones have been experienced high degrees of seawater alteration by their high $^{87}Sr/^{86}Sr$ ($\sim$0.7080) and δO^{18} ($\sim$13.0$^{o}/_{oo}$) values. A similar conclusion is reached based on the high δO^{18} values ranging from 9.0 to 10.0$^{o}/_{oo}$ of eclogite samples(Gao et al., 1999). Covariation patterns in the Sr and Nd isotopic compositions of the metabasites suggest that they might have experienced a long period of intensive seawater alteration before they were subducted and metamorphosed under high- to ultrahigh-pressure conditions. A similar pattern has been resolved in the Sr-Nd isotopic systematics of the pillow basalts within the ophiolite zone.

V21E MCC: 3008 Tuesday 1020h

State of the Art in Theory of Materials: Methods and Applications III *(joint with P, MR, DI)*

Presiding: **R Cohen,** Carnegie Institution of Washington**; B Militzer,** Carnegie Institution of Washington

V21E-01 1020h INVITED

FIRST PRINCIPLES PHASE DIAGRAM CALCULAIONS WITH THE MAPS PACKAGE

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The MAPS, MIT ab initio software package (http://cms.northwestern.edu/Group.html) was used to perform first principles phase diagram calculations (FPPD) for the mineral systems: $CaCO_3 - MgCO_3$; $CdCO_3 - MgCO_3$; $CaCO_3 - MgCO_3$; and NaCl-KCl. General characteristics of FPPD calculations will be reviewed and details of specific calculations will be discussed. Particular attention will be given to: the prediction of new stable ordered phases; metastable ordered phases; and the role of vibrational entropy in phase stability.

V21E-02 1035h

First Principle Study of Olivine Solid Solutions

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Intra-crystalline cation exchange between two octahedral M-sites in olivine [$(Fe,Mg)_2SiO_4$] has received considerable attention because of its importance on thermodynamics, transport and other physical properties of this major mantle mineral. Moreover, the pure Fe end-member, fayalite displays anti-ferromagnetic ordering below room temperature. The presence of magnetic ordering at such low temperatures may still have a significant impact on thermodynamic properties of solid solution at high temperatures. In order to gain further insight, olivine solid solution (Fe-Mg) is investigated using *ab initio* total energy calculations based on local density approximation (LDA) and generalized gradient approximation (GGA) of density functional theory. The nature of Fe-Mg order-disorder across crystallographically distinct M1 and M2 sites were studied. We performed spin-polarized calculations, treating Fe^{2+} in a high-spin state. Initially various configurations of Mg and Fe in M1 and M2 sites were generated in order to construct an effective Hamiltonian and to obtain the atomic interaction parameters (J) between M1-M1, M1-M2 and M2-M2 sites. We used Monte Carlo simulation to obtain the equilibrium cation arrangements for various compositions across the Mg-Fe join. In agreement with experiments, our calculations show that at low temperature, Fe^{2+}, prefers the M1 site over the M2 site, and disorders at higher temperature. However, unlike neutron diffraction experiments, we do not find high temperature reversal (Fe in M1 at low temperature to Fe in M2 at high temperature). We are exploring the possible cause of such discrepancies. We intend to explore the effects of ordering of magnetic spins both at the Fe end-member and across the Fe-Mg join, and its interaction with the atomic ordering. We are also extending the present findings to higher pressures of geophysical relevance.

V21E-03 1050h

A statistical approach to atomistic simulation of geophysical solid solutions

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Many materials of geophysical importance are solid solutions rather than pure minerals. Mascropic modeling of the thermodynamic properties of these minerals often necessitates ideal mixing assumptions. While atomistic models make it possible to model solid solutions without the ideal mixing approximation, such calculations were not computationally feasible until recently. Nevertheless, no convenient methodology for studying the configurational aspects of geophysical solid solutions currently exists, especially for the high temperatures of the earth. We introduce a technique for studying solid solutions at high temperature and apply it to the $MgSiO_3$-Al_2O_3-MgO system at lower mantle conditions. We use a statistical mechanics based approach that samples calculated Gibbs free energies of the solid solutions corresponding to different, and often very numerous, mixing configurations (*i.e.* ways to arrange atoms in mixing sites). Vibrational contributions to the Gibbs free energies are calculated from phonon spectra calculated under the quasiharmonic approximation. We then use the sampled configurational free energies to estimate configurational thermodynamic properties of the solid solutions. We first discuss the choice of an appropriate unit cell size that properly samples a space of mixing configurations and avoids imposing artificial ordering. We then compare Boltzmann-derived entropies of mixing with those resulting from ideal mixing. We also discuss the role of configurational heat capacity on the energetics of solid solutions at high temperatures. Finally, we introduce a technique for approximating configurational high temperature thermodynamic properties of solid solutions from 0 Kelvin energy distributions (over mixing configurations). Combining these results with only a few high temperature configurations greatly reduces the number of computations necessary to determine the full high temperature thermodynamic properties of complex mineral assemblages.

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Spectroscopic and thermal properties of minerals from density-functional perturbation theory

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Ab-initio calculations based on density-functional theory have provento give a highly accurate description of structural and elastic properties of minerals under pressure. To evaluate spectroscopic, dielectric and thermal properties it is necessary to compute the second derivatives of the energy with respect to a displacement or electric field perturbation. While the Hellman-Feynmann theorem makes the computation of forces (first derivatives of the energy) straightforward, second derivatives depend on the linear response of the orbitals and density to the perturbation. I will sketch the variational formulation of density-function perturbation theory, and it's implementation in the CASTEP plane-wave code. The capabilities will be illustrated with calculation of the full phonon dispersion spectra and dielectric properties of a-quartz, ZrO_2 and $NaHF_2$.

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Ab initio studies of phonon softening at high pressure in quartz SiO_2

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The silica polymorph quartz exhibits several interesting properties including pressure induced amorphization, high pressure phase transitions, anomalous elastic properties, negative Poisson ratios, soft mode behavior, etc. *Ab initio* density functional calculations of quartz are used to understand the changes in phonon frequencies and elastic properties under bulk and uniaxial compression. Non-hydrostatic stresses are believed to play an important role in the pressure induced amorphization.