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.

V21E-04 1105h INVITED

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 $NaHF_2$.

V21E-05 1120h

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.

We have undertaken density functional LDA calculations of quartz using extended norm conserving pseudopotentials to compute the phonon frequencies at various points in the Brillouin zone as a function of pressure. The calculated equation of state and phonon frequencies are found to be in good agreement with experimental data. A 466 cm^{-1} Raman active A_1 mode shifts considerably under uniaxial pressure along the c-axis as compared to bulk compression in agreement with reported Raman data. This mode involving symmetric bending of the Si-O-Si bond is believed to have a principal role in the compression mechanism of quartz. A zone boundary (1/3, 1/3, 0) K-point phonon mode becomes soft at high pressures. The mode softening is related to the high pressure amorphization and phase transitions of quartz and these studies suggest that the mean amorphization pressure can be lowered under non-hydrostatic conditions.

V21E-06 1135h INVITED

Solid state magnetic resonance from first principles: applications to silicates

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I will describe a recently developed technique for the prediction of magnetic resonance properties (NMR and EPR/ESR) of the solid state. The method is implemented within density functional theory, and periodic boundary conditions, and uses the efficient plane-wave basis and pseudopotential combination. I will demonstrate the method by reference to applications to the silicates: the assignment of the NMR spectra of the zeolite Ferrierite, and EPR g-tensor measurements of defects in quartz.

V21E-07 1150h

Theoretical study on structural factors correlated with ^{23}Na NMR parameters

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Ab initio NMR calculations at the HF/6-311+G(2df,p) GIAO level are performed on many Na-centered clusters with different O-ligands. Several aspects of the relationship between local structure and ^{23}Na NMR parameters have been carefully investigated. The accuracy of ^{23}Na NMR calculation is checked by calculating ^{23}Na NMR shieldings for similar crystalline materials with known experimental shieldings. The largest Na-O distance which can still contribute to the Na shielding is found to be about 3.5 Å. Quantitative contributions to the Na shielding from different individual O-ligands are emphasized in this paper. These contributions are carefully calculated and compared to establish the order of decreasing deshielding as: OH, NBO(Al)>Al-O-Si>NBO(Si)>Al-OH >H2O>Si-O-Si>Si-OH Na-clustering effects from other cations nearby are also found to tremendously increase the shielding of Na. Finally, the relationship between local structure and the Na NMR has been used to explain the Na NMR data for hydrous albite glasses.

V21E-08 1205h INVITED

Mineral Surfaces From First principles: Structure, Adsorption and Hydration

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Atomic scale phenomena occurring at the interface of minerals and water are, on one hand, very important in Earth and Environmental Sciences, and, on the other, extremely difficult to address, either from experiments or from simulations. The altered chemical bonds at surfaces demand quantum-mechanical first-principles simulation tools, while the complexity of the mineral surfaces and of water itself demand large simulation cell sizes and long simulation times, respectively. We approach the problem from two opposite starting points: (i) from the dry side: studying the effect of the first water layers on mineral surfaces, and (ii) from the wet side: studying liquid water and its response to the presence of ions and surfaces. This double route is justified by the very different characteristic time scales in the wet surface problem: some water molecules bind to the surface for very long times as compared to typical simulation times (picoseconds), while other molecules diffuse quite freely in the liquid. After a brief description of the methodology we use, based on linear-scaling density-functional theory, results will be presented for (i) the adsorption of pollutants onto dry clay surfaces and how the adsorption characteristics are modified by water molecules;(ii) the adsorption of water on calcite surfaces; and (iii) the characteristics of liquid water as described by our method.

V21F MCC: 3001-3003 Tuesday 1020h

The Origins of Hot Spots, LIPs, Seamount Chains, and Volcanic Ridges III *(joint with OS, T)*

Presiding: **D Forsyth,** Brown University**; D Naar,** University of South Florida

V21F-01 1020h

Shear-wave splitting as a diagnostic tool for resolving plume-related mantle flow around hotspots

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The plate tectonics hypothesis successfully explains most of Earth's geological and geophysical features. However, mantle hotspots, regions often associated with large magmatic provinces, linear age progressions of volcanism, and/or large topographic swells, do not fit into a simple plate-tectonic model. Most hotspots are explained by a simple plume model, i.e. a conduit of hot buoyant upwelling material that originates from a deeper thermal boundary layer, the origin of which is often assumed to be in the lower mantle. Past global seismic tomography has had little success in resolving plume-like structures due to resolution limitations. Recent regional teleseismic imaging above hotspots has had limited success in imaging plume-like conduits down to depths of ~400 km. Receiver function and SS precursor studies have also had limited success in detecting the thinning of the transition zone beneath hotspots, which is expected on physical grounds due to the penetration of hot plume material from below. It has been proposed recently that some of these features associated with hotspots can be explained by more complicated plate tectonic models, leading to significant debate. We analyze shear-wave splitting of upward propagating shear waves through the seismically anisotropic upper mantle around the Hawaii and Eifel hotspots, and southwest of Yellowstone along the hotspot axis. If plumes exist beneath these hotspots, these data may resolve the geometry and magnitude of upper-mantle flow and anisotropy associated with the interaction between the moving plate and upwelling plume material. Each of the hotspots we investigate is in a unique geophysical setting. For each study region, we observe an approximately parabolic pattern in map view of the splitting fast directions that is predicted by a simple kinematic plume model. The common pattern we observe, along with inferences about the location of anisotropy, suggests that plume conduits exist in at least the upper mantle beneath Hawaii, Eifel, and eastern Nevada. The best plume model for Hawaii fits the few observations well, but more data are needed to critically test it. The optimum Eifel plume model predicts the splitting fast directions fairly well, with complexity observed between nearby stations that suggests contributions from lithospheric and/or shallow asthenospheric sources. Fast directions from six stations in Idaho, in addition to splitting data collected across eastern Idaho, western Utah, and Nevada are predicted well by a plume model centered in eastern Nevada, but not beneath Yellowstone. We show that shear-wave splitting may be resolving plume-related mantle flow around some hotspots, and therefore if enough splitting data are collected, they could be used as a diagnostic tool to help resolve between plume and non-plume sources for other hotspots. A helpful complement to such future splitting investigations are regional surface-wave anisotropy investigations to better determine the depth extent of azimuthal anisotropy, and the development of better tools that more accurately predict fast directions and delay times from numerical mantle flow models.

V21F-02 1040h

Joint inversion of short- and long-period P traveltimes reveals a variety of plumes in the mantle.

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Diffraction theory predicts that traveltimes of finite-frequency waves are affected by heterogeneities within a narrow region around the ray-theoretical path, called Fresnel zone. Because of wavefront healing, heterogeneities whose scale-length is smaller then the size of the Fresnel zone do not significantly affect the traveltimes. Dahlen et al. (GJI, Vol 141, 157, 2000) show how to correct for wavefront healing effects with a method we refer to as finite-frequency modeling. We perform a global tomographic study by using the finite-frequency modeling, which allows to combine data of different dominant frequencies. To enhance the resolution, we combine long- and short-period data, and we introduce an irregular model parameterization. Our new tomographic model shows a strong correlation between low velocity anomalies and the location of a large number of known hotspots. To test the reliability of these anomalies, an extensive resolution analysis was performed. As result, we can confidently say that deep mantle plumes are located beneath Ascension, Azores, Canary, Easter, Hawaii, Samoa and Tahiti. Other plumes, among which is Iceland, originate at much shallower depth. Newly discovered plumes-like features are located beneath the Mid-Atlantic Ridge, the Southeast Indian Ridge, beneath the Seychelles and the Coral Sea.

V21F-03 1100h

The Upper Mantle Under the South Pacific Super-Swell from Multimode Surface Waveform Tomography

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The South Pacific contains a swarm of volcanic island chains superimposed on a broad bathymetric high known as the South Pacific Superswell. The islands and swell are thought to be the surface manifestation of a "superplume" beneath the the region. We present a Sv-wave speed tomographic model for the South Pacific derived from multi-mode waveform inversion of more than 17,000 vertical component seismograms. Most of the data are from the Global Digital Seismic Network but we include important data from ten broadband seismographs deployed in French Polynesia as part of the PLUME experiment (Polynesia Lithosphere and Upper