V42E MC: 305 Thursday 1330h

New Directions in Experimental Mineralogy and Petrology II *(joint with T, MR, HG)*

Presiding: **J Parise,** SUNY, StonyBrook**; J Tyburczy,** Arizona State University

V42E-01 1330h INVITED

Application of Inelastic X-ray Scattering to Measurements of Acoustic Wave Velocities in Geophysical Materials at Very High Pressure

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Inelastic x-ray scattering (IXS) is a growing field which largely benefited from the availability of 3^{rd} generation synchrotron sources. It can be divided into two main fields, which address different areas in condensed matter physics. *IXS from electronic excitations* aims at the study of electronic properties, whereas *IXS from collective ion excitations* aims at the study of phonons and phonon-like excitations. This technique is complementary to inelastic neutron scattering, but was only developed in the past ten years due to extreme requirements in terms of x-ray instrumentation and brilliance of the x-ray beam. IXS is in particular very powerful for the study of high frequency dynamics of disordered systems such as liquids and glasses [*e.g.*, Sette F. et al., *Science* **280**, 1998]. The application of such inelastic x-ray scattering techniques at high pressure recently made available at the European Synchrotron Radiation Facility at Grenoble (France) also offers a new and unique opportunity for measuring acoustic wave velocities in the terahertz frequency range and phonon dispersion curves in geophysical materials submitted to very high pressures in diamond-anvil cells [Krisch M. et al., *Phys. Rev. B* **56**, 8691, 1997 ; Fiquet G. et al., *Science* **291**, 468, 2001]. To illustrate measurements of importance to geophysics, we describe experiments that have been carried out on polycrystalline materials at the inelastic scattering beamline ID28 using incident monochromatic radiation of 15.618 and 17.794 keV with an overall energy resolution of 5.5 meV and 3 meV, respectively.
We will first show measurements performed on iron samples (*bcc* and *hcp* forms) up to 110 GPa. Unit cell volumes and preferred orientations were characterized by x-ray diffraction measurements carried out at the ID30 beamline. The longitudinal wave velocity is shown to follow closely a Birch law linking linearly velocity and density. These results are found in good agreement with previous measurements by shock wave techniques [Brown and McQueen, *J. Geophys. Res* **91**, 7485, 1986], which shows that there is no intrinsic temperature dependence of the longitudinal acoustic wave velocity. Extrapolation to higher pressures confirms previous predictions that the inner core may not be constituted of pure *hcp* iron. Preliminary results obtained on iron silicide, pyrite and polycrystalline iron-free magnesium silicate perovskite will be presented as well.
In addition, it has recently been shown that single crystal dynamical properties could be investigated by IXS under very high pressures in a diamond-anvil cell [Occelli et al., *Phys. Rev. B* **63**, 224306, 2001], thus opening the possibility to measure elastic constants and acoustic wave propagation anisotropy in opaque materials at pressures.

V42E-02 1400h

Time-resolved in-situ measurements at high pressures and temperatures: new opportunities at synchrotron radiation beamlines for crystal structure, elasticity and rheology studies with large-volume press

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Technological developments for high-pressure research at synchrotron radiation beamlines have greatly advanced experimental Mineralogy and Petrology studies in the past decade. Simultaneous and real-time measurements of x-ray diffraction, imaging, absorption and physical properties such as acoustic velocity offer the prospect of more accurate information on phase equilibria, crystal structure, equation of state and elasticity of minerals in the pressure and temperature regimes relevant to Earth. The addition of the time variable allows resolution of time-dependent properties such as phase transition dynamics, rheological flow, and elasticity change during structural kinetics process (e.g. cation ordering).
The technical developments enabling these experiments include combining translating imaging plate and charge-coupled device (CCD) detectors to the large volume press. Using this apparatus monochromatic data suitable for Rietveld structure refinement reveals the dynamic mechanism of the phase transformation from olivine to spinel. Microscopic stress deconvolution from diffraction peak broadening provides data suitable for modeling the rheological flow of minerals. In a proof-of-concept experiment using a conical slit arrangement with a multi-element energy-dispersive detector, simultaneous measurements of the macroscopic strain and stress obtained from x-ray imaging and diffraction along different vectors, provided data suitable for the derivation of a flow law. These experiments take the advantage of x-ray transparency of sintered cBN anvils for large-volume presses.
Discussions will also focus on preliminary design concepts for combining structure refinement and acoustic measurements. For many minerals, structural changes cause large changes in elastic properties. Integrating the existing techniques offers an opportunity to couple crystallographic measurements with the estimation of acoustic travel time at simultaneously maintained high pressure and temperature. Structure refinements based on the x-ray diffraction data provide information on the state of cation ordering, for example, while the acoustic measurements provide simultaneous determinations of P and S-wave velocities. The latter measurements are crucial because elastic constants (K, m) can be derived at a given P-T condition, therefore there is no need to measure EoS by varying P-T condition which may result in changes of cation ordering.

V42E-03 1415h

X-ray Spectroscopy at Ultra-High Pressure: Present and Future

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High pressure research has entered the era of high-end state of the art measurements, especially in the field of synchrotron x-ray research. Nowadays, a large number of techniques are readily available and applicable in conjunction with the most widely used high pressure apparatus, namely the diamond anvil cell.
In the past years, diffraction constituted the largest part of high-pressure synchrotron-based x-ray research, along with limited efforts in the field of x-ray absorption spectroscopy. The appearance of high-energy third generation x-ray sources (ESRF, APS, SPring-8) allowed extremely brilliant x-ray beams to be focused down to very small sizes, due to the conjunction of high flux, small source size and divergence, and high coherence.
With the help of x-ray spectrometers and low-Z (x-ray transparent) gaskets, a wide variety of high-resolution spectroscopic techniques can be accessed.
We will briefly present techniques such as x-ray emission spectroscopy, as well as resonant x-ray scattering (x-ray Raman) and nuclear resonnance spectroscopy. Inelastic x-ray scattering with ultra-high resolution allows us to access the vibrational properties (acoustic and optical phonons) of materials. Applications on deep Earth materials such as iron and iron-bearing compunds (FeS, FeO, Fe_2O_3) will also be presented.

URL: http://james.badro.free.fr

V42E-04 1430h

Gigahertz Ultrasonic Interferometry and its Potential Application in Geosciences

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Knowledge of the elastic properties and crystal chemistry of minerals plays an important role in interpreting the composition and mineralogy of Earth's interior. GHz-ultrasonic interferometry (GUI) is a rapidly evolving tool among acoustical methods for measuring elastic-wave travel times, and is a natural compliment to existing optical methods such as Brillouin scattering in that opaque samples may be used. Here we describe some of our recent accomplishments, as well as existing problems in the context of applications to Earth science.
GUI now features both P and S elastic waves with near-optical wavelength, thereby reducing the sample-size requirements for single-crystal ultrasonics to about 50 microns. The recent addition of shear waves to this method by P-to-S conversion last year resulted in determination of the complete set of ambient *P-T* elastic constants (c_{ij}) of magnesiowüstite-(Mg,Fe)O with varying ferrous- and ferric-iron contents spanning the solid solution. Successful shear generation also prompted construction of Al_2O_3 shear buffer rods for use at high pressures in the diamond anvil cell, which are now in the final stages of production. Compression wave experiments are already routine in the DAC up to ∼6 GPa and have been used to measure parameters such as $\partial c_{11}/\partial P$ in MgO (=9.35±0.13) and $(Mg_{0.423}Fe_{0.5410.036})O$ (=7.6±0.3).
However, for direct application to Earth's interior, cross-pressure cross-temperature derivatives of the elastic moduli are required. The biggest challenge to GUI (in addition to finding an adequate high-temperature pressure standard) will be to maintain acoustic coupling between the sample and the diamond anvil in a hydrostatic liquid or gas pressure medium at high temperature. Already we have obtained excellent ultrasonic signals through a sample of San Carlos olivine to 250°C at ∼2.5 GPa in alcohol using a resistance-heated DAC, without the use of a bonding agent such as glue. We are now exploring the use of low density silica gel (aerogel) as a pressure medium to hold the sample against the acoustic transmitting diamond anvil. To test this idea, we synthesized wet aerogel (alcogel) in a 4:1 methanol:ethanol solution and loaded it in a diamond cell along with a crystal of quartz and several rubies. Based on the *c/a* axial ratio of the quartz measured by single-crystal X-ray diffraction and the peak widths of ruby fluorescence, the alcogel pressure medium remained hydrostatic to the highest measured pressure of 4.5 GPa. Alumina alcogels may also be synthesized for high temperature application. We

have also recently adapted the ultrasonic attachments to a miniature X-ray diamond cell (60° cone) so that in the future both static and dynamic elasticity measurements may be carried out during the same experiment. Independent volume (X-ray) and length (ultrasonic) measurements at high *P-T* would have intriguing implications for an absolute pressure scale, and remains one of the larger goals of our technique.

V42E-05 1445h

Determination of the elastic properties at high pressure without pressure scale

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Pressure and temperature are the key parameters for determining the physical properties of earth materials in the interior of the Earth. In many laboratory studies, the determination of pressure requires pressure-standards , for example, NaCl, Au, or Pt. Recent evidence from the phase boundaries of perovskite-forming reactions suggests that the equations of state for these materials may be in error by as much as 10%.

Ultrasonic-base laboratory studies to determine elasticity require measurement of P and S-wave travel times, density and length of sample at the experimental conditions. Combining in-situ X-radiation and ultrasonic measurements, now it is possible to collect all of these parameters simultaneously and directly. This enables pressure scale-free measurements of the equation of state of the sample using a parameterization such as the Birch-Murnaghan equation of state. In addition, pressure at the experimental condition is defined by the sample X-ray volume. Therefore, this technique can be used to re-determine the equations of state for cohabitating pressure standards.

We report elasticity data for ferropericlase (Mg,Fe)O with 17 mol% Fe, a potential mantle composition. The ultrasonic velocities have been measured at high pressure and the equation of state has been determined using the pressure-scale free method. Compared with MgO, the bulk modulus and its pressure derivative of (Mg,Fe)O are comparable. But the shear modulus and pressure derivative have been reduced. The pressure suggested by the sample is higher by more than 10% than that calculated from the coexisting NaCl using the Decker pressure scale.

V42E-06 1530h INVITED

New Thermochemical Adventures in Modern Mineralogy

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Much current interest in mineralogy involves complex, hydrated, and often poorly crystalline materials found in the low temperature environment found as products of both natural processes and human activity. Examples of such materials include zeolites, clays, hydrotalcites, manganese oxides, iron-aluminum oxyhydroxides, and sulfate minerals. Such materials are active as catalysts, ion exchangers, and transport agents for contaminants. Both structural and thermodynamic characterization of such materials has been difficult in the past, but advances in spectroscopy, diffraction, and oxide melt solution calorimetry make much more definitive studies possible at present. Systematic energetic trends have been recently observed for the formation and hydration of framework-structured zeolites and manganese oxides. Similar trends are being sought for the layered materials, clays, and hydrotalcites. The role of water in the stabilization of low temperature phases reflects a close balance between energetically favorable bonding and loss of entropy during hydration. Detailed compositional, structural, and thermochemical analysis of the same samples is required to properly interpret calorimetric data.

V42E-07 1600h

Recent Advances in Research on Silicate Solid Solutions

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The Earth, as well as other solid planets and meteorites, is largely made up of solid-solution minerals. An understanding of their microscopic, mesoscopic and macroscopic properties and their behavior under different P-T conditions is a challenge for all disciplines concerned with the solid state. A major goal of mineral physics is to investigate how microscopic and mesoscopic properties control or affect the thermodynamic and bulk physical properties of minerals.

Advances in different spectroscopic methods such as IR, Mssbauer, Raman, NMR, and X-ray and optical absorption make this possible. In addition, developments in computational methods are increasing rapidly and allow detailed microscopic properties to be investigated. For example, 29Si NMR investigations are showing that many silicate solid solutions (e.g. pyroxene, garnet, feldspar) are characterized by short-range cation order. Previously, the question of short-range order had largely been ignored in thermodynamic modeling studies because its determination by diffraction methods is very difficult. Raman and IR spectra are being used to characterize structural heterogeneity and thus lattice strain over different correlation lengths. Lattice strain, resulting from size differences of mixing atoms, is largely responsible for nonideal thermodynamic behavior in the volume and enthalpy of mixing for most silicate solid solutions. Chemical effects such as crystal field stabilization energies can also play role in affecting thermodynamic properties, but they are generally second-order compared to strain. Local-site relaxation and localized strain properties in solid solutions can also be studied with element specific methods such as XAS or optical absorption spectroscopy. Third generation synchrotrons allow XAS studies even at the trace element level in minerals.

The aluminosilicate garnet and the Na-K feldspar solid solutions have received much structural and thermodynamic study using many different experimental and computational methods. Both systems are characterized by positive excess mixing with respect to volume, enthalpy and vibrational entropy. The thermodynamic properties can be explained partly by their microscopic structural properties. These two solid-solution systems will be addressed and recent experimental results, largely spectroscopic based, will be presented and discussed with regards to their solid-solution behavior.

V42E-08 1615h INVITED

Future directions in Mössbauer spectroscopy

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Since the discovery of the Mössbauer effect more than 40 years ago, a wide range of applications in a number of different disciplines has been described. One great advantage of the Mössbauer effect is its high energy resolution, which enables its use as a highly sensitive probe of the atomic environment, providing information on valence state, site occupancies, site coordination and distortion and magnetic structure, and processes such as phase transitions, relaxation, lattice dynamics and diffusion.

Properties that have not been fully exploited include spatial and time resolution. The milliprobe, for example, enables a two orders of magnitude increase in spatial resolution. Further improvement may be anticipated with developments in synchrotron studies of nuclear forward scattering. Other possibilities on the horizon include development of a Mössbauer electron microscope which would focus conversion electrons using conventional electron optics, and development of focusing lenses for gamma rays on a laboratory scale. Time resolution has also not been widely exploited. Studies with conventional techniques are possible over a wide range of time scales, from *in situ* investigations of phase transitions, oxidation and other chemical reactions, to diffusion studies, to studies at the intrinsic time scale of the Mössbauer effect to investigate processes such as electron transfer. Existing facilities for forward nuclear scattering at synchrotron installations reduce this timescale even further.

Mössbauer spectroscopy can be performed under a wide range of P,T conditions, and the limits have not yet been reached. Developments in nuclear forward scattering could expand the pressure and temperature limits, raising the tantalising possibility of measuring Mössbauer parameters at mantle temperatures and pressures.

V42E-09 1645h INVITED

Experimental Mineralogy and the Origin of Life

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The origin of life on earth was a geochemical event. The first living entity must have emerged from chemical reactions of air, water and rock. Of those three raw materials, the atmosphere and oceans have been the focus of most origins research, but rocks and minerals are receiving increased attention for their potential chemical and structural roles in assembling life. Recent research elucidates five possible roles for minerals in life's origin; each of these roles is the subject of ongoing experimental research.

(1) Porous rocks and minerals, including vesiculated volcanic rocks and weathered feldspars, may play relatively passive roles as protective environments for the concentration of organic molecules.

(2) Minerals may also serve as scaffolds for the organization and assembly of these molecules into larger structures. Clays and double-layer hydroxides are especially efficient in this regard.

(3) Mineral templates may play a more direct role in molecular selection and assembly. In recent studies we observe that scalenohedral crystal faces of calcite are chirally selective for left- and right-handed amino acids. Atomic force microscopy reveals chiral growth structures and etch morphology on these faces, and points to a mechanism for selection.

(4) Transition metal oxides and sulfides serve as catalysts for organic synthesis in hydrothermal environments. We observe two contrasting mechanisms for carbon-carbon bond formation. All transition metal minerals studied promote methylation through Fischer-Tropsch type reactions. In addition, nickel and cobalt sulfides efficiently promote carbonylation reactions, including the synthesis of carboxylic acids.

(5) Sulfide minerals may dissolve in hydrothermal systems to become reactants in organic synthesis reactions. In experiments with iron sulfides at 250C and 0.2 GPa, for example, we observe the formation of organic di- and tri-sulfides, methyl thiol, and a variety of carbonylated iron complexes in hydrothermal solutions. These reactive aqueous species, some of which resemble the active centers of metabolic enzymes, point to the possibility that minerals may have played a critical role in jump-starting the earliest metabolic cycles.

Taken together, these experiments demonstrate a central, dynamic role for minerals in the origin of life.

V42F MC: 304 Thursday 1330h

Geochemical and Isotopic Tracers of Earth Processes: Geochronology and Time Scale Issues (a session in honor of Gil Hanson) *(joint with H, T, GC, MR)*

***Presiding:* S R Hemming,** Lamont-Doherty**; T Rasbury,** SUNY Stony Brook

V42F-01 1330h

Dating Fluvial Terraces by ^{230}Th/U on Pedogenic Carbonate, Wind River Basin, Wyoming

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Reliable and precise ages of Quaternary pedogenic carbonate can be obtained with ^{230}Th/U dating by TIMS applied to large suites of carefully selected small samples. Datable carbonate can form within a few thousand years of surface stabilization allowing ages of Quaternary deposits and surfaces to be closely estimated. We have dated pedogenic carbonate from glacio-fluvial terraces of the Wind River Basin to better constrain the age of the penultimate glaciation in the central Rocky Mountains.

Dense pedogenic carbonate clast-rinds from gravels of middle to late Quaternary terraces in the Wind River Basin contain 5-35 ppm U and 0.01-0.3 ppm ^{232}Th, with (^{230}Th/^{232}Th)=5-7500, making them extremely suitable for ^{230}Th/U dating. Complexities in the textures of the Wind River clast-rinds emphasized the importance of sampling horizons as thin as 0.5 mm from polished slabs to avoid averaging long (10^4-10^5 yr) and potentially discontinuous depositional histories. Samples meeting straightforward textural criteria

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