Dynamical Properties of Earth and Planetary Materials

CECAM-HQ-EPFL, Lausanne, Switzerland

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Sponsors: CECAM and Psi-k

Organizers: Razvan CARACAS, Bjoern WINKLER and Lars STIXRUDE

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The exponential development of powerful algorithms, implementations and computational power over the last decade has seen the application of first-principles calculations in solving critical problems of mineral physics expand at an unprecedented pace. Theoretical mineral spectroscopy, high-pressure thermodynamics, construction of phase diagrams, determination of melts and melting curves go hand in hand today with experimental investigations. The thermodynamic and thermochemical conditions that we are able to successfully reproduce in the computer simulations cover the entire range existent in our planet, our solar system or in other distant worlds.

Our workshop aimed at advancing exchanges among theorists using different approaches, as well as between theorists and experimentalists, in order to enhance and broaden the use of first principles calculations in geosciences. In particular we featured mini-sessions on:

- melts and glasses, with experimental contributions about the structure of silicate and borosilicate glasses at ambient pressure conditions, with atomistic simulations about the behavior of geologic fluids and melts and with first-principles molecular-dynamics approach on the state of the primordial magma ocean;

- experimental overviews, covering a wide range of topics: a infrared and raman study of the magnetic transitions in ilvaite, a synchrotron study on the diffuse scattering and its use in understanding phonon band dispersion and phase transitions, a review of the behavior of molecular solids under pressure, a study about the kinetics of a solid-solid reaction in silicates at mid-mantle conditions, a study of the elasticity of MgO, a review about the plasticity of MgO and the methods used to describe it, and a study on determining melting and thermodynamical properties of materials at ultra-high pressure using nuclear resonant inelastic x-ray scattering measurements;

- computational techniques, including advances and illustrations of the use of the SIESTA and CASTEP packages, an overview of the computation of Moessbauer and NMR spectra from ab initio calculations, and a study about the determination of infrared spectra

- iron-bearing high-pressure phases, covering computational and experimental studies of the spin transition in mantle minerals at extreme conditions, its effect on elasticity, seismic properties, thermodynamical and spectroscopic properties, as well as a detailed description and understanding of the associated structural changes

- isotope partitioning, with experimental and theoretical contributions on determining isotope partitioning between minerals and between fluids and solids, including isotopes of B, Li, Si and Fe.

Programme

Day 1 - October, 10th 2011

SESSION I: Melts and Glasses

13:50 to 14:00 - Welcome

14:00 to 14:50 - Neuville Daniel

Structure and properties of silicate melts: From volcanic activity to industrial processes

14:50 to 15:40 - Sung Keun Lee

Universal behavior in pressure-induced melt-polymerization in silicate melts in EarthÁøs interiors

15:40 to 16:10 - Coffee Break

16:10 to 17:00 - Lars Stixrude

Dynamics of silicate liquids at high pressure

17:00 to 17:50 - Sandro Jahn

Structure and properties of geological melts and fluids: A combined experimental and computational approach

17:50 to 18:40

Day 2 - October, 11th 2011

SESSION II: Experimental approaches

09:00 to 09:50 - Monika Koch-Mueller

Pressure-induced phase transitions in Ilvaite studied by In-situ Mid/Far Micro-FTIR spectroscopy

09:50 to 10:40 - Alexei Bosak

Diffuse scattering in ÒsimpleÓ materials: modeling and interpretation

10:40 to 11:10 - Coffee Break

11:10 to 12:00 - Roberto Bini

Tuning of the electronic properties of simple model molecules by pressure and their implications in high pressure chemistry

12:00 to 14:00 - Lunch Break

14:00 to 14:50 - David Dobson

Kinetics of the reaction perovskite + ferropericlase = ringwoodite

14:50 to 15:20 - Sergio Speziale

Elastic properties of deep Earth materials by Brillouin scattering of polycrystalline materials at high pressures: The role of grain size and of texturing in MgO

15:20 to 15:50 - Coffee Break

15:50 to 16:40 - Cordier Patrick

Modeling plastic deformation of MgO under mantle conditions

16:40 to 17:30 - Jennifer Jackson

Melting behavior and phonon measurements of earth materials above 1 megabar

Day 3 - October, 12th 2011

SESSION III: Advances in computational techniques

08:30 to 09:20 - Alberto Garcia

New and forthcoming functionalities in the SIESTA code

09:20 to 10:10 - Josef Zwanziger

Computational Approaches to Moessbauer and Magnetic Resonance Spectroscopies

10:10 to 10:30 - Coffee Break

10:30 to 11:20 - Keith Refson

Vibrational spectroscopy with the CASTEP code

11:20 to 12:30 - Marc Blanchart

Infrared spectroscopy of minerals from first-principles

SESSION IV: Iron-bearing high-pressure phases

14:00 to 14:50 - Jung-Fu Lin

Electronic and Elastic Properties of Iron-Containing Minerals in EarthÕs Interior

14:50 to 16:40 - Stuart Gilder

Magnetic properties of iron and iron-bearing phases at high pressure

16:40 to 17:00 - Coffee Break

17:00 to 17:50 - Razvan Caracas

Spin transition in Fe-bearing perovksite

17:50 to 18:40 - Boffa Ballaran Tiziana

Effect of Fe and Al substitution on the elastic properties of perovskite: a single-crystal diffraction study up to 75 GPa.

19:30 to 22:30 - Dinner

Day 4 - October, 13th 2011

SESSION V: Isotope partitioning

09:00 to 09:50 - Mathieu Roskosz

Experimental and spectroscopic approach to the determination of equilibrium Fe isotopic fractionation factors in planetary materials

09:50 to 10:40 - Piotr Kowalski

First principles calculation of B and Li equilibrium isotope fractionation between minerals and aqueous solutions

10:40 to 11:10 - Coffee Break

11:10 to 12:00 - Merlin MŽheut

The structural determinants of silicon fractionation properties of silicate minerals : a First-Principles Density Functional Study

Abstracts of Presented Papers

Structure and properties of silicate melts: from volcanic activity to industrial processes

Neuville Daniel[1], Charles Le Losq 1, Pierre Florian2 and Dominique Massiot2

CNRS-Institut de Physique du Globe de Paris

1) CNRS-IPGP, GŽochimie et Cosmochimie, 4 place Jussieu, 75252 Paris Cedex05, France
E-mail : neuville@ipgp.fr

2 CNRS-CEMHTI UPR3079 & UniversitŽ dÕOrlŽans, 1D av. Recherche Scientifique, 45071 OrlŽans

3) CINaM, UniversitŽ de Marseille, Marseille

Viscosity is a most important physical property of silicate melts as it controls mass and heat transfer in the EarthÕs interiors, as well as in high temperature industrial processes such as glass making. Although viscosity models are of fundamental importance for both glass making and volcanology, prediction of viscosity is difficult because of it extremely strong dependences on temperature and chemical composition. In fact the viscosity of melts varies generally by more than 10 orders of magnitude between superliquidus conditions and the glass transition range. Similarly, at constant temperature, one can observe comparable differences as a function of composition. For example, at 1500K, the viscosity of pure SiO2 is about 10 orders of magnitude higher than that of window glass. Recent work has provided a theoretical framework for understanding viscosity variations in terms of configurational entropy, which in addition, give valuable macroscospic and microscopic information on the structure of melts. In this presentation, I will give an extensive overview of the viscosity of silicate melts as a function of temperature and chemical composition. Particular interest will be paid to : - the speciation of aluminum as a function of temperature and chemical composition. This element has a crucial influence in Earth systems, and its environment is still questioned. We present new results using XANES and Raman spectroscopies and 27Al Nuclear Magnetic Resonance on CAS, MAS and CMAS glasses. We propose an Al/Si tetrahedral distribution in the glass network in different Qn species for Si and essentially in Q4 for Al in the MAS and CMAS system. In the CAS system Al, can be distributed in more complex Q species. In the CMAS glasses system, an increase of [5]Al and [6]Al is clearly visible as a function of the increase of Mg/Ca ratio. In the MAS and CAS systems, the proportion of [5]Al and [6]Al increases with decreasing SiO2 and according to results on the calcium aluminosilicate glasses, the maximum of [5]Al is in the center of the ternary system. The distribution of Al and Si in different neighbor can be link to the thermodynamic property variations. These results raise the question about the role played by [5]Al in the structure and properties of silicate melts.- theoretically mixing Na-K in aluminosilicate melts produce the so-called Òmixed alkali effectÓ. On the basis of some new rheological results, the Na-K mixing canÕt be explained with this Òmixed alkali effectÓ. To go further and as rheological properties are directly linked with structural properties, we will present our first results obtained by Raman and NMR spectroscopy. These last ones provide important structural informations on the polymerization of glasses and melts, and also on the environment of tetrahedral coordinated cations. These structural results are directly linked with viscosity measurements and shown that substituting Na by K in aluminosilicate melts induces structural changes in both alkali environment and aluminosilicate network. This implies that Na and K atoms are non-randomly distributed in the aluminosilicate network. Na silicate melts present a network with some channels and a random distribution of Al and Si, while K silicate networks are different. They present a non-random distribution of Al and Si, with two sub-networks: one rich in Si and fully polymerized, the other containing Al and K. On this view, mixing Na and K melts returns to change theses configurations and induces complicated and non-linear effects.

Universal behavior in pressure-induced melt-polymerization in silicate melts in earthÁøs interiors

Sung Keun Lee[1]

School of Earth and Environmental Sciences, Seoul National University, Seoul, Korea, 151-742

Pressure-induced changes in melt-composition, configurational entropy, viscosity, and solubility of elements in silicate melts in magma oceans provided a unique situation in which significant chemical differentiation of the silicate earth could have occurred and formed unrecycled partial melts by forming a hidden reservoir in EarthÁøs mantle. Although the structures of silicate melts have been linked to these key properties, the melt structures at high pressure remained largely unknown. Even more challenging is to reveal the structure of natural multi-component magmas in the earthÁøs interior because any experimental effort to reveal the complex structure tends to be hampered by inhomogeneous broadening in experimental data associated with such complexity. Therefore, chemical constraints such as the non-bridging oxygen (NBO) content at 1 atm, rather than the real structural parameters for melt polymerization at high pressure, are commonly used to account for pressure-induced changes in the melt properties in EarthÁøs interior. Here, we show that the pressure-induced NBO fraction in diverse silicate melts show a universal behavior where all the reported experimental NBO fractions at high pressure can be simplified into a single decaying function, regardless of melt composition. This simplicity in the pressure-induced changes in melt polymerization enables us to account for the non-linear variations in thermodynamic and the transport properties of multi-component and thus natural silicate melts at high pressure. The current results with universality in melt polymerization thus provide atomistic insights into the melt densification in the EarthÁøs mantle and a formation of hidden reservoir with distinct chemical composition [1].

[1] S. K. Lee, Proceedings of the National Academy of Sciences, 108 6847 (2011)

Dynamics of silicate liquids at high pressure

Lars Stixrude[1]

Department of Earth Sciences, University College London, London WC1E 6BT, United Kingdom

Viscosity and chemical diffusion in silicate liquids at high pressure are important for understanding a number of geophysical processes including thermal evolution, crystal settling, and melt percolation as the magma ocean cooled to a solid state, and chemical equilibration between melts and crystals, and between molten silicates and iron during core formation, as well as geophysical observations including those of enhanced electrical conductivity at depth. Existing experimental data show that the transport properties of silicate liquids may behave non-monotonically with increasing pressure, rendering

extrapolation to pressures typical of a global magma ocean impossible. We have taken a different approach, using ab initio molecular dynamics based on density functional theory to predict the viscosity and self-diffusion coefficients in silicate liquids over the entire pressure-temperature regime of the magma ocean. Our results confirm the non-monotonic dependence of transport properties with increasing pressure and show that anomalies are associated with the dominance of five-fold Si-O coordination at intermediate compression. Over most of the mantle pressure-temperature regime, viscosity increases with pressure, and is approximately one order of magnitude higher at the core-mantle boundary. Applying our results to the dynamics of the magma ocean, we find that this state probably cooled very quickly initially, with surface heat flux exceeding that incoming from the Sun. Self-diffusion of hydrogen is essentially de-coupled from the silicate framework, leading to enhanced electrical conductivity that can explain geophysical anomalies associated with melt atop the 410 km discontinuity, and forming a superionic state. Simulations reveal the mechanism of enhanced H diffusion, which includes hopping between non-bridging oxygens.

Structure and properties of geological melts and fluids: a combined experimental and computational approach

Sandro Jahn[1]

[1] GFZ German Research Centre for Geosciences, Potsdam, Germany

The structure determination of geological melts and fluids is a challenging task because (1) there is no long-range atomic ordering as in crystals, (2) they usually contain multiple components and (3) their structure changes continuously with pressure, P, temperature, T, and chemical composition. Furthermore, to model their behavior under relevant conditions of the Earth's interior, investigations have to be performed in situ at high P and T. There is no single experimental technique, from which the structure of a melt or a fluid can be derived unambiguously. However, sophisticated in situ methods, such as neutron and x-ray diffraction, Raman, infrared and x-ray absorption spectroscopies, provide unique fingerprints of melts and fluids at extreme conditions, which contain information on the atomic structure and the chemical bonding. First-principles modeling and molecular dynamics techniques have become powerful tools to link experimental data to the actual atomic structure or to the molecular vibrations. Once the structural model has been verified, physical and chemical properties of the melt or fluid can be derived from the simulations. They can provide new insight into the role of melts and fluids in geological processes. In this presentation, I will show a few examples of combined experimental-computational studies, which includes the structure of oxide and aluminosilicate melts [1] as well as the speciation in aqueous fluids at high P and T [2]. Implications of specific structural features on isotope fractionation or trace element partitioning between minerals, fluids and melts and on the transport properties of melts will be discussed [3].

[1] S. Jahn, Am. Mineral. 93, 1486 (2008); J. W. E. Drewitt et al., J. Phys. Condens. Matter 23, 155101 (2011).

[2] S. Jahn and B. Wunder, Geochim. Cosmochim. Acta 73, 5428 (2009); S. Jahn, C. Schmidt, J. Phys. Chem. B 114, 15565 (2010); G. Spiekermann et al., submitted to Geochim. Cosmochim. Acta (2011).

[3] B. Wunder et al., Eur. J. Mineral. 23, 333 (2011); P. Kowalski and S. Jahn, Geochim. Cosmochim. Acta, in press, doi:10.1016/j.gca.2011.07.039 (2011).

Pressure-induced phase transitions in ilvaite studied by in-situ mid/far micro-ftir spectroscopy

Monika Koch-Mueller[1], Maria Mrosko1, Ulrich Schade2

1Deutsches GeoForschungsZentrum, Sektion 3.3 Chemie und Physik der Geomaterialien, Telegrafenberg, 14473 Potsdam, mrosko@gfz-potsdam.de

1Deutsches GeoForschungsZentrum, Sektion 3.3 Chemie und Physik der Geomaterialien, Telegrafenberg, 14473 Potsdam, mrosko@gfz-potsdam.de

2Helmholtz-Zentrum Berlin fŸr Materialien und Energie - Speicherring BESSY II, Albert-Einstein-Stra§e 15, 12489 Berlin

Infrared spectroscopy is a sensitive probe for information on the local microscopic structure and bonding in minerals. Combined with experiments in diamond-anvil-cells (DAC) it provides important insights in pressure-induced structural changes such as phase transitions, cation order and disorder etc. We applied this technique to study the high pressure behaviour of ilvaite by in-situ spectroscopy using (i) a Hyperion FTIR microscope with a conventional MIR light source and (ii) a custom-made vaccum FIR microscope (Mrosko et al. 2011) with synchrotron light at the infrared beamline IRIS (BESSY II).Ilvaite is a mixed-valence iron sorosilicate with the ideal formular CaFe22+Fe3+[Si2O7/O/(OH)]. In the past it has been the subject of intense research in respect to its physical, chemical and structural properties. It shows a variety of temperature-induced electronic, structural and magnetic phase transitions. Between 333 and 343 K it undergoes with increasing temperature a structural phase transition from monoclinic to orthorhombic similar to the Verwey transition in magnetite. However, its high-pressure behaviour is still not well understood: pressure-induced structural changes were proposed for natural ilvaite at 1.2 and 1.9 GPa (Finger and Hazen 1987) and for a synthetic pure Fe-endmember ilvaite at 2.25 GPa (Ghazi-Bayat et al. 1993). To study the high-pressure behaviour of ilvailte in more detail we collected Mid- and Far-infrared spectra of a natural ilvaite sample in-situ in a diamond-anvil cell (DAC) as a function of pressure up to 31 GPa. The composition of the natural material is (Fe2+0.61Mn2+0.40)(Fe3+1.01 Fe2+0.96 Al3+0.02Mg2+0.01)[Si2.03 O7/O/(OH)] as determined by electron microprobe. One series of DAC experiments were performed at GFZ in the Mid-IR using Argon as pressure medium and a Globar as light source. Four pressure series were performed at Bessy II in the Far-IR region using petroleum jelly as pressure medium and synchrotron light. Pressure-induced changes in the Mid- and Far-IR spectra were analysed via the autocorrelation function (Salje et al. 2000) for all five pressure series. All five series confirm the phase transition at about 2.3 GPa already known from X-ray diffraction studies. For the first time a second pressure-induced phase transition at much higher pressure (between 10 and 11 GPa) could be observed. Both transitions are clearly visible throughout the whole spectral ranges: in the OH-stretching region, Mid-IR region from 1400 to 400 cm-1 and the Far-IR region down to 50 cm-1. Above 11 GPa and up to 20 GPa no further discontinuities could be detected. One series going in pressure up to 31 GPa indicate an additional structural change above 20 GPa. Computational studies to reproduce the pressure effects are highly appreciated.

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[3] E.K.H. Salje, M.A. Carpenter, T. Malcherek, T. Boffa Ballaran, Eur. J. Mineral, 12, 503-519 (2000).

Diffuse scattering in ÒsimpleÓ materials: modeling and interpretation

Alexei Bosak[1]

ESRF, Grenoble, France

Many physical properties of technological or scientific interest are a function of the regular atomic arrangement, symmetry aspects of phase transitions and a notion of order parameter being defined on a basis of the crystal structure may serve as an example. In a diffraction experiment, the crystal structure manifests itself as a set of sharp Bragg reflections. However, any real material only approximates an ideal crystal: structural disorder and vibrational motion of atoms in a crystal give rise to a diffuse scattering (DS) located on and between Bragg reflections. Structural disorder is usually not completely random but correlated at short distances on a scale of nanometers. Critical fluctuations, nucleation and percolation processes strongly depend of these correlations, as well as many mechanical, magnetic, electronic and optical properties.For some cases, in particular in the absence of long-range interactions, the diffuse scattering can be rationalized using ab initio models. In turn, the experimental diffuse scattering can serve as a validation tool for the given lattice dynamics description. We have successfully tested this approach for a number of silica polymorphs.The modelling of disordered systems is computationally much more expensive, but for the metals with long-range interactions some essential features of correlated disorder can be successfully explained via the q-dependent electronic susceptibility, as we could demonstrate for magnetite and Ni-W alloys.

Tuning of the electronic properties of simple model molecules by pressure and their implications in high pressure chemistry

Roberto Bini[1]

LENS, European Laboratory for Non-linear Spectroscopy, Via N. Carrara 1, I-50019 Sesto Fiorentino, Firenze, Italy;

Dipartimento di Chimica dell'Universitˆ degli Studi di Firenze, Via della Lastruccia 3, I-50019 Sesto Fiorentino, Firenze, Italy.

The Diamond Anvil Cell has been diffusely employed to study chemical reactions occurring even in the simplest molecular systems at high pressure conditions. The reactivity of these systems is a complex interplay of several factors that rule the choice of specific reactive paths in general different, sometimes unexpected, from those taking place at ambient conditions. The continuous improving of the probing techniques employed to characterize the chemical changes occurring in molecular systems under high pressure conditions made possible, in the last years, new experiments where the contributions of the relevant parameters ruling the reactivity, i.e. pressure, temperature and radiation, could be successfully disentangled. Among the several issues emerged from these studies (crystalline environment, role of lattice phonons) appears particularly relevant the role of visible and near UV radiation that was found in several cases effective to lower the reaction threshold pressure and to introduce a great selectivity in the reaction. Important modifications of the excited states with rising pressure have been evidenced and found to play a key role in the reactivity of simple model molecular systems. For example, the employment of molecules characterized by dissociative excited states, such as the simplest R-OH systems, once suitably prepared by absorption of laser light can give rise to the formation of radicals able to trigger the reaction in otherwise inert systems. The efficiency of these processes has been found incredibly high also at pressures of few kilobars opening interesting perspectives also in view of practical applications. These results evidence also the lack of computational studies able to reproduce the pressure effects on the excited states even of the simplest molecules in high density condensed phases.

Kinetics of the reaction perovskite + ferropericlase = ringwoodite

David Dobson[1], JAMES BADRO2, ERS MEIBOM3 ELISABETTA MARIANI4

University College of London, London, UK

2IPGP Paris, France.

3MNHN, Paris, France

4University of Liverpool, UK

The kinetics of solid-state disproportionation reactions can be strongly assymetric due to the different diffusive length scales ofdisproportionation versus recombination. Transport of material from the lower mantle into the transition zone requires the reaction of perovskite (pv) plus ferropericlase (fp) to produce ringwoodite (rw); this reaction is diffusive on the grain-length scale and hence might allow a significantly wide region where metastable phases exist. We present experiments to investigate the kinetics of this reaction. We have assumed that the transformation from pv to majorite (mj) is fast (being diffusive at the unit-cell length scale) and hence performed coupled reaction experiments of MgO with (Mg,Al)(Al,Si)O3 mj at a pressure of 20 GPa (in the rw and mjstability fields) at temperatures of 1773 to 2123 K. The reaction is, as expected, mediated by diffusion of chemical components through the growing rw layer, with growth rate of the layer being linear with t2. Rw grows with strong topotactic relations to the MgO which would, on completion of thereaction, result in single (or twinned) crystals of rw replacing the MgO grains. However, the kinetics of the reaction is further complicated by the incompatibility of aluminium in rw.

As the rw layer grows, a double-diffusive instability develops with the rw-mj interface becoming fingered to maximise the surface area from which to diffuse aluminium into the garnet. The mean grain-size of regions with this texture is ~2 micrometres, which shows little coarsening due to zenner pinning. Reaction continues until all of the MgO is replaced leaving fine-grained reaction rims between these rw regions and the remaining excess (Mg,Al)(Al,Si)O3 garnet. Two ways to estimate the grain size of the lower mantle might arise from this:1) Seismological estimates of the thickness of the 670-km discontinuity are consistent with the equilibrium reaction. This means that the width of the region where the metastable mj + fp = rw reaction occurs is below seismological resolution. 2) The reaction texture might (occasionally) survive in porphyroclastic mantle xenoliths. Both these estimates are consistent with a maximum lower-mantle grain size of about 1 cm.

Elastic properties of deep earth materials by brillouin scattering of polycrystalline materials at high pressures: the role of grain size and of texturing in mgo

Sergio Speziale[1], H. Marquardt, H.J. Reichmann

Deutsches GeoForschungsZentrum, Potsdam

Our knowledge of the structure of the deep Earth is mainly based on seismology. Understanding the observed heterogeneity in the lower mantle requires fine knowledge of the elastic properties of the minerals that are present in the rocks of this remote region of our planet. For non-quenchable phases such as Ca-silicate perovskite and Mg-silicate postperovskite, it is impossible to isolate single-crystals to perform a study of the complete elastic anisotropy. However, average elastic properties of aggregates of these minerals have been determined by few techniques in the diamond-anvil cell. Recent measurements of aggregate shear acoustic velocities of MgSiO3 perovskite and postperovskite and MgO have been performed by Brillouin scattering at pressures of the lowermost mantle (Murakami et al, 2007a,b, 2009). New measurements at simultaneous high pressure and high temperatures have been already reported (Murakami et al., 2008). The prerequisite to obtain relevant information about the aggregate shear modulus from such measurements is that the sample behaves as an isotropic aggregate of crystals on the probing scale of Brillouin spectroscopy. In order to test this assumption, we have performed a series of Brillouin scattering measurements of MgO powder samples in a wide range of pressures. We have systematically measured low velocities compared with the expected aggregate values from single-crystal results. Our, someway surprising results, have oriented our attention to both preferred orientation, uniaxial stress effects, and then to an investigation of grain-size reduction during compression in the diamond-anvil cell. Based on our results, grain-size reduction to the nanoscale can be a major source of inaccuracy in the measured velocities of oxides such as MgO. Our findings imply that sample microstructure characterization is required to interpret the results of Brillouin scattering measurements of polycrystalline samples, especially for materials of unknown elastic properties.

[1] M.Murakami et al. Earth Planet. Sci. Lett. 256, 47 (2007); ibid. 259, 18 (2007); ibid. 277, 123 (2009).

[2] M.Murakami et al. Physics Earth Planet. Inter. 174, 282 (2008).

Modeling plastic deformation of mgo under mantle conditions

Cordier Patrick[1], J. Amodeo and Ph. Carrez

UniversitŽ Lille 1

Mantle convection involves plastic deformation of minerals and rocks under extreme conditions that are very difficult to reproduce in the laboratory. In particular, experimental strain-rates are at least 6 orders of magnitude larger than in nature. Extrapolation to natural conditions of semi-empirical constitutive flow laws parameterized on laboratory data is thus very unsafe and leads to significant discrepencies with observations (e.g. post-seismic deformation). Here we describe a physically-based model able to describe the rheology of MgO (the magnesium end-member of the second most abundant phase of the lower mantle) under mantle temperatures and pressures, but also under very low strain-rates representative of mantle convection. Our multiscale numerical model involves : (i) dislocation core modeling based on the Peierls-Nabarro-Galerkin model, (ii) thermal activation modeling of dislocation glide based on the kink-pair theory, (iii) critical resolved shear stress modeling based on the Orowan equation (in ther thermally-activated regime) or on Dislocation Dynamics modeling (in the athermal regime). The kink-pair theory allows to describe the mobility of dislocations under very low stresses without extrapolations. We show that decreasing the strain-rate counteract the influence of high-pressure and emphasizes the athermal regime for MgO in lower mantle conditions.

Melting behavior and phonon measurements of earth materials above 1 megabar

Jennifer Jackson[1]

California Institute of Technology

In this contribution, we will present recent nuclear resonant inelastic x-ray scattering measurements on iron-bearing silicates, oxides, and metals, and their application towards our understanding of EarthÕs interior. Specifically, we will present measurements on silicates and oxide minerals that are important in EarthÕs upper and lower mantles, as well as iron to over 1 megabar in pressure. The nuclear resonant inelastic x-ray scattering method provides specific vibrational information, e.g., the phonon density of states, and in combination with compression data permits the determination of sound velocities and other vibrational information under high pressure and high temperature [1,2]. For example, accurate determination of the sound velocities and density of chemically complex Earth materials is essential for understanding the distribution and behavior of minerals with depth [3,4,5]. The high statistical quality of the data in combination with high energy resolution and a small x-ray focus size permit accurate evaluation of the vibrational quantities of iron-bearing Earth materials as a function of pressure, such as the Grueneisen parameter and thermal pressure [6]. Finally, we will present a novel method detecting the solid-liquid phase boundary of compressed iron at high temperatures using synchrotron Moessbauer spectroscopy. Our approach is unique because the dynamics of the iron atoms are monitored. This process is described by the Lamb-Moessbauer factor, which is related to the

mean-square displacement of the iron atoms. We will discuss the implications of our results as they relate to EarthÕs core-mantle boundary regions.

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[2] J. M. Jackson, E.A. Hamecher, W. Sturhahn, Eur. J. Min. 21, 551-560 (2009).

[3] J. K. Wicks, J. M. Jackson, W. Sturhahn, Geophys. Res. Lett. 37, L15304 (2010).

[4]D.J. Bower, J.K. Wicks, M. Gurnis, J.M. Jackson, Earth Planet. Sci Lett. DOI 10.1016/j.epsl.2010.12035 (2011)

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New and forthcoming functionalities in the siesta code

Alberto Garcia[1]

[1] Institut de Ciencia de Materials (ICMAB-CSIC), Barcelona, Spain

The SIESTA program (www.uam.es/siesta) has opened up new opportunities in many disciplines by offering the possibility of treating large systems with first-principles electronic-structure methods. The code's efficiency for large problems stems from the use of strictly localized basis sets and from the implementation of linear-scaling algorithms which can be applied to non-metallic systems. The program can perform a full range of molecular dynamics simulations, structural optimizations, and vibrational analysis, making it suitable for a wide spectrum of research topics in geosciences. This talk will highlight new and forthcoming functionalities in SIESTA that enhance its usefulness to the community: -- Support for a van der Waals density functional [1].-- New QM-MM functionality for hybrid quantum-classical simulations [2].-- Improvements to the scripting and multi-level parallelization that enhance the throughput of calculations and allow new types of simulations.-- Electronic structure enhancements: DFT+U, spin-orbit interaction.-- Revamping of the linear-scaling sub-system to make it more robust for a wider variety of systems.-- Analysis tools The talk should also serve to help identify particular areas in which to focus the future development of the program. (This work was carried out by a number of SIESTA developers)

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Computational approaches to moessbauer and magnetic resonance spectroscopies

Josef Zwanziger[1]

[1] Dept. of Chemistry, Dalhousie University, Halifax, Canada

An important class of methods for studying structure in materials centers around the electron distribution near the atomic nuclei. Included in this class are Moessbauer, Nuclear Quadrupole Resonance, and Nuclear Magnetic Resonance. I will review our developments in these fields, some of which are mature[1,2,3] and others of which are in progress, and show how the methods are used to compute experimental observables. Time permitting I will also discuss our recent work on electric fields, including both an approach based on density functional perturbation theory and an approach based on the modern theory of polarization. Examples here will focus on computation of photoelastic response [4].

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Vibrational spectroscopy with the castep code

Keith Refson[1]

STFC Rutherford Appleton Laboratory

First principles quantum mechanical approaches have become a vitalpart of the study of spectroscopic and thermal properties of bothengineering and natural materials. The CASTEP code offers a range of approaches to phonon physics within the well-established and robust framework of density functional theory and the plane-wavepseudopotential method. A multiplicity of methods, incorporating bothfinite-difference and density-functional perturbation theoryapproaches allow studies across a wide range of materials andstates including molecular, insulating and metallic, and with aselection of Hamiltonians, including DFT and hybrid functionals. I will survey the current and some forthcoming new capabilities, andillustrate with calculations including a full spectroscopic assignmentof crystalline C60, high-pressure dynamics of a newly synthesizedrhenium nitride. Finally I will describe the application of lattice dynamics to thecalculation of thermal diffuse scattering (TDS) in Titanite andpresent a comparison with X-Ray and neutron diffraction results. This allows the extraction of phonon physics from relatively inexpensive diffraction experiments.

Infrared spectroscopy of minerals from first-principles

Marc Blanchart[1], Etienne Balan

Institut de MinŽralogie et de Physique des Milieux CondensŽs (IMPMC), Paris, France

Infrared (IR) spectroscopy provides information at the molecular level on the structure of minerals (Farmer 1974). It is widely used to investigate the structure of clay minerals and other disordered hydrous phases, which typically form in soils and weathering environments.

It provides valuable information about the location and concentration of OH defects in nominally anhydrous minerals. Other applications include the mineralogical quantification in complex samples, the detection of mineral transformations in geological environments and the investigation of their interfacial properties, through the adsorption of probe molecules. IR spectroscopy can be performed using a wide variety of experimental setups. For powder samples, spectra are most often recorded in transmission mode. However, other configurations can be used, such as diffuse reflectance or attenuated total reflectance to investigate the interface between solids and aqueous solutions. In complex natural samples, spectra may also be recorded from thin sections using IR microscopy techniques.The straightforward interpretation of vibrational IR spectra is often difficult. In particular, there is not always an evident relation between the microscopic atomic structure and measured vibrational bands when considering poorly ordered minerals or isolated OH defects in complex structures. An additional complexity of powder spectra arises from the influence of macroscopic parameters on the vibrational spectra. In polar insulators, atomic vibrations can be associated with oscillating macroscopic electric fields that are determined by the macroscopic shape of the particles. For these reasons, a theoretical determination of the vibrational frequencies and intensities is an ideal tool to establish unambiguous relations between the vibrational spectrum and the microscopic structure of minerals. In this context, first-principles computational methods based on density functional theory are very useful. The vibrational spectrum of a polar insulator can be obtained knowing the analytical part of the dynamical matrix and dielectric quantities such as the Born effective charges and the electronic dielectric tensor. These quantities can be calculated as the second-order derivatives of the total energy with respect to atomic displacements and/or an external uniform electric field, using the linear response theory (Baroni et al. 2001). The dependence of the vibrational spectroscopic properties on the dielectric properties is then determined by macroscopic parameters depending on the considered system. Combining first-principles calculations of crystal properties with a model taking into account experimental and sample-dependent parameters, it is possible to significantly improve the comparison between theory and experiment. Several applications of this approach will be presented, including the speciation and quantification of OH defects in nominally anhydrous minerals (Balan et al. 2008a, 2011a, Blanchard et al. 2009), the interpretation of the OH spectrum of Al hydroxides (Balan et al. 2006, 2008b, Delattre et al. 2011), the order/desorder in apatite crystal structure (Balan et al. 2011b), and the investigation of radiation effects in clay minerals (Fourdrin et al. 2009).

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Electronic and elastic properties of iron-containing minerals in earthÕs interior

Jung-Fu Lin[1]

Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, TX 78712, USA

As the most abundant 3d transition metal in the EarthÕs interior, ironÕs existence in the lower-mantle and core phases affects a broad range of physical and chemical properties in these regions. Thus, comprehension of the electronic and elastic properties of Fe-containing compounds under relevant pressure-temperature conditions is essential for interpreting seismological, geochemical, geodynamic, and geomagnetic observations deep in the EarthÕs interior. Herein, I will discuss the electronic spin and valence states of iron in the lower-mantle minerals, and the elasticity of candidate iron alloys in the EarthÕs core. Specifically, recent studies have shown that lower-mantle minerals such as ferropericlase [(Mg,Fe)O], silicate perovskite [(Mg,Fe)SiO3], post-perovskite, and ferromagnesite [(Mg,Fe)CO3] can contain iron in very distinct electronic spin and valence states at high pressure-temperature (P-T) conditions. The electronic spin and valence states of iron in these minerals have been investigated using synchrotron Mšssbauer, X-ray diffraction, and emission spectroscopies in high-pressure diamond anvil cells. In particular, I will address the spin states of ferric and ferrous iron in perovskite and post-perovskite as a function of P-T-composition in the lower mantle, focusing on the use of the hyperfine parameters, quadrupole splittings (QS), and chemical shifts (CS), seen in Mšssbauer spectroscopic analyses. Furthermore, precise measurements on the elasticity of candidate iron alloys at simultaneously high P-T conditions are needed to provide reliable constraints on the composition and seismic features of the EarthÕs core. The Vp-density relation of Fe and its alloys have been recently measured at extremely high P-T using in situ high-energy resolution inelastic X-ray scattering and X-ray diffraction in external heated diamond anvil cells at the Advanced Photon Source. Combining these results with theoretical calculations and thermodynamic modeling, I will discuss how the existence of iron affects the elastic and thermodynamic properties of iron-containing minerals, and our understanding of the geochemistry, geophysics, and geodynamics of the deep Earth.

Magnetic properties of iron and iron-bearing phases at high pressure

Stuart Gilder[1]

Department of Earth and Environmental Sciences, Ludwig Maximilians UniversitŠt, Munich, Germany

Although fluid motion in the outer core is commonly thought to generate the EarthÕs magnetic field, its geometry and secular variation may not rely on fluid mechanics alone. A strongly paramagnetic, or potentially ferromagnetic, inner core could have an important influence on the magnetic field surrounding it. Previous studies on the magnetic state of hexagonal closed packed (hcp) Fe, a likely candidate for the phase of iron in the core, have come to diverse conclusions. To help solve this problem, we studied the magnetic properties of Fe at high pressures employing three different approaches. The first allowed direct visual characterization of the magnetization by immersing Fe particles in a fluid pressure medium then observing the interaction (or lack thereof) of the particles with an external magnet. Stress in the cell was perfectly hydrostatic, e.g., no stress gradient existed. The attraction of Fe to an applied magnetic field at 17.7 GPa and 262 C suggests hcp Fe could exist in a ferromagnetic state. In the second approach, we built a system that measures reversible magnetic hysteresis parameters in a diamond anvil cell. We measured the magnetic hysteresis loops of 99\% pure Fe under pressure from 0 to 21 GPa. In the third technique, we directly measure the full magnetic vector of iron under pressure by inserting a diamond anvil cell into the bore of a three-axis superconducting magnetometer. The three analytical techniques and their results will be discussed.

Spin transition in Fe-bearing perovksite

Razvan Caracas[1]

CNRS, ENS Lyon

The interior of our planet is characterized by a succession of concentric layers, with distinct properties, which are in a continuous interaction. The largest of these layers, the EarthÕs mantle extends from the base at the crust (varying from 8 to 150 km) all the way down to the boundary with the core (CMB), situated at about 2900 km depth. The ranging thermodynamic conditions, about 3500K and 135 GPa, make CMB largely unattainable in current experimental setups. Here we focus on some of the most recent exciting applications of first-principles calculations based on density-functional theory and density-functional perturbation theory to the study of major minerals of the EarthÕs mantle: the phase diagrams of perovskites and their physical properties. In Fe-bearing perovskite (pv) (the most abundant mineral of the mantle by volume) the Fe2+ component exhibits a spin transition under pressure whose nature and outcome is still a matter of debate. We use lattice dynamical calculations to disentangle a part of its complex phase diagram and the spin behavior. To do this we investigate the dynamic stability of Pbnm FeSiO3 pv and show the existence of unstable phonon modes. We track the eigen-displacements of the phonons modes to find low-spin and intermediate spin states. On solid-state physical basis we explore a set of hypothetical structures with various spin configurations and considerably lower enthalpy than the parent orthorhombic Pbnm structure. We show that the spin evolves along a high-spin to mixed high- and intermediate spin to low-spin transition sequence. We also analyze the thermal behavior of both high-spin and low-spin phases along the entire

Mg-Fe solid solution and we discuss a first thermal phase diagram. We discuss at length the implication of the spin transition for modeling the mantle. We continue with the phase transition towards the post-perovskite (ppv) phase, its high-pressure polymorph. The phase diagram of the (Mg,Fe2+)SiO3 pv-ppv system shows a preferred partitioning of Fe in pv and a decrease of the transition pressure accentuated by the presence of Fe2+. In the presence of Al, the Fe3+ exhibits a spin transition associated with an Al Fe3+ site exchange and the pv-ppv transition.

Effect of fe and al substitution on the elastic properties of perovskite: a single-crystal diffraction study up to 75 gpa.

Boffa Ballaran Tiziana[1], Alexander Kurnosov1, Konstantin Glazyrin1, Daniel J. Frost1, Marco Merlini2 M. Hanfland2, Razvan Caracas3

BGI, Univ. Bayreuth. Germany

1. BGI, Univ. Bayreuth. Germany

2. ESRF Grenoble, France

3. CNRS, ENS Lyon, France

A number of studies have identified seismic velocity anomalies extending from the base to the middle of the lower mantle, so called large low shear velocity provinces (LLSVP), that likely have a chemical in addition to a thermal origin (Masters et al. 2000; Ni et al. 2005; Garnero et al. 2007) . If such anomalies have a chemical origin then they will inevitably contain perovskite with a composition which is distinct from the surrounding mantle. An understanding of the plausible chemical variation of perovskite in addition to its effect on density and elastic properties is, therefore an important issue. Here we present the results of room temperature compression experiments on single crystals of MgSiO3, (Mg,Fe)SiO3 and (Mg,Fe)(Al,Si)O3 perovskite containing substansial substitution of Fe3+-Al and with a composition analogous to that expected for a perovskite formed within subducted oceanic crust in the lower mantle. The data were collected employing a diamond anvil cell, in a helium pressure transmitting medium and a synchrotron X-ray source. Unit cell parameters for the 3 perovskite samples were measured up to 75 GPa. No broadening of reflection has been observed up to the maximum pressure reached, allowing accurate determination of the unit-cell parameters and a detailed examination of the effect of different chemical substitutions on the compression mechanism of perovskite as well as on its equation of state (EoS). The bulk modulus and first pressure derivative determined for MgSiO3 perovskite obtained by fitting a 3rd order Birch-Murnaghan are found to be quite insensitive to the maximum pressure to which the data are fitted. The EoS parameters obtained by fitting data from room preessure to 10, 40 or 75 GPa are almost identical. This insensitivity of fitting range, however, is not found to be the case for either (Mg,Fe)SiO3 or (Mg,Fe)(Al,Si)SiO3 perovskites, where the EoS fitted to data up to 40 GPa deviates with the actual measured data when extrapolated to higher pressure. In the case of (Mg,Fe)SiO3 perovskite this deviation appears to be related to the change in compression of the octahedral tilting as revealed by analysis of the lattice strain variation with pressure and is likely a consequence of the high-spin to intermediate spin transition of Fe2+. In the case of (Mg,Fe)(Al,Si)SiO3 perovskite, instead such effect is clearly due to a change in the compressibility of the c-axis and no evidence for effects due to a change in Fe spin state is observed. The two types of substitutions affect differently the elastic properties of MgSiO3 perovskite, Fe2+ in fact has a large negative effect on the bulk sound velocity and a large increase in density in contrast with Fe3+-Al which have a very modest effect both on the bulk sound velocity and on density. The latter may be, therefore, more compatible with causing the observed seismic anomalies in the lower mantle.

Experimental and spectroscopic approach to the determination of equilibrium fe isotopic fractionation factors in planetary materials

Mathieu Roskosz[1], N. Dauphas (2), E.E. Alp (3)

UnitŽ MatŽriaux et Transormations, UniversitŽ de Lille 1, CNRS UMR 8207, 69655
Villeneuve dÕAscq, France

2) Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute,
The University of Chicago, 5734 South Ellis Avenue, Chicago IL 60637, USA

3) Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue,
Argonne, IL 60439, USA

Isotopes distribution is commonly used to shed light on interactions and dynamics of planetary reservoirs. During the last decade, significant isotopic fractionation of heavy elements were measured in materials produced in high temperature environments such as planetary mantles. In this respect, the contrasted Fe isotopes signature of the Earth and Mars mantles is still enigmatic and may point to very specific features of these planetary bodies. A major difficulty for interpreting iron isotope variations is that most equilibrium fractionation factors are poorly known. Several approaches can then be used to estimate these factors: (1) quantum chemical calculations, (2) Analysis of laboratory experiments, (3) the direct investigation of vibrational properties of iron in solids by using nuclear resonance inelastic X-ray scattering (NRIXS). In this contribution, we will focus on the two last approaches. Melting experiments corresponding to the conditions inferred for core differentiation in an early silicate magma ocean were performed at 1750 and 2000 ¡C, and from 1 to 7.7 GPa. The compilation of all experiments conducted at 2000 ¡C yields a very small 57Fe metalÐsilicate fractionation of 0.047±0.063ä. Nonetheless, such data are extremely difficult to collect because experimental results can be fundamentally flawed by several kinetic effects. This pitfall therefore requires an extensive characterization of kinetic fractionation processes. Our recent results on the effect of Fe valence state on isotope dynamics in molten silicates will be used to illustrate this aspect of the experimental study of isotopes fractionation in high temperature and pressure environments. A special emphasis will also be paid to the last, new and most promising approach. The NRIXS uses a synchrotron X-ray source to probe the vibrational properties of iron atoms in the solid lattice. Polyakov and coworkers first proposed to use the kinetic energy derived from the partial phonon density of state (PDOS) of the Fe sublattice to estimate fractionation factors. In the present contribution, we outline an alternative approach based on the determination of the average force constant of the bonds involving iron atoms , which can be calculated from the 3rd order moment of the raw NRIXS spectrum. Because this force constant and its uncertainty are almost always given in papers reporting NRIXS data, our approach should be easy to implement. Nevertheless, we will show that the energy range over which PDOS must be recorded, the accuracy and the processing method required to extract accurate values from PDOS imposes specific operating conditions. Some revisions of equilibrium fractionation factors determined from existing data collected for other purposes with other analytical protocols are therefore anticipated

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First principles calculation of b and li equilibrium isotope fractionation between minerals and aqueous solutions

Piotr Kowalski[1], S, RO JAHN, BERND WUNDER

GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany (email: kowalski@gfz-potsdam.de)

GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany (email: kowalski@gfz-potsdam.de)

B and Li are important geochemical tracers widely used in petrology. Their isotopes strongly fractionate between minerals and aqueous fluids during fluid-rock interaction processes, leaving pronounced isotopic signatures in the interacting materials. Because of that these light elements are widely used as tracers of mass transfer processes in the subduction cycle. One of the most important mechanisms driving the formation of isotopic signatures is the mass-dependent equilibrium isotope fractionation, which nowadays can be modelled on the atomic scale by modern computational methods and hardware. For that purpose we have developed an efficient ab initio based computational approach, which allows for prediction of the equilibrium isotope fractionation factors in complex high pressure and temperature minerals, melts and fluids [1]. In our method these media are modelled as continuous media, which is important for the investigation of the thermal expansion and pressure-driven compression effects that influence the isotope fractionation process in high -T and -P materials. We will show the performance of our method in the prediction of the B and Li isotope fractionation factors between complex Li/B-bearing crystalline solids (staurolite, spodumene, tourmaline and micas) and aqueous solutions. A comparison of the results with the existing experimental data [1-4] will be provided. Among other findings, we will show that we are able to reproduce correctly the experimentally found isotope fractionation sequences: fluid-tourmaline-B[4] micas for B and staurolite-fluid-mica-spodumene for Li. The computed values agree with the measured data often within 1 ä and the computational uncertainty is comparable to the experimental error. In addition to that we will demonstrate that by ab initio simulations we are able to deliver an unique picture of the processes governing the isotope fractionation on the atomic scale, such as the role of coordination environment and pressure-induced change in the local environment of the fractionating element. Our work indicates that such ab initio based investigations complement the experimental works leading to better understanding of isotope fractionation processes in the Earth and planetary environment.

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The structural determinants of silicon fractionation properties of silicate minerals : a first-principles density functional study

Merlin MŽheut[1]

GŽosciences Environnement Toulouse, OMP - UniversitŽ Paul Sabatier, 14 avenue Edouard Belin, 31400 Toulouse, FRANCE

Ab initio methods based on density functional theory have proven to be successful in reproducing the physical and chemical properties of complex systems. Within this framework, we have recently developed a methodology to predict equilibrium fractionation factors as a function of temperature (1). We use PBE functionals, combined with the use of pseudopotentials and planewave basis sets. Our previous work focused on the effect of the polymerization of the silicate network on Si-isotope fractionation (2), which had previously been predicted to be a determining factor. Our work does not confirm this assumption. To investigate the origin of this fractionation, we studied minerals with identical polymerization structures such as talc, pyrophyllite, muscovite, phlogopite or clinochlore. In the case of muscovite and phlogopite, the calculated quartz-mineral fractionations are in qualitative agreement with natural estimates. In this family of silicates, a correlation can be shown between the mineral-quartz fractionation of silicon and cationic content. Together with the simple shape of the fractionation laws, this permits to propose the following approximate law, valid for any temperature T (in K): In α (phyllo.,qtz,Si,T)=a(T)*[Mg(o)]+b(T)*([Al(o)]+[Al(t)]), where [Mg(o)], [Al(o)] and [Al(t)] represent the content of octahedric magnesium, aluminium and tetrahedric aluminium relative to 4 tetrahedral units, and a(T)=-12.834x2+14.39x3; b(T)=-5.040x2+4.20x3, with x=10^2/T We will discuss the interpretation of this relationship in terms of cationic force field effects, and the extent to which it can be generalized to other silicate structures.

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List of Participants

Organizers

Caracas Razvan - CNRS-Laboratory of Earth Sciences, Ecole Normale SupŽrieure Lyon, France

Stixrude Lars - University College London, United Kingdom

Winkler Bjoern - Johann Wolfgang Goethe University, Frankfurt, Germany

Participants

Bini Roberto - University Florence, Italy

Blanchart Marc - Institut de MinŽralogie et de Physique des Milieux ConsensŽs (IMPMC), Paris , France

Bosak Alexei - European Synchrotron Radiation Facility (ESRF), Grenoble, France

Daniel Neuville - CNRS-Institut de Physique du Globe de Paris, France

Dobson David - University College London, United Kingdom

Garcia Alberto - Institute of Materials Science, Barcelona, Spain

Gilder Stuart - Ludwig Maximilians University, Munich, Germany

Jackson Jennifer - Caltech, Pasadena, USA

Jahn Sandro - German Research Centre for Geosciences, Potsdam, Germany

Koch-Mueller Monika - German Research Centre for Geosciences, Potsdam, Germany

Kowalski Piotr - Helmholtz Centre Potsdam, Germany

Lee Sung Keun - Seoul National University, South Korea

Lin Jung-Fu - University of Texas, Austin, USA

MŽheut Merlin - CNRS-Institut de MinŽralogie et de Physique des Milieux CondensŽs (IMPMC), Paris, France

Patrick Cordier - UniversitŽ Lille 1, France

Refson Keith - Rutherford-Appleton Laboratory, United Kingdom

Roskosz Mathieu - Univ. Lille 1, France

Speziale Sergio - German Research Centre for Geosciences, Potsdam, Germany

Tiziana Boffa Ballaran - University Bayreuth, Germany

Zwanziger Josef - Dalhousie University, Halifax, Canada