

FA2-MS15-T01

Shear deformation and phase transitions in mantle minerals studied by atomic scale simulations. Sandro Jahn. *GFZ German Research Centre for Geosciences, Telegrafenberg 14473 Potsdam, Germany.*
E-mail: jahn@gfz-potsdam.de

Investigations of the physical properties of silicates and their thermodynamic stability under extreme conditions of pressure and temperature are indispensable to obtain a better understanding of the structure and dynamics of the Earth. In recent years, substantial progress has been made in this field through the development of new methods in high pressure mineral physics using both experimental and atomic scale modeling approaches. The latter are especially powerful when they are used to predict properties or phase behavior at conditions where experiments are difficult to perform or to reveal some of the underlying principles of measured properties or processes. Here, we use a combined approach of atomic scale modeling techniques to shed light on the mechanisms of non-elastic deformation and polymorphic phase transitions of mantle silicates. While first-principles calculations in the framework of density-functional theory provide the most accurate information on the crystal structures and their thermodynamic stabilities, a combination of classical molecular dynamics and metadynamics is employed to study the actual deformation or transformation process. Examples include phase transformations between various polymorphs of MgSiO₃ pyroxenes [1-3] and between the Mg₂SiO₄ polymorphs olivine and ringwoodite. Shear deformations observed in the metadynamics simulations will be related to rheological properties of the corresponding silicates. For Mg₂SiO₄ olivine, a change of slip system is predicted towards high pressure and/or high temperature.

[1] Jahn S., Martonak R., *Phys. Chem. Minerals*, 2008, 35, 17. [2] Jahn S., Martonak R., *Am. Mineral.*, 2009, 94, 950. [3] Jahn S., *Acta Cryst. A*, 2010, in press.

Keywords: High-pressure minerals, Molecular dynamics, Phase transitions

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Interplay Between Structural and Electronic Behavior in Iron Bearing Earth Lower Mantle Minerals. L. Dubrovinsky^a, C. McCammon^a, K. Glazyrin^a, O. Narygina^a, M. Merlini^b, I. Kantor^c, M. Hanfland^c, A. Chumakov^c. ^a*Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany.*
^b*Dipartimento di Scienze della Terra, Università degli Studi di Milano Via Botticelli 23, 20133 Milano, Italy.*
^c*ESRF, Boîte Postale 220, 38043 Grenoble, France.*
E-mail: Leonid.Dubrovinsky@uni-bayreuth.de

A major goal in the geosciences is to understand (and predict) how the Earth works, which requires a detailed knowledge of how the mineral phases which make up the Earth behave under high pressure and high temperature conditions. Much attention has been focused on the silicate perovskite and magnesium-iron oxide phases, since they make up major part of the Earth's interior. Special attention has been focused on possible phase transformations of the materials due to their

significant implications for mantle behavior. The majority of measurements have been made on *pure* MgSiO₃ perovskite, however, and almost exclusively using X-ray powder diffraction. Although the importance of Fe and Al as minor components of the silicate perovskite phase has been well documented in the past decade in numerous papers including many published in *Science* and *Nature*, the few studies using methods sensitive to these elements (e.g., X-ray emission spectroscopy and nuclear forward scattering) were not sufficiently systematic and/or sensitive to recognize any significant changes in the pressure range below 100 GPa. We studied silicate perovskites (Mg_{0.88}Fe_{0.12})SiO₃ and (Mg_{0.9}Fe_{0.1})(Si_{0.975}Al_{0.025})O₃ and series of magnesiowüstites by means of high resolution X-ray single crystal and powder diffraction in laser-heated diamond anvil cells, Mossbauer spectroscopy, and nuclear forward scattering at pressure up to 120 GPa and temperature above 2000 K. We will discuss effects of changes in iron electronic state on structure of mantle minerals.

Keywords: mantle mineralogy, laser-heating, DACs, single crystals, structure

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P₂/c to C₂/c phase transition in clinopyroxenes and the geodynamic implications. Matteo Alvaro^a, Fabrizio Nestola^b, Fernando Camara^c, Chiara M. Domeneghetti^d, Vittorio Tazzoli^d, Ross J. Angel^a. ^a*Crystallogr. Lab., Virginia Tech, Blacksburg, U.S.A.* ^b*Dip. di Geoscienze, Università di Padova, PD, Italy.* ^c*C.N.R. – IGG – Unita' di Pavia, PV, Italy.* ^d*Dip. di Scienze della Terra, Univ. di Pavia, PV, Italy.*
E-mail: malvaro@vt.edu

Clinopyroxenes are chain silicate minerals, in which there are two chains, made up by corner-sharing SiO₄ - tetrahedra running parallel to the *c* - axis. The two chains are crosslinked by M1 (containing Mg, Fe²⁺, Fe³⁺, and Al) and M2 (containing Ca, Fe²⁺, Mg and Na) polyhedra. There are three polymorphs (HT-C₂/c, P₂/c, HP-C₂/c) stable at different pressure and temperature conditions. At ambient conditions the space group is P₂/c, which transforms to HT-C₂/c and HP-C₂/c at high-temperature and high-pressure conditions respectively. The HP and HT C₂/c structures have the same Wyckoff positions as one another but different geometries. Moreover both the high-pressure and high-temperature phase transitions are strongly dependent upon composition. Clinopyroxenes represent about 12% of the upper mantle of the Earth, and are involved in many geodynamic processes. Therefore the knowledge of their structural, physical-chemical and thermodynamic properties will be crucial in interpreting the structure and dynamics of the upper mantle.

Pure clinoenstatite MgSiO₃ is stable at least up to 8-8.5 GPa (240-255 km depth) and it undergoes a phase transformation from P₂/c to C₂/c at about 6.2 GPa accompanied by a strong and discontinuous change in density. Such a density change would cause a sudden jump in the seismic velocity waves at the upper mantle close to 180-190 km depth. But a more realistic composition for upper-mantle P₂/c clinopyroxene would include a small but significant amount of both Ca and Fe in its structure. Both Ca and Fe separately strongly decrease the pressure of the transformation. The average M2 ionic radius is of course the only parameter which allowed us to evaluate the effect of Ca and Fe together. We have

determined the structural evolution and phase transition behaviour of two natural pigeonites with composition $\text{Wo}_6\text{En}_{76}\text{Fs}_{18}$ and $\text{Wo}_{10}\text{En}_{43}\text{Fs}_{47}$ (ie Ca and Fe) by single-crystal diffraction. Both undergo a first order phase transition, and show that the transition pressure is controlled by the average M2 ionic radius.

Keywords: High-pressure phase transition, pyroxenes, Earth's upper mantle.

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Structural studies of $\gamma\text{-Fe}_2\text{SiO}_4$ ringwoodite and its high-pressure polymorph. E. Greenberg^{a,b}, J.

Rouquette^c, C.A. McCammon^b, I. Kantor^d, V. Prakapenka^d, L.S. Dubrovinsky^b, G.Kh. Rozenberg^a, M.P. Pasternak^a. ^a*Physics and Astronomy, Tel-Aviv University, Israel.* ^b*Bayerisches Geoinstitut, Universitaet Bayreuth, Germany.* ^c*Institut Charles Gerhardt, Université Montpellier II Sciences et Techniques du Languedoc, France.* ^d*GSECARS, Argonne National Laboratory, USA.*

E-mail: erangre@gmail.com

One of the most abundant minerals in Earth's mantle is $(\text{Mg,Fe})_2\text{SiO}_4$ olivine. The properties of olivine and its transformation to spinel have been extensively studied due to the effect this transition has on seismic wave velocities. The purpose of this study is to obtain an equation of state for the Fe end-member of ringwoodite (Fe_2SiO_4 spinel) and to determine the high-pressure post-spinel structure. Synchrotron x-ray diffraction and Mössbauer spectroscopy were used to study the structural properties of ringwoodite up to 60 GPa. Starting at ~ 30 GPa, x-ray diffraction shows splitting of several peaks, marking a phase transition to a rhombohedrally distorted spinel structure. According to Mössbauer spectroscopy measurements, this new high-pressure phase has two different Fe sites; each characterized by different quadrupole splitting and isomer shift values. These two sites have an intensity ratio of 3:1, in agreement with the structure determined from x-ray diffraction studies.

Keywords: high-pressure phase transitions, Mossbauer spectroscopy, powder x-ray diffraction

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Solid solution behaviour of lower mantle minerals.

Daniel Y. Jung^a, Max Schmidt^b. ^a*Laboratory of Crystallography, Dept. Materials, ETH Zürich, Switzerland.* ^b*Institut for Mineralogy and Petrology, Dept. Earth Sciences, ETH Zürich, Switzerland.*

E-mail: Daniel.Jung@mat.ethz.ch

Under the assumption that the Earth's lower mantle is pyrolytic and isochemical to the upper mantle, $(\text{Mg,Fe})\text{SiO}_3$ perovskite ($\sim 70\%$) is thought to be the most abundant phase in the lower mantle, followed by magnesiowüstite $(\text{Mg,Fe})\text{O}$ with $\sim 20\%$ and CaSiO_3 with between 6 and 12 vol%. One of the open questions concerning Ca in the lower mantle is whether with increasing temperature and depth, the entire amount of Ca could be incorporated into MgSiO_3 perovskite such that the CaSiO_3 perovskite phase would vanish.

Using density-functional simulations within the generalized gradient approximation and projector-augmented wave method (as implemented in the VASP [1] software package) together with thermodynamic modelling, the reciprocal solubilities of MgSiO_3 and CaSiO_3 perovskites were calculated for pressures and temperatures of the Earth's lower mantle from 25 to 100 GPa and 0 to 6000 K, respectively. The solubility of Ca in MgSiO_3 results to be less than 0.02 atoms per formula unit, the solubility of Mg in CaSiO_3 is even lower, and, most important, the extent of solid solution decreases with pressure. To dissolve CaSiO_3 perovskite completely in MgSiO_3 perovskite, a solubility of 7.8 or 2.3 mol% would be necessary for a fertile pyrolytic or a depleted harzburgitic mantle. Thus, for any reasonable geotherm, two separate perovskites will be present in fertile mantle, suggesting that Ca-perovskite will be residual to low degree melting throughout the entire mantle. However, at the solidus, CaSiO_3 perovskite might completely dissolve in MgSiO_3 perovskite in a depleted mantle with <1.3 wt% CaO. These implications may be modified if Ca solubility in MgSiO_3 is increased by other major mantle constituents such as Fe and Al.

[1] Kresse G., Furthmüller J., *Physical Review B*, 1996, 54, 11169.

Keywords: solid solution, high-pressure phases, ab-initio calculations