



Experiment title: High-pressure low-temperature X-ray diffraction of silicate perovskite: an alternative window to the lower mantle

Experiment number:
HS 1124

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Report:

During the available beam time, two experiments were performed. The first one aimed to obtain the structure of MgSiO₃-perovskite at different pressures, and temperature conditions as close as possible from 0 K, in order to get read of all thermal contributions, since such structure refinements may have important impacts for theoretical models of the MgSiO₃-pv structure. We believe that this experiment will also provide a low temperature Eos of MgSiO₃-pv with a precision not yet available. This is necessary for providing precise very high-temperature EoS calculated by the thermal pressure method.

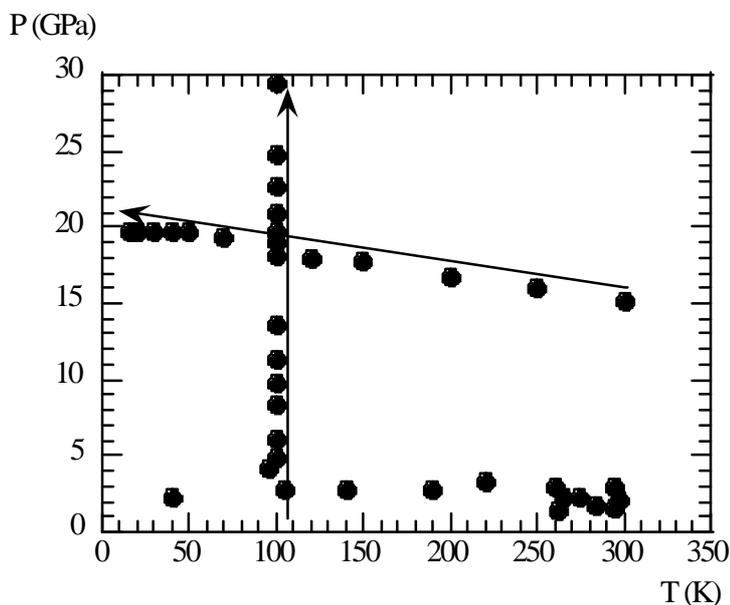


Fig. 1: Experimental pressure-temperature conditions under which MgSiO₃-pv diffraction patterns were taken.

We recorded ~40 diffraction patterns [Fig. 1] on polycrystalline samples ($40 \times 400 \times 20 \mu\text{m}^3$) pressurized under static conditions in a membrane diamond anvil cell up to 30 GPa, using He as a pressure-transmitting medium and a ruby chip to measure pressure. The cell was placed in a helium flow cryostat which allowed to cool the sample from 300 K down to 10 K. Temperature was measured with a Cu/constantan thermocouple down to 40 K and a Au-0.07% Fe/chromel couple for lower temperatures. A cross check of the actual temperature of the sample was also obtained in the 100-10 K range with the relative intensities of the fluorescence lines of the ruby.

Hence, we do have high-quality data along one isotherm (100 K) up to 30 GPa, and along a pseudo-isobar down to 10 K. These data are currently being processed.

A second experiment was performed to estimate the influence of Aluminium on the bulk modulus of MgSiO_3 perovskite, at ambient temperature, down to pressure conditions relevant of the lower mantle. The results of this work have been submitted to Geophysical Research Letter, and have been presented at the ESRF workshop ‘Science at high pressure: Latest trends from 3rd generation sources’.

Abstract. Aluminium oxide (Al_2O_3) is estimated to amount 4 to 5 mol% in all mantle compositional models, and is believed to be incorporated into $(\text{Mg,Fe})\text{SiO}_3$ -perovskite under the pressure and temperature conditions of the lower mantle. Hence, using synchrotron X-ray diffraction, we have measured the 300 K equation of state of a perovskite with $X_{\text{Al}} = \text{Al}/(\text{Al}+\text{Mg}+\text{Si}) = 0.077$, up to 32 GPa, in order to estimate the influence of Al on the compressibility of perovskite. A least square adjustment of two independent data sets yields the following equation of state parameters [$V_0 = 163.52(3) \text{ \AA}^3$, $K_0 = 229(4) \text{ GPa}$, and $K'_0 = 2.5(4) \text{ GPa}$] [Fig. 2 and 3]. The high compressibility of aluminous perovskite deduced from the present work, together with available experimental results from Zhang and Weidner [1999] and *ab initio* calculations from Brodholt [2000], allow to assess the most probable substitution mechanism for aluminium into perovskite at pressures characteristics of the shallow lower mantle [Fig. 4]. Al^{3+} is likely to be incorporated in place of Si^{4+} in the octahedral site of perovskite, hence requiring the creation of oxygen vacancies for charge balance. As a consequence, aluminous perovskites may have a higher affinity for water than pure MgSiO_3 -perovskite. The enhanced compressibility of aluminous perovskite certainly has also strong geophysical and geochemical implications, as it may revive perovskite-rich lower mantle models. Also, the transformation of garnet into compressible Al-rich perovskite at the top of the lower mantle may be responsible for the high-P-and -S velocity gradients observed between 660 and 760 km depth.

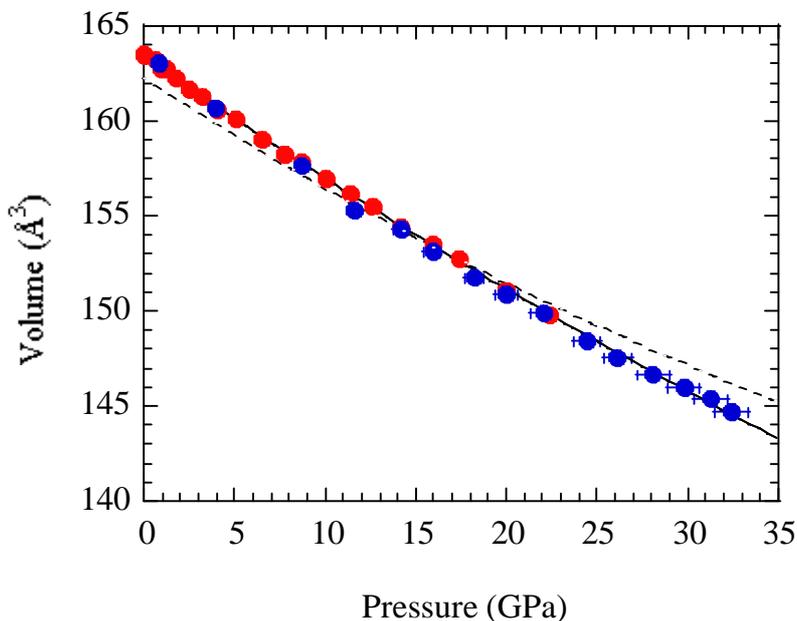


Fig. 2 Birch-Murnaghan equation of state of $\text{Al}_{0.077}$ -perovskite (solid line). Red circles: experiment in He; blue circles: experiment in Ar. $\text{Al}_{0.077}$ -perovskite becomes denser than pure MgSiO_3 -perovskite (dashed line) [Fiquet et al., 2000] above approximately 17 GPa at 300 K.

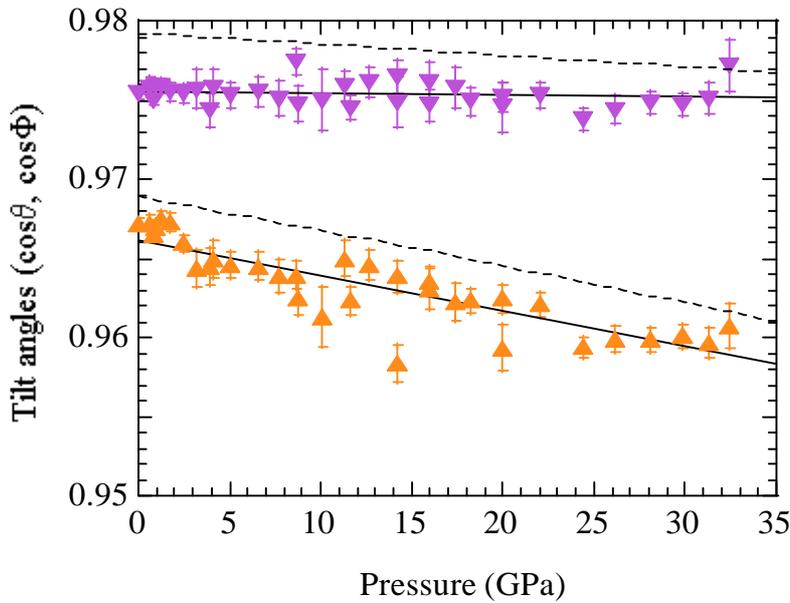


Fig. 3 Variation of $\cos\theta=a/b$ () and $\cos\Phi=2a/c$ () for $\text{Al}_{.077}$ -perovskite as a function of pressure. Notice that a linear fit to the data (solid line) indicates that Φ remains almost constant up to 32 GPa. The evolution of the tilt angles for pure MgSiO_3 -perovskite (dashed line) have been reported for comparison [Ross and Hazen, 1990; Fiquet et al., 2000]. This indicates a very different compression mechanism of aluminous perovskites along the c-axis, supporting the proposed substitution mechanism.

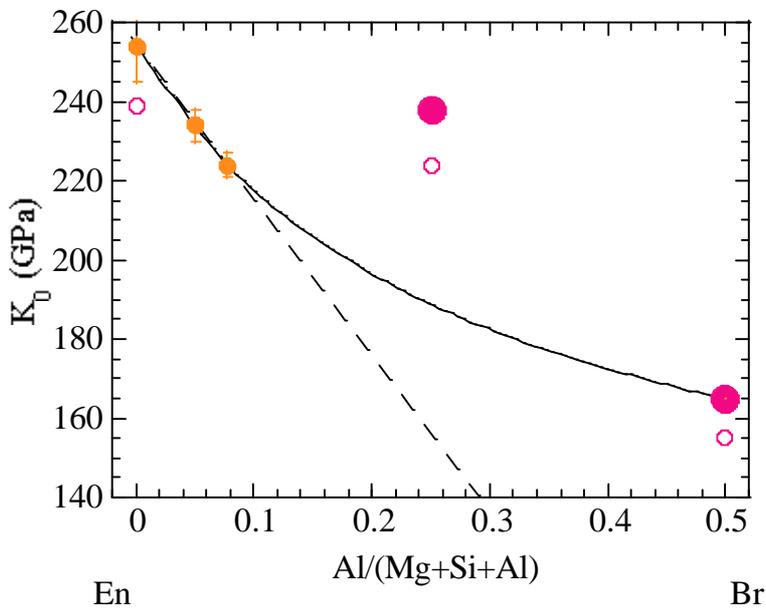


Fig. 4 Evolution of the compressibility of perovskite as a function of its Al-content $X_{\text{Al}}= \text{Al}/(\text{Mg}+\text{Si}+\text{Al})$. All bulk moduli reported are valid within the 0-10 GPa range, assuming a pressure derivative $K'_0= 4$. Filled orange circles include the bulk moduli experimentally determined by Ross and Hazen [1990], Zhang and Weidner [1999], and the present results. While empty squares depict the bulk moduli calculated by Brodholt [2000], for the vacancy-free MgSiO_3 , $(\text{Mg}_3\text{Al})(\text{Si}_3\text{Al})\text{O}_{12}$ perovskites, and for the oxygen deficient $\text{Mg}_2\text{Al}_2\text{O}_5$ brownmillerite, large filled circles represent the corresponding experimental values approximately 7-8% higher [Brodholt, 2000]. The solid line is only an interpolation between the available experimental and calculated bulk moduli. A linear fit to the experimental data (dashed line) indicates a very steep dependence of K_0 $-3.9(1) 10^2$ GPa on the aluminum content in perovskite. This is only compatible with the incorporation of Al^{3+} in place of Si^{4+} in the octahedral site of perovskite, charge-balanced by the creation of oxygen vacancy.

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Brodholt, J.P., Pressure-induced changes in the compression mechanism of aluminous perovskite in the Earth's mantle, *Nature*, 407, 620-622, 2000.

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