ESRF	**Experiment title:** Crystal structure of silicate perovskites at megabar pressures and 2500 K from single - crystal data refinements.	**Experiment number**: HS 4177
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Report:

Two different types of experiments were conducted at the ID09 beam line one at high-pressure and room temperature and the other at both high-pressure and high-temperature with the aim to elucidate the structural distortion of MgSiO3 perovskite both with the end-member composition and with some Fe^{2+} and Fe^{3+} and Al substitution at pressure and temperature conditions of the Earth's lower mantle.
Several crystals were tested at room pressure in order to find those with optimal orientation for single crystal structural study in the diamond anvil cell.

The experiments at high-pressures and room temperature were conducted on two well carachterised single-crystals of MgSiO3 and Fe2+-bearing (4%) perovskites loaded in membrane-type diamond anvil cells (DAC) using He as pressure transmitting medium. For both samples we reached pressure of **90** GPa, without noticing any broadening of reflections which can be caused by non-hydrostatic stresses and/or bridging of the crystals. The longest dimension of the two crystals was smaller than 15 μm, therefore they were always completely inside the X-ray beam and thanks to the beam line set up we were able to collect high-quality data up to the maximum pressure reached. Structural refinements were performed at several pressures and all converged with discrepancy factors of 4-5% for $MgSiO_3$ perovskite end-member and of 2-3% for the Fe-bearing perovskite crystal.
These experiments together with those conducted in Februar 2010 on a Fe-Al-bearing perovskite up to 70 GPa allow us to constrain precisely the effect of cation substitution on the structural behaviour of $MgSiO_3$ perovskite at pressures of the lower mantle.

An accurate analysis of the structural refinements still needs to be completed, however, the data collected so far indicate that the orthorhombic distortion expressed in terms of tilting angle B-O1-B and B-O2-B is very similar for the MgSiO3 end-member perovskite and for the Fe2+-bearing perovskite. This distortion increases with pressure in a similar way for the two samples (Fig. 1). The distortion of Fe,Al-bearing perovskite is more pronounced already at room pressure (note that at 90 GPa the B-O1-B and B-O2-B angles of both MgSiO3 and Fe-MgSiO3 perovskites have values similar to those that the Fe,Al-bearing perovskite structure presents at room pressure) and as a consequence its variation with pressure is smaller especially for the B-O1-B angle (Fig. 1).

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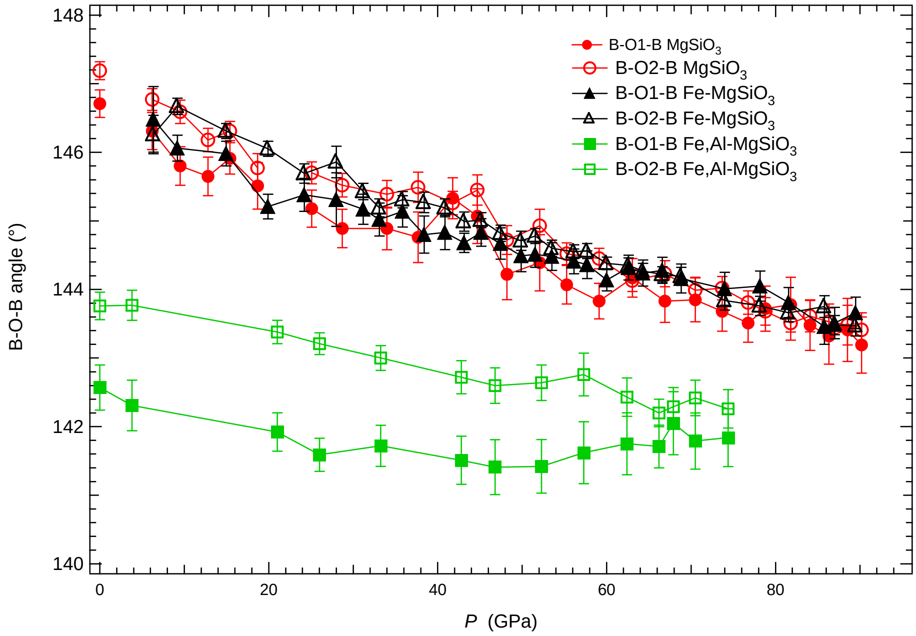

Fig. 1: Variation of the octahedral tilting angles B-O1-B and B-O2-B of $MgSiO_3$ perovskite end-member (red), of Fe^{2+}-bearing perovskite and of Fe-Al-bearing perovskite as a function of pressure

Although several studies have been conducted so far on the high-pressure behaviour of Mg-silicate perovskite, they have mostly dealt with powdered samples, especially when conducted at pressure conditions of the lower mantle. The results obtained during this experiment are therefore unique in their ability to experimentally constrain the structural changes of perovskites with compositions ranging from peridotitic to basaltic at elevate pressures with the precision and accuracy of the single-crystal diffraction technique.

A second set of experiments was carried out at both high-pressures and temperatures using a portable laser heating system developed by Dubrovinsky and co-workers (see experimental report HS3934). Such system has the advantage of being fixed to the goniometer of the ID09 beam line and of moving together with the diamond anvil cell during the omega scans necessary for the collection of intensity data from single-crystals. In this way the laser spot, which in our experiments always was larger than the crystal loaded in the DAC, was heating the whole sample minimising in this way the temperature gradients and giving sharp diffraction profiles. In particular we have studied a crystal of the Fe,Al-bearing perovskite at pressure above 63 GPa and temperature of 1700 K in order to investigate the possibility of Fe^{3+} and Al disorder between the octahedral and the A site of the perovskite structure. Fe^{3+} and Al are usually ordered into the A and the B site respectively in perovskite samples recovered from multi-anvil synthesis experiments. It has, however, been postulated (Catalli et al. 2010) that at pressures above 60 GPa Fe^{3+} in a low spin state may compete with Al for the octahedral site. We have collected two sets of high-pressure and high-temperature intensity data at pressure of 67 and 78 GPa and at 1700 K. In both cases the structural refinements give a discrepancy factor of about 6% for more than 120 unique reflections. An attempt to refine a structural model with variable occupancy of Si and Fe in the octahedral site resulted in a negative occupancy for Fe suggesting that even at those pressure and temperature Fe is preferentially distributed in the A site. Intensity data also were collected at room temperature before and after the heating cycles and will be used to better constrain any possible structural change occurred in the Fe,Al-bearing perovskite due to laser heating.

In spite of the challenge of conducting experiments with single-crystals at extreme conditions, the set up at ID09A appears perfectly suitable for such studies and gives a unique opportunity at the moment for better constraining the structural behaviour of the Earth's interior.

References

Catalli K., Shim S.-H., Prakapenka V.B., Zhao J., Sturhahn W., Chow P., Xiao Y., Liu H., Cynn H., Evans W.J (2010) Spin state of ferric iron in $MgSiO_3$ perovskite and its effect on elastic properties. Earth Planet Sci Lett, 289, 68-75.