ESRF	**Experiment title:** Structural changes associated with the spin crossover transition in Fe and Al – bearing $MgSiO_3$ perovskite determined through single – crystal X-ray diffraction refinements.	**Experiment number**: HS 3920
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Report:

The aim of the high-pressure measurements conducted at ID09A was to study the structural changes occurring with pressure in an Fe-Al-bearing perovskite to quantify the polyhedral distortions that might be associated with a spin crossover transition in Fe.
Several crystals were tested at room pressure in order to find those with optimal orientation for single crystal structural study in the diamond anvil. The diamond anvil cells were subsequently loaded with He and intensity data were collected at different pressures. Lattice parameters were also determined at each pressure using approximately 90-110 strong reflections. Two samples were studied: $MgSiO_3$ perovskite end-member and a $Mg_{0.59}Fe_{0.42}Al_{0.34}Si_{0.65}O_3$ perovskite from a tholeitic MORB bulk composition, both synthesized using a multi-anvil press at the Bayerisches Geoinstitut. Structural refinements at room pressure clearly indicate that the cation substitution in the latter sample follows a coupled substitution mechanism with Fe^{3+} replacing Mg in the A site and Al^{3+} replacing Si in the B octahedral site of the perovskite structure.

We succeeded in reaching 30 GPa with the diamond anvil cell loaded with the $MgSiO_3$ perovskite end-member and **70** GPa with the Fe-Al-bearing perovskite. The data collected are of exceptional quality thanks to the careful set up of the ID09A beam line and even the structural refinements of the highest-pressure data converged after a few cycles with discrepancy factors of approximately 3-4 %. As soon as the crystal is bridged between the diamonds or against the gasket, however, the structural refinements give very poor results. This occurred, for example, with the $MgSiO_3$ sample above 30 GPa, causing us to end the experimental compression at this pressure. The experiments so far conducted allow us to constrain precisely the structural behaviour of the Fe-Al-bearing perovskite at pressures of the lower mantle.

No discontinuity was observed in the unit-cell lattice parameters of the two investigated samples up to the maximum pressures reached. An accurate analysis of the structural refinements still needs to be completed, however, the data collected so far indicate that the *c* axis of Fe-Al-bearing perovskite is much more compressible than that of the perovskite end-member. This is due to the fact that the B-O1 octahedral bond distance, which is along the *c* axis of the orthorhombic perovskite, is more compressible than the B-O2 bond distances, which lie in the basal plane of the octahedron (Fig. 1). In contrast the compressibility of all octahedral bond distances of the $MgSiO_3$ perovskite end-member are practically the same.

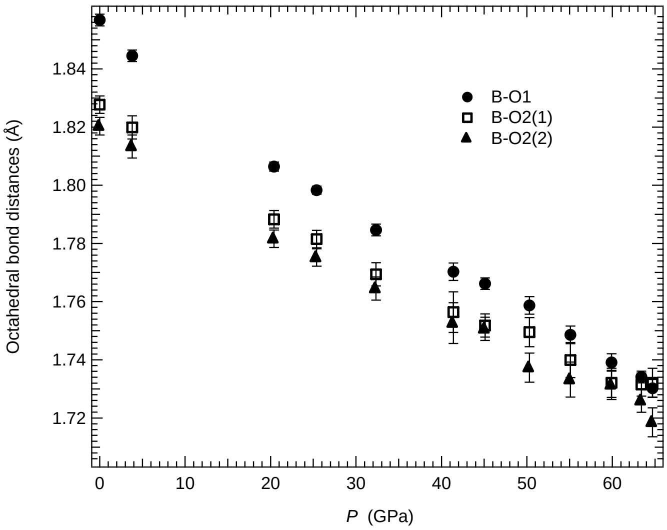

Fig. 1: Octahedral bond distances of Fe-Al-bearing perovskite as a function of pressure.

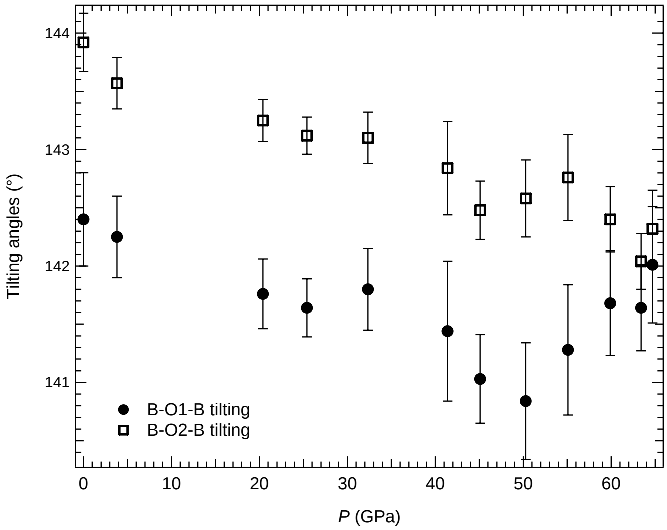

Fig. 2: Octahedral tilting angles of Fe-Al-bearing perovskite as a function of pressure

The distortion of both samples increases with pressure as indicated by the decrease in the octahedral tilting angles. In the case of the Fe-Al-bearing perovskite, however, there is a clear change in the behaviour of the B-O1-B tilting angle, which starts to increase at about 50 GPa (Fig. 2). This behaviour may be due to the possible high-spin low-spin transition of the Fe atoms.

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 perovskite at elevate pressures with the precision and accuracy of the single-crystal diffraction technique. Although the single-crystal experiments are still challenging, the set up at ID09A is clearly suitable for such studies and open a new series of experiments aimed at better constraining the behaviour of the Earth's interior.