

Structural distortion of MgSiO₃ perovskite and the influence of Fe and Al at pressures of the Earth's lower mantle

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The MgSiO₃ perovskite-type structure is considered the dominant phase in the Earth's lower mantle. As such a detailed understanding of its elastic properties and density as well as how such properties are affected by chemical substitutions are of great importance to mineral physics, seismology and geodynamics. Many studies have reported the compressibility of MgSiO₃ perovskite with or without additional element (mainly Fe and Al) substitution [1, 2, 3]. It has also been proposed that changes in the spin state of Fe at high-pressures may influence the compressibility of perovskite [4, 5]. Little is known, however, about the structural state of perovskite at very high pressures. Such knowledge is essential not only for constraining its physical-properties at lower mantle conditions, but also for understanding the structural instability leading to the perovskite to post-perovskite phase transition, which may cause complex seismic signatures within the D' layer.

We have studied three single-crystals of MgSiO₃ with the end-member composition and containing either Fe²⁺ or Fe³⁺ and Al by means of X-ray diffraction at the ID09 beam line of the European Synchrotron Radiation Facility. Intensity data have been collected up to 90 GPa at room temperature with diamond anvil cells loaded with He as pressure transmitting medium and ruby chips as pressure calibrants. All perovskites display with increasing pressure only a small increase of the octahedral tilting, but undergo major octahedral distortions, which are more pronounced in the Fe³⁺, Al-bearing perovskite. No evident structural changes associated with the Fe spin transition have been observed.

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Modelling the aqueous Al³⁺ System using Density Functional Theory

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We have shown (1) that the speciation of aqueous Al³⁺ is well described over a wide range of solution pH by Density Functional Theory calculations on gas phase Al(OH)_x(H₂O)_y^{(3-x)+} clusters embedded in a continuum solvent. Cluster geometry, electronic structure and Gibbs Free Energies all display similar trends suggesting increased acidity as the coordination number decreases. These results are in complete agreement with the observed cooperativity of Al³⁺ hydrolysis products (2).

Extending our model (3) to include coordination by an F⁻ counterion shows that this ligand coordinates the Al³⁺ cation in a similar way to the OH⁻ ligands thus inducing important changes in AlF(OH)_x(H₂O)_y^{(2-x)+} complexes in the direction of increased acidity, in agreement with the observed elevated acidity of natural waters in which AlF²⁺ species occur (4). Furthermore, in light of recent NMR observations (5) of a fast proton-coupled water exchange mechanism on Al³⁺ aqueous complexes, we suggest this mechanism is also present in the aqueous AlF²⁺ system.

Finally, a large array of Al₂(OH)_x(H₂O)_y^{(6-x)+} aqua/hydroxo Al³⁺ dimer species have been investigated. Our results suggest that many species are possible and their stability may be understood in terms of the number of coordinating water and hydroxide ligands and the hydroxide bridging geometry. This novel approach thus provides a revealing picture of the extremely complex aqueous Al³⁺ environment and may thus be of great use to the geochemical and environmental chemistry communities.

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