

Iron spin transition in bridgmanite revisited

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Iron is the most abundant transition metal in Earth minerals such as carbonates and silicates. When exposed to the high pressures and high temperatures that are expected in the Earth's mantle their electronic structure, e.g. the spin state of iron, can change. Both, Fe²⁺ and Fe³⁺ species in such minerals are in the high spin electronic state at ambient conditions and may undergo transitions from high spin to low spin state with increasing pressure as observed for e.g. siderite (FeCO₃), magnesiosiderite ((Mg,Fe)CO₃), and bridgmanite ((Fe,Mg)SiO₃).

In the case of the Fe-bearing magnesium silicate perovskite, recently named as bridgmanite, the Fe spin transition is complicated by the crystal chemistry, because Fe may occupy the A and B-site of the lattice and the Fe oxidation state may vary. The high spin to low spin transition was first observed using K β x-ray emission (XES) showing a gradual change of the iron's high spin and low spin fractions in the 30-70 GPa range and a sharp transition to the low spin state at 120 GPa [1]. Originally the gradual transition was assigned to the Fe³⁺ on the B-site and the sharp one to that of Fe²⁺ on the A-site [1,2]. Fe³⁺ on the A site is at all mantle pressures in the high spin state but due to diffusion from the A-site and oxidation of Fe²⁺ the Fe³⁺ content on B-site increases and is almost never negligible. [3,4]. This assignment above was challenged by later Mössbauer measurements that suggest the gradual transition [3] over a large pressure range to be due to the formation of Fe²⁺ with intermediate spin state on the A-site, based on the appearance of a doublet with unusually high quadrupole splitting above 30 GPa [5]. At 120 GPa the Fe²⁺ on the A-site converts to the low-spin state [6] consistent with earlier observations XES [1]. Despite those many studies on the transition in bridgmanite, the controversy still lingers on, as documented by latest review articles [2,4,7].

Here, our recent results on the spin-state of ferrous (Fe²⁺) and ferric (Fe³⁺) iron in bridgmanite will be presented and discussed in context to the results obtained by Badro et al. [1]. Preliminary analysis of the ferrous iron data implies that the results there [1] cannot be explained by a combination of our ferrous data and results obtained by Liu et al. [8] on ferric iron. In order to study the course of the spin transition and corresponding changes in local coordination we combine complementary x-ray spectroscopies, i.e. x-ray absorption (XAS) at the iron K-edge, iron K β and valence-to-core (vtc) x-ray emission (XES). Tracking changes in the coordination state and oxidation state we evaluate the Fe K-edge pre-edge feature position and intensity [9] from XAS. The XES experiments were performed using an energy dispersive

von Hamos type spectrometer in combination with a Pilatus area detector for simultaneous acquisition of Fe K β and vtc XES [10] together with XAS measurements. In previous experiments our group demonstrated a good agreement between x-ray emission and x-ray absorption like analysis of Fe L- and M-edge x-ray Raman scattering (XRS) [11]. Consequently, the combination of these methods will help to further constrain the spin state, local coordination and oxidation state of iron in ferrous and ferric bridgmanite at pressure aiming to solve the controversy on the iron's spin state in bridgmanite.

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