The spin state of Fe^{3+} in lower mantle bridgmanite

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As the most abundant mineral, the crystal chemistry of $MgSiO_3$–rich bridgmanite is fundamentally important to expand our knowledge on the Earth's interior and its evolution. Recent experiments and theory suggest that spin crossover of iron occurs in bridgmanite within the middle part of the lower mantle, however, the depth of the crossover is highly controversial so far. This is mainly due to two possible valence states (Fe^{2+} and Fe^{3+}) and the variable site occupancy of iron in bridgmanite. Here, we studied the valence and spin state of iron in well characterized Al-free Fe^{3+}-rich bridgmanite by Mössbauer spectroscopy to understand the effect of Fe^{3+} concentration on the spin state. We found that a minor amount (~ 15 % in total iron) of Fe^{3+} is in the low spin state above 36 GPa, and that the proportion does not largely increase up to 83 GPa. This is consistent with recent experimental studies by Mössbauer and X-ray emission spectroscopy in well characterized bridgmanite. The proportion of low spin iron was saturated at 40 GPa, and such saturation was observed at higher pressure in a previous study with higher amount of Fe^{3+}. In the Earth's deep lower mantle, spin crossover may take place below 900 and 1200 km depth in pyrolite and MORB, respectively. However, its effect on physical properties may be small due to the limited amount of Fe^{3+} in the low spin state.