

Partitioning of FeSiO₃ and FeAlO₃, Fe-spin state and elasticity for bridgmanite and post-bridgmanite

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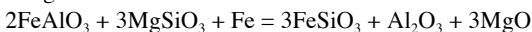
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Configurational Boltzmann averaging in the Gibbs ensemble with DFT (at GGA, GGA+U and HSE06 levels of theory) for compositions in the MgSiO₃-FeSiO₃ (MS-FS) and MgSiO₃-FeAlO₃ (MS-FA) systems, indicate that FS and FA partition in opposite directions, toward post-bridgmanite (pbm) and bridgmanite (bm), respectively. Our computational data are broadly consistent with the majority of experimental results.

Fe²⁺ and Fe³⁺ occupy the larger A-site in both minerals, whereas Al occupies the B-site. Our derived cation-oxygen distances and chemical bond analysis provide a plausible explanation for the partitioning and spin-state. Fe³⁺ (in FA) remains high spin at all relevant mantle conditions, since low spin configurations of Fe³⁺ are thermally inaccessible.

An isochemical bm-pbm transition within the investigated solid solution range (up to 25 mol% FS and FA) would imply decreasing bulk and increasing shear modulus. At a reference pressure of 100 GPa, the bulk modulus for bm and pbm increases by 1.4% and 1.0%, respectively, from MS to MS-FS_{12.5} and decreases by 0.4% and 0.2%, respectively, from MS to MS-FA_{12.5} (subscripts indicate mol%). The shear modulus decreases for both phases along both of the solid solution series from the pure MS composition, with the largest decrease along the FA-join. For bm and pbm the shear moduli decrease with 2.4% and 1.3%, respectively from MS to MS-FS_{12.5} and with 4.4% and 3.0%, respectively, from MS to MS-FA_{12.5}.

We determined a Clapeyron slope for the bm-pbm transition of 9.6 MPa/K for MS, decreasing to 8.4 and 8.1 MPa/K at 6.3 and 12.5 mol% FS and to 8.2 and 7.3 MPa/K at 6.3 and 12.5 mol% FA. A reaction from FA-rich bm and Fe-metal to FS-rich pbm produces additional Al₂O₃ and MgO:



In peridotite, the excess MgO and Al₂O₃ may dissolve in ferropericline and pbm, respectively. If pbm becomes Al-saturated, Ca-ferrite- (CF-) or Ca-titanite- (CT-) structured phases with the MgAl₂O₄-component may form. In basaltic rocks, MgAl₂O₄ will enter the CF-CT-phases, with excess MgO reacting with SiO₂ from silica-dominated phases to increase the MS-component of ppv.