

The redox state of the Earth's lower mantle

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The major lower mantle mineral bridgmanite has a strong affinity for Fe₂O₃. This appears to arise from an energetically favourable coupled substitution of Fe³⁺ and Al in the structure. In experiments performed at conditions of the top of the lower mantle in the presence of metallic iron bridgmanite has been found to contain significant amounts of Fe₂O₃. This means that bridgmanite contains a significant Fe₂O₃ component even at the lowest oxygen fugacity plausible for the lower mantle. If bridgmanite was formed at these conditions from material initially poor in Fe₂O₃ then disproportionation of FeO would have to occur to produce an assemblage of Fe₂O₃-bearing bridgmanite and iron metal. As the lower mantle likely was in place before the end of core formation it would have formed from material initially poor in Fe₂O₃. Iron metal should, therefore, have formed with bridgmanite. To provide sufficient Fe₂O₃ in the bridgmanite structure to balance a coupled substitution with Al₂O₃ would require the formation of approximately 1 weight % metallic iron.

A thermodynamic model has been developed to describe the speciation of FeO and Fe₂O₃ in minerals of the lower mantle as a function of pressure, temperature and oxygen fugacity. The model employs experimental data on the partitioning of iron components between ferropiclsase and garnet and determinations of the major bridgmanite substitution mechanisms. Using volume and equation of state data on end-member components this model can be extrapolated to conditions prevailing throughout most of the lower mantle. The results can be compared with the sparse experimental data obtained over these conditions. The model is used as a basis to calculate plausible seismic wave velocity profiles through the lower mantle. The implications for the early redox evolution of the mantle and the speciation of volatiles in the lower mantle can also be examined.