

The W-WO₂ Oxygen Fugacity Buffer at High Pressures and Temperatures: Implications for fO₂ Buffering and Metal-silicate Partitioning.

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Oxygen fugacity (fO₂) controls multivalent phase equilibria and partitioning of redox-sensitive elements, and it is important to understand this thermodynamic parameter in experimental and natural systems. The coexistence of a metal and its oxide at equilibrium constitutes an oxygen buffer which can be used to control or calculate fO₂ in high pressure experiments. Application of 1-bar buffers to high pressure conditions can lead to inaccuracies in fO₂ calculations because of unconstrained pressure dependencies.

Extending fO₂ buffers to pressures and temperatures corresponding to the Earth's deep interior requires precise determinations of the difference in volume (ΔV) between the buffer phases. Synchrotron x-ray diffraction data were obtained using diamond anvil cells (DAC) and a multi anvil press (MAP) to measure unit cell volumes of W and WO₂ at pressures and temperatures up to 70 GPa and 2300 K. These data were fitted to Birch-Murnaghan 3rd-order thermal equations of state using a thermal pressure approach; parameters for W are $K_T = 306$ GPa, $K_T' = 4.06$, and $\alpha K_T = 0.00417$ GPa K⁻¹. Two structural phase transitions were observed for WO₂ at 4 and 32 GPa with structures in P2₁/c, Pnma and C2/c space groups. Equations of state were fitted for these phases over their respective pressure ranges yielding the parameters $K_T = 190, 213, 300$ GPa, $K_T' = 4.24, 5.17, 4$ (fixed), and $\alpha K_T = 0.00506, 0.00419, 0.00467$ GPa K⁻¹ for the P2₁/c, Pnma and C2/c phases, respectively.

The W-WO₂ buffer (WWO) was extended to high pressure by inverting the W and WO₂ equations of state to obtain phase volumes at discrete pressures (1-bar to 100 GPa, 1 GPa increments) along isotherms (300 to 3000K, 100 K increments). The slope of the absolute fO₂ of the WWO buffer is positive with increasing temperature up to approximately 70 GPa and is negative above this pressure. The slope is positive along isotherms from 1000 to 3000K with increasing pressure up to at least 100 GPa. The WWO buffer is at a higher fO₂ than the IW buffer at pressures lower than 40 GPa, and the magnitude of this difference decreases at higher pressures. This qualitatively indicates an increasingly lithophile character for W at higher pressures. The WWO buffer was quantitatively applied to W metal-silicate partitioning by using the WWO-IW buffer difference in combination with literature data on W metal-silicate partitioning to model the exchange coefficient (K_D) for the Fe-W exchange reaction. This approach captures the pressure dependence of W metal-silicate partitioning using the WWO-IW

buffer difference and models the activities of the components in the silicate and metallic phases using an expression of the Gibbs excess energy of mixing. Calculation of K_D along a peridotite liquidus predicts a decrease in W siderophility at higher pressures that supports the qualitative behavior predicted by the WWO-IW buffer difference, and agrees with findings of others. Comparing the competing effects of temperature and pressure on W metal-silicate partitioning, our results indicate that pressure exerts a greater effect.