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The W-WO_2 oxygen fugacity buffer (WWO) at high pressure and temperature: Implications for f_{O2} buffering and metal-silicate partitioning

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Abstract

Synchrotron X-ray diffraction data were obtained to simultaneously measure unit-cell volumes of W and WO_2 at pressures and temperatures up to 70 GPa and 2300 K. Both W and WO_2 unit-cell volume data were fit to Mie-Grüneisen equations of state; parameters for W are K_T = 307 (±0.4) GPa, K'_T = 4.05 (±0.04), γ_0 = 1.61 (±0.03), and q = 1.54 (±0.13). Three phases were observed in WO_2 with structures in the $P2_1/c$, *Pnma*, and $C2/c$ space groups. The transition pressures are 4 and 32 GPa for the $P2_1/c$-*Pnma* and *Pnma*-$C2/c$ phase changes, respectively. The $P2_1/c$ and *Pnma* phases have previously been described, whereas the $C2/c$ phase is newly described here. Equations of state were fitted for these phases over their respective pressure ranges yielding the parameters K_T = 238 (±7), 230 (±5), 304 (±3) GPa, K'_T = 4 (fixed), 4 (fixed), 4 (fixed) GPa, γ_0 = 1.45 (±0.18), 1.22 (±0.07), 1.21 (±0.12), and q = 1 (fixed), 2.90 (±1.5), 1 (fixed) for the $P2_1/c$, *Pnma*, and $C2/c$ phases, respectively. The W-WO_2 buffer (WWO) was extended to high pressure using these W and WO_2 equations of state. The T-f_{O2} slope of the WWO buffer along isobars is positive from 1000 to 2500 K with increasing pressure up to at least 60 GPa. The WWO buffer is at a higher f_{O2} than the iron-wüstite (IW) buffer at pressures lower than 40 GPa, and the magnitude of this difference decreases at higher pressures. This implies 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 non-linear pressure dependence of W metal-silicate partitioning using the WWO-IW buffer difference. 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 the results here indicate that pressure exerts a greater effect on W metal-silicate partitioning.

Keywords: High pressure, tungsten, oxygen fugacity buffer, equation of state, metal-silicate partitioning