W-WO joins the deep Earth electrochemical series ⚓

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Abstract. The short-lived ^{182}W-^{182}Hf isotope system is useful for constraining early mantle and core differentiation processes (e.g., Klein et al. 2002), if its siderophile behavior is understood. With the publication of the bulk thermoelastic properties of the high-pressure polymorphs of WO_2 in the January issue of *American Mineralogist*, Shofner et al. (2016) determine the relative energetics of the W-WO system as a function of pressure and temperature, thus defining the W-WO redox equilibrium relative to Fe-FeO, Ni-NiO, and Co-Co, at deep Earth conditions. **Keywords:** Oxygen fugacity buffer, high pressure, equation of state, metal-silicate partitioning

The core/mantle boundary is the major interface governing mechanical and thermal mixing of the entire planet. The equilibrium position of this boundary, and the associated equilibrium compositions of the overlying oxide mantle and underlying metal core are determined by planetary-scale redox thermodynamics. The observed and inferred abundances of transition metals in the Earth's mantle can be interpreted in terms of core formation and core/mantle evolution processes if armed with the relevant thermodynamics: such as an analog of the familiar table of aqueous standard reduction potentials, but for geologically relevant metals, oxides, and silicates at conditions of planetary interiors. This "deep Earth electrochemical series" defines the relative thermodynamic stability of end-member metal-metal oxide equilibria (buffers[1]) and maps them as a function of pressure and temperature. The current library of relative energetics of metal-metal oxide systems extended to conditions of the Earth's deep mantle includes Fe-FeO (Fischer et al. 2011), Ni-NiO (Campbell et al. 2009), and Co-CoO (Armentrout et al. 2013). With the publication of Shofner et al. (2016), the W-WO system can be added as well. Thus the entire electrochemical series for transition metals throughout the pressure and temperature conditions of planetary interiors can begin to be assembled.

Shofner et al. use both multi-anvil press and laser-heated diamond-anvil cell techniques in conjunction with synchrotron-based X-ray diffraction to determine the phase diagram of WO_2, discovering an additional high-pressure polymorph. In addition, the bulk thermoelastic properties of the WO_2 polymorphs up to

~55 GPa and 2500 K were determined. Three parameters determine the pressure-volume relationship at a reference temperature (usually 300 K), and an additional three parameters determine the thermal pressure as a function of temperature at each volume, using a Mie-Gruneisen-Debye formalism. Together, the six parameters determine the density of each tungsten dioxide phase as a function of pressure and temperature—thus providing the total information of density, bulk modulus, and thermal expansion as a function of pressure and temperature, including cross derivatives. Because W was used as a reference material in these experiments, the relative *P-V* energetics of the W-WO buffer system can be calculated to pressures and temperatures of ~70 GPa and ~2250 K.

The energetics of metal-metal oxide systems can be equivalently determined in terms of the (Helmholtz) free energy difference, the oxygen fugacity, f_{O_2}, or as a standard reduction potential (e.g., Kavner et al. 2007). All of these conventions have an implicit reference state, which may be fictive, as in the case of f_{O_2} at deep Earth conditions. Figure 1 plots the energetics of four M-MO systems as a function of pressure and temperature down an Earthlike-adiabat. This plot shows that for all systems, the combination of pressure and temperature increases the free energy difference between the oxide and the metal—to first approximation, these four transition metals become increasingly siderophile in the Earth (a higher f_{O_2} is required to oxidize the metals). However, the curves on Figure 1 are not perfectly parallel, indicating that the buffer system energetics have different
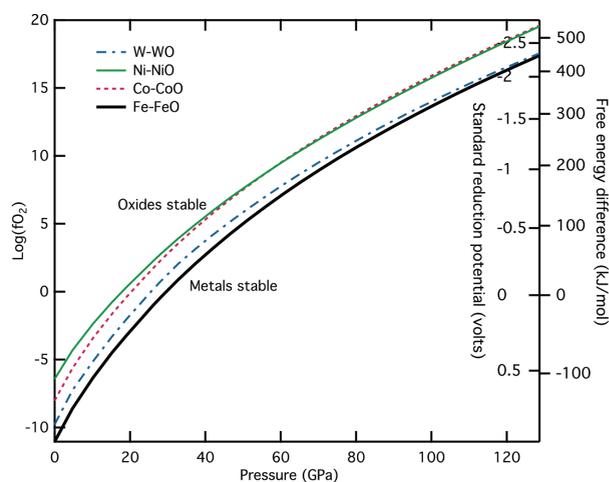
FIGURE 1. The energetics of metal-metal oxide systems as a function of pressure down a mantle adiabat. The left axis shows f_{O_2}. The right hand axis shows two equivalent measures of equilibrium energetics—free energy difference and a standard reduction potential for an electron transfer reaction.

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[1] Three qualifications permit a metal-metal oxide system to be useful as a buffer within a chemical system: (1) both metal and metal oxide are present in equilibrium. (2) The reservoirs of both the metal and metal oxide are large compared with the size of the system. (3) The kinetics of the metal-metal oxide reactions in both forward and reverse directions are fast compared with the rest of the system kinetics.
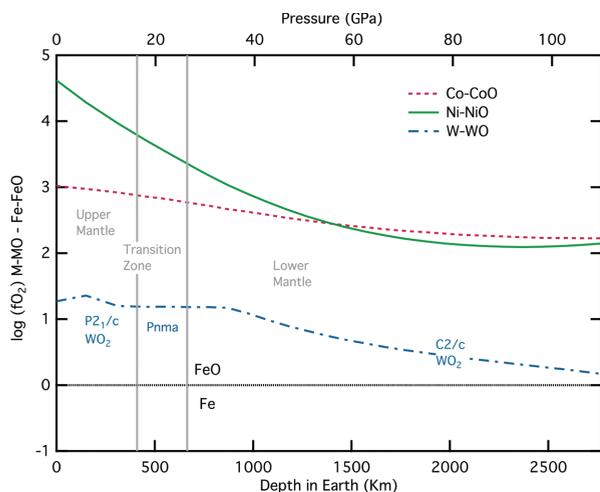
Figure 2. Metal-metal oxide equilibria with respect to the Fe-FeO equilibrium as a function of depth in the Earth (down an adiabat). The three polymorphs of WO_2 are seen as changes in slope. Crossovers are predicted in the W-Fe systems at depths corresponding to the core/mantle boundary and in the Ni-Co system at pressures and temperatures in the mid-lower mantle.

dependencies on pressure and temperature.

Figure 2 plots these different dependencies, showing the energetics of the buffer systems relative to iron-wustite as a function of depth. At lower pressures, the W, Ni, and Co equilibria all are above the I-W buffer, indicating their siderophile nature, and approach the Fe-FeO equilibrium with increasing pressure along a present-day Earth-interior adiabat, though with different behaviors. At pressures below 35 GPa, the W-WO system parallels the iron-wustite system, indicating little change in relative oxygen fugacity between the two systems in that pressure range, consistent with the conclusions from partitioning measurements between the Mo and W and iron systems by Wade et al. (2011). However, at lower mantle conditions, Shofner et al. show that W becomes less siderophile—predicting a crossover with the Fe-FeO at conditions close to the core-mantle boundary. To calculate the partition coefficients of W between core and mantle phases, Shofner et al. combine the W-WO equilibrium energetics with

estimates of the mixing energetics of multicomponent phases and determine a nonlinear pressure dependence of W partitioning between peridotite liquidus and core.

The real Earth is a multicomponent mixture, and end-member thermodynamics play only a partial role in determining partitioning behavior in a system that must include multiple phases, mixing energetics, and possibly non-ideal and/or non-stoichiometric behavior. This requires experimental tests targeting the systems of interest. One of the powers of Figure 2 is that it suggests optimal pressure and temperature ranges where more detailed petrological partitioning experiments can be performed. For example, the Ni-CoO = Co-NiO exchange reaction is predicted around 58 GPa and 2200 K, corresponding to a depth of 1400 km in the mantle. These crossover predictions are subject to solution effects and should thus be tested by a series of targeted high-pressure and temperature partitioning experiments to investigate the effects of speciation and solubility.

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