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Oxygen fugacity buffering in high-pressure solid media assemblies from IW-6.5 to IW+4.5 and application to the V *K*-edge oxybarometer

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Abstract

Control of oxygen fugacity during high-temperature phase equilibrium experiments is required to simulate the conditions that exist in natural systems. At high pressures, oxygen fugacity may be imposed using solid buffer equilibria via the classic "double capsule" technique. This design becomes untenable, however, at temperatures above the melting points of commonly used noble metal capsule materials and/or where buffer assemblages may alloy with the capsule or contaminate the sample. Here we introduce and test a modified double capsule approach that includes a solid metal-oxide buffer in close proximity to but separate from the sample of interest. Buffers used include (in order of most oxidized to reduced) Ni-NiO, Co-CoO, W-WO_3, Fe-FeO, Mo-MoO_2, Cr-Cr_2O_3, V-V_2O_3, Ta-Ta_2O_5, and Nb-NbO. At a fixed temperature, these buffers span a wide range—up to 10 log f_{O_2} units. To demonstrate the buffering capacity of this double capsule approach, secondary redox equilibria and V-doped CaO-MgO-Al_2O_3-SiO_2 system glasses were studied in experiments using the double capsule geometry. The secondary equilibria provide an independent verification of the oxygen fugacity established in the double capsule environment. The glasses proved difficult to interpret, and our results provide guidance to future efforts to utilize the glass oxybarometer at reducing conditions. Application of this modified double capsule technique to studies of V valence in $MgAl_2O_4$ spinels led to the recognition of several factors that will affect V valence in this system: temperature of equilibration, duration of experiment, and spinel bulk composition. We have synthesized V-bearing $MgAl_2O_4$ spinel at the reduced conditions of the Cr-Cr_2O_3, (IW-3.51), Ta-Ta_2O_5, (IW-5.37), and Nb-NbO buffers (IW-5.44). This spinel exhibits a very small V^{3+} pre-edge peak consistent with its reduced nature. The absence of evidence for V^{2+} suggests that $MgAl_2O_4$ spinel excludes V^{2+} due to the preference of V for octahedral sites. This finding is supported by DFT calculations for spinels of variable composition, and in agreement with some other indirect evidence for preference for V^{3+} in aluminous spinels (Bosi et al. 2016; Paque et al. 2013).

Keywords: Oxygen fugacity, spinel, XANES, solar nebula