

OXYGEN BUFFERING IN HIGH PRESSURE SOLID MEDIA ASSEMBLIES: NEW APPROACH ENABLING STUDY OF fO_2 FROM IW-4 TO IW+4.5.

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Introduction: Oxygen fugacity is an intensive parameter that controls some fundamental chemical and physical properties in planetary materials [1]. In terrestrial magmas high fO_2 promotes magnetite stability and low fO_2 causes Fe-enrichment due to magnetite suppression. In lunar and asteroidal basalts, low fO_2 can allow metal to be stable. Experimental studies will therefore be most useful if they are done at a specific and relevant fO_2 for the samples under consideration. Control of fO_2 in the solid media apparatus (piston cylinder multi-anvil) has relied on either sliding sensors or graphite capsule buffering, which are of limited application to the wide range of fO_2 recorded in planetary or astromaterials. Here we describe a new approach that allows fO_2 to be specified across a wide range of values relevant to natural samples.

Experimental approach: The approach taken is use of a double capsule where the outer capsule is the metal of the buffer, and inside the bottom of the outer capsule is a layer of the oxide portion of the buffer. The inner capsule is a standard MgO capsule that contains the sample of interest (Fig. 1). This inner capsule could be alumina or graphite as well, but here it is MgO. Metal-oxide pairs used for the initial series were – in order of most oxidized to most reduced – Ni-NiO, Co-CoO, Mo-MoO₂, Fe-FeO, W-WO₂, Cr-Cr₂O₃, V-V₂O₃, and Nb-Nb₂O₅. The fO_2 defined by these pairs was calculated using thermodynamic data, mainly from [2], as well as [3-5] (Fig. 2). The samples were loaded into a 13 mm non-end-loaded piston cylinder assembly, with BaCO₃ pressure medium, a graphite furnace, with temperature monitored using a Type C thermocouple [6]. Samples were pressurized to 1 GPa, and heated to 1400 °C, and held for 6 hours before power quenching to room temperature.

Results: Results fell into several categories: a) simple buffer intact (Cr-Cr₂O₃, Mo-MoO₂, Fe-FeO, Ni-NiO, and Co-CoO), b) metal reacted with MgO to form a third phase that participates in the buffering (MgWO₄), and c) oxide entirely reduced (V₂O₃ and Nb₂O₅) leaving only the metal (V, Nb). Buffering in the latter two did not work, but we plan repeat attempts to stabilize the oxide part of the buffer.

Applications: Our samples in the inner capsule were MgAl₂O₄ spinel doped with a small amount of V, with the goal to calibrate the vanadium valence with fO_2 for spinels of this composition and then apply the results to natural systems such as CAIs, and other small primitive clasts or particles for which standard redox barometers may be absent. Additional applications are numerous and might include metal-silicate or mineral-melt element partitioning, phase equilibria studies, or mineral or melt syntheses.

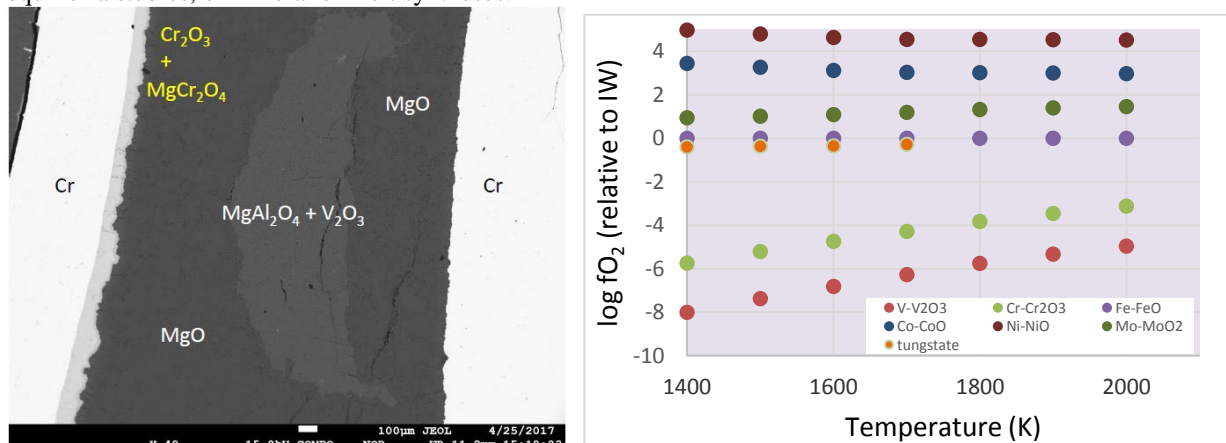


Figure 1 (left): BSE image of double capsule experiment with a Cr outer capsule (white), Cr₂O₃ layer at left inside edge of Cr capsule (light gray), and MgO inner capsule containing MgAl₂O₄+V₂O₃. Figure 2 (right): Calculations of fO_2 for each of the buffers used, relative to iron-wustite. At the temperature of our experiments (1673 K), the range of fO_2 covered is from IW+4.5 to IW-4; temperature dependence of most buffers is weak.

References: [1] Righter, K. et al. (2016) Amer. Mineral. 101, 1928-1942. [2] Barin, I. (1995) Thermochemical Data of Pure Substances, 3rd Ed., Wiley-VCH Verlag GmbH, Germany. [3] Raghavan, S. and Kay, D.A.R. (1990) Thermochim. Acta, 170, 13-17. [4] O'Neill H. St.C. and Pownceby, M. I. (1993) Contrib Mineral Petrol 114, 296-314. [5] Jacob, K.T. et al. (2010) J. Chem. Eng. Data 55, 4854–4863.