

Vanadium valence in MgAl_2O_4 spinels at reducing conditions (IW to IW-5). K. Righter¹, A.L. Butterworth², Z. Gainsforth², K. Iacovino³, T. Erickson³, C. E. Jilly-Rehak⁴, R. Rowland^{3,5}, S. Fakra⁶, A.J. Westphal²; ¹Mailcode XI2, NASA Johnson Space Center, Houston, TX 77058; kevin.righter-1@nasa.gov. ²Space Sciences Laboratory, University of California Berkeley, Berkeley, CA 94720. ³Jacobs-JETS, ARES NASA Johnson Space Center, 2101 NASA Pkwy., Houston, TX 77058; ⁴Dept. of Geological Sciences, Stanford University, Stanford CA 94305; ⁵Los Alamos National Laboratory, Mail Stop P952, Los Alamos, NM 87545; ⁶Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720,

Introduction: Vanadium is commonly a major or minor element in spinel structured oxides from a wide range of planetary materials [1-3]. Vanadium is stable in multiple valence states of 5+, 4+, 3+, and 2+ in natural systems, and spinel-structured oxides are known to host vanadium in 4+, 3+, and 2+ [4-6]. The relation between $f\text{O}_2$ and valence has been utilized as an oxybarometer at IW-1 and above [5]. However, the extension of the oxybarometer to low $f\text{O}_2$ conditions, in the stability field of 2+ has been hindered by lack of experiments at or below IW-1 conditions [5]. These experimental data are lacking due to the difficulty in controlling $f\text{O}_2$ at reducing conditions in general and to the lack of appropriate standards for comparison to natural materials. Our progress on controlling $f\text{O}_2$ in high pressure experimental samples has allowed us to create reducing conditions at specific $f\text{O}_2$ values appropriate to studying V valence in spinels at low $f\text{O}_2$ relevant to chondrules, CAIs, and reduced differentiated bodies [7]. Here we extend this approach to study V in reduced conditions at high temperatures and pressures. Results from experiments at multiple temperatures and durations demonstrate the need for equilibration times > 6 hours at 1600 °C in order to approach equilibrium. Only then can we produce highly equilibrated samples that provide new insights into V valence at low $f\text{O}_2$.

Experimental approach: To create reducing conditions, we used Cr-Cr₂O₃, Ta-Ta₂O₅, and Nb-NbO metal-oxide buffers, which define $f\text{O}_2$ at IW-3.5, IW-5.2, and IW-5.4, respectively, as calculated using thermodynamic data [8]. We used a double capsule design where the outer capsule is the metal of the buffer. A bottom layer of the companion buffer oxide was placed inside the outer [7]. A sample of high purity spinel $\text{MgAl}_2\text{O}_4 + 1 \text{ wt\% V}_2\text{O}_3$ was packed within an MgO inner capsule.

The samples were loaded into a 13 mm non-end-loaded piston cylinder apparatus, using a BaCO₃ pressure medium, graphite furnaces, and temperature monitored with either a Type C (up to 1400 °C) or Type B thermocouple (1400-1600 °C). Samples were pressurized to 1 GPa, heated to the run temperature, and held for the desired length of time (up to 70 hrs) before turning the power off to quench to room temperature. Run products were mounted in epoxy and sectioned for analysis by SEM, EMPA, and X-ray Absorption Near Edge Structure (XANES) spectroscopy.

Analytical approach: Run product textures and overall mineralogy was surveyed using a JEOL 7600F FEG-SEM, and metal-oxide and silicate phases were analyzed with a JEOL 8530 FE Hyperprobe. V in glasses was analyzed at the hard X-ray synchrotron beamline 10.3.2, situated at a bend magnet source at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The ALS operates at 1.9 GeV, 500 mA current, and beamline 10.3.2 provides up to 10⁹ photons/s at 6 keV. We took 2 μm spatial resolution X-ray fluorescence multi-element maps to select a single phase area, then acquired cumulative V K-edge XANES spectra from one to three spots on each sample (5 x 2 μm). The spectra were deadtime corrected, energy-calibrated with a V metal foil standard, and normalized following the method in [9].

Results: Verification of the buffer was done by SEM, EBSD, and EMPA. SEM was used to image the textures and EMPA to confirm stoichiometry of the oxide phase. For example, the experiment with the Ta-Ta₂O₅ buffer had a ~100 μm thick layers of Ta metal and Ta₂O₅. The use of a Mo outer capsule in some cases was to maintain capsule integrity while including the metal half of the buffer along with the oxide in the bottom of the outer Mo capsule. NbO was the oxide recovered in many experiments which is critical to calculation, because Nb₂O₅ was used as a starting material and anticipated at stable oxide at run conditions. Confirmation of the cubic structure of the NbO was made using non-destructive EBSD on the run products (Fig. 1).

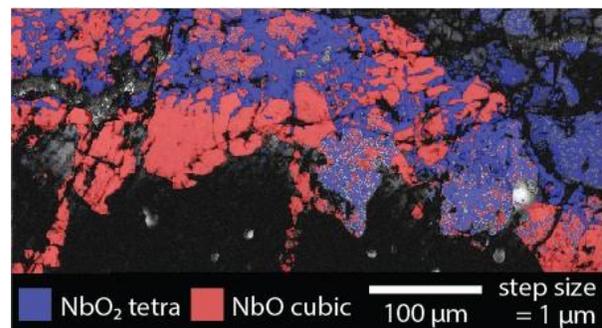


Figure 1: EBSD imaging highlighting in red the distinctive cubic structure of NbO.

Equilibration times of spinels must consider the generally slower diffusion rates of many transition or trivalent elements such as Cr, Fe³⁺, Al [10,11]. Experiments at low temperatures (1400 °C) and 6 hr duration had some unreacted or less equilibrated portions, suggesting that longer equilibration times and/or higher temperatures were required to equilibrate MgAl₂O₄ spinels at these conditions (Fig. 2). Therefore we carried out 6-hr experiments at 1500 and 1600 °C in addition to a time series of experiments with run durations ranging from 0.5 to 70 hrs at 1600 °C. Experiments of longer duration and higher temperatures utilized the Type B thermocouples because the Type C thermocouples oxidized and failed after very short (30 min) run times. Products from all 1600 °C runs longer than 6 hrs exhibited equilibrated textures without any evidence for zoning or unreacted material (Fig. 3).

Analyses of the V K-edge XANES pre-edge peaks (Figure 4) following the method of [9] calculated an effective vanadium valence (V*) of 2.3±0.2. Thus these results extend beyond the spinel V* calibration in [5]. This low V* confirms the successful equilibration of spinel in a highly reduced (IW-5) environment.

Conclusions: Spinel equilibrated at reducing conditions exhibit evidence for low V contents. The reduced spinels have a very small K XANES pre-edge peak. The magnitude of the peak seems to decrease at low fO₂, but not at the same slope as V pre-edge peaks change at higher fO₂. The low fO₂ range must be calibrated specifically within the range rather than extrapolated from more oxidized conditions.

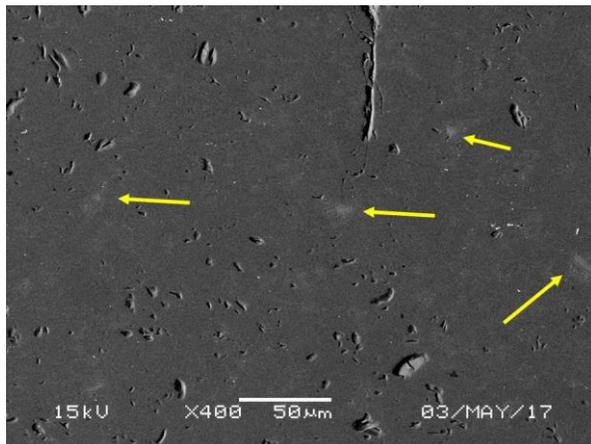


Figure 2: 1400 °C experiment (6 hrs) with bright patches indicating unreacted materials and zoning of V.

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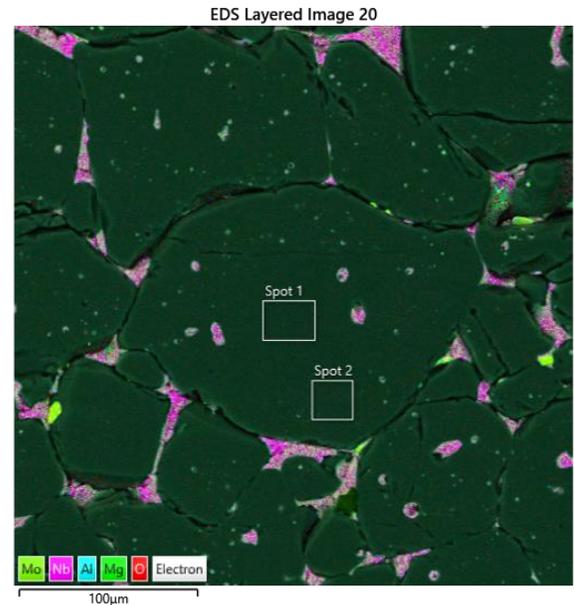


Figure 3: 1600 °C experiment at Nb-NbO buffer (70 hrs) with more equilibrated textures and lack of zoning seen at lower temperatures.

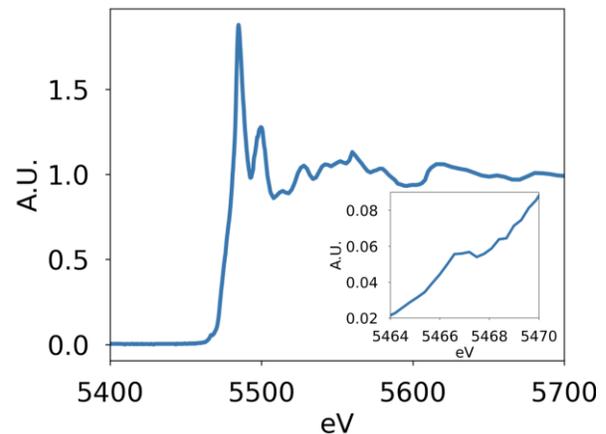


Figure 4: V-K XANES spectrum of spinel from Spot 1 of Figure 3. Inset shows that the pre-edge intensity (estimated 0.015 height) is very low.

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