DEVELOPING V-XANES OXYBAROMETRY FOR PROBING MATERIALS FORMED IN REDUCING ENVIRONMENTS IN THE EARLY SOLAR DISK. A.L. Butterworth[1], Z. Gainsforth[1], C. E. Jilly-Rehak[1], K. Righter[2], and A. J. Westphal[1]. [1]University of California Berkeley, Space Sciences Laboratory, 7 Gauss Way, Berkeley, CA 94720. [2]Johnson Space Center, Houston, TX 77058. Email: annab@ssl.berkeley.edu.

Introduction: Vanadium exhibits four oxidation states (V^{2+}, V^{3+}, V^{4+}, and V^{5+}) that have been shown to preferentially partition between melt phases dependent on redox conditions, spanning oxygen fugacity across more than 10 log units [1]. We are developing synchrotron-based x-ray absorption spectroscopy of low-fugacity standards for the determination of V oxidation state in highly reducing conditions relevant to the early solar nebula.

Development of V oxybarometers has progressed significantly in recent years, particularly for V^{3+}, V^{4+} and V^{5+}, equivalent to environments with log(fO_2) > -12. A V K-edge XANES oxybarometer was calibrated (@1400°C) with glasses [2] then expanded to chromian spinels [3] and spinel-olivine-glass melts [4].

K-edge based oxybarometers depend on pre-edge features (1s–3d transitions) and edge position to probe oxidation states. Advantages of a K-edge based oxybarometer includes the relative simplicity of interpreting pre-edge features. Modeling tools to interpret K-edge spectra have been well established, for example first-principles calculations based on the density functional theory (DFT) [5].

One limitation of the V K-edge oxybarometer is the calibrated oxygen fugacity range. The glasses available to constrain the initial calibrations range between log (fO_2) ~ -5 (mainly V^{5+}) down to log (fO_2) ~ -12, at 1400°C, (mainly V^{3+}). The oxybarometer [2] extrapolated from V^{3+} to V^{2+} assuming a V^{2+} pre-edge peak height of zero.

Another potential limitation of K-edge synchrotron techniques is spatial resolution. High resolution, sub-micron hard X-ray *micro*XANES applications (approaching 100 nm beamspot) must still consider several-μm penetration depth. Thicker rock sections or sample fine-scale heterogeneity may hide sub-surface inclusions that could contaminate spectra.

L-edge techniques include soft X-ray synchrotron XANES and TEM EELS. Both techniques are capable of higher spatial resolution than K-edge XANES (<10 nm) at V L-edge.

The $L_{2,3}$ 2p-3d multiplet structure is sharp and more sensitive to combined effects of valence state, site symmetry, and crystal field strength than K-edge features. V^{2+} L-edge spectra also show strong features in contrast to 1s-3d pre-edge. This is especially important for low abundance V (<0.3 wt%) in primitive meteorite spinels.

Interpretation of L-edge spectroscopy is generally less well-developed than for K-edge simulations. In contrast with the K-edge approach, the entire L_{23} spectrum must be analyzed for interpretation. High quality ab initio calculations of the L-edge of metal oxide compounds, including Ti and V, are being actively developed [6,7]. So far, models apply to a relatively narrow range of mineral structures and compositions, meaning no universal models exist for V $L_{2,3}$ spectra. As far as we know, there is no tool to determine precise (fO_2 determination within ±0.5 log units) V^{2+}/ V^{3+} calibrated for spinels appropriate for probing micro-environments of primitive, reduced solar system materials (such as spinels in chondrules and CAIs).

Our approach is to continue the development of V, Ti oxybarometers for astromaterials, focusing on magnesian spinel formed in reducing environments, log (fO_2) < -12. We are beginning with existing standards [3], and also synthesizing new standards, with V^{2+} or Ti^{3+}, to probe lower fO_2.

Samples and Methods: We have analyzed chromian spinel samples, which were previously used to extend the V K-edge oxybarometer [3], Table 1. We acquired multi element spectra at both K- and L-edges: Fe, Cr, Ti, V K-edge XANES and EXAFS at ALS Beamline 10.3.2, and Fe, Cr, Ti, V L-edges plus Al, O K-edges XANES at ALS 11.0.2. For μXAS Beamline 10.3.2, we used the original polished samples of spinel/melt pairs embedded in epoxy. We prepared FIB sections of these samples for L-edge work at ALS 11.0.2 (Scanning Transmission X-ray Microscope, STXM) and TEM. FIB and TEM work was carried out at the National Center for Electron. FIB liftouts were cut using an FEI DualBeam FIB with Ga^+ at 30 and 6 keV. Atom

Location by CHanelling Enhanced Microanalysis (ALCHEMI) was done on the Titan to determine the sites of cations.

Using this approach we aim to anchor our V K-spectra to previous results, and enabling quantitative interpretaion of L-edge spectra.

Table 1: Samples analyzed, from [3]

Spinel/Melt Buffer & Dopant	Log fO_2, 1300°C	ΔIW 1300°C
IW	–11.15	–0.40
IW, V+5%	–11.15	–0.40
IW, Ti+10%	–11.13	–0.38
IW-1	–12.09	–1.51

IW = Iron-Wüstite buffer

The IW-1 sample microprobe characterization was (in wt%) 43.3 Cr_2O_3, 1.0 V_2O_3. 16.22 FeO, 13.99 MgO [3].

Results: Figs 1 and 2 show example V spectra taken from one sample, "Experiment IW-1", which is our lowest fO2 available standard. In Fig. 1, we also show for comparison an L-edge XANES spectrum for Stardust particle "Iris", thought to be a fragment of a Type II chondrule [8]. The spectra are qualitatively similar, predominantly V^{3+}.

We now have a complete description of the four chromian spinel-structure oxides, including formation fO_2, composition, site occupancy and multi-element K-edge spectra, we will use DFT and multiplet theory to simulate each of the spinels. Vanadium composition ranges from major element to minor abundance.

Discussion: The K-edge simulations will provide the basis for developing a model for L-edge interpretation. We are preparing low oxygen fugacity spinel standards at JSC, aiming to create samples with significant V^{2+} (and Ti^{3+} [9]). Subsequent availability of lower fO_2 V-bearing spinel samples will then allow us to extend the range of the K-edge oxybarometer.

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References: [1] Papike, P. V. et al., (2005) *Am. Min.* 90, 277.. [2] Sutton S. R. et al. (2005) *GCA 69*, 2333-2348. [3] Righter K. et al. (2016) *Am. Min. 101,* 1928-1942. [4] Papike, P. V. et al., (2013) *Am. Min.* 98, 2193. [5] Cabaret, D. et al., (2010) *Phys. Chem. Chem. Phys.*, 12, 5619. [6] Hoche T., et al., (2013) Am. Min. 98, 665. [7] Brik M. G., et al., (2006). *The Euro. Phys. J. B* 51: 345. [8] Gainsforth Z. et al, (2015), *MaPS* 50, 976. [9] Righter et al., (2017) LPSC.

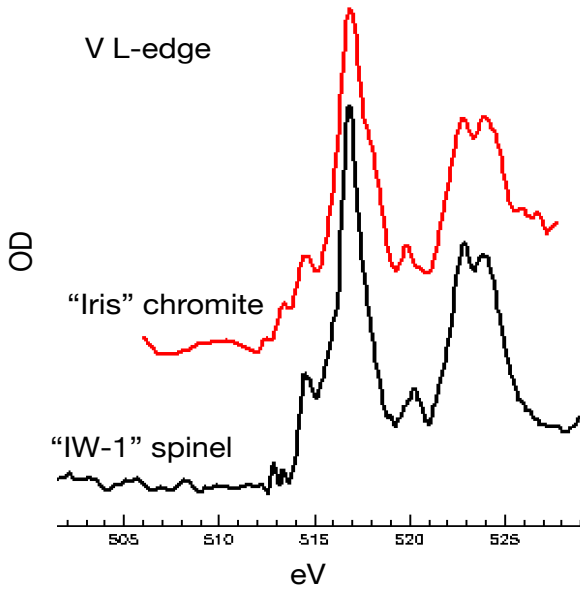

Fig 1. V L- XANES spectra of Stardust particle "Iris" [8] and qualitatively similar spectra acquired on chromian spinel "IW-1" from [3].

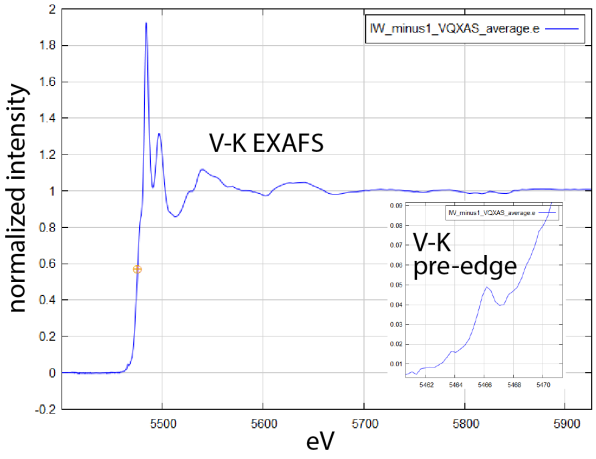

Fig 2. V K-edge spectra the same chromian spinel "IW-1" from [3]. Spectrum is high resolution EXAFS, the inset shows pre-edge XANES region for comparison with [1]).