V XANES IN SPINELS AS AN OXY-BAROMETER IN METEORITES WITH IMPLICATIONS FOR REDOX VARIATIONS IN THE INNER SOLAR SYSTEM.

K. Righter[1], S. Sutton[2], L. Danielson[3], K. Pando[4], L. Le[3], and M. Newville[2]. [1]NASA-JSC, 2101 NASA Pkwy., Houston, TX 77058 (kevin.righter-1@nasa.gov), [2]GSECARS University of Chicago, 9700 South Cass Avenue, Bldg. 434A, Argonne, IL 60439; [3]ESCG, Jacobs Engineering, Houston, TX 77058; [4]ESCG, Hamilton Sundstrand, Houston, TX 77058

Introduction: The variation of oxygen fugacity within inner solar system materials spans a range of nearly 15 orders of magnitiude [1]. Igneous and metamorphic rocks commonly contain a mineral assemblage that allows oxygen fugacity to be calculated or constrained such as FeTi oxides, olivine-opx-spinel, or some other oxybarometer [2]. Some rocks, however, contain a limited mineral assemblage and do not provide constraints on fO2 using mineral equilibria. Good examples of the latter are orthopyroxenites or dunites, such as diogenites, ALH 84001, chassignites, or brachinites. In fact it is no surprise that the fO2 of many of these achondrites is not well known, other than being "reduced" and below the metal saturation value. In order to bridge this gap in our understanding, we have initiated a study of V in chromites in achondrite. Because the V pre-edge peak intensity and energy in chromites varies with fO2 (Fig. 1) [3], and this has been calibrated over a large fO2 range, we can apply this relation to rocks for which we otherwise have no fO2 constraints.

Samples: We have selected a suite of samples for which there are no phases for use of standard oxybarometers, and for which there are large and accessible chromites: ALH84001 (martian orthopyroxenite), EET 99402 and ALH 84025 (brachinites), GRA 06128/129 (ungrouped achondrites), ALH 77256 and GRA 98108 (diogenites), ALH 77081, EET 84302, MAC 88177, MET 01198, RBT 04228 (acapulcoites/lodranites), and QUE 99679 (CK chondrite).

XANES and EMPA measurements: All major elements in spinels were analyzed with a CAMECA SX100 electron microprobe, using an accelerating voltage of 20 kV, sample current of 20 nA, and standardization and corrections as described in [3]. Measurements of the valence of V were made using synchrotron microXANES (*X*-ray *A*bsorption *N*ear-*E*dge *S*tructure) spectroscopy (SmX), at the Advanced Photon Source (APS), Argonne National Laboratory (beamline 13-ID, the Consortium for Advanced Radiation Sources or CARS). SmX measurements are made by focusing a monochromatic (cryogenic, Si (111) double crystal monochromator) X-ray beam (3x3 μm) from the synchrotron onto a spot on the sample and measuring the fluorescent X-ray yield from that spot as a function of incident X-ray energy. Changes of fluorescent X-ray intensity and energy of features in the XANES spectrum (notably the pre-

edge peak) depend on oxidation state and coordination (e.g., [4,5]). In the present work, the intensity of the XANES pre-edge
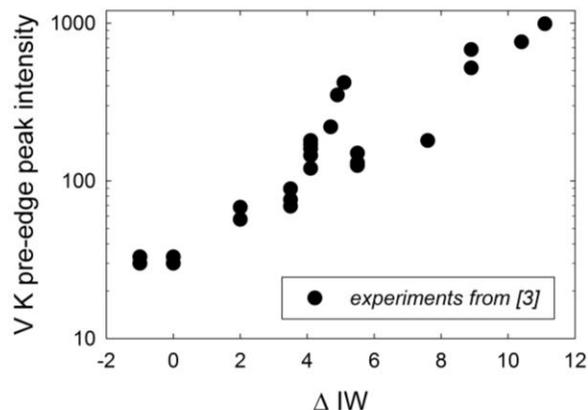
Figure 1: Correlation of V K pre-edge peak intensity with ΔIW for spinels in the experiments of [3].

peak at ~5470 eV was used to determine V oxidation state based on the technique described by [3], where analyses of spinel and glass produced under known fO2 conditions are used for calibration.

Results: The V pre-edge peak intensity for all samples measured ranges from 14 at the low end (defined by the acapulcoite-lodranite group) to ~ 75 at the high end (defined by the CK chondrite QUE 99679). (Fig. 2). In general, the acapulcoites are most reduced progressing to more oxidized diogenites, GRA 06128, brachinites, ALH 84001, to CK chondrites (Fig. 2). There are several noteworthy points here. First, the lodranite-acapulcoite suite seems very reduced, perhaps as much as 2 log fO2 units below the IW buffer. Second, GRA 06128 and the brachinites are similar and oxidized near IW, but distinctly different from each other. The similarity of oxidation state but different Mg# could be the result of differentiation processes. Third, our measurements of chromites in ALH 77256 and GRA98108 yield values betweem IW-1.5 and -0.5, in agreement with the range estimated for eucrites formation (ΔIW = -1 [6]). Fourth, ALH 84001 is more oxidized than these metal-bearing meteorites. There has been debate regarding its oxygen fugacity; some have argued an oxidized fO2 near FMQ [7], while others have argued a more reduced value, well below FMQ [8,9]. The pre-edge peak intensities measured here are consistent with values of

FMQ-2.7 estimated for ALH 84001 by other techniques such as mineral equilibria or Eu/Gd partitioning in pyroxenes [8]. Finally, CK chondrite spinels are the most oxidized, in agreement with calculations of [10]. There is a correlation of Mg# with oxidation state of V that is consistent with the general idea of oxidation in the presence and absence of metal (Fig. 2).
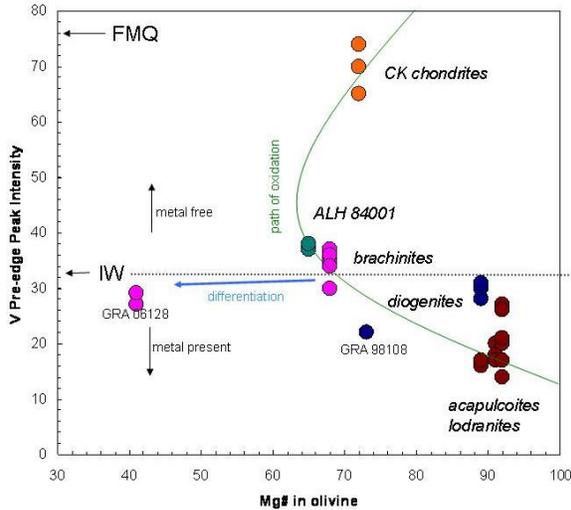
Figure 2: V K pre-edge peak intensity and Mg# in olivines from samples measured in this study. Arrows on the vertical axis show the pre-edge peak intensities corresponding to two valence ratios and FMQ, the former determined by a glass/spinel calibration [5] and the latter determined by synthetic spinels [3]. FMQ and IW refer to the fayalite-magnetite-quartz and iron-wüstite buffers.

These results imply that there may be substantial V^{2+} in spinels at low fO_2s. However, the vanadium valence calibration for spinel at low pre-edge peak intensities needs more work and should be extended to $fO_2 < IW-2$. As the pre-edge peak intensity decreases going from V^{3+} to V^{2+}, there should be an accompanying energy shift to lower energies in the main edge region and the main edge spectral shape should change to some extent. For example, comparing VO and V_2O_3 in [4], the main edge shifts by about 1 eV. Energy shifts of that magnitude were not observed for these spinels, and the main edge region of all these spectra is pretty similar. Spinel may behave differently in this regard compared to other oxides. It is also conceivable that the pre-edge peak intensity is lowered because the symmetry of the V crystallographic site (largely responsible for the intensity of the pre-edge) is changing without valence reduction. We will carry out additional experiments targeted in this low fO_2 region in an attempt to better constrain the valence calibration.

Summary: Our new measurements allow fO_2 estimates to be made for several achondrite groups for which traditional barometry is not possible. These new values are compared to previous measurements and calculations for achondrite groups. Current and previous work is in good agreement for HED and acapulcoites. Altogether these groups define 8 log fO_2 units and exhibit nearly continuous variation from the reduced aubrites to the most oxidized angrites (Figure 3).

References: [1] Righter et al. (2006) MESS II paper. [2] Frost, B.R. (1991) RIMS 25, 1-9; [3] Righter, K. et al. (2006) *American Mineralogist* 91, 1643-1656; [4] Wong, J. et al. (1984) Phys. Rev. B, 30, 5596-5610; [5] Sutton, S.R. et al. (2005) GCA 69, 2333-2348; [6] Stolper, E. (1977) GCA 41, 587-611; [7] Herd C. D. K. and Papike J. J. (1999) LPS XXX, 1503; [8] Righter, K. et al. (2008) *Met. Planet. Sci.* 43, 1709-1723; [9] Righter, K. and Drake, M.J. (1996) *Icarus* 124, 513-529; [10] Righter, K. and Neff, K. (2007) *Polar Sci.* 1, 25-44; [11] Righter, K. et al. (1990) *GCA 54*, 1803-1815; [12] Goodrich, C.A. et al. (2013) *GCA 122*, 280-305.
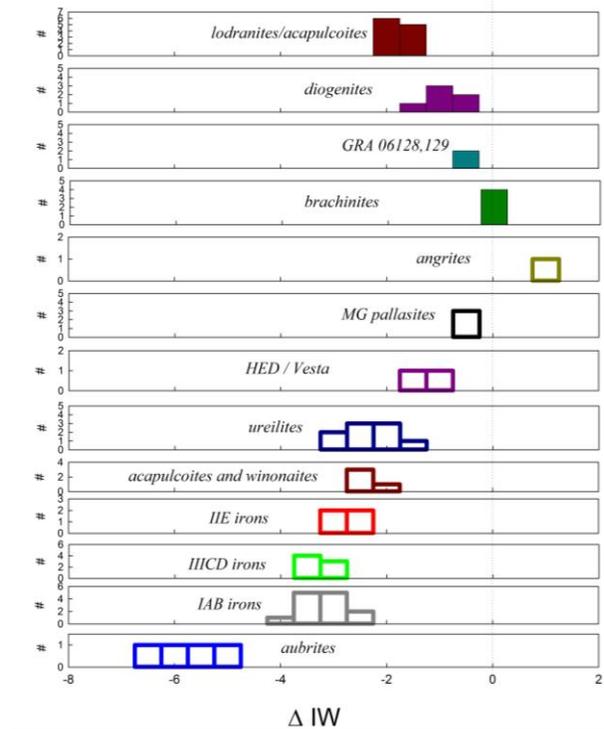
Figure 3: Histogram of ΔIW values from this work (solid bars) and values from previous work determined by thermodynamic calculations, electrochemical measurements, and Cr XANES (open bars); the latter are from references in [1], [9], and [11],[12].