USING VANADIUM IN SPINEL AS A SENSOR OF OXYGEN FUGACITY IN METEORITES: APPLICATIONS TO MARS, VESTA, AND OTHER ASTEROIDS. 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: 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 [1]. Some rocks, however, contain a limited mineral assemblage and do not provide constraints on fO_2 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 fO_2 of many of these samples 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 natural meteorite samples. Because the V pre-edge peak intensity and energy in chromites varies with fO_2 (Fig. 1) [2], and this has been calibrated over a large fO_2 range, we can apply this relation to rocks for which we otherwise have no fO_2 constraints.

Samples: We have selected a suite of samples for which there are no available phases for standard oxybarometers, and for which there are large and accessible chromites. ALH84001 is a martian orthopyroxenite, for which there has been some debate regarding its oxygen fugacity; some have argued an oxidized fO_2 near FMQ [3], while others have argued a more reduced value, well below FMQ [4,5]. Brachinites are olivine-rich achondrites that also contain chromite, plagioclase and pyroxene. They have recently been linked to the ungrouped achondrite GRA 06128/129, via O isotopes, age, and composition [6-8]. Chromites in EET 99402, ALH 84025, and GRA 06129 were measured and compared to assess whether they record comparably oxidized conditions. Diogenites contain orthopyroxene and chromite, and although they have been linked to eucrites and the HED parent body which is thought to be ~ IW-1 [9], there have not been redox estimates for diogenites. We have measured chromites in ALH 77256 and GRA98108, and can compare the results to previous estimates related to the HED parent body. Finally, we have analyzed a suite of lodranites and acapulcoites again because the redox conditions in this parent body have not been discussed in detail, yet seem to be of fundamental importance on understanding and constraining the processes that led to their formation. All samples were provided by MWG except for the acapulcoites/lodranites (J. Herrin), GRA 06128 (A. Treiman), and ALH 84001 (M. Righter).

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 [2]. Measurements of the valence of V were made using synchrotron micro-XANES (***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., [10,11]). In the present work, the intensity of the XANES pre-edge peak at ~5470 eV was used to determine V oxidation state based on the technique described by [2], where analyses of spinel and glass produced under known fO_2 conditions are used for calibration.

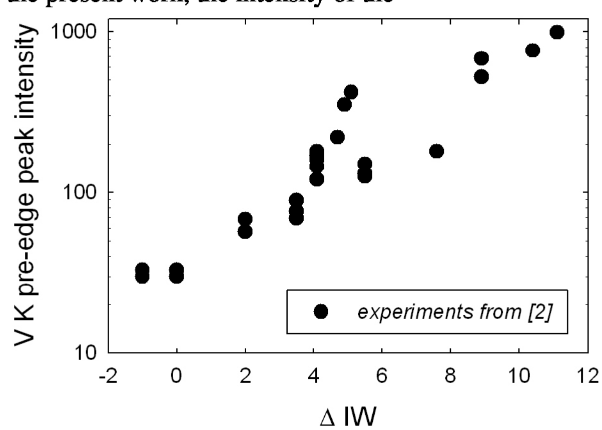

Figure 1: Correlation of V K pre-edge peak intensity with oxygen fugacity for spinels in the experiments of [2].

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). There is a general progression from the acapulcoites to diogenites to GRA 06128 to brachinites to ALH 84001 to terrestrial basalts to the CK chondrites (Fig. 2). There are several noteworthy points here. First, the lodranite-acapulcoite suite seems very reduced, perhaps as much as 2 log fO_2 units below the IW buffer. Second, GRA 06128 and the brachinites are similar, but distinctly different from each other. They are more oxidized than the acapulcoites, lodranites, and GRA 98108 diogenite, however, which suggests that they may both have come from a more oxidized parent body. Third, ALH 84001 is more oxidized than these metal-bearing meteorites, but more reduced than terrestrial basalts that have equilibrated at FMQ-2. These 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 [4]. Finally, CK chondrite spinels are the most oxidized, in agreement with the calculations of [12]. 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. 3).

These results imply that there may be substantial V^{2+} in spinels at low fO_2s. However, the vanadium valence calibration for spinel at these very low pre-edge peak intensities may not be well constrained. 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 [10], 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. However, 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.

References: [1] Frost, B.R. (1991) RIMS 25, 1-9; [2] Righter, K. et al. (2006) *American Mineralogist* 91, 1643-1656; [3] Herd C. D. K. and Papike J. J. (1999) LPS XXX, 1503; [4] Righter, K. et al. (2008) *Met. Planet. Sci.* 43, 1709-1723; [5] Righter, K. and Drake, M.J. (1996) Icarus 124, 513-529; [6] Shearer, C.K. et al. (2008) Amer. Mineral. 93, 1937-1940; [7] Ash, R.D. et al. (2008) LPS XXXIX, 2271; [8] Zeigler, R. et al. (2008) LPS XXXIX, 2456; [9] Stolper, E. (1977) GCA 41, 587-611; [10] Wong, J. et al. (1984) Phys. Rev. B, 30, 5596-5610; [11] Sutton, S.R. et al. (2005) GCA 69, 2333-2348; [12] Righter, K. and Neff, K. (2007) Polar Sci. 1, 25-44.

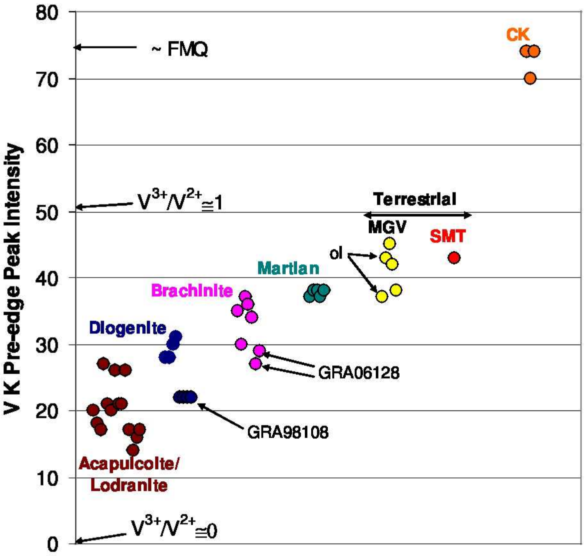

Figure 2: V K pre-edge peak intensity for acapulcoites, lodranites, diogenites, brachinites, martian orthopyroxenite ALH 84001, two terrestrial basalts, and CK chondrites. FMQ refers to the fayalite-magnetite-quartz buffer. Arrows on the vertical axis show the pre-edge peak intensities corresponding to two valence ratios and FMQ, the former determined by a glass/spinel calibration [2] and the latter determined by synthetic spinels as part of this work (figure 1).

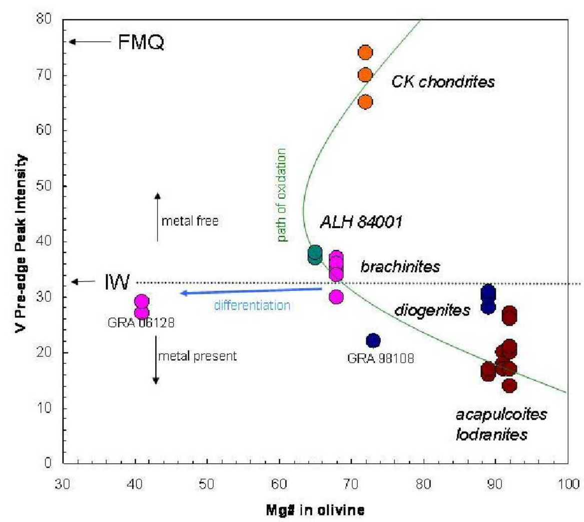

Figure 3: V K pre-edge peak intensity and Mg# in olivines from samples measured in this study. The variation in Mg# with oxidation is as expected in the metal-present field. This trend reverses in the metal-free field above IW [12]. The similarity of oxidation state in GRA 06128 and brachinites, but different Mg# could be the result of differentiation processes.