UNGROUNDED ACHONDRITE NWA 7325: TITANIUM, VANADIUM AND CHROMIUM XANES OF MAFIC SILICATES RECORD HIGHLY-REDUCED ORIGIN. S.R. Sutton1,2, S. Wirick2, and C.A. Goodrich3. 1Dept. of Geophysical Sciences and 2Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637 USA (sutton@cars.uchicago.edu). 3Planetary Science Institute, 1700 E. Ft. Lowell, Tucson, AZ 85719 USA.

Introduction: NWA 7325 is an ancient refractory achondrite suggested to be a possible Mercury sample based on bulk element ratios, very low Fe content and comparison with Messenger data [1,2]. Because of its apparent refractory nature, we have applied microscale XANES spectroscopy methods to define Ti, V and Cr valences in its mafic silicates (olivine and pyroxene) in an attempt to constrain the oxidation state of the crystallizing igneous system. Redox buffers involving multivalent elements are useful for this purpose because they are sensitive to differing oxygen fugacity regimes and therefore can record a wide dynamic range in oxidation state conditions [3].

Methods: The sample consisted of a thin section of NWA 7325 and derived from a few gram fragment of the meteorite. The Zeiss EVO 50 XVP scanning electron microscope at U. Mass, was used for SEI/BEI/EDS observations. The Cameca SX-50 electron microprobe at U. Mass was used to determine mineral compositions. Olivine (Fo 97.5) and pyroxene (diopside, Wo 45.3, mg# 98.2) grains for XANES analysis were identified using BEI.

Vanadium and Cr XANES spectra were collected using the X-ray microprobe at Beamline X26A at the National Synchrotron Light Source (NSLS), Upton, NY. A channel-cut Si(111) monochromator was used to feed monochromatic, bending magnet X-rays to a dual K-B mirror system which focused the beam to ~7 μm [4]. Titanium XANES spectra were collected using the X-ray microprobe at Beamline 13-ID-E (GSECARS) at the Advanced Photon Source (APS), Argonne, IL. A channel-cut Si(111) monochromator was used to feed monochromatic, undulator X-rays to a dual K-B mirror system which focused the beam to ~1 μm [5]. XANES spectra were measured in fluorescence mode using quad Vortex Silicon Drift Detectors (SDD) to collect Kα intensities as the incident energy was scanned through the appropriate absorption edges.

Vanadium valence method (offering determinations for V2+, V3+, V4+ and V5+) followed that of [6] using the normalized intensity of the 1s→3d pre-edge peak. Chromium valence method (Cr2+, Cr3+) used the normalized intensity of the derivative spectrum peak near 5994 eV produced by a 1s→4s electronic transition [4]. Titanium valences (Ti3+, Ti4+) were obtained using the energy and intensity of the 1s→3d pre-edge peak [7]. Estimated valence precisions were near 0.05 (1σ) in all cases.

Results: Here we report the valence results for Ti, V and Cr in olivine and pyroxene.

Chromium: Seventeen (17) analyses were obtained on 13 olivine grains, each consisting of a merged spectrum combining 3 or 4 spectra at different crystal orientations [4]. The mean Cr valence was 2.12 with a standard deviation of 0.04, i.e., highly reduced and Cr2+-dominated. Four pyroxene spots were analyzed with a mean valence of 2.67 ± 0.05, i.e., somewhat more oxidized than the olivine and Cr2+-dominated. The pyroxene result assumes that the valence calibration demonstrated to be valid for olivine [4] is also valid for pyroxene, a reasonable assumption considering that Cr occurs in octahedral sites in both phases.

Vanadium: Vanadium spectra were obtained for the same 13 olivine grains and 3 of the 4 pyroxene spots. All olivine spectra were merged to obtain a single valence result and similarly for the pyroxene, a process intended to correct for orientation effects, although the similarity of the spectra suggested that orientation effects are minor. The olivine spectra were dominated by V2+ and the pyroxene spectra by V3+ (Fig. 1). Significantly, these are the most reduced natural V K XANES spectra ever measured by us. The valence results for olivine and pyroxene were 2.34 ± 0.05 and 2.60 ± 0.05, respectively, highly reduced consistent with the Cr results. The table in Fig. 1 shows the peak energies of the derivatives of the two merged spectra are consistent with those of V3O2 and V5O3, respectively [8].

Titanium: Ti K XANES spectra were obtained at the APS on three olivines and one pyroxene. Surprisingly, the valence of 3.44 ± 0.06 obtained for a merge of the three olivine spectra indicated a significant content of Ti3+. High levels of Ti3+ have been observed in olivine from other reduced meteorites, such as enstatite chondrites [9] and low metamorphic grade ordinary chondrites [7, 10] as well as in CAI fassaite [5]. Pyroxene yielded a valence of 3.84 ± 0.09, i.e., Ti4+-dominated.

Discussion: The olivine is dominated by Cr2+ and V2+ with roughly equal proportions of Ti3+ and Ti4+, i.e., highly reduced, whereas the pyroxene has a more oxidized valence state, mostly Cr2+, V3+ and Ti4+. Some of the valence difference between the two phases might be due to differences in valence state partitioning, in particular that olivine may incorporate species approximately equally but pyroxene may have a
preference for the smaller, more oxidized member of a redox pair. For example, lunar basalts have significant Cr$^{2+}$ in olivine but only Cr$^{3+}$ in pyroxene [11], and experimental work shows that basaltic olivine incorporates both Cr$^{2+}$ and Cr$^{3+}$ [12].

Fig. 2 is an attempt to estimate $f_{O_2}$ from the olivine results using the typical redox buffer conditions of Papike et al. [3]. In this scheme, the Ti valence suggests ~IW-7, vanadium ~ IW-5 and chromium ~IW-2 to -3. The Cr result is consistent with our $f_{O_2}$ estimate for high–Fo ureilite olivine with the same valence [4]. Thus, there is some discrepancy between the three redox indicators. Most likely, these differences reflect the buffer modifications by the precise conditions of the NWA 7325 igneous system, such as melt composition and structure. Another possibility is that Cr, and possibly V, have been slightly oxidized during the secondary event in this rock (shock reheating? [1, 14]) whereas the Ti redox has been unchanged (sluggishness of Ti$^{3+}$ oxidation has been suspected in CAIs [e.g. 13]). Also, shown in Fig. 2 is the “Cr metal-Cr oxide” buffer at ~IW-4.5 [12]. Since metal appears to be rare in this rock [1, 14], this buffer would seem to represent a $f_{O_2}$ lower limit, unless metal was present during olivine crystallization and subsequently consumed in the secondary metamorphism. Thus, the olivine data suggest $f_{O_2}$ near the “Cr metal-Cr oxide” buffer or possibly slightly lower. Cr-bearing sulfides are quite common supporting a reduced environment. Rare Cr$^{3+}$-bearing phases (chromite, eskolaite) have been observed [1] suggesting somewhat more oxidizing conditions perhaps related to the secondary event.

A similar comparison for pyroxene is consistent with an $f_{O_2}$ near the “Cr metal-Cr oxide” buffer for Ti and V but Cr is more oxidized, most likely reflecting the preference of pyroxene for Cr$^{3+}$.

Overall, the XANES results indicate that NWA 7325 has an highly-reduced oxidation state. This is consistent with the near-Sun environment of Mercury, but also with some components of ureilites or a previously unsampled achondrite parent body [14].