MICROANALYSIS OF NIOBIUM IN IRON METEORITES. M. Humayun[1] and A. J. Campbell[1], [1]Dept. of the Geophysical Sciences, The University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637, USA (hum8@midway.uchicago.edu).

Introduction: Niobium and tantalum are generally regarded to be lithophile incompatible elements occurring in chondritic relative proportions in planetary materials [1]. Precise Nb/Ta data have indicated that Nb may be depleted in the Earth's mantle [2, 3] which may be evidence for sequestering in an eclogite reservoir [2], or for its removal into the core [3, 4]. Metal-silicate partitioning experiments have indicated that Nb, but not Ta, may behave in a weakly siderophile manner, and predict abundances of 15-50 ppb in iron meteorites [4]. Bulk analysis of iron meteorites by spark source mass spectrometry reported Nb abundances of 7-40 ppb correlated with V and Cr abundances [5], apparently consistent with the predictions above. We report the results of a microanalytical investigation of V, Cr, Nb, Zr, Hf and Ta abundances in metal, troilite, schreibersite and cohenite from iron meteorites using laser ablation ICP-MS. The elements above (with the exception of Cr) were found to be below detection limits in metal, phosphide and carbide phases, but V, Cr and Nb were found to be present in troilite, particularly from IAB irons.

Analytical Methods: Polished slabs of iron meteorites were obtained, and phases identified using a JEOL JSM5800LV Scanning Electron Microscope. Laser ablation ICP-MS analysis of mineral phases was performed at The University of Chicago using a CETAC Transgenomics LSX-200 laser ablation system coupled to a ThermoFinnigan Element1 high resolution ICP-MS. A large spot size (50-100 μm) was used in line scan mode [6] to produce a bright, stable ion signal from the sample. Peaks monitored in low resolution included ^{7}Li, ^{29}Si, ^{31}P, ^{34}S, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{89}Y, ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{93}Nb, ^{94}Mo, ^{95}Mo, ^{180}Hf, ^{181}Ta, and ^{182}W. Intensities were normalized to Fe, and converted to abundances using intensities determined on NIST SRM 1263a, a V-Cr steel doped with Zr, Nb, Mo, Hf, Ta and other trace elements. A terrestrial pyrite was used for S calibration. Blanks were determined prior to each measurement, and the 3σ variability of the blank used to determine the detection limits which were 1-3 ppm for V, Cr and Mn, and 0.1-2.0 ppb for Y, Zr, Nb, Hf, and Ta, depending on the spot size used.

Following the identification of Nb in IAB troilites at very substantial count rates (up to 8×10^3 cps), the Canyon Diablo troilite mass spectrum was scanned at mass resolving power of M/ΔM~5000 at m/e= 88-96 to confirm the identity of the peaks. Mass calibration was checked using the positions of the Mo peaks (92, 94, 95, 96).

Results: Metal from the Group IIAB irons Negrillos, Coahuila, Filomena and Mount Joy had Nb below detection limits of <0.1 ng/g. Similarly, metal from Hoba (IVB), Santa Luzia (IIA), Cape York (IIIA), Canyon Diablo (IAB) and Youndegin (IAB) all had V, Y, Zr, Nb, Hf and Ta below detection limits. Schreibersite (Fe, Ni_3P) from Santa Luzia and Youndegin had Zr, but no detectable V, Nb, Hf or Ta. Cohenite (Fe_3C) from Youndegin had no detectable V, Nb, Hf or Ta. The elements V, Cr and Nb were found in all troilites measured, including those from Youndegin, Canyon Diablo, Santa Luzia, and Cape York, but high abundances of Nb (400-700 ppb) were found only in troilites from Canyon Diablo and Youndegin (**Fig. 1**). Neither Zr nor Ta (**Fig. 1**) were detected in these troilites, with Ta <0.1-2 ppb. To confirm the presence of Nb, measurements were repeated with larger spot sizes which showed that the ^{93}Nb+ signal correlated with beam size. Both Cr and Nb correlate with V abundances in the various troilites. The correlation between V and Cr obtained by LA-ICP-MS is more precise than, but identical to, that observed by XRF measurements of troilite nodules from iron meteorites [7].

Potential interferences: Since Nb is monoisotopic, the peak position of ^{93}Nb+ was checked in the Canyon Diablo troilite at a mass resolving power of M/ΔM~5000 to eliminate possible interferences from ^{186}W++, ^{53}Cr^{40}Ar+, ^{61}Ni^{32}S+ or polyatomic ions. NIST SRM 612 glass, which has ~40 ppm Y, Zr, Nb, Mo, etc., was scanned under the same conditions for comparison. A slight mass offset between actual mass positions and those measured was corrected using the peak positions of Mo+ ions at m/e= 92, 94, 95 and 96, bracketing the peak position of ^{93}Nb+. No resolvable interferences were found. Mass scans of the spectrum in low resolution showed that isobaric interferences from Cr, Mn, Fe, Co and Ni were limited to ^{56}Fe^{40}Ar+ at 96. No detectable interferences of the other three isotopes of CrAr+ were observed at other masses monitored in the 89-96 region, and a MAr+/M+ $<10^{-5}$ was obtained for the first-row transition metal argides in this mass range.

Discussion and Implications: Niobium is a refractory element and, therefore, all meteoritic or planetary bodies have approximately similar Nb abundances (250-500 ppb). The presence of Nb, but the exclusion of Ta, in troilites is a surprising result from an elemental partitioning standpoint. Niobium has the same charge (+5) as V and Ta, but its ionic radius is similar to that of Ta (0.064 nm), and larger than that of V (0.054 nm) in octahedral coordination. The chalcogenic tendencies of V and Cr were well known [e.g., 7], and both Nb and Ta will form sulfides [8]. Carbides of Nb and Ta are well known too, but the absence of these elements from cohenite indicates that partitioning as carbides is not important, here. The absence of Nb from the metal phase of even the most reduced iron meteorite group (IIA), and from the metal phase of other irons, is evidence against a siderophile character. Low pressure experiments (2.5 GPa) [4] had indicated the presence of 15-50 ppb of Nb at oxygen fugacities that may characterize iron meteorites, while SSMS results indicated 7-40 ppb in bulk irons [5]. The LA-ICP-MS results show that this Nb is not present in Fe-Ni metal, but that Nb may be present in troilite inclusions within bulk iron meteorites. Further, minor amounts of S (3.5%) present in the experiments of Wade and Wood [4] may have played a more important role in Nb partitioning into Fe-FeS metal than the role of pressure. The one issue that is not readily understood here is the presence of Nb mainly in troilite from IAB irons. The elements V, Cr and Nb mutually correlate. Of these, only Cr partitions into Fe-Ni metal at the 10-100 ppm level. The other major hosts for these elements are the silicate phases in planetary bodies. The partitioning of V, Cr and Nb between silicate and sulfide phases must be controlled by the sulfur fugacity of the system, and in this regard it is noteworthy that IABs are the irons from which ubiquitous sulfide nodules are best known. A simple prediction of our findings would be that silicate phases from IABs should exhibit Nb/Ta depletions, which is testable. Since IAB irons are not inferred to derive from large parent bodies, such Nb depletions if observed could not be attributed to a high pressure effect [4], as has been argued for the Earth and Mars [e.g., 5].

In addition to the large observed Nb/Ta ratio, the LA-ICP-MS data indicate that the Nb/Zr ratio is extremely large, too, making troilite a phase of potential interest for ^{92}Nb-^{92}Zr chronometry in the early solar system [9, 10, 11, 12]. The p-process nuclide ^{92}Nb, present at ^{92}Nb/^{93}Nb~ 10^{-3} [9, 10], decays to ^{92}Zr with a half-life of 36±3 m.y. This offers a potentially important means of determining the timing of isotopic closure of IAB troilites, including Canyon Diablo troilite, the established source of the solar system's initial Pb isotopic composition [13]. The $f^{Nb/Zr}$ in the two troilites measured were >430 (Youndegin) and >1755 (Canyon Diablo). By comparison, the highest $f^{Nb/Zr}$ reported from rutiles from IABs is <35 [9]. Using the formalism of [9], the inferred ^{92}Zr enrichments are >15% (Youndegin) and >70% (Canyon Diablo), but the measurements will be challenging given the very low Zr contents, and the high Mo/Zr ratios in these troilites.

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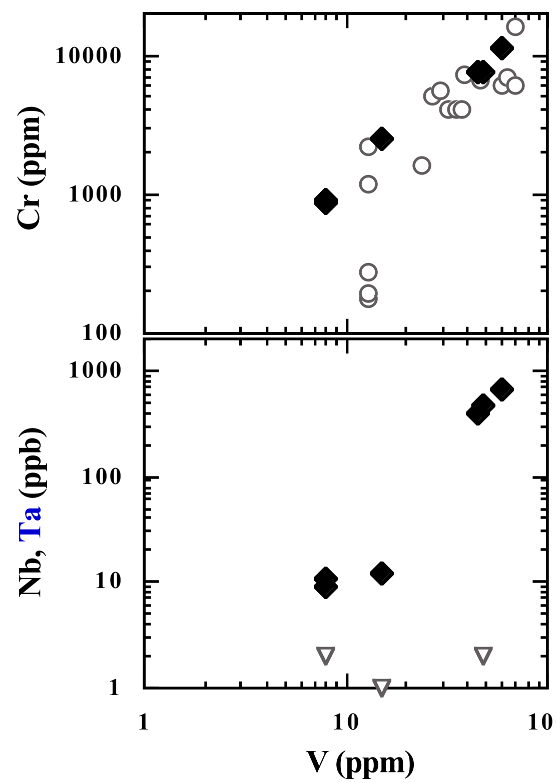

Fig. 1: V vs. Cr, Nb (diamonds) and Ta (inverted triangles, detection limits only) in meteoritic troilites by LA-ICP-MS. In order of decreasing V abundances: Youndegin IAB, Canyon Diablo IAB (duplicates), Santa Luzia (IIAB), and Cape York (IIIAB, duplicates). XRF measurements of V vs. Cr (open circles [7]) shown for comparison.