**THE DISTRIBUTION OF MOLYBDENUM IN THE INDARCH EH4 CHONDRITE.** D. L. Cook<sup>1</sup>, M. Humayun<sup>1</sup>, and A. J. Campbell<sup>1</sup>, <sup>1</sup>Department of the Geophysical Sciences, The University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637, davecook@uchicago.edu.

**Introduction:** The enstatite chondrites are highly reduced meteorites, characterized by abundant Fe-Ni metal, nearly Fe-free silicates, and unusual sulfides [1]. Due to the extreme degree of reduction, elements more siderophile than Fe should be expected to be wholly contained in the metal phase. However, abundance data for bulk metal separates from EH and EL chondrites reported by [2] showed that the siderophile elements Ir, Os, Ru, and Mo were depleted, whereas W was enriched. Equilibrium condensation of these elements from a gas of solar composition is not predicted to form an Fe-Ni alloy enriched in W yet depleted in Ir, Os, Ru, and Mo, which are all more refractory than Ni and Fe [3]. Thus, a volatility controlled process is unlikely to be solely responsible for the observed pattern in enstatite chondrite metal. Furthermore, W and Mo, which have nearly identical redox behavior [4], were fractionated by a factor of approximately 1.7. [2] suggested the Mo depletion in the metal may be due to a sulfide host phase. Molybdenum was detected in troilite separates from the Khairpur EL6 chondrite, but the absolute abundances were unknown [5]. Moreover, sulfide-silicate partitioning experiments showed that Mo does not behave as a strongly chalcophile element and that partitioning into iron sulfide decreased with increasing S and Ni contents of the sulfide phase [6]. Thus, it is unclear whether the sulfide phases in enstatite chondrites provide a significant sink for Mo. In order to determine if the Mo depletion and the W-Mo fractionation observed in the bulk metal phase of enstatite chondrites is due to chalcophile behavior of Mo, we performed in-situ analyses of potential host phases in the Indarch EH4 chondrite using laser ablation ICP-MS. We report abundances of Mo in Fe-Ni metal, troilite (FeS), niningerite ((Mg,Mn,Fe)S), oldhamite (CaS), and pyroxene.

Analytical Methods: A polished thick section of Indarch (ME 1403) was first examined via scanning electron microscopy (JEOL 5800-LV, University of Chicago) to select phases suitable for laser ablation analysis. Grains were chosen based on two criteria. First, analyses were restricted to mineral grains  $\geq 50$ µm in order to avoid ablation of adjacent grains and to ensure accurate analysis of the target grains. Second, only grains free of inclusions of additional phases were chosen.

Analyses of the individual phases were performed at The University of Chicago using a CETAC LSX-200 laser ablation system in conjunction with a Finnigan Element magnetic sector ICP-MS [7]. Single point analyses were made on individual grains using a laser spot size 25  $\mu$ m in diameter, which produced ablation pits 15 to 30  $\mu$ m deep. The isotopes monitored included <sup>7</sup>Li, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>60</sup>Ni, <sup>95</sup>Mo, and <sup>101</sup>Ru. During each analysis, the mass spectrometer was repeatedly swept across the mass range of interest, with sampling times of 30 ms (<sup>7</sup>Li, <sup>57</sup>Fe, <sup>60</sup>Ni, and <sup>55</sup>Mn) or 60 ms (<sup>95</sup>Mo and <sup>101</sup>Ru) per peak per sweep.

Instrumental sensitivity factors for each isotope relative to <sup>57</sup>Fe were determined by measuring the signal intensity of standards with known concentrations of the elements of interest. Two standards were employed: the National Institute of Standards and Technology standard reference material 1263a (Fe, Ni, Mn, and Mo) and the IIA iron meteorite Filomena (Ru). Intensities were converted to elemental abundances using internal standardization [7] by normalizing to Fe, for which the concentration was independently determined previously during the SEM reconnaissance via EDS analysis.

All analyses were blank corrected. Blank values were determined from the average of six measurements of the background; three measurements were made before the first grain analysis, and three additional measurements were made after approximately two-thirds of the selected grains were analyzed. Detection limits were set as three standard deviations of these six background measurements. Data were corrected for an isobaric interference on <sup>95</sup>Mo due to <sup>55</sup>Mn<sup>40</sup>Ar<sup>+</sup>. This correction was significant only for the niningerite analysis, in which case Mo was below the detection limits.

**Results:** Molybdenum measured in three metal grains ranged from  $2.6 \pm 0.3$  (1 $\sigma$ ) to  $3.3 \pm 0.4$  ppm, with an average value of  $2.9 \pm 0.2$  ppm, in agreement with the average value for EH bulk metal reported by [2]. Concentrations measured in four troilite grains ranged from  $4.1 \pm 0.4$  to  $7.8 \pm 0.6$  ppm, with an average value of  $5.1 \pm 0.3$  ppm. The molybdenum concentration in an oldhamite grain was  $0.5 \pm 0.2$  ppm. Molybdenum was below detection limits (0.3 ppm) in niningerite (one analysis) and pyroxene (two analyses).

The average Ru concentration in the metal grains  $(3.1 \pm 0.2 \text{ ppm})$  is similar to the average value for EH bulk metal reported by [2]. Ruthenium was below detection limits (0.4 ppm) in all sulfide phases analyzed and in pyroxene (0.3 ppm). Nickel was present in all troilite grains and ranged from 965 ± 8 to 8210 ± 22

ppm. Concentrations were lower in niningerite  $(105 \pm 9 \text{ ppm})$  and oldhamite  $(229 \pm 6 \text{ ppm})$  and were below detection limits (32 ppm) in pyroxene.

Discussion: The presence of Mo in troilite indicates that Mo displays chalcophile, as well as siderophile, behavior in Indarch. Such behavior could explain the Mo depletion and W-Mo fractionation observed in bulk metal from enstatite chondrites (Fig. 1) [2]. All three metal grains analyzed in Indarch exhibit Mo depletions similar to those in the metal from other enstatite chondrites [2]. Furthermore, the absence of Mo in Indarch pyroxene and the low Mo concentration in oldhamite, coupled with the low abundance of oldhamite in Indarch [1], suggest that other than Fe-Ni metal, troilite is the only additional major host phase for Mo. However, because pyroxene is the dominant phase in enstatite chondrites [1], pyroxene could potentially host a substantial portion ( $\approx 14\%$ ) of the Mo budget even if Mo is present at a concentration below the detection limits (e.g., 0.2 ppm). Conversely, given the highly reduced nature of the enstatite chondrites, Mo is unlikely to occur in silicates.

[5] estimated that the relative Mo concentration in troilite from the Khairpur EL6 chondrite was about one-third of the concentration in the metal, but a lack of standards prevented the calculation of absolute abundances. Conversely, we find that Mo in Indarch is enriched in troilite relative to metal. The average values for the concentrations in the metal and troilite correspond to a D<sup>sulfide-metal</sup> value of approximately 1.8. Thus, Mo behaves as a weakly chalcophile element in Indarch. Such behavior is consistent with the partitioning of Mo into iron sulfide observed by [6].

No bulk Mo data for enstatite chondrites have been reported. Therefore, we calculated the bulk Mo concentration for Indarch using our average concentration data for metal and troilite and the concentration in old-hamite and the published mineral modes for Indarch [1]. The whole rock Mo concentration is approximately  $882 \pm 40$  ppb. Thus, despite the weakly chalcophile behavior of Mo, troilite accounts for 42% of the Mo budget in Indarch.

The average W/Mo abundance ratios in enstatite chondrite bulk metal [2] normalized to the CI ratio [8] are 1.70 and 1.65 for EH and EL chondrites, respectively. Using our estimate for the Mo whole rock concentration and the whole rock W data for Indarch [9], we calculated a bulk, CI-normalized W/Mo ratio of  $1.41 \pm 0.33$  (2 $\sigma$ ). Hence, the W-Mo fractionation observed in enstatite chondrite metal may not be representative of enstatite chondrites at the whole rock scale. The bulk W/Mo ratio for Indarch is nearly chondritic within the uncertainty and suggests that W and Mo may

not have been significantly fractionated from one another. However, this conclusion is not definitive because our bulk Mo value depends on modal abundances which may be non-representative of the bulk rock. Whole rock measurements of Mo in enstatite chondrites are needed to unambiguously determine if W and Mo were fractionated in these chondrites. Also, the paucity of reported bulk W measurements for enstatite chondrites would benefit from additional studies.

The absence of Ru from the sulfides and pyroxene in Indarch indicate that the Ru depletion in enstatite chondrite metal [2] is not due to sequestration in another identifiable host phase. These results are consistent with the findings of [5]. Furthermore, PGE partitioning experiments in the Fe-Ni-S system showed that minor amounts of Ru partition into Ni-bearing troilite but that Os and Ir do not; the overall siderophile behavior was Os  $\geq$  Ir > Ru [10]. Hence, if the Ru depletion in enstatite chondrite metal is not due to chalcophile behavior of Ru, it is highly unlikely that the corresponding Os and Ir depletions are due to partitioning into troilite.

**References:** [1] Keil K. (1968) *JGR*, *73*, 6945-6976. [2] Kong P. et al. (1997) *GCA*, *61*, 4895-4914. [3] Kelly W. R. and Larimer J. W. (1977) *GCA*, *41*, 93-111. [4] Chase M. W. et al. (1985) *JANAF thermochemical tables, J. Phys. Chem. Ref. Data 14, Suppl. 1.* [5] Allen R. O. and Mason B. (1973) *GCA*, *37*, 1435-1456. [6] Lodders K. and Palme H. (1991) *EPSL*, *103*, 311-324. [7] Campbell A. J. and Humayun M. (1999) *Anal. Chem.*, *71*, 939–946. [8] Anders E. and Grevesse N. (1989) *GCA*, *53*, 197-214. [9] Lee D. –C. and Halliday A. N. (2000) *Science*, *288*, 1629-1631. [10] Fleet M. E. and Stone W. E. (1991) *GCA*, *55*, 245-253.



**Fig. 1:** Measured elemental abundances in bulk EH metal [2] (circles) and in Indarch metal (triangles), and the calculated Mo abundance that would be in Indarch metal (diamond), if Mo were not present in other phases.