PALLADIUM-SILVER ISOTOPIC SYSTEMATICS IN MUONIONALUSTA AND FRACTIONATION IN THE IVA IRON METEORITE PARENT BODY. M. F. Horan[1], R.W. Carlson[1], C. M. O'D. Alexander[1] and J. Blichert-Toft[2], [1]Department of Terrestrial Magnetism, Carnegie Institution of Washington (5241 Broad Branch Road NW, Washington DC 20015. horan@dtm.ciw.edu), [2]Ecole Normale Supérieure de Lyon, Université Claude Bernard Lyon 1 and CNRS (69007 Lyon, France).

Introduction: Group IVA iron meteorites provide some of the most definitive evidence for live ^{107}Pd ($t_{1/2}$ = 6.5 Ma) in the early Solar System [1]. One IVA, Gibeon provided a Pd-Ag isochron between various pieces of metal that indicated a ^{107}Pd/^{108}Pd = (2.40 ± 0.05) x 10-5; among the highest observed for any iron meteorite [1]. Silver isotopic compositions in low-Pd/Ag troilite from some of the same meteorites, however, show little correlation with Pd/Ag, probably as a result of resetting during shock or cooling [2].

Troilite from Muonionalusta, a Group IVA iron meteorite, recently has provided the oldest Pb-Pb age yet measured for a differentiated planetesimal [3]. This Pb-Pb age (4565.3±0.1 Ma), its Hf-W metal-silicate segregation age (2.4 ±2.0 Ma) and a calculated cooling rate suggest its parent body accreted within 2-3 Ma of the formation of CAIs and that troilite from Muonionalusta, unlike Gibeon, escaped isotopic resetting by shock [3].

Despite recent advances in Ag isotopic analysis of iron meteorites and chondrites by multicollector ICP-MS [4], the Pd-Ag isotope systematics in the IVA irons have not been re-examined since the original TIMS work, primarily because of their low Ag abundances [1,4]. Given the high-precision Pb-Pb age for Muonionalusta troilite, the only iron for which such precise absolute age information is available, we undertook a Pd-Ag isotopic study of Muonionalusta in order to better constrain the chronology of its formation, the timing of its extreme Pd/Ag fractionation, and the Solar System initial abundance of ^{107}Pd [1].

Analytical Techniques: Samples for this study were taken from two slabs of Muonionalusta described in [3]. Approximately 25-gram samples of metal were sawn from the slabs using a BN cutting wheel. Approximately 2 g from a large (~4 cm) troilite nodule contained within the metal of one of the two slabs were removed with a chisel. The metal samples were polished with SiC sandpaper to remove rust and previous etching that exposed Widmanstätten bands.

Chemistry. Chemical procedures were similar to those given in [4]. Samples were rinsed with ethanol, then leached in aqua regia for 1-5 minutes. Between 0.2-2% of the metal and 21% of the troilite was removed during leaching. The residues were then rinsed in ethanol and dissolved in hot aqua regia or 12M HCl. After complete dissolution, aliquots (40-50%) were removed and spiked with ^{109}Ag and ^{110}Pd for concentration determinations by isotope dilution. Spiked and unspiked solutions were dried and re-dissolved in 0.5M HCl. Silver and palladium were purified using anion exchange resin as described in [4,6]. Separate sets of columns and beakers were used for spiked and unspiked samples. Total analytical blanks were 5-20 pg for Ag and 20 pg for Pd.

Mass spectrometry. Purified Ag was analyzed on the Nu Plasma multi-collector ICP-MS at the Department of Terrestrial Magnetism, Carnegie Institution of Washington. To minimize Ag background and improve washout, the spray chamber and torch were boiled in HNO_3 between analytical sessions. Isotopes of Ag from metal samples were simultaneously collected using ion multipliers in counting mode. Corrections for Ag background used on-mass measurements of the wash and sample dilution acid. Troilite Ag was measured in Faraday cups using simultaneous collection. Silver isotope compositions in samples were corrected for mass fractionation using averages of adjacent standard measurements. External reproducibility of the Ag standard (NIST SRM 978a) measured using ion multipliers was better than ±1.5 per mil (2σ) for each analytical session. Replicate mass spectrometric measurements of unspiked and spiked samples analyzed during different analytical sessions and corrected in this way varied by less than ±1 per mil. External reproducibility of the same standard, measured using the Faraday cups at intensities similar to those obtained during the troilite analysis (100 mV on ^{107}Ag) was ±0.4 per mil (2σ). Isotope dilution determinations of the abundances of Pd and Ag also were measured on the Nu Plasma using Faraday cups and ion multipliers, respectively, in analytical sessions separate from those in which unspiked Ag was measured.

Results: One sample of metal from Muonionalusta yielded a low Ag abundance of 0.320(±0.002) ng/g and a correspondingly radiogenic ^{107}Ag/^{109}Ag ratio of 1.373(±0.002). The Pd abundance was 6.934 µg/g, resulting in a ^{108}Pd/^{109}Ag ratio of 13,800(±150). A second metal sample yielded 0.105 (±0.002) ng/g Ag and an ^{107}Ag/^{109}Ag ratio of 1.804(±0.015). The Pd concentration in this metal split was 6.976 µg/g corresponding to a ^{108}Pd/^{109}Ag ratio of 50,200 (± 1000). Troilite from Muonionalusta contained 11.75 (±0.04) ng/g Ag and had a ^{107}Ag/^{109}Ag ratio of 1.0833 (±0.0004). The Pd concentration in the troilite was 0.291 (±0.1) ng/g corresponding to a ^{108}Pd/^{109}Ag of 13.9 (±0.1). All errors given above are 2σ and include the internal error of the measurement, the uncertainty in the fractionation correction, and the uncertainty in the blank correction. Correction for the analytical blank was the largest contributor, by far, to uncertainties in Ag isotopic compositions in both metal samples and the Ag concentration in the second metal sample.

The data are plotted in Figure 1. The three points do not lie on a single isochron. Connecting the troilite to the two metal data provides slopes corresponding to $^{107}Pd/^{108}Pd$ ratios of 2.1 x 10^{-5} and 1.4 x 10^{-5}. These ratios translate into ages 1.3 and 4.8 Ma younger than Gibeon [1], or to ages 9.7 and 13.2 Ma younger than the $^{107}Pd/^{108}Pd$ ratio of 5.9 x 10^{-5} inferred for carbonaceous chondrites [7].

The troilite-metal reference lines intersect the y-axis at an initial $^{107}Ag/^{109}Ag$ ratio of 1.0830 (ε = 30±4). This ratio is resolvably higher than the chondritic initial ratio of 1.07943 (ε = -3.1 ±0.6) [7]. Nevertheless, its Ag is less radiogenic than sulfides from other IVA meteorites [1,2], and is consistent with the suggestion that troilite in Muonionalusta escaped isotopic resetting by shock [3].

Discussion: As noted by [3], the Pb-Pb age for the troilite requires that the parent body of Muonionalusta accreted and differentiated its core and mantle prior to 4565.3±0.1 Ma. Tungsten isotope data is consistent with metal-silicate segregation at 2.4±2.0 Ma after CAI formation (4567.1-4568.7 Ma). A calculated cooling rate of 500K/Ma for the metal suggests a duration of 2-3 Ma between melting/differentiation and cooling to the Pb blocking temperature for troilite of 300°C. This chronology thus requires accretion and differentiation after 0.4Ma, but no later than about 1 Ma [3].

From a chondritic initial $^{107}Ag/^{109}Ag$ ratio [7] and solar system initial $^{107}Pd/^{108}Pd$ = 2.4 x 10-5 [1], the elevated $^{107}Ag/^{109}Ag$ of the troilite would be reached in 2.4 Ma (the Hf-W age) with a Pd/Ag (atomic) of 1200, or in 1 Ma with Pd/Ag of 2400. Given the Pd and Ag concentrations measured here for troilite and metal, these ratios would correspond to a modal abundance of 12-21% troilite (or 8% S) in the bulk Muonionalusta. This indicates that the parental materials of Muonionalusta could not have existed with Pd/Ag ratios as high as typical of IVA metal nor as low as chondritic in the time interval prior to segregation of the troilite. For example, at a Pd/Ag of 20000, similar to the metal, the $^{107}Ag/^{109}Ag$ of the troilite would be reached in less than 0.2 Ma. The high Pd/Ag ratio inferred for Muonionalusta and its parent body results not from elevated Pd (because its Pd contents are similar to those of other iron meteorite groups), but from its low Ag concentration [2]. This extreme depletion may result from early depletion in volatile elements [1,2] as well as depletion in redox-sensitive elements [9].

Quick formation and cooling cannot be reconciled with the Pd-Ag data if the Solar System initial $^{107}Pd/^{108}Pd$ is as high (5.9 x 10^{-5}) as inferred for carbonaceous chondrites [7]. Assuming the Pd-Ag system closed at the same time as the Pb-Pb system in the troilite would suggest initial Solar System $^{107}Pd/^{108}Pd$ ratios of (1.8 x10^{-5}) to (2.7 x 10^{-5}) at 4568 Ma. Such a range in initial ratios indicates that the Pd-Ag system in Muonionalusta metal is not recording the same event as the Pb-Pb system in its troilite. The ~3.5 Ma difference between the model ages of the two metal data suggests either a later disturbance or prolonged cooling.

The inconsistency between the U-Pb and Pd-Ag results for Muonionalusta may not be surprising. The U-Pb system in troilite is relatively unaffected by exchange with surrounding metal, as a result of the low U and Pb concentrations in the latter. In contrast, although the troilite has over 100 times the Ag concentration of the metal, the Ag in the metal has $^{107}Ag/^{109}Ag$ up to 66% higher than that in the troilite. Consequently, any diffusional exchange of Ag between metal and sulfide will have a significant effect on the Ag isotopic composition of both phases.

References: [1] Chen J.H. and Wasserburg G.H. (1990) GCA 54, 1729-1743. [2] Chen J.H. and Wasserburg G.H. (1996) Geophysics Monograph 95, AGU. [3] Blichert-Toft J. et al. (2010) EPSL 296, 469-480. [4] Carlson R.W.and Hauri E.H. (2001) GCA 65, 1839-1848. [5] Woodland S.J. et al. (2005) GCA 69, 2153-2163. [6] Schönbächler M. et al. (2007) Int. J Mass Spec 261, 183-191. [7] Schönbächler M. et al. (2008) GCA 72, 5330-5341. [8] Schönbächler M. et al. (2010 Abstract Met Soc. [9] McCoy et al. (in preparation for GCA)

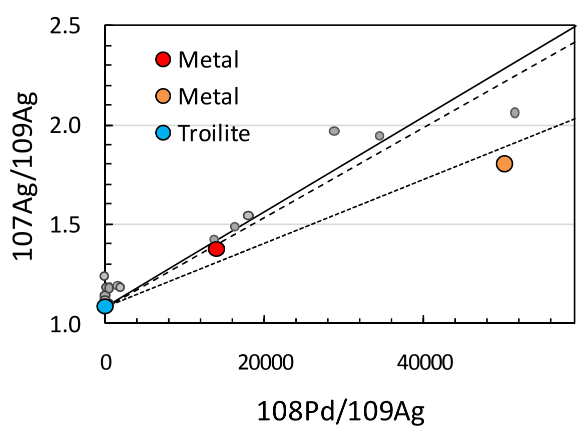

Figure1. Pd-Ag isotope data for Muonionalusta are shown with colored symbols. Small gray symbols are data for sulfide and metal from other Group IVA iron meteorites [1,2]. The solid line is a regression of data for Gibeon (IVA) metal samples [1]; the dashed line is a regression of data for Group IIA iron meteorites [8]; the dotted line is a regression of data for Grant, a Group III iron meteorite [4].