

**AN EVALUATION OF THE PALLADIUM-SILVER ISOTOPE SYSTEMATICS IN THE OLDEST DIFFERENTIATED PLANETESIMAL: BEYOND SHOCK.** M.F. Horan<sup>1</sup>, R.W. Carlson<sup>1</sup> and J. Blichert-Toft<sup>2</sup>  
 Department of Terrestrial Magnetism, Carnegie Institution of Washington (5241 Broad Branch Road NW, Washington DC 20015. horan@dtm.ciw.edu), <sup>2</sup>Ecole Normale Supérieure de Lyon, Université Claude Bernard Lyon 1 and CNRS (69007 Lyon, France).

**Introduction:** Troilite from Muonionalusta (iron meteorite group IVA) gives the oldest absolute age yet measured for a differentiated planetesimal (4565.3±0.1 Ma) which suggests that the IVA parent body accreted, differentiated, and cooled within 2-3 Ma after CAI formation [1]. The aim of this study is to use the quick evolution and volatile-depleted (high Pd/Ag) composition of IVA irons to better constrain the initial Solar System abundance of <sup>107</sup>Pd (<sup>107</sup>Pd → <sup>107</sup>Ag with  $t_{1/2} = 6.5$  Ma). Most Pd/Ag ages have been referenced to  $^{107}\text{Pd}/^{108}\text{Pd} = (2.40 \pm 0.05) \times 10^{-5}$  obtained on metal from Gibeon, also a Group IVA meteorite [2]. Interpreting this slope as an initial ratio for the Solar System is complicated by the non-zero age of Gibeon and the presence in Gibeon troilite of unsupported radiogenic Ag. Carbonaceous chondrites, by contrast, imply a higher Solar System initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of  $(5.9 \pm 2.2) \times 10^{-5}$ . Using this initial suggests that the Pd-Ag system in differentiated meteorites was open for 8-20 Ma [3]

Muonionalusta is one of ~50 Group IVA iron meteorites whose trace element contents suggest they initially crystallized in a single asteroidal core [4]. Metallographic cooling rates of IVAs reflect a later history of multiple episodes of shock fragmentation, reheating, and cooling without overlying mantle [5]. Sorting out the effects of this complicated history on the Pd-Ag isotope system is critical to determining a more accurate initial Solar System abundance of <sup>107</sup>Pd.

**Samples and Methods:** Metal and troilite samples were taken from two slabs of Muonionalusta [1]. Pd and Ag concentrations, determined by isotope dilution, and Ag isotopic compositions, measured on unspiked aliquots, were analyzed using a Nu Plasma MC-ICP-MS [3, 6]. The ancient Pb-Pb age [1] was obtained from a piece of a 2-cm diameter troilite nodule from slab 1.

**Results:** Three metal samples from slab 1 and three metal samples from slab 2 contained Ag abundances between 0.1062 and 0.3227 ng/g, <sup>107</sup>Ag/<sup>109</sup>Ag between 1.373 and 1.804, and Pd abundances between 5822 and 6368 ng/g. Corresponding  $^{108}\text{Pd}/^{109}\text{Ag}$  ratios ranged from 12,570 to 45,900. One additional metal sample, taken adjacent to the troilite in slab 1, contained 1.46 ng/g Ag with <sup>107</sup>Ag/<sup>109</sup>Ag of 1.131 and 5612 ng/g Pd, corresponding to  $^{108}\text{Pd}/^{109}\text{Ag}$  of 2201.

Troilite from slab 1 contained 5.612 ng/g Ag with <sup>107</sup>Ag/<sup>109</sup>Ag of 1.127±0.002, and 0.780±0.002 ng/g Pd, corresponding to  $^{108}\text{Pd}/^{109}\text{Ag}$  of 0.05946 ±0.00010. HCl-insoluble inclusions (probably schreibersite) within this troilite yielded 1.758±0.006 ng/g Ag with <sup>107</sup>Ag/<sup>109</sup>Ag of 1.130±0.002, and 5168±10 ng/g Pd, corresponding to  $^{108}\text{Pd}/^{109}\text{Ag}$  of 1691±8. Troilite from slab 2 contained 11.75±0.04 ng/g Ag and had a <sup>107</sup>Ag/<sup>109</sup>Ag ratio of 1.0833±0.0004 [6]. The Pd concentration was 0.291±0.1 ng/g corresponding to  $^{108}\text{Pd}/^{109}\text{Ag}$  of 13.9±0.1. The Ag isotopic compositions for all samples are inversely correlated with Ag abundances, suggesting that the Ag in the measured metal samples represents a mixture between 1-10% troilite containing unradiogenic Ag with metal dominated by purely radiogenic <sup>107</sup>Ag; the metal sampled adjacent to slab 1 troilite contained 26% troilite.

New data and those previously given in [6] are plotted in Figures 1 and 2. The metal samples, except one, and the troilite from slab 2 are well-correlated and provide a slope that corresponds to  $^{107}\text{Pd}/^{108}\text{Pd}$  of 2.14 (±0.26) × 10<sup>-5</sup>. This slope is within uncertainty of that obtained from Gibeon [2], and just outside the uncertainty of the slope inferred from carbonaceous chondrites [3]. The reference line between slab 2 troilite and metal intersects the y-axis at an initial <sup>107</sup>Ag/<sup>109</sup>Ag ratio of 1.0830, resolvably higher ( $\epsilon = 30 \pm 4$ ) than the chondritic initial ratio. The elevated <sup>107</sup>Ag/<sup>109</sup>Ag of the troilite would be reached within 2-3 Ma if the  $^{108}\text{Pd}/^{109}\text{Ag}$  ratio of its parental melt were between 400 and 800. This range of  $^{108}\text{Pd}/^{109}\text{Ag}$  ratios, combined with the Pd and Ag abundances measured for troilite and metal, suggests that the precursor to Muonionalusta was a melt having 9-15% S and a Pd/Ag ratio about 100x higher than chondrites [6]. This Pd/Ag ratio is consistent with trace element models for the composition of the IVA source, provided Ag was depleted to the same extent as Ga, which has a similar condensation temperature [4].

Despite its very low  $^{107}\text{Pd}/^{109}\text{Ag}$  ratio, slab 1 troilite has a Ag isotopic composition similar to its HCl-insoluble inclusions and adjacent metal (Figure 2), suggesting that these phases were isotopically homogenized after <sup>107</sup>Pd became extinct. Slab 1 troilite's <sup>107</sup>Ag/<sup>109</sup>Ag ratio of 1.13 would be reached after c. 50 Ma for a  $^{108}\text{Pd}/^{109}\text{Ag}$  ratio of approximately 2000. This

ratio is higher than that calculated for the precursor to Muonionalusta, but lower than that typical for metal, and indicates that unsupported radiogenic Ag in this troilite was obtained from nearby metal. A 2-cm diameter troilite nodule, for example, could obtain sufficiently radiogenic Ag by diffusional exchange with a 0.6 cm shell of surrounding metal that had 0.1 ng/g Ag and  $^{107}\text{Ag}/^{109}\text{Ag} = 2$  prior to exchange. After exchange, the surrounding metal would be expected to lie below the reference line defined by unaffected metal aliquots if its  $^{108}\text{Pd}/^{109}\text{Ag}$  remained unchanged. The  $^{108}\text{Pd}/^{109}\text{Ag}$  measured in the adjacent metal sample here, however, suggests that its Ag was effectively overwhelmed by physical admixture with troilite.

One metal sample in Figure 1 lies below the metal-troilite reference line with a significantly lower slope of  $1.58 \times 10^{-5}$ . Although we cannot rule out the possibility of an unidentified analytical artefact, this composition could imply that the Pd-Ag system in this sample closed at least a few Ma later than other Muonionalusta metal, after partial exchange of its Ag with less radiogenic Ag from troilite.

**Discussion:** Shock melting may offer an explanation for both the presence of isotopically reset Ag and the preservation of ancient Pb in the same troilite nodule from slab 1. Shock compression can melt and disperse troilite which may include or dissolve other minerals including silicates [7]. Troilite in Muonionalusta is reported to have stishovite inclusions and petrographic evidence for melting and recrystallization by shock [7,8]. In slab 1, the boundary between the troilite nodule and adjacent metal is irregular, with deformed swathing kamacite and infiltration of troilite melt into the metal. Such deformation may have facilitated exchange of Ag between troilite having ~100 times the Ag concentration of the metal and metal having  $^{107}\text{Ag}/^{109}\text{Ag}$  up to 66% higher than that of the troilite, resulting in troilite with unsupported radiogenic Ag. Silicate material bearing ancient, radiogenic Pb may have been included in the troilite melt. In contrast to the Pd-Ag system, the U-Pb system may have been relatively unaffected by shock melting and exchange with surrounding metal, as a result of the low U and Pb concentrations in the latter.

Using the higher Solar System initial  $^{107}\text{Pd}/^{108}\text{Pd}$  inferred for chondrites implies that the Pd-Ag system in Muonionalusta metal is at least 9 Ma younger than its troilite Pb-Pb age. If the Pd-Ag system closed at the same time as the Pb-Pb system in the troilite (i.e., 2-3 Ma after CAI formation), then an initial Solar System abundance of  $^{107}\text{Pd}/^{108}\text{Pd}$  of  $(2.8 \pm 0.4) \times 10^{-5}$  can be inferred. This initial Solar System composition can then be used to recalculate Pd-Ag ages of other meteorites. Metal from Gibeon [2] and metal-troilite from

Canyon Diablo (Group IAB) [9] have Pd-Ag ages that are indistinguishable from Muonionalusta, at 2-3 Ma after CAI. Metal from Group IVB irons [2], a mineral isochron from the pallasite Brenham [9], and metal-troilite from the Group IIIAB meteorite Grant [9, 10] yield Pd-Ag ages that are 2-3 Ma younger than Muonionalusta.

**References:** [1] Blichert-Toft J. et al. (2010) EPSL 296, 469-480. [2] Chen J.H. and Wasserburg G.H. (1990) GCA 54, 1729-1743. [3] Schönbächler M. et al. (2008) GCA 72, 5330-5341. [4] McCoy et al. GCA 75, 6821-6843. [5] Yang et al., (2008) GCA 72, 3043-3061. Rasmussen et al. (1995) GCA 59, 3049-3059. [6] Horan M.F. et al. (2011) LPS XLII Abstract #1311 [7] Buchwald (1975) Iron Meteorites. [8] Holtstam et al. (2003) MAPS38, 1579-1583. [9] Carlson R.W. and Hauri E.H. (2001) GCA 65, 1839-1848. [10] Woodland S.J. et al. (2005) GCA 69, 2153-2163.

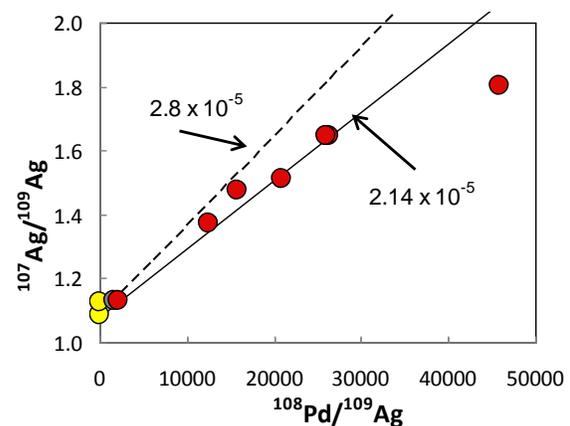


Fig. 1 Pd-Ag data for Muonionalusta. Metal data shown in red; troilite data in yellow; data for HCl-insoluble phase in gray.

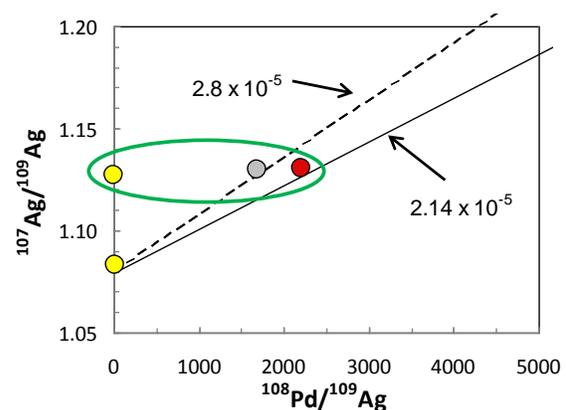


Fig 2. (Inset to Fig 1.) Inside the green area are data for troilite from slab 1 (yellow), HCl-insoluble inclusions in troilite (gray) and adjacent metal (red). The other troilite sample is from slab 2.