

PALLADIUM-SILVER ISOCHRON FOR THE IVA IRON MUONIONALUSTA: SOLAR SYSTEM INITIAL $^{107}\text{Pd}/^{108}\text{Pd}$ AND THE COOLING OF PROTOPLANETARY CORES. M. Matthes¹, M. Fischer-Gödde¹, T.S. Kruijer¹ and T. Kleine¹, ¹Institut für Planetologie, University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany, (max.matthes@uni-muenster.de).

Introduction: The short-lived ^{107}Pd - ^{107}Ag system ($t_{1/2} = 6.5$ Ma) is a powerful tool to date the cooling of the parent metal cores of iron meteorites [1]. However, the full potential of the Pd-Ag system has yet to be realized, mainly because (i) precise Pd-Ag isochrons are only available for a handful of irons and (ii) the solar system initial $^{107}\text{Pd}/^{108}\text{Pd}$ is not well constrained. The most precise Pd-Ag isochron obtained so far is for the IVA iron Gibeon with an initial $^{107}\text{Pd}/^{108}\text{Pd} = (2.40 \pm 0.05) \times 10^{-5}$ [1]. In the past, Pd-Ag ages were calculated relative to this value, but because the age of Gibeon is not known independently, it was not possible to calculate Pd-Ag ages relative to the beginning of the solar system. More recent studies attempted to determine the solar system initial $^{107}\text{Pd}/^{108}\text{Pd}$ using either carbonaceous chondrites [2] or the IVA iron Muonionalusta [3], for which a precise Pb-Pb age is available [4]. However, these two approaches resulted in different estimates for the solar system initial $^{107}\text{Pd}/^{108}\text{Pd}$ of $(5.9 \pm 2.2) \times 10^{-5}$ and $(2.8 \pm 0.5) \times 10^{-5}$, respectively. This difference would correspond to a time difference of ~ 7 Ma, making Pd-Ag ages calculated relative to the beginning of the solar system very uncertain.

To address these issues, we initiated a Pd-Ag study of the IVA iron Muonionalusta. In a companion study, we also determined the U isotopic composition of Muonionalusta troilite [5], which resulted in a revision of its Pb-Pb age from the previously reported value of 4565.3 ± 0.1 Ma [4] to 4558.4 ± 0.5 Ma. Combined, the results provide a new and precise solar system initial $^{107}\text{Pd}/^{108}\text{Pd}$ and make it possible to resolve differences in cooling ages for IVA and other iron meteorites.

Samples and analytical methods: Twelve metal pieces (~ 6 to ~ 13 g) and one troilite nodule (~ 0.5 g) from three different slabs of Muonionalusta were investigated. Prior to digestion in reverse aqua regia, the samples were cleaned using SiC abrasives and leached in warm 6M HCl. After complete dissolution, three aliquots were taken for the determination of Ag and Pd concentrations and Pt isotopic compositions; the remaining 60% of each sample solution was used for the Ag isotopic measurements. The separation of Ag, Pd and Pt followed our established procedures [6].

All isotope measurements were performed using the Thermo Scientific[®] Neptune Plus MC-ICPMS at Münster, using either an ESI APEX-Q (Ag) or a Cetac Aridus II desolvating system (Pt). The Ag fractions were doped with Pd to correct for instrumental mass

bias and all Ag isotopic data are given relative to the mean $^{107}\text{Ag}/^{109}\text{Ag} = 1.08048$ obtained for the NIST 978a standard. The reproducibility of the $^{107}\text{Ag}/^{109}\text{Ag}$ measurements is $\pm 0.4\%$ (2s.d.), as estimated from four separate aliquots of the same sample solution processed individually through the chemistry. The reproducibility of the Ag isotope dilution measurements varied between $\pm 1\%$ and $\pm 7\%$ (2s.d.). Silver blanks were 12 ± 6 pg and 7 ± 3 pg for the measurements of $^{107}\text{Ag}/^{109}\text{Ag}$ and Ag concentrations; the resulting blank corrections were $< 1\%$ for the isotopic compositions and $< 4\%$ for the Ag concentrations. The Pt isotope compositions of each sample were determined to assess neutron capture effects on measured $^{107}\text{Ag}/^{109}\text{Ag}$ [6]. The Pt isotope results are given in $\epsilon^{196}\text{Pt}$ as the parts per 10^4 deviations from terrestrial $^{196}\text{Pt}/^{195}\text{Pt}$.

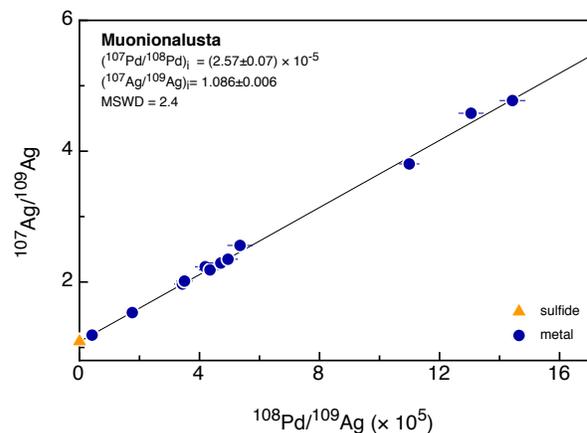


Fig. 1: Pd-Ag isochron for the IVA iron Muonionalusta. Regression calculated using IsoPlot.

Results: Most of the metal samples are characterized by relative uniform Pd concentrations, but exhibit low and varying Ag contents between ~ 67 and ~ 239 ppt, resulting in $^{108}\text{Pd}/^{109}\text{Ag}$ between $\sim 17,000$ and $\sim 140,000$. One metal sample with a macroscopically visible troilite inclusion yielded a Ag concentration of ~ 935 ppt and a lower $^{108}\text{Pd}/^{109}\text{Ag}$ of ~ 4200 . The troilite has ~ 2.63 ppb Ag and a low $^{108}\text{Pd}/^{109}\text{Ag}$ of ~ 23 . The $^{107}\text{Ag}/^{109}\text{Ag}$ ratios of the samples vary between 1.091 and 4.774 and correlate well with $^{108}\text{Pd}/^{109}\text{Ag}$, yielding an isochron with a slope corresponding to an initial $^{107}\text{Pd}/^{108}\text{Pd} = (2.57 \pm 0.07) \times 10^{-5}$ (Fig. 1). This value is higher than an earlier reported value of $(2.15 \pm 0.30) \times 10^{-5}$ [3]; note, however, that compared to this study we obtained much more radiogenic $^{107}\text{Ag}/^{109}\text{Ag}$ and a much larger range in $^{108}\text{Pd}/^{109}\text{Ag}$. Finally, none of the

metal samples shows a resolvable Pt isotope anomaly and the mean $\epsilon^{196}\text{Pt}$ of all samples is 0.01 ± 0.02 (95% conf., $N = 13$). Thus, no correction for neutron capture effects is necessary for the Muonionalusta data.

Discussion: *Solar system initial $^{107}\text{Pd}/^{108}\text{Pd}$.* The revised Pb-Pb age of Muonionalusta—corrected using its measured U isotopic composition—is 4558.4 ± 0.5 Ma [5]. Using this Pb-Pb age and a CAI age of 4567.2 Ma combined with our newly determined $^{107}\text{Pd}/^{108}\text{Pd}$ of Muonionalusta results in a solar system initial $^{107}\text{Pd}/^{108}\text{Pd}$ of $(6.6 \pm 0.4) \times 10^{-5}$. This value is significantly higher compared to a value of $(2.8 \pm 0.5) \times 10^{-5}$ previously determined based on Muonionalusta [3]. However the new value is consistent with, but more precise than the value of $(5.9 \pm 2.2) \times 10^{-5}$ obtained from a carbonaceous chondrite whole-rock isochron [2].

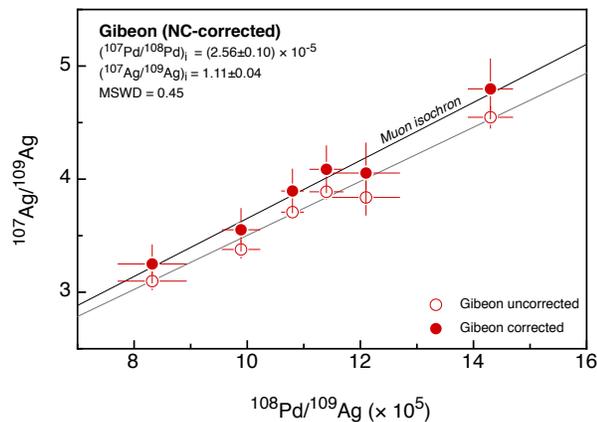


Fig. 2: Section of the Pd-Ag isochron for the IVA iron Gibeon. Pd-Ag data are from [1]. After correction for neutron capture, Gibeon plots on the Muonionalusta isochron.

Comparison to Gibeon and implications for the cooling of the IVA core. The IVA iron Gibeon has an initial $^{107}\text{Pd}/^{108}\text{Pd}$ of $(2.40 \pm 0.05) \times 10^{-5}$ [1], slightly lower than that obtained for Muonionalusta in the present study. However, cooling of the IVA core should have been isothermal, unless the IVA core cooled without an insulating mantle [7]. Detailed thermal modeling shows that in the latter case Gibeon should have a Pb-Pb closure age ~ 2 Ma *older* than Muonionalusta [7]; however, the Pd-Ag age for Gibeon seems to be slightly *younger*. Thus, it seems unlikely that the lower $^{107}\text{Pd}/^{108}\text{Pd}$ of Gibeon reflects slower cooling compared to Muonionalusta.

Secondary neutron capture during cosmic ray exposure might lead to apparent lower slopes of Pd-Ag isochrons [6]. Such effects are absent for Muonionalusta (see above), but may have been important for Gibeon. Indeed, different pieces of Gibeon show slightly different Pt isotope anomalies [9] and so combined Pd-Ag and Pt isotope analyses on the exact same pieces of Gibeon would be necessary to quantify neutron

capture effects. However, most Gibeon samples analyzed so far have an $\epsilon^{196}\text{Pt}$ of ~ 0.07 [9]. We, therefore, corrected the Gibeon data from [1] for neutron capture effects using $\epsilon^{196}\text{Pt} = 0.07 \pm 0.07$. The corrected Gibeon data points plot well on the Muonionalusta isochron (Fig. 2), and regression of all corrected Gibeon data results in an isochron corresponding to an initial $^{107}\text{Pd}/^{108}\text{Pd}$ of $(2.56 \pm 0.10) \times 10^{-5}$, indistinguishable from the value for Muonionalusta (Fig. 2). Thus, neutron capture is a likely cause for the small difference in measured $^{107}\text{Pd}/^{108}\text{Pd}$ for Gibeon and Muonionalusta and both probably cooled below Pd-Ag closure at about the same time. This is not easily reconciled with the ~ 2 Ma age difference between these two samples predicted from metallographic cooling rates and thermal models of an exposed IVA core [7].

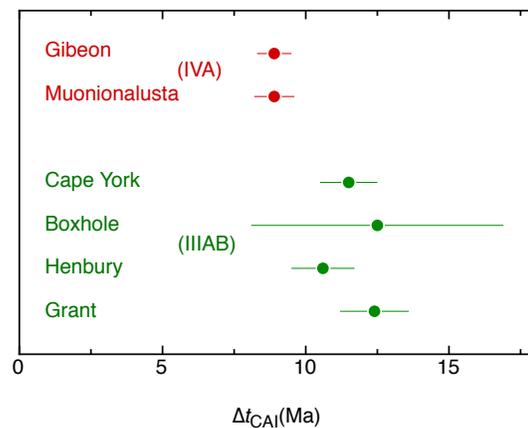


Fig. 3: Pd-Ag ages of IVA and IIIAB iron meteorites, calculated relative to the new solar system initial $^{107}\text{Pd}/^{108}\text{Pd}$.

Resolved Pd-Ag age differences between different groups of irons. Figure 3 shows Pd-Ag ages for IIIAB and IVA irons; only ages based on internal isochrons are shown, and where necessary the Pd-Ag data were corrected for neutron capture effects [6]. Evidently, cooling of at least some cores occurred on a ~ 10 Ma timescale (Fig. 3). Moreover, there are resolved differences in the cooling ages for different iron groups; while the IIIAB core cooled below Pd-Ag closure at ~ 12 Ma after CAI, the IVA core had cooled ~ 3 Ma earlier. These different cooling timescales probably reflect differences in one or several of the following factors: (i) parent body sizes, (ii) Pd-Ag closure temperatures [8], and (iii) cooling rates.

References: [1] Chen, J.H. and Wasserburg, G.J. (1990) *GCA*, 54, 1729-1743. [2] Schönbachler, M. et al. (2008) *GCA*, 72, 5330-5341. [3] Horan, M.F. et al. (2012) *EPSL*, 351, 215-222. [4] Blichert-Toft, J. et al. (2010) *EPSL*, 296, 469-480. [5] Brennecka and Kleine, *this meeting* [6] Matthes, M. et al. (2015) *GCA*, 169, 45-62 [7] Moskovitz, N.A. and Walker, R.J. (2011) *EPSL* 308, 410-416. [8] Matthes et al., *this meeting*. [9] Kruijer, T.S. et al. (2014) *Science*, 344, 1150-1154.