

**PALLADIUM-SILVER ISOTOPE SYSTEMATICS OF IIIAB IRON METEORITES.** M. Matthes, M. Fischer-Gödde, T. Kleine, Institut für Planetologie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany (max.matthes@uni-muenster.de).

**Introduction:** The accretion, differentiation and cooling history of iron meteorite parent bodies can be quantified by using long- and short-lived isotope systems. Of these, the extinct  $^{107}\text{Pd}$ - $^{107}\text{Ag}$  system ( $t_{1/2} \sim 6.5$  Ma) is well suited to investigate the cooling history of iron meteorites [1, 2]. Palladium is siderophile and has a condensation temperature of  $\sim 1324$  K, whereas Ag is chalcophile and volatile with a condensation temperature of  $\sim 996$  K. The major processes fractionating Pd and Ag, therefore, are volatilization/condensation and metal-sulphide separation. Consequently, magmatic irons and in particular those strongly depleted in volatile elements exhibit high Pd/Ag and highly radiogenic Ag isotopic compositions [1-3].

The strong fractionation of Pd and Ag between metal and sulphide makes it possible to obtain precise internal Pd-Ag isochrons based on sulphide-metal pairs. So far internal isochrons have been obtained only for a very few iron meteorites, including the IIIAB irons Cape York [1] and Grant [1, 4, 5], and the two IVA irons Gibeon [2] and Muonionalusta [3]. To better constrain the cooling history of the parent bodies of magmatic iron meteorites and to ultimately define a high-precision chronology of the crystallization, cooling and volatile element depletion history of differentiated protoplanets, we initiated a study of the Pd-Ag isotope systematics of iron meteorites. Here we present first results for the IIIAB irons Cape York and Grant.

**Analytical Techniques:** Two metal pieces ( $\sim 3$  g) and one sulphide sample ( $\sim 0.2$  g) from Cape York as well as a  $\sim 3$  g sample of metal and  $\sim 1.8$  g of a metal-sulphide slab from Grant were investigated for this study. All samples were cleaned with abrasives and leached in 6 M HCl prior to digestion in hot aqua regia. Two aliquots were taken for Ag and Pd concentration determination by isotope dilution. Silver was purified using anion exchange chromatography following [6]. To avoid any contamination, spiked and unspiked samples were processed using different sets of beakers and columns. Total analytical blanks were  $< 20$  pg Ag for the determination of Ag isotopic composition and  $< 8$  pg Ag and Pd for the concentration measurements.

All isotope measurements were conducted on the ThermoScientific Neptune *Plus* MC-ICPMS at the University of Münster. For the Ag isotope measurements samples were introduced into the mass spectrometer using an ESI Apex-Q desolvating nebulizer, resulting in total ion beams of  $\sim 2 \times 10^{-11}$  A for  $\sim 10$  ppb Ag. Instrumental mass fractionation was corrected us-

ing admixed Pd with a  $^{106}\text{Pd}/^{107}\text{Ag}$  signal intensity ratio of about 1, and using the exponential law and  $^{108}\text{Pd}/^{106}\text{Pd} = 0.97237$ . The Ag isotope results are reported in  $\epsilon^{107}\text{Ag}$  units, which represent the deviation of  $^{107}\text{Ag}/^{109}\text{Ag}$  in a sample from the mean  $^{107}\text{Ag}/^{109}\text{Ag}$  measured for two standard runs bracketing the sample run. The reproducibility of the Ag isotopic measurements for a  $\sim 10$  ppb Ag solution during one measurement session was  $\pm 0.4 \epsilon^{107}\text{Ag}$  (2 SD). The mean  $^{107}\text{Ag}/^{109}\text{Ag}$  obtained for the NIST SRM978a standard during the course of this study is  $1.080109 \pm 0.000013$  (2 SE), in good agreement with results reported for this standard previously [2, 4-6].

Purified Ag and Pd from the spiked aliquots were introduced into the mass spectrometer using an ESI SIS spray chamber. Instrumental mass fractionation was corrected relative to bracketing standard runs. Typical precisions of  $^{108}\text{Pd}/^{109}\text{Ag}$  are better than  $\sim 0.5\%$ .

**Results:** Two metal samples from Cape York have Ag abundances of  $\sim 7$  ng/g and Pd abundances of  $\sim 3$   $\mu\text{g/g}$ , resulting in  $^{108}\text{Pd}/^{109}\text{Ag}$  between  $\sim 211$  and  $\sim 254$ . The  $\epsilon^{107}\text{Ag}$  of these two metal samples is  $\sim 48$ . The Cape York sulphide yielded a high Ag abundance of  $\sim 90$  ng/g and a low Pd abundance of  $\sim 536$  ng/g, resulting in  $^{108}\text{Pd}/^{109}\text{Ag} \sim 3$  and  $\epsilon^{107}\text{Ag} \sim 4$ . A metal sample from Grant yielded Ag and Pd concentrations of  $\sim 4$  ng/g and  $\sim 4.6$   $\mu\text{g/g}$ , corresponding to  $^{108}\text{Pd}/^{109}\text{Ag} \sim 630$ , while the metal-sulphide slab has  $\sim 100$  ng/g Ag and  $\sim 3$   $\mu\text{g/g}$ , resulting in a much lower  $^{108}\text{Pd}/^{109}\text{Ag}$  of  $\sim 16$ . Both Grant samples display radiogenic Ag isotopic compositions with  $\epsilon^{107}\text{Ag} \sim 132$  for the metal and  $\epsilon^{107}\text{Ag} \sim 27$  for the metal-sulphide sample.

**Discussion:** The results are displayed in isochron diagrams in Fig. 1 (Cape York) and 2 (Grant) together with data obtained previously for these two meteorites. The new data are in good agreement with previously reported results, but are more precise than most of the earlier data. This improved precision on  $^{107}\text{Ag}/^{109}\text{Ag}$  primarily reflects advances in analytical techniques by MC-ICPMS, which allows precise correction of instrumental mass fractionation using admixed Pd [4-6].

*Cape York:* The two investigated metal samples from Cape York have somewhat lower  $^{108}\text{Pd}/^{109}\text{Ag}$  and  $\epsilon^{107}\text{Ag}$  compared to metal pieces analyzed by Chen and Wasserburg [1]. This most likely reflects the presence of tiny sulphide inclusions in the metal samples analyzed in the present study, consistent with the slightly higher Ag content of these samples compared to the metal samples investigated by Chen and Wasserburg

[1]. The Ag isotopic composition of the Cape York troilite analyzed here appears less radiogenic but overlaps with the lower error bound of the  $^{107}\text{Ag}/^{109}\text{Ag}$  reported for a Cape York troilite by Chen and Wasserburg [1]. As to whether troilites in Cape York have different  $^{107}\text{Ag}/^{109}\text{Ag}$  and, hence, contain unsupported radiogenic  $^{107}\text{Ag}$ , as has been observed for sulphides from other iron meteorites [2], requires further investigation.

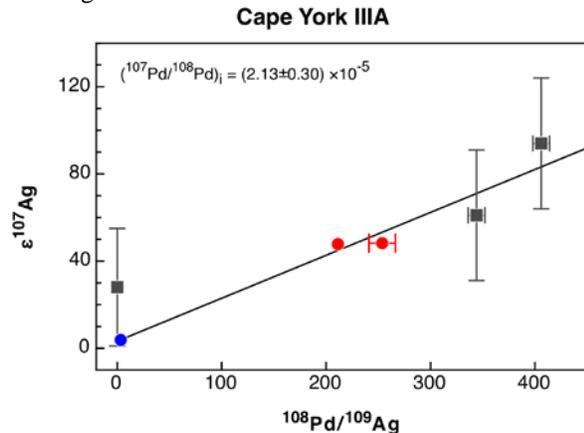


Figure 1. Pd-Ag isochron for Cape York. Data from this study shown as red (metal) and blue (sulphide) circles, those from Chen and Wasserburg [1] as grey squares. Regression calculated using IsoPlot.

A regression through the Pd-Ag data for Cape York presented here and in Chen and Wasserburg [1] results in an initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of  $(2.13 \pm 0.30) \times 10^{-5}$ , identical to  $^{107}\text{Pd}/^{108}\text{Pd} = (2.15 \pm 0.30) \times 10^{-5}$  reported for the IVA iron Muonionalusta [3] and slightly lower but not resolved from  $^{107}\text{Pd}/^{108}\text{Pd} = (2.40 \pm 0.05) \times 10^{-5}$  reported for the IVA iron Gibeon [2].

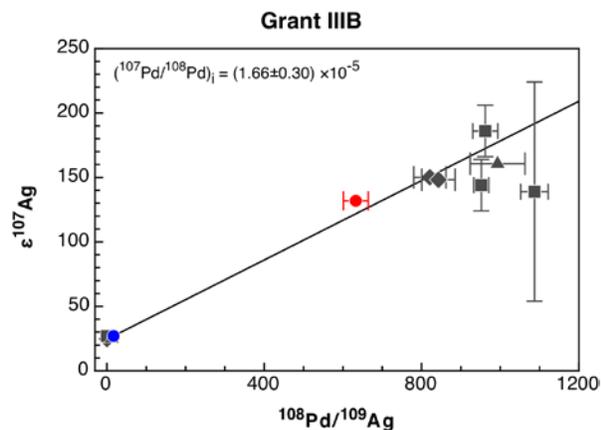


Figure 2. Pd-Ag isochron for Grant. Data from this study shown as red (metal) and blue (sulphide) circles. Literature data: triangles [5]; diamonds [4]; squares [1].

**Grant:** The investigated metal piece from Grant has slightly lower  $^{108}\text{Pd}/^{109}\text{Ag}$  and  $\epsilon^{107}\text{Ag}$  compared to Grant metals investigated in previous studies. Again this most likely reflects the presence of sulphide inclu-

sions in the metal piece investigated here. The Grant sulphide analyzed by us has slightly higher  $^{108}\text{Pd}/^{109}\text{Ag}$  and  $\epsilon^{107}\text{Ag}$  than sulphides analyzed previously, which is not surprising because we only analyzed a sulphide-metal mixtures, not a pure sulphide separate.

A regression through the Pd-Ag data for Grant from this and previous studies results in an initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of  $(1.66 \pm 0.11) \times 10^{-5}$ , significantly lower than the initial  $^{107}\text{Pd}/^{108}\text{Pd}$  obtained for Cape York.

**Chronological interpretation:** The difference in initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of Grant and Cape York indicates that Grant cooled below the Pd-Ag closure temperature  $\sim 2$ -3 Ma later than Cape York. This is consistent with the early crystallization of Cape York and the late crystallization of Grant as derived from trace element systematics and fractional crystallization models of the IIIAB irons [7]. The Pd-Ag results thus indicate that different portions of the IIIAB core, which had solidified at different stages in the crystallization sequence, cooled below Pd-Ag closure within less than  $\sim 2$ -3 Ma of each other.

Linking the Pd-Ag ages to an absolute time scale and to the timing of core formation (as constrained by Hf-W) and thus to ultimately constrain the cooling rate of the IIIAB core is more difficult. This is because the initial  $^{107}\text{Pd}/^{108}\text{Pd}$  at the start of the solar system is not well known. It has been customary to calculate Pd-Ag ages relative to the IVA iron Gibeon with its well constrained initial  $^{107}\text{Pd}/^{108}\text{Pd}$ , although the age of Gibeon relative the formation of the solar system is not known. More recently, a solar system initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of  $(5.9 \pm 2.2) \times 10^{-5}$  was inferred based on Pd-Ag data for chondrites [8], suggesting that the Pd-Ag ages for Gibeon and Muonionalusta postdate the formation of the solar system by  $\sim 8$  Ma. This is difficult to reconcile with the ancient Pb-Pb age of  $4565.3 \pm 0.1$  Ma reported for Muonionalusta [9], however. Horan et al. [3] combined their Pd-Ag data for Muonionalusta with the Pb-Pb age of this sample to obtain a solar system initial  $^{107}\text{Pd}/^{108}\text{Pd}$  of  $(2.8 \pm 0.5) \times 10^{-5}$ . Relative to this initial, the  $^{107}\text{Pd}/^{108}\text{Pd}$  ratios of Cape York and Grant obtained in the present study correspond to ages of  $\sim 2.6$  and  $\sim 4.9$  Ma after the beginning of the solar system. This would imply a very rapid cooling of the IIIAB core, consistent with evidence based on metallographic cooling rates of IIIAB irons [10].

**References:** [1] Chen J.H. and Wasserburg G.J. (1983) *GCA*, 47, 1725-1737. [2] Chen J.H. and Wasserburg G.J. (1990) *GCA*, 54, 1729-1743. [3] Horan M.F. et al. (2012) *EPSL*, 351, 215-222. [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] Schönbacher M. et al. (2007) *IJMS*, 261, 183-191. [7] Scott E.R.D. (1972) *GCA*, 36, 1205-1236. [8] Schönbacher M. et al. (2008) *GCA*, 72, 5330-5341. [9] Blichert-Toft J. et al. (2010) *EPSL*, 296, 469-480. [10] Yang J.J. and Goldstein J.I. (2006) *GCA*, 70, 3197-3215.