

**THE EFFECT OF COSMIC RAY IRRADIATION ON PLATINUM AND PALLADIUM ISOTOPES IN IRON METEORITES.** A. C. Hunt<sup>1</sup>, M. Ek<sup>1</sup> and M. Schönbächler<sup>1</sup>. <sup>1</sup>ETH Zürich, Institute for Geochemistry and Petrology, Clausiusstrasse 25, 8092 Zürich, Switzerland. E-mail: [alison.hunt@erdw.ethz.ch](mailto:alison.hunt@erdw.ethz.ch).

**Introduction:** Dating of early solar system processes such as differentiation and core formation of planetesimals and planets frequently relies on short-lived decay systems such as <sup>182</sup>Hf-<sup>182</sup>W [e.g. 1] or <sup>107</sup>Pd-<sup>107</sup>Ag [e.g. 2,3]. However, these systems are susceptible to the effects of galactic cosmic rays (GCR) and hence, acquiring correct ages requires knowledge of the exposure history of the meteorite. Exposure to GCR causes secondary neutron capture on isotopes with large neutron cross sections, which can result in large shifts in the measured isotope ratios [4].

Platinum is a highly siderophile element with six naturally occurring isotopes (<sup>190</sup>Pt, <sup>192</sup>Pt, <sup>194</sup>Pt, <sup>195</sup>Pt, <sup>196</sup>Pt and <sup>198</sup>Pt). Platinum isotopes are a powerful neutron dosimeter as a result of the burnout of <sup>195</sup>Pt on to <sup>196</sup>Pt [4]. Platinum isotopes are also affected by neutron capture by <sup>191</sup>Ir, which can result in the production of <sup>192</sup>Pt [4]. Therefore, depending on the Ir/Pt ratio of the sample, as well as shielding and exposure age, it is possible to produce large <sup>192</sup>Pt excesses. This relationship is demonstrated for the IVA, IVB, IIAB and IID iron meteorites [5, 6, 7], highlighting that Pt isotopes are a powerful tool for correcting the effects of GCR irradiation.

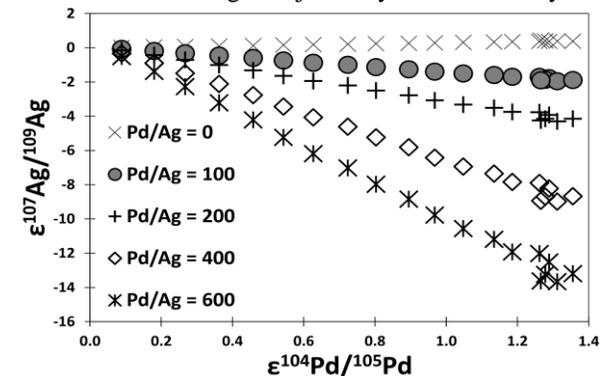
Palladium is also a highly siderophile element with six naturally occurring isotopes (<sup>102</sup>Pd, <sup>104</sup>Pd, <sup>105</sup>Pd, <sup>106</sup>Pd, <sup>108</sup>Pd and <sup>110</sup>Pd). Neutron capture by <sup>106</sup>Pd can potentially lead to disturbances to the <sup>107</sup>Pd-<sup>107</sup>Ag chronometer (Fig. 1). Large excesses in <sup>104</sup>Pd can also be generated if Rh/Pd ratios of the sample are sufficiently elevated, due to the burnout of <sup>103</sup>Rh to <sup>104</sup>Rh, followed by  $\beta$ -decay to <sup>104</sup>Pd (Fig. 1). Therefore Pd can potentially be used as a neutron dosimeter to correct for cosmogenic Ag.

In this study we aim to collect Pt and Pd isotopes from the same sample aliquot in order to assess the effects of neutron capture on both elements in various iron meteorite groups. Previous studies reported a good agreement between variations in <sup>104</sup>Pd and more established dosimeters such as <sup>192</sup>Pt [8, 9]. We present new data for the IIAB, IIIAB, IVA and IVB iron meteorites, including the samples North Chile, Sikhote-Alin, Henbury, Cape York, Gibeon, Muonionalusta, Tawallah Valley and Santa Clara.

**Methods:** Fusion crust and weathered edges were removed from all samples before digestion. Additionally, samples were leached in cold 2 M HCl, before dissolution in aqua regia. Primary separation of Pd from Pt (and general matrix elements) was achieved using

AG1-X8 anion exchange resin following a procedure modified from [10].

**Platinum.** A second ion exchange column was developed for further purification and removal of Ir from Pt [11]. This is important as Ir causes tailing effects onto Pt isotopes during measurement by MC-ICPMS. In previous studies Ir tailing resulted in corrections of between 2 and 15 to  $\epsilon^{192}\text{Pt}/^{195}\text{Pt}$  [5]. Iridium was reduced before the samples were loaded onto anion exchange resin and then separated from Pt. This procedure was repeated in order to achieve a <sup>191</sup>Ir/<sup>195</sup>Pt ratio of less than 0.16, thus minimizing the effect of tailing from Ir isotopes onto Pt. Finally, Pt cuts were dried in a mixture of aqua regia and perchloric acid in order to volatilize remaining Os, which generates isobaric interferences on Pt isotopes. After chemistry, both Os and Ir are removed to an adequate level. In particular, <sup>191</sup>Ir/<sup>195</sup>Pt ratios are less than 0.02 such that no additional correction for tailing of Ir onto Pt is necessary, therefore overcoming a major analytical uncertainty.



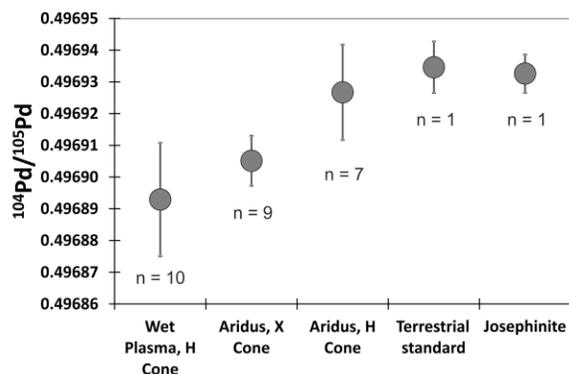
**Figure 1.** Isotopic shifts predicted by [4] for an iron meteorite with a pre-atmospheric radius of 40 cm and an exposure age of 625 Ma. Variations in  $\epsilon^{107}\text{Ag}/^{109}\text{Ag}$  vs.  $\epsilon^{104}\text{Pd}/^{105}\text{Pd}$  for a range of Pd/Ag ratios and Rh/Pd = 2 are shown.

**Palladium.** Ruthenium causes isobaric interferences on <sup>102</sup>Pd and <sup>104</sup>Pd. Doping experiments show that it is vital to achieve Ru/Pd ratios of < 0.005 in order to ensure an accurate interference correction when measuring by MC-ICPMS [12]. Separation of Pd from Ru was achieved by drying the sample in a mixture of aqua regia and perchloric acid. The sample was then loaded onto anion exchange resin where Pd was successfully separated from remaining Ru and other matrix elements. This procedure typically yields Ru/Pd ratios < 0.0005.

For both Pt and Pd, yields after anion exchange chemistry are 70 % or better, and total procedural blanks are less than 1 ng.

**Isotopic analyses.** All Pt and Pd analyses were made using a Thermo Scientific Neptune Plus MC-ICPMS with a Cetac Aridus II desolvating nebulizer and standard H cones, operated in low-resolution mode. Additionally, the MC-ICPMS is fitted with two  $10^{12} \Omega$  resistors which were employed for collecting  $^{190}\text{Pt}$  and  $^{188}\text{Os}$ , or  $^{101}\text{Ru}$  and  $^{111}\text{Cd}$  for interference corrections.

For Pt analyses, all isotopes were collected simultaneously. In addition,  $^{188}\text{Os}$  and  $^{200}\text{Hg}$  were monitored to correct for isobaric interferences, and  $^{191}\text{Ir}$  was monitored to check tailing effects onto Pt isotopes. Analyses were corrected for instrumental mass bias using the exponential law, and were internally normalized to both  $^{198}\text{Pt}/^{195}\text{Pt}$  ('8/5') = 0.2145 and  $^{196}\text{Pt}/^{195}\text{Pt}$  ('6/5') = 0.7464 [5, 6]. Samples were measured relative to NIST SRM 3140 Pt standard solution. The daily external precision (2 S.D.) of a 260 ppb Pt standard is typically better than 0.8 for  $\epsilon^{192}\text{Pt}/^{195}\text{Pt}$  (8/5). Reproducibility for SRM 3140 passed through ion exchange chemistry is  $\epsilon^{192}\text{Pt}/^{195}\text{Pt}$  (8/5) =  $0.2 \pm 0.8$  (2 S.D., n = 6).

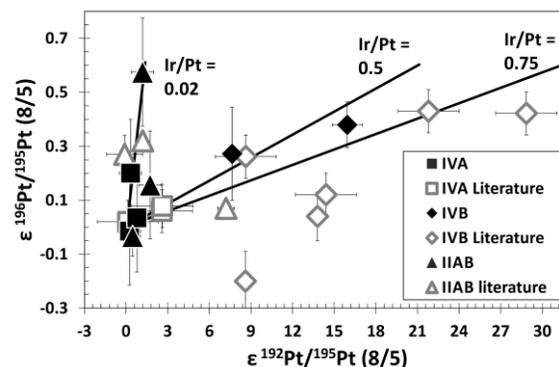


**Figure 2.** The  $^{104}\text{Pd}/^{105}\text{Pd}$  ratios for SRM 3138 measured using a Neptune MC-ICPMS in wet plasma mode, compared to an Aridus II introduction system. The Aridus II was tested with both standard H cones and an X skimmer cone. Also shown are data for SRM 3138 and a terrestrial Pd-bearing mineral (Josephinite) which had been passed through column chemistry.

All Pd isotopes were simultaneously analysed. Additionally,  $^{101}\text{Ru}$  and  $^{111}\text{Cd}$  were monitored to correct for potential isobaric interferences. Instrumental mass bias was corrected for using the exponential law and  $^{108}\text{Pd}/^{105}\text{Pd} = 1.18899$  [13]. All samples were measured relative to the NIST SRM 3138 standard. The daily external precision (2 S.D.) of a 100 ppb Pd standard solution is typically better than 15 and 10 ppm for  $^{104}\text{Pd}/^{105}\text{Pd}$  and  $^{106}\text{Pd}/^{105}\text{Pd}$ , respectively (Fig. 2).

**Discussion: Palladium.** Our results using the Aridus II introduction system for the Pd SRM 3138 standard (both untreated and passed through ion exchange chemistry) and the Josephinite yielded identical Pd isotope compositions (Fig. 2). This shows that our new analytical method provides accurate and precise results.

**Platinum.** New data for the IVA meteorite group confirm previous analyses by [5, 7], which suggest that these meteorites were weakly exposed to the effects of neutron capture due to GCR (Fig. 3). Many IIAB samples were also weakly exposed, but their low Ir/Pt ratios result in a limited spread in  $\epsilon^{192}\text{Pt}/^{195}\text{Pt}$ . IVB samples show larger variations, in particular for  $\epsilon^{192}\text{Pt}/^{195}\text{Pt}$ , which is due to their higher and more variable Ir/Pt ratios (Fig. 3). Our new data correlate well with GCR models of [4], and confirm that Pt isotopes can be used to correct GCR effects without prior knowledge of exposure time and depth in sample.



**Figure 3.**  $\epsilon^{196}\text{Pt}/^{195}\text{Pt}$  vs.  $\epsilon^{192}\text{Pt}/^{195}\text{Pt}$ . Modelled GCR exposure trends from [4] are also shown for Ir/Pt ratios of the analysed samples. New data for the IVA, IVB and IIABs overlap with literature data [5, 6, 7].

**References:** [1] Kleine T. et al. (2009) *Geochim. Cosmochim. Acta*, 73, 5805-5818 [2] Chen J. H. and Wasserburg G. J. (1990) *Geochim. Cosmochim. Acta*, 54, 1729-1743 [3] Theis K. et al. (2013) *Earth. Planet. Sci. Letters*, 361, 402-411 [4] Leya I. and Masarik J. (2013) *Meteoritics & Planet. Sci.*, 48, 665-685 [5] Kruijer, T. S. et al. (2013) *Earth. Planet. Sci. Letters*, 361, 162-172 [6] Wittig, N. et al. (2013) *Earth. Planet. Sci. Letters*, 361, 152-161 [7] Kruijer et al. (2014) *Science*, 344, 1150-1154 [8] Wittig N. et al. (2013) *LPSC 44*, Abstract #2355 [9] Mayer B. et al. (2014) *LPSC 45*, Abstract #2581 [10] Rehkämper M. and Halliday A. N. (1997) *Talanta*, 44, 663-672 [11] Hunt et al. (2014) *77<sup>th</sup> Metsoc*, Abstract #5260 [12] Ek et al, (2014) *77<sup>th</sup> Metsoc*, Abstract #5262 [13] Kelly W. R. and Wasserburg G. J. (1978) *Geophys. Res. Lett.*, 5, 1079-1082.