

## NEUTRON CAPTURE ON PLATINUM AND TUNGSTEN ISOTOPES IN IRON METEORITES: IMPLICATIONS FOR HF-W CHRONOMETRY

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**Introduction:** The extinct  $^{182}\text{Hf}$ - $^{182}\text{W}$  decay system ( $t_{1/2} = 8.9$  Myr) is ideally suited for dating metal segregation in planetesimals. For instance, magmatic iron meteorites exhibit strong  $^{182}\text{W}$  deficits, indicating that they represent fragments of some of the oldest planetesimals formed in the solar system [e.g., 1-3]. However, a reliable chronological interpretation of the Hf-W data is hampered by neutron-capture reactions on W isotopes in iron meteoroids [1-4]. Determining accurate core formation ages thus requires the quantification of cosmic-ray induced W isotope shifts. Corrections involving  $^3\text{He}$  and/or exposure ages [e.g. 2,3] are imperfect monitors for these effects, because cosmogenic noble gases are primarily produced by higher energy nuclear reactions that occur near the surface of a meteoroid, while W isotopes are predominantly affected by neutron-capture reactions at (epi)thermal energies occurring at larger depth [5]. Nevertheless, cosmogenic noble gases are useful for identifying iron meteorite samples with minor to absent (epi)thermal neutron fluences. In a previous study we showed that magmatic irons with very low concentrations of cosmogenic noble gases have  $^{182}\text{W}/^{184}\text{W}$  ratios indistinguishable from the initial of CAI, but higher than those of other magmatic irons [5]. This observation suggests that iron meteorite samples with very low concentrations of cosmogenic noble gases have only minimal cosmic-ray effects [5]. An accurate quantification of cosmic-ray effects on W isotopes, however, requires the use of a direct neutron dose monitor [4].

**Aim and Approach:** In the present study we explore the potential of Pt isotopes as a neutron fluence monitor in iron meteorites. Due to the large resonance integrals of the Ir isotopes, the reactions  $^{193}\text{Ir}(n,\gamma)^{194}\text{Ir}(\beta^-)^{194}\text{Pt}$  and  $^{191}\text{Ir}(n,\gamma)^{192}\text{Ir}(\beta^-)^{192}\text{Pt}$  can induce positive anomalies in  $^{194}\text{Pt}$  and very large anomalies in  $^{192}\text{Pt}$ .

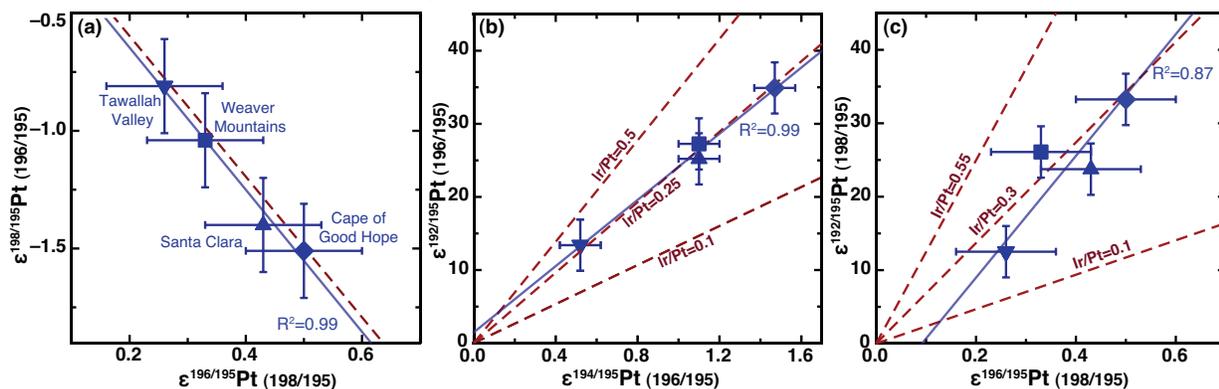
The magnitude of anomalies in  $^{192}\text{Pt}$  and  $^{194}\text{Pt}$  also depends on the Ir/Pt of the meteorite. Moreover, the reaction  $^{195}\text{Pt}(n,\gamma)^{196}\text{Pt}$  generates isotope anomalies in

$^{195}\text{Pt}$  and  $^{196}\text{Pt}$  that are independent on the Ir/Pt ratio, while  $^{198}\text{Pt}$  is the only isotope that is (mostly) unaffected by neutron capture. Both Pt and W isotopes are mainly affected by neutron capture reactions in the epithermal energy range. Therefore Pt isotope compositions are a promising proxy for cosmic-ray induced neutron-capture reactions on W isotopes.

Here we present the first precise Pt isotope data for extraterrestrial materials and report the first findings of neutron capture induced Pt isotope anomalies in iron meteorites. The combined Pt and W isotope analyses on IVB iron meteorites are used to quantify the effects of neutron capture on the W isotopes, and these results are then compared to the  $^{182}\text{W}/^{184}\text{W}$  of magmatic irons that were most likely unaffected by cosmic-rays [5].

**Samples and Analytical Methods:** IVB iron meteorites exhibit the lowest  $^{182}\text{W}/^{184}\text{W}$  among magmatic iron meteorites, indicating substantial modification of their W isotope budgets by neutron-capture reactions. They also show relatively high concentrations of cosmogenic noble gases. IVB irons, therefore, are ideal targets for an initial search for neutron-capture induced Pt isotope anomalies in iron meteorites.

Selected IVB irons (Fig. 1) were dissolved in  $\text{HNO}_3:\text{HCl}$  and aliquots were taken for Pt and W isotope analyses. The purification of Pt involved solvent extraction of Os from reverse aqua regia into  $\text{CCl}_4$  [6] and ion exchange chromatography [7]. Platinum isotopes were measured using a ThermoScientific Neptune Plus<sup>®</sup> MC-ICPMS at the University of Münster, equipped with an APEX<sup>®</sup> nebulizing system.



**Fig. 1** Platinum isotope variations in IVB irons. (a)  $\epsilon^{192}\text{Pt}$  vs.  $\epsilon^{194}\text{Pt}$ , (b)  $\epsilon^{192}\text{Pt}$  vs.  $\epsilon^{196}\text{Pt}$ , (c)  $\epsilon^{192}\text{Pt}$  vs.  $\epsilon^{198}\text{Pt}$ . The modeled correlations for neutron capture (red dashed lines) are generally consistent with the regression through the data (blue solid line). Modeled correlations also account for neutron capture effects on the normalizing ratios (i.e.  $^{196}\text{Pt}/^{195}\text{Pt}$  and  $^{198}\text{Pt}/^{195}\text{Pt}$ ). Error bars represent 2SD external uncertainties.

Isobaric Os interferences on  $^{192}\text{Pt}$  were corrected by monitoring  $^{189}\text{Os}$ . Instrumental mass bias was corrected by normalizing to  $^{196}\text{Pt}/^{195}\text{Pt}$  or  $^{198}\text{Pt}/^{195}\text{Pt}$  using the exponential law. The analytical methods for W isotope analyses are described in [5]. Platinum and W isotope ratios are reported as  $\epsilon^{191/195}\text{Pt}$  and  $\epsilon^{181/184}\text{W}$ , i.e., in parts per  $10^4$  deviations from terrestrial W and Pt.

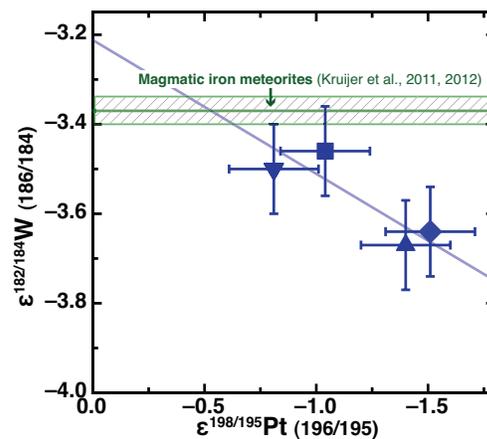
**Results:** The new Pt isotope data are displayed in Fig. 1. All studied IVB iron meteorites show small but well resolved anomalies in  $\epsilon^{196}\text{Pt}$  (8/5) and  $\epsilon^{198}\text{Pt}$  (6/5) that are negatively correlated (Fig. 1a). Very large anomalies are observed for  $\epsilon^{192}\text{Pt}$ , ranging from  $\sim 13$  to  $35$  (Fig. 1bc), while  $\epsilon^{194}\text{Pt}$  anomalies are significantly smaller ( $\sim 0.5$ - $1.5$ ) (Fig. 1b). The  $\epsilon^{182}\text{W}$  values of the same samples range from  $-3.5$  to  $-3.2$ , and  $\epsilon^{183}\text{W}$  values are  $\sim 0.10$ , consistent with previous results [8].

**Discussion:** The mass-independent Pt isotope variations in the IVB irons may either be due to nucleosynthetic anomalies or may reflect capture of (epi)thermal neutrons during cosmic-ray exposure of the IVB iron meteoroid. Diagnostic are the large  $^{192}\text{Pt}$  anomalies of up to  $35$   $\epsilon$  observed for the IVB irons from this study. These cannot be nucleosynthetic in origin because the collateral deficit of  $\sim 7$   $\epsilon^{198}\text{Pt}$  predicted by astrophysical models [9] is not observed. Instead, the observed positive shifts in  $^{192}\text{Pt}$  and  $^{194}\text{Pt}$  are fully consistent with neutron capture reactions on  $^{191}\text{Ir}$  and  $^{193}\text{Ir}$ . Further evidence that the Pt isotopic anomalies are caused by neutron-capture within the IVB iron meteoroid comes from the observation that the  $\epsilon^{196}\text{Pt}$  and  $\epsilon^{198}\text{Pt}$  values are variable among the four investigated IVB irons. As nucleosynthetic anomalies arise from a heterogeneous distribution of isotopically distinct presolar components, all IVB irons should carry the same anomaly (because they all derive from the same parent body). This is not observed, however. Instead, the  $\epsilon^{196}\text{Pt}$  (8/5) and  $\epsilon^{198}\text{Pt}$  (6/5) variations are well correlated and can be fully explained by the neutron capture reaction  $^{195}\text{Pt}(n,\gamma)^{196}\text{Pt}$  (red dashed line in Fig. 1a).

The  $\epsilon^{183/184}\text{W}$  values of the studied IVB irons are positive, and consistent with previously reported s-process deficits for this group of samples [8]. After correction for these nucleosynthetic effects using [9], the  $\epsilon^{182}\text{W}$  values of the IVB irons range from  $-3.46$  to  $-3.67$ . These  $\epsilon^{182}\text{W}$  values are reasonably well correlated with the Pt isotope anomalies (Fig. 2), indicating (i) that the  $^{182}\text{W}$  variations are due to neutron capture effects, and (ii) that Pt isotopes are a suitable proxy for such effects on the W isotopes. Using the correlation between  $\epsilon^{182}\text{W}$  and  $\epsilon^{198}\text{Pt}$ , an intercept of  $\epsilon^{182}\text{W} = -3.21 \pm 0.28$  is obtained for  $\epsilon^{198}\text{Pt} = 0$ . Despite its large uncertainty, this value is in good agreement with a more precise, independent average for magmatic iron

meteorites of  $\epsilon^{182}\text{W} = -3.37 \pm 0.03$  from the aforementioned combined noble gas – W isotope study [5].

The interpretation of the neutron capture-induced  $\epsilon^{192}\text{Pt}$  and  $\epsilon^{194}\text{Pt}$  anomalies is more complicated, because their magnitude depends on the Ir/Pt of the respective meteorite sample. This results in a larger scatter in variation diagrams involving  $\epsilon^{192}\text{Pt}$  or  $\epsilon^{194}\text{Pt}$  (e.g., Fig. 1c), which results from the different Ir/Pt of the iron meteorites. Current research focuses on obtaining more precise  $^{192}\text{Pt}$  data, and on developing a model to interpret neutron capture induced  $^{192}\text{Pt}$  and  $^{194}\text{Pt}$  anomalies in greater detail.



**Fig. 2**  $\epsilon^{182}\text{W}$  vs.  $\epsilon^{198}\text{Pt}$  for the iron meteorites studied here. Also shown (green hashed area) is the value for magmatic irons which are largely unaffected by cosmic-rays [5].

**Conclusions:** We demonstrate the first neutron capture induced Pt isotope variations in iron meteorites resulting from cosmic-ray exposure. Thus, Pt isotope analyses provide a powerful means for identifying and correcting neutron capture induced shifts in W isotope compositions, a prerequisite for a reliable interpretation of Hf-W data of iron meteorites. The first results presented here are consistent with the conclusion from [5] that magmatic iron meteorites segregated their cores within less than  $\sim 1$  Myr after CAI formation.

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**References:** [1] Kleine, T. et al. (2005) *Geochim. Cosmochim. Acta*, 69, 5805-5818. [2] Markowski, A. et al. (2006) *EPSL* 250, 104-115. [3] Qin, L. et al. (2008) *EPSL* 273, 94-104. [4] Leya, I. et al. (2003) *Geochim. Cosmochim. Acta*, 67, 529-541. [5] Kruijjer, T. et al. (2011) *LPSC #1712*. [6] Cohen, H.S. and Waters, F.G. (1996) *An. Chim Acta* 332, 269-275. [7] Rehkämper, M. and Halliday, A.N. (1997) *Talanta* 44, 663-672. [8] Qin, L. et al. (2008) *Astrophys. J.* 674, 1234-1241. [9] Arlandini C, et al. (1999) *Astrophys. J.* 525, 886-900.