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Coupled W–Os–Pt isotope systematics in IVB iron meteorites: In situ neutron dosimetry for W isotope chronology

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ABSTRACT

Tungsten isotope compositions of magmatic iron meteorites yield ages of differentiation that are within ± 2 Ma of the formation of CAIs, with the exception of IVB irons that plot to systematically less radiogenic compositions yielding erroneously old ages. Secondary neutron capture due to galactic cosmic ray (GCR) irradiation is known to lower the ε^{182}W of iron meteorites, adequate correction of which requires a measure of neutron dosage which has not been available, thus far. The W, Os and Pt isotope systematics of 12 of the 13 known IVB iron meteorites were determined by MC-ICP-MS (W, Os, Pt) and TIMS (Os). On the same dissolutions that yield precise ε^{182}W, stable Os and Pt isotopes were determined as in situ neutron dosimeters for empirical correction of the ubiquitous cosmic-ray induced burn-out of ^{182}W in iron meteorites. The W isotope data reveal a main cluster with ε^{182}W of ~ -3.6, but a much larger range than observed in previous studies including irons (Weaver Mountains and Warburton Range) that show essentially no cosmogenic effect on their ε^{182}W. The IVB data exhibits resolvable negative anomalies in ε^{189}Os (-0.6ε) and complementary ε^{190}Os anomalies ($+0.4\varepsilon$) in Tlacotepec due to neutron capture on ^{189}Os which has approximately the same neutron capture cross section as ^{182}W, and captures neutrons to produce ^{190}Os. The least irradiated IVB iron, Warburton Range, has ε^{189}Os and ε^{190}Os identical to terrestrial values. Similarly, Pt isotopes, which are presented as ε^{192}Pt, ε^{194}Pt and ε^{196}Pt range from $+4.4\varepsilon$ to $+53\varepsilon$, $+1.54\varepsilon$ to -0.32ε and $+0.73\varepsilon$ to -0.20ε, respectively, also identify Tlacotepec and Dumont as the most GCR-damaged samples. In W–Os and W–Pt isotope space, the correlated isotope data back-project toward a 0-epsilon value of ε^{192}Pt, ε^{189}Os and ε^{190}Os from which a pre-GCR irradiation ε^{182}W of -3.42 ± 0.09 (2σ) is derived. This pre-GCR irradiation ε^{182}W is within uncertainty of the currently accepted CAI initial ε^{182}W. The Pt and Os isotope correlations in the IVB irons are in good agreement with a nuclear model for spherical irons undergoing GCR spallation, although this model over-predicts the change of ε^{182}W by $\sim 2\times$, indicating a need for better W neutron capture cross section determinations. A nucleosynthetic effect in ε^{184}W in these irons of -0.14 ± 0.08 is confirmed, consistent with the presence of Mo and Ru isotope anomalies in IVB irons. The lack of a non-GCR Os isotope anomaly in these irons requires more complex explanations for the production of W, Ru and Mo anomalies than nebular heterogeneity in the distribution of s-process to r-process nuclides.

1. Introduction

The ^{182}Hf–^{182}W chronometer ($t_{1/2}$=8.9 Ma) is important for dating metal-silicate fractionation events in the first 60 Ma of solar system history (Jacobsen, 2005; Kleine et al., 2009). The initial W isotope composition and the $(^{182}Hf/^{180}Hf)_0$ ratio are essential for calibration of this chronometer. In the first attempts to apply the Hf–W isotope chronometer, the least radiogenic W in solar system material was obtained from precise W isotopic analyses of iron meteorites yielding initial ε^{182}W~ -4 (Harper and Jacobsen, 1996; Lee and Halliday, 1996). Precise Hf–W isochrons on Allende CAIs have yielded refined values of ε^{182}W$=-3.28 \pm 0.12$ (Burkhardt et al., 2008), although this value may be compromised by metamorphism of Allende (Humayun et al., 2007). Recently, the CAI initial ε^{182}W has been revised (-3.51 ± 0.10 2σ) to account for nucleosynthetic anomalies in the

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original data (Burkhardt et al., 2012), yielding a value similar to that determined earlier by Kleine et al. (2005); -3.47 ± 0.09 2σ. Precise W isotope compositions of iron meteorites are used to determine the timing of core formation (magmatic irons) or of metal-silicate differentiation (non-magmatic irons) in their parent bodies. Using the Allende CAI initial ε^{182}W value proposed by Burkhardt et al. (2008), the timing of core differentiation in the majority of magmatic iron meteorites has been bracketed from -2.8 to $+1.4$ Ma, since the time of formation of CAIs (Kleine et al., 2009). All of the magmatic irons are systematically biased to apparently older ages (less radiogenic initial ε^{182}W) than CAI in the compilation of Kleine et al. (2009). Average ε^{182}W for most magmatic iron meteorite groups (Qin et al., 2008b) are within error of the Allende CAI initial ε^{182}W value, with the notable exception of group IVB irons which record ε^{182}W (-3.57 ± 0.10, excluding Tlacotepec) resolvably less radiogenic than the CAI initial ε^{182}W (Burkhardt et al., 2008), and barely within error of the revised Allende CAI initial ε^{182}W (Burkhardt et al., 2012). Given the currently unsettled CAI initial ε^{182}W (Kleine et al., 2005; Humayun et al., 2007; Burkhardt et al., 2008, 2012), and that some magmatic iron meteorites formed within 1–2 Ma of CAIs (Blichert-Toft et al., 2010), iron meteorites may be expected to constrain the upper limit on the solar system initial ε^{182}W.

The ε^{182}W of iron meteorites is known to be lowered by neutron capture reactions from secondary neutrons due to cosmic-ray spallation of the iron masses during space exposure as <1 m diameter objects (Kleine et al., 2005; Markowski et al., 2006a, 2006b; Masarik, 1997; Scherstén et al., 2006). The extent of secondary neutron capture has to be precisely determined if iron meteorites are to be useful in examining either the initial ε^{182}W of the solar system or small time differences between various iron meteorite groups. The neutron fluence in an iron meteorite is not uniformly distributed but is peaked $\sim$30–40 cm below the pre-atmospheric exposure surface (Masarik, 1997), while spallogenic nuclides (e.g. noble gases) are peaked in abundance near the original exposure surface (Ammon et al., 2009). Thus, existing noble gas measurements in iron meteorites do not provide adequate corrections for neutron capture effects on ^{182}W in iron meteorites but allow upper limits to be placed on the maximum effect on ε^{182}W (Markowski et al., 2006b; Qin et al., 2008b). Precise knowledge of the neutron capture modification of isotope ratios in iron meteorites has been limited by a lack of information on the neutron fluence experienced by an iron sample cut from a <1 m iron mass. Several elements have isotopes with high neutron capture cross-sections that function effectively as neutron dosimeters including B, Cd, Sm and Gd (e.g., Schulz et al., 2012). All of these elements are lithophile except, possibly, Cd which has been investigated in iron meteorites without definitive results (Kruijer et al., 2011).

The approach taken here has been to develop new in situ neutron dosimeters involving siderophile elements in the W–Au mass region that have a comparable response to secondary neutrons as ^{182}W so that the initial ε^{182}W of IVB irons may be determined independently from the CAI initial value (Burkhardt et al., 2008, 2012; Kleine et al., 2005). The neutron capture cross-section of ^{189}Os is comparable to that of ^{182}W, and it produces ^{190}Os, which has a low neutron capture cross-section creating a positive anomaly in ε^{190}Os (Fig. 1). This reaction was successfully exploited by Huang and Humayun (2008), and more recently by Walker (2012), who showed the presence of anti-correlated isotope anomalies in ε^{189}Os and ε^{190}Os in IVB irons with a maximum effect in Tlacotepec, the iron meteorite with the lowest ε^{182}W (-4.5 to -4.0, Horan et al., 1998; Markowski et al., 2006a, 2006b; Scherstén et al., 2006; Qin et al., 2008b). However, W isotope compositions of most of the IVB irons analyzed for Os isotopes were not available in the literature, and direct measurement of W isotopes on the same aliquots analyzed for Os isotopes is important since neutron fluence varies significantly within a single iron meteorite. Another GCR reaction that has potential for neutron dosimetry is the neutron capture of ^{191}Ir to form ^{192}Pt, since the resulting isotope has a low natural abundance (0.78%) and the large amplification of the neutron capture reaction makes this a potentially sensitive neutron dosimeter (Fig. 1).

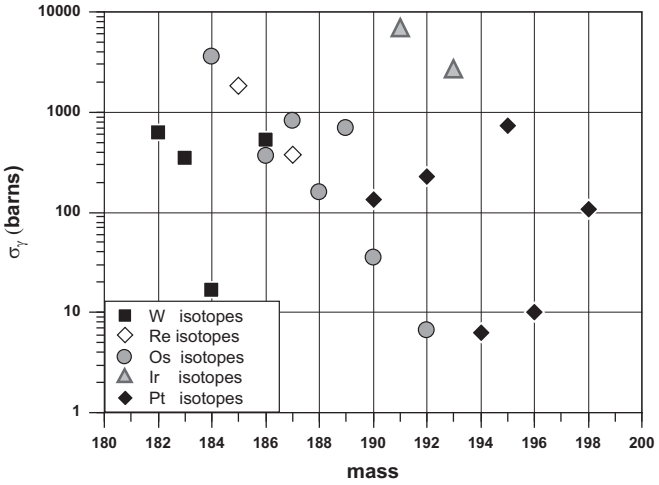

Fig. 1. Thermal neutron capture cross sections of W (black squares), Re (open diamonds), Os (grey circles), Ir (grey triangles) and Pt isotopes (black diamonds) given as $\sigma\gamma$ (barns) (Mughabghab, 2003).

In this study, we report precise isotope compositions of W, Os and Pt on 12 of the 13 known IVB iron meteorites (Tenera was not obtainable for this project). From correlations of ε^{182}W with ε^{189}Os and ε^{192}Pt, we calculate a precise and consistent value for the pre-irradiation ε^{182}W for the IVB magmatic iron meteorite group. We also confirm that there appears to be a small nucleosynthetic effect in ε^{184}W in IVB irons as reported previously (Qin et al., 2008a, 2008b). We use the Os isotope data to evaluate whether nucleosynthetic anomalies in Os isotopes are resolvable, which may be expected from the isotope anomalies observed in Mo (Burkhardt et al., 2011), Ru (Chen et al., 2010; Fischer-Gödde et al., 2012) and W (Qin et al., 2008a, 2008b) for IVB irons. This provides important constraints on the likely origins of nucleosynthetic effects in bulk iron meteorites.

2. Analytical methods

Between 0.3 and 0.9 g of 12 IVB iron meteorites were sawn from larger pieces using a jewellers' handsaw with stainless steel blades, hand-polished with Al_2O_3 sand paper to remove saw marks, rinsed with DI water and immediately digested in pre-cleaned Carius tubes with inverse Aqua Regia (iAR, HCl–HNO_3 [1:3]) (Shirey and Walker, 1995). After digestion (230 °C, >48 h), the Carius tubes were opened and Os was removed by established solvent extraction procedures (Cohen and Waters, 1996) and purified by micro-distillation prior to analysis by N-TIMS or MC-ICP-MS.

After the extraction of Os, aliquots of the sample iAR solution ($\sim$10%) were dried down and dissolved in 0.1 M HCl–0.01 M HF–1% H_2O_2 and loaded onto columns with 2 mL cation resin (AG 50W-X8 [200–400 mesh]) in order to retain Fe, Ni and other matrix cations on the column, whereas W and Pt and other anions were collected in the elutant (Puchtel and Humayun, 2001). W separation procedures were modified from Kleine et al. (2004) and Markowski et al. (2006a, 2006b). After drying down the cation column elutant, the samples were dissolved in 0.5 mL 2 M HCl-0.5 M HF and W (and Mo) was separated in 6 M HNO_3