

INVESTIGATIONS OF THE ^{182}Hf - ^{182}W SYSTEMATICS; C. L. Harper Jr. & S. B. Jacobsen, Dpt. Earth & Planet. Sci., Harvard Univ., 20 Oxford St., Cambridge, MA 02138 USA

Introduction: The ^{182}Hf - ^{182}W chronometer is likely to become a powerful tool in studies of the accretion and very early differentiation histories of planets. Careful investigation of the ^{182}Hf - ^{182}W system is also important in astrophysics because a determination of the initial abundance of ^{182}Hf will provide a key constraint on models of the molecular cloud environment within which the sun formed. The 9 Ma half-life of ^{182}Hf provides an excellent timescale for studies of both star-forming and planet-building processes. Several geochemical aspects also make the ^{182}Hf - ^{182}W systematics particularly well suited for dating planetary accretion-related (as opposed to nebular) processes. First, in contrast to the U/Pb, Rb/Sr, I/Xe and Pu/Xe parent/daughter pairs, both elements in the Hf/W parent/daughter pair are refractory. Therefore nebular fractionations involving episodes of volatile loss are unlikely to have modified the initial budgets of Hf and W in bulk planetary reservoirs (which are expected to have been present in chondritic proportions). Second, W is a moderately siderophile element, and its factor of 10-30 depletions in the silicate mantles of planets (Earth, Mars, Moon, eucrite parent body) is a consequence of the partitioning of W into planetary cores during core formation. In the case of the highly siderophile element chronometries, ^{187}Re - ^{187}Os and ^{244}Pu -Ru,Pd [1], this relatively simple fractionation history is complicated by the likelihood that a significant part (up to >99%) of their silicate mantle budgets were supplied by a "late veneer" component of material accreted well after the epoch of core formation, and later admixed geodynamically. While this aspect of multistage complexity makes the ^{187}Re - ^{187}Os and especially the ^{244}Pu -Ru,Pd systematics particularly attractive for studying early planetary geodynamics, any putative veneer contributions to W budgets in planetary silicate mantles are insignificant (<1%); consequently W isotopes should provide a clear window into the epoch of core formation. As we expect core formation to have been rate-limited by accretion during most of the major mass accumulation epochs of the silicate planets, ^{182}Hf - ^{182}W provides an apparently unique source of potential information with which to test planetesimal coagulation models. Complexity arises in the context of large-scale giant-impact-type accretion events (mergers), in which planetary cores and mantles merge without chemically homogenizing (and thereby isotopically equilibrating). In the pure case of this mode of accretion, chronometric information in W isotopes in the final planetary silicate mantle approximates a mass-average over the differentiation histories of the pre-merged bodies, so the chronology of the late stages of hierarchical accretion series is not recorded. However, because giant impact events probably generate whole-mantle melting and mixing, the date of the last such event can in principle be constrained from the ^{146}Sm - ^{142}Nd (silicate differentiation) chronometer (*cf.*, [2], & companion abstract by Jacobsen & Harper). In summary, W isotopes are capable of supplying information about the history of accretion (Fig. 1a,b) prior to any late stages of merger-type planet building.

^{182}W Measurements: W isotopic measurements by the negative thermal ionization mass spectrometry (NTIMS) method using WO_3^- beams were developed by Köppe (1989), Heumann *et al.* (1989) and Völkening *et al.* (1991) [3]. The first high precision W isotopic measurements of meteoritic W by NTIMS were reported by Harper *et al.* (1991) [4] as a comparison series of 12 runs each of standard tungsten and tungsten separated from the iron phase of the Toluca iron meteorite. Relative to a $^{183}\text{W}/^{184}\text{W}$ normalization, an apparent shift of -3.0 ± 0.9 epsilon-units in $^{182}\text{W}/^{184}\text{W}$ was observed in the Toluca W relative to the standard (Fig. 2) with the $^{186}\text{W}/^{184}\text{W}$ ratio found to be normal within an uncertainty of $\sim \pm 3$ epsilon-units. After consideration of various possible sources of error (interferences and/or $^{18,17}\text{O}/^{16}\text{O}$ fractionation), the shift was concluded to be a real effect. It can be interpreted as a result of two possible processes: (i) neutron capture modification of the W isotopic composition during space exposure, or (ii) radiogenic growth of ^{182}W in the silicate portion of the Earth (= the high-Hf/W reservoir source of the standard) due to ^{182}Hf decay after removal of W to the Earth's core. In the latter case, Toluca W would approximate the non-radiogenic initial isotopic composition for $^{182}\text{W}/^{183}\text{W}$ in the solar system. In order to confirm the effect and study the fine structure of the non-radiogenic mass abundances of W from Toluca and other iron meteorites, we have developed a high precision multicollector technique for W isotopic measurements utilizing a 7-cup configuration allowing simultaneous monitoring of oxygen

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isotope fractionation and ReO_3^- interference (Figs. 3 & 4). Reproducibility for a suite of standard $^{182}\text{W}/^{183}\text{W}$ measurements normalized to $^{184}\text{W}/^{183}\text{W}$ is shown in Figure 5 and indicate an $\sim\pm 1\epsilon$ -unit level of precision. One measurement of Toluca W from a new separation is also shown. This measurement appears to confirm the finding of Harper *et al.* (1991) [3], but is imprecise due to a degradation of beam stability from impurity in the sample. Efforts are underway to obtain highest quality measurements with a new purified sample. **REFS:** [1] Harper C. L. Jr. (1993). *Meteoritics*, 28, 359; [2] Harper C. L. Jr. and Jacobsen S. B. (1992). *Nature*, 360: 728; [3] Köppe M. (1989). Ph. D. Chem. Thesis, Regensburg, F.R.G.; Heumann K. G. *et al.* (1989). *Proc. 37th ASMS Conf. Mass Spectrometry & Allied Topics*, p. 414; Völkening J. *et al.* (1991). *Int. J. Mass Spec. Ion Proc.*, 107: 361; [4] Harper C. L. *et al.* (1991). *LPS XXII*: 515.

