INITIAL ^{182}Hf/^{180}Hf AND W-ISOTOPIC SYSTEMATICS OF THE EARLY SOLAR SYSTEM.

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The ^{182}Hf – ^{182}W decay scheme has a number of attributes that make it a highly useful chronometer for early solar system processes. Both Hf and W are refractory and thus are not susceptible to perturbations caused by high-temperature processing in the early solar system. The half-life of 9 million years is close to the possible lifetime of the solar nebula allowing suitable time-points to be determined. Hf and W have quite different geochemical affinities, Hf is lithophile while W is significantly more siderophile, and hence Hf-W systematics might be used for constraining the timing of planetary core formation. It is this latter aspect that has attracted great interest in cosmochemistry [1-5]. The presence of a ^{182}W deficit in iron meteorites (relative to bulk chondrite meteorites) suggests that Fe meteorites formed, that is Hf was fractionated away from W, prior to the complete decay of ^{182}Hf to ^{182}W (half life of 9 Ma). The deficit provides strong evidence of the presence of ^{182}Hf in the early solar system, although determining the ^{182}Hf/^{180}Hf from this data requires a cosmochemical model relating W isotopic compositions with Hf/W ratios.

Lee and Halliday [1] determined that the W isotopic composition of chondrites was the same as terrestrial, and along with a Hf/W cosmochemical model, determined that the initial ^{182}Hf/^{180}Hf of the solar system was approximately 2×10^{-4}. The similarity of terrestrial and chondritic compositions required sufficient time to essentially allow all ^{182}Hf to decay to ^{182}W and for that ^{182}W to be homogeneously distributed in Earth. Thus, terrestrial core formation, which causes Hf-W fractionation, can only take place after all ^{182}Hf has decayed to suitably low levels, approximately 60 Ma.

Recently, a number of new measurements [4,5] draw into question the inferences previously drawn and suggest that the Hf-W isotope systematics of the early solar system are not as straightforward as previously proposed. Specifically, the new observations suggest that the chondritic ^{182}W/^{183}W is 2ε units lower than terrestrial. If correct, this chondritic value would have the effect of lowering the initial ^{182}Hf/^{180}Hf of the early solar system and shortening the delay interval between accretion and core formation. Yin et al. [4] suggest a ^{182}Hf/^{180}Hf of ca 1.0×10^{-4} and delay of less than 15 Myr is viable.

This low initial ^{182}Hf/^{180}Hf is supported by zircon Hf-W systematics. We have previously attempted to measure ^{182}W in meteoritic zircons with high Hf/W ratios [6,7] and have consistently found low apparent ^{182}Hf/^{180}Hf. These low values have been questioned and interpreted as being due to a variety of causes associated with the zircon petrogenesis, including possible resetting of zircons, and the analytical technique. Through a variety of permissible effects and uncertainties, reconciliation between meteoritic zircon and whole-rock W-isotopic effects could be made.

The data of Yin et al. [4] show that the zircon data are compatible with bulk W isotopic systematics and such efforts at reconciliation were based on the wrong premise.

Nevertheless, additional possibilities for a matrix effect in Hf-W calibration from zircon have been examined that could affect the determination of ^{182}Hf/^{180}Hf values. The problem is that no zircon exists that contains sufficient W for calibration purposes. This is somewhat surprising given that W^{4+} is similar in size to Zr^{4+} and Hf^{4+} but likely reflects the presence of W in the W^{6+} oxidation state. The Hf-W calibration has been resolved into two dominant effects that affect ion yields. The first is the relative sensitivity factor due to the chemistry of Hf relative to W. This can be measured from NIST SRM 610 glass [7]. The second effect is the structural effect of the zircon matrix and the effect of Hf as a major element. This can be addressed by using another trace element as a proxy for W, in this case Yb was used. The Yb can act as a proxy because trace elements typically scale within a matrix and their relative ionization probabilities remain constant. The analysis of standard zircons with measured Hf and Yb concentrations indicates that the Hf matrix effect is relatively minor in zircon wrt NIST 610 glass with Hf being underproduced relative to Yb by about 7 %. Such a correction factor does not significantly affect the ^{182}Hf/^{180}Hf values reported previously [7].

The meteoritic zircons come from the Simmern chondrite (^{182}Hf/^{180}Hf $= 8 \pm 2 \times 10^{-5}$) and the Pomozdino eucrite ((^{182}Hf/^{180}Hf $= 2.5 \pm 0.5 \times 10^{-5}$). The Pomozdino zircons have an ion probe $^{207}Pb/^{206}Pb$ age of 4559 ± 5 Ma ($2\sigma_m$).

The Simmern zircon has a fractionated REE pattern both wrt the typical zircon heavy REE enrichments, but also shows ultrarefractory-enriched pattern with a Tm anomaly. Such systematics are typically found in CAI so it is probable that this inclusion is related in some way to CAI formation rather than chondrule formation. In either case, this will not affect the initial $^{182}Hf/^{180}Hf$ and this is likely to be close to the value for the early solar system. The zircon data are consistent with W isotopic systematics of Yin et al. [4], who suggest a $^{182}Hf/^{180}Hf$ for the early solar system of $1.00 \pm 0.08 \times 10^{-4}$.

The Pomozdino zircon is consistent with a closure period of 15 ± 7 Ma after the Simmern zircon, broadly consistent with the time difference for the U-Pb systematics wrt CAI formation (8 ± 5 Ma).

Hf-W fractionation in the early solar system is generally ascribed to parent body fractionation, specifically, core formation of planetesimals and larger planetary bodies. Tungsten is moderately siderophile and so partitions into the metal whereas hafnium is strongly lithophile and partitions into the silicate. Thus the segregation of metal into planetary cores essentially freezes the W isotopes, while the silicate mantle will evolve according to the residual amount of ^{182}Hf.

Of potentially greater significance for Hf/W fractionation is metal-silicate differentiation in the solar nebula. Substantial evidence exists for high temperatures within the solar nebula and while probably insufficient to fractionate Hf from W directly, temperatures are sufficient to melt rereactory objects (c. 2000 K). Furthermore, the temperatures required to melt a chondrule or CAI will lead to volatilization of Fe and Ni. Some of this metal will back react with the chondrule leading to higher fayalite contents in rim materials or other Fe rims, but it is likely that a large fraction of Fe is removed and condenses elsewhere as metal. Indeed metal-rich chondrites are found which show evidence of condensation through volatility-fractionated siderophile elements with indications of changing conditions within individual grains [8,9].

The W isotopic composition of Fe metal is quite uniform despite analysis from a wide range of meteorites with different inferred ages. The metal has the lowest $^{182}W/^{184}W$ values measured. The most straightforward interpretation of these observations is that early segregation in the solar system through fractional condensation has frozen the W isotopic composition. Equilibration with silicate at later time will cause an elevation in the $^{182}W/^{184}W$ ratio and will move towards the chondritic value if mass balance between the silicate and metal is maintained. Evidently this has not happened. Once the metal and silicate were segregated they have not been able to exchange W isotopes. There is a likelihood that the chondrite W isotopic systematics are dominated by metal-silicate mixing lines. Given the age of the chondritic components, the mixing line will be very close to an isochron. However, chondrites are breccias and the nature of the silicate mixing component along with CAI has not been fully examined.

The eucrite zircon Hf-W data are consistent with their relative age to CAI whereas the bulk rock W isotopic systematics suggest less evolved W isotopic values [e.g. 4, 10]. If metal segregated early in the solar system it will act as a primitive reservoir in Hf-W evolution of planetesimals. The situation will then be quite analogous to the case of mineral versus whole-rock isochrons encountered in Sr isotopes in complex metamorphic terranes on Earth. The mineral isochrons give the last age of closure, whereas the whole-rock isochron yields the age of regional scale fractionation of Rb-Sr. This situation is also possible for the eucrite system. The zircon age reflects the crystallization age of the eucrite whereas the whole-rock isochron reflects the metal-silicate fractionation in the early solar system as well.

Hf-W isotopes have been used to deconvolve chronology of planetary differentiation, but such an interpretative scheme is perhaps premature given the uncertainties involved in modeling the Hf-W isotopic evolution of the early solar system.

References:

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