

ON THE PROBLEM OF METAL-SILICATE EQUILIBRATION DURING PLANET FORMATION: SIGNIFICANCE FOR Hf-W CHRONOMETRY. S. B. Jacobsen¹, (jacobsen@neodymium.harvard.edu), Q.-Z. Yin², and M. I. Petaev^{1,3} ¹Dept. of Earth & Planetary Sci., Harvard Univ., Cambridge, MA 02138. ²Dept. of Geology, Univ. of California, One Shields Avenue, Davis, CA 95616. ³Harvard-Smithsonian Center for Astrophysics.

Introduction: The metallic cores of the terrestrial planets formed by physical separation of metal from silicate during the process of accretion. The chemical composition of the Earth's mantle provides strong evidence that the separation of the metal occurred in a magma ocean [1]. It is also thought that the rate of core growth was limited by the rate of accretion over most of the Earth's accretion interval. The ¹⁸²Hf-¹⁸²W chronometer is uniquely suited to determine the time-scale of this process [2]. Our Hf-W results show that the main phase of core formation happened within 10 Ma of the origin of the solar system and that accretion must have been terminated by about 30 Ma [3]. Recently it has been suggested [4] that inconsistency with results from other systems (U-Pb, I-Pu-Xe, Rb-Sr) requires a disequilibrium process for Hf-W that does not affect U-Pb. Here we show that the constraints from other systems are entirely consistent with the new Hf-W age of the Earth and no revision of the interpretation is necessary.

The process of metal-silicate segregation during accretion: The metal in a planetary core may be a mixture of several components with different trace element patterns: (i) a component formed in small precursor bodies during relatively low T, low P metal-silicate equilibration at a very early stage; (ii) a component equilibrated with magma at the base of a magma ocean at higher P and T, (iii) a component derived from a superheated magma ocean immediately after a giant impact, and (iv) a component derived directly from the core of a giant impactor. Also, some metal in chondrites may have condensed directly in the solar nebula. While such metal is not transported directly into the cores of planetesimals it may play a role in setting the redox conditions in planetary mantles at which FeNi metal cores form. The consistency of Hf-W and Mn-Cr chronometry tells us that the metal in both chondrites and iron meteorites formed close to the time of formation of the solar system. The process of reduction probably involved both H₂ and C, but the exact mechanism is unknown; we only know that it has occurred. The Mo and Pd concentrations in iron meteorites show that the fractions of the cores in their parent bodies can vary from ~10% to 30% (presumably due to oxidized Fe being retained in the silicate mantle).

Hf-W chronometry of the Earth: The ϵ_W -value

of the silicate Earth is 1.9 ϵ -units higher than that of average chondrites ($\epsilon_W = -1.9$). Thus, by mass balance, the Earth's core must have a present ϵ_W -value of -2.2, substantially higher than the initial solar ϵ_W -value of -3.5. This requires a 2-stage model age of 30 Ma for the time of core-formation assuming complete isotopic equilibration of the core and the mantle at that time. Such complete equilibration is not physically realistic, so models of core-segregation that do not assume complete isotopic equilibration between the core and the mantle have been developed [5].

Local-equilibrium model: In this scenario the metal and silicate in a small parcel, after its addition to the Earth, are in a local isotopic equilibrium, but the metal is transported to the core without further equilibration with the remaining mantle. In this case the mean time of core formation is 110 Ma and 90 % is formed by 250 Ma. However, the residual siderophile trace element pattern of the mantle requires equilibration at high P and T in a magma ocean, thus making this type of model unlikely. Furthermore, recent modeling of metal sinking through a magma ocean points to their full equilibration before core segregation [6].

Magma-ocean equilibration: During accretion of planetesimals the impactor is largely vaporized and its mass is transported into the atmosphere in the form of hot expanding vapor. In the case of impact into a hot magma ocean this process should be even more efficient due to greater vaporization of the target region. Global recondensation of evaporated material will efficiently mix it with the entire magma ocean; subsequent precipitation of FeNi metal from the magma ocean assures isotopic equilibration, before segregation of metal into the core [2]. In this case Hf-W system yields a mean Earth accretion time of 10 Ma and a total accretion time of ~30 Ma.

Growth by Giant Impacts: The final consideration is the role of giant impacts in the accretion process and the extent to what it is recorded by Hf-W chronometry. For the Earth, a giant impact may be defined as sudden accretion of a body, ~1% to 10% of the Earth's mass. In the past a core-penetrative accretion without isotopic equilibration was considered possible during giant impacts implying that giant impacts may result in a third form of Hf/W partitioning by penetrative core mergers. In such a case the Hf-W chronometer might not record this event at all if the Earth's mantle and the

mantle of the giant impactor had the same ϵ_W values. The SPH modeling by Cameron and Benz [7] suggests that cores during giant impacts may merge penetratively without mixing and equilibration with their mantles. However, more recent calculations by Canup [8] suggest the impactor's core is mostly disrupted before it is added to the Earth. The disrupted core in the model simulation rains through the mantle as large metal blobs which would also likely be isotopically equilibrated with the mantle.

Thermodynamics of metal-silicate separation:

What is the behavior of Fe metallic liquid in equilibrium with silicate liquid at extreme temperature? Will a giant impact lead to a closure of the miscibility gap between the metal and silicate liquids and consequent re-homogenization of the stratified (metallic and silicate) liquids? How do we estimate the critical temperature and how does the solubility change as temperature decreases? Constraining this question would be of interest because, in the case of total re-homogenization, a model of the Hf-W chronology of accretion reduces to the simple two stage case which determines the time of the giant impact. Also, how is the siderophile pattern of residual mantle affected by the equilibration between mantle and core-forming melt? Was the bottom of a magma ocean the place of last equilibration of core forming liquid with mantle? A better thermodynamic model of metal-silicate behavior at high P and T is clearly desirable.

The U-Th-Pb chronometer: It was once thought that the concentration of Pb in the silicate portion of the Earth was depleted primarily by partitioning of Pb into a metal-sulfide core, whereas U (a lithophile element) left behind. Consequently, the apparently young U/Pb-age of the silicate Earth has been widely assigned to core formation. However, it is now known that the U/Pb ratio was also strongly fractionated in the Earth's precursor materials by incomplete condensation and/or volatilization in the nebula. The earliest Pb isotope evolution in the Earth, therefore, corresponds to a chronological model with at least two stages of fractionation: (1) nebular partitioning followed by (2) partitioning of Pb into the core. These stages are a consequence of Pb being both volatile and chalcophile. The Pb abundance in the bulk silicate Earth plots very close to a volatility-related depletion trend defined by the elements which are believed not to partition into the core. It seems clear that the nebular fractionation is dominant and that the core-related fractionation would have to be accurately deconvoluted from it in order to obtain a credible result for the timing of core formation. The fact that the isotopic composition of Pb in the depleted mantle plots to the right of the 4.57 Ga "geo-

chron" in a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot can also be explained by the dominance of its Pb budget by recycled subducted Pb derived from both hydrothermally altered MORB crust and sediments formed by weathering of the upper continental crust. Therefore, Pb isotope systematics of mantle-derived basalts do not imply "late" formation of the Earth by up to a 100 Ma, as was once widely believed. The ultimate causes of the observed shift to the right of the geochron in mantle Pb, are: (i) the vertical differentiation of the continental crust into an upper crust and a lower, (ii) partitioning of continentally-derived U into MORB. Both altered MORB and upper crust have U/Pb ratios higher than the BSE value and develop a radiogenic bulk composition over time. Crustal recycling of Pb provides a much more likely explanation of the Pb isotope-shift in the modern mantle than delayed core formation. Also, if Hf-W was affected by disequilibrium, so was U-Pb. There is no reason to believe that U-Pb gives a better estimate for core formation than Hf-W because the disequilibrium will affect both systems. Because of these problems Pb isotopes do not provide strong constraints on the chronology of core formation and accretion.

The I-Xe and Pu-Xe chronometers: These chronometers record fractionation caused principally by open system Xe transport from both the mantle and early atmosphere as well as by late veneer addition. The gases derived from the Earth's mantle by degassing associated with partial melt extraction to the surface may have been lost to space at very early times before closure of the atmosphere. Xe degassing or closure of the atmosphere can directly track accretion, because as a proto-planet grows larger, more atmosphere is being retained. Thus, the Xe chronometers can provide upper limits to the accretion/core formation interval for the Earth. However, some crucial parameters necessary for the calculation are not well known.

Conclusion: The Hf-W system is the only reliable accretion/core formation chronometer and it demonstrates that the Earth accreted rapidly. The short timescale of core formation solves a longstanding discrepancy between astronomical observations and geochemical estimates of the timescales of terrestrial planet formation.

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