TUNGSTEN (W) SELF-DIFFUSION AND METAL-SILICATE EQUILIBRATION. Benjamin Jacobsen1, Qing-zhu Yin1, David Tinker2, and Charles E. Lesher1, 1Department of Geology, University of California, Davis, One Shields Avenue, Davis, CA 95616 (jacobsen@geology.ucdavis.edu; qyin@ucdavis.edu), 2Department of Geology and Geophysics, Yale University, New Haven, CT 06520-8109 USA.

Introduction: The extent to which the material that accreted to the proto-Earth and segregated to form the core chemically and isotopically equilibrated with the silicate mantle is an outstanding problem in planetary science. This question is particularly important when trying to assign a meaningful age for planetary accretion and core formation based on the Hf-W isotope systematics [1,2,3,4]. The Earth and other terrestrial planets are likely to have formed by accretion of previously differentiated planetesimals. For the planetesimals themselves, the most important thermal energy source for the metal-silicate differentiation is the combined radioactive heating due to decay of $^{26}$Al (half-life 0.7 Ma) and $^{60}$Fe (half-life 1.5 Ma). It is expected that the fractionation of Hf and W during planetesimal core formation leads to a divergence in the W isotopic compositions of core and silicate portions of these bodies. This expectation is supported by the radiogenic $^{182}$W signatures compared to chondrites reported for basaltic eucrites [3,5,6]. The observation that the W isotopic compositions of silicate portions of Earth, Moon and Mars are similar and markedly less radiogenic than eucrites suggests that during planet accretion the pre-differentiated metallic core material with low $^{182}$W must have interacted extensively with the more radiogenic (high $^{182}$W) silicate material to subdue the ingrowth of $^{182}$W.

The standard theory of planet formation predicts that after runaway and oligarchic growth, the late stage of planet formation is characterized by impact and merging of Mars-sized objects [7]. This would have been a tremendously energetic process, raising the temperature of the proto-Earth to ~7000K [8,9], and indiscriminately ionizing everything. Stevenson (1990) [10] showed that emulsification caused by large-scale Rayleigh-Taylor instabilities following giant impacts breaks the metallic core of the impactor into centimeter-sized droplets within a few minutes. If these models are correct, the opportunity exists for intimate interaction between the impactor’s core and the proto-Earth’s silicate mantle as metal droplets descend through the terrestrial magma ocean.

In order to characterize the timescales of metal-silicate equilibration and therefore understand the processes involved in the late giant impact stage of planetary formation, we have conducted a series of W self-diffusion experiments in basaltic liquid to understand the rate of isotope exchange between metal and silicate during planetary accretion and core formation. The purpose of these experiments is to critically evaluate the constraints provided by the Hf-W isotopic analyses of meteoritic and terrestrial materials. These simple self-diffusion experiments provide constraints on the intrinsic mobility of W in silicate liquids, which is not complicated by the inter-diffusion of chemical species. The experiments give a first-order, conservative approximation of the W isotopic exchange and re-equilibration in a magma ocean scenario.

Experimental setup: In our experiments, we used natural basalt [11] doped with isotopically-normal and isotopically-enriched $^{183}$W. Cylinders of the isotopically distinct basalt were juxtaposed to form a simple diffusion couple. The diffusion couples were loaded into a graphite capsule (1 mm I.D. x 2 mm long). Our experiments were conducted using the Walker-design 6/8 multianvil device [12]. The W self-diffusion experiments were conducted at 3 GPa between 1500 -1700 °C. After each run, samples were immediately quenched to glass. The complete assembly was removed from the multianvil device, sectioned longitudinally to expose the diffusion couple, mounted in epoxy, and polished. The self-diffusion profiles for the W-isotopic composition of the charges were analyzed using laser ablation system coupled either to a quadrupole ICP-MS or the MC-ICP-MS, at the Interdisciplinary Center for Plasma Mass Spectrometry (UCD/ICPMS) at University of California, Davis. Laser ablation line-scans and spot analyses were conducted perpendicular to the diffusion interface using an incident laser beam with 20 µm diameter. Line-scan traverses were conducted with speed of 10-15 µm/sec. Distance between laser spots analyses were either 80 µm or 100 µm.

Data reduction: The self-diffusion coefficient (D) was calculated using the solution for diffusion in a semi-infinite medium [13]. The values for D were derived from the slopes of a best-fit line to plot of y vs. z, where

$$y = \text{erf}^{-1}\left(\frac{2C - C1 + C2}{C1 - C2}\right) = \frac{z}{2\sqrt{Dt}}$$

is the inverted solution to the diffusion equation, as described by [14]. C1 and C2 are the isotope...
composition for $^{183}$W in the enriched and normal sample, respectively, and C is the measured isotope composition at a distance z from the normal-enriched interface at time t. The inflection of the isotopic profile is taken as the diffusion interface, and is treated here as $z = 0$. The linearized solution to the equation gives an isotopic gradient across the normal-enriched interface, the slope of which is used to calculate the diffusion coefficient.

![Graph](image_url)

**Fig. 1:** Arrhenius temperature dependence on the W self-diffusion coefficients.

**Results:** Our measurements for the W self-diffusion in basaltic liquid are the first of their kind. The results show that, for the particular basalt composition used, the W self-diffusion coefficient increases by a factor of ~2 for every 100 °C increase in temperature. The data show good Arrhenian behavior with activation energies ($E_a$) of 221 ± 28 kJ/mol for W. In Table 1, the activation energy ($E_a$) and pre-exponential factor $D_0$ for W are compared with those for other elements [15]. The activation energy for W is comparable to Zr and Ti.

**Table 1. Arrhenius parameters**

<table>
<thead>
<tr>
<th>Element</th>
<th>$D_0$ (cm$^2$/s)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W*</td>
<td>1.54</td>
<td>221</td>
</tr>
<tr>
<td>Zr**</td>
<td>0.57</td>
<td>216</td>
</tr>
<tr>
<td>Ti**</td>
<td>0.48</td>
<td>206</td>
</tr>
<tr>
<td>Mg**</td>
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<td>173</td>
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<tr>
<td>Ca**</td>
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<td>172</td>
</tr>
<tr>
<td>Nd**</td>
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<td>181</td>
</tr>
<tr>
<td>Yb**</td>
<td>0.04</td>
<td>169</td>
</tr>
</tbody>
</table>

* This work
**LaTourette, Wasserburg and Fahey (1996)

**Model Setup:** Consider a single spherical metal droplet of radius r, settling through silicate liquid with settling velocity $v_s$. The characteristic time $\tau$ for reaction between metal and silicate is defined as $2r/v_s$. Assuming that equilibration is rate-limited by diffusion in silicate liquid, equilibration of the metal droplet with the surrounding silicate liquid will occur over a distance $dr$, where $dr = (D_W t)^{1/2} = (2D_W r/v_s)^{1/2}$ and $D_W$ is the self diffusivity for W in the silicate liquid. Because the settling velocity of the droplet, $v_s$, can be approximated by Stokes’ equation, $v_s = \Delta \rho g r^2 / 9 \eta$, where $\Delta \rho$ is the density difference between metal and silicate, g is the gravitational constant, and $\eta$ is viscosity of silicate liquid (magma ocean). The volume of equilibrated silicate liquid surrounding the metallic droplet integrated over the column height H (magma ocean depth) can be expressed as $V_{eq} = \pi \Delta \rho (2D_W r/v_s)^{1/2}/H$. Summing the volumes of equilibrated melt associated with all descending metallic droplets normalized to the total volume of the magma ocean (both target’s and impactor’s mantle) provides us with a measure for the extent of isotopic equilibration.

**Conclusion:** Using a reasonable estimate of viscosity from the literature, applying the above derived diffusion coefficients we can calculate and show that the degree of equilibration approaches 100% when the metallic droplet size is small (<30 cm). This is a reasonable droplet size to achieve during the giant impact [10]. From this size dependency, the minimum degree of equilibration after giant impact could also be constrained and compared with the observations of lunar W isotope data.