**Ag isotopic evolution of the mantle during accretion: new constraints from Pd and Ag metal-silicate partitioning.**

K. Righter[1] and M. Schönbächler[2], [1] NASA-JSC, 2101 NASA Parkway, Houston, TX 77058; kevin.righter-1@nasa.gov, [2] ETH Zürich, Inst. Isotope Geology and Mineral Resources, 8092 Zürich, Switzerland.

**Introduction:** Decay of $^{107}$Pd to $^{107}$Ag has a half-life of $6.5 \times 10^6$ Ma [1]. Because these elements are siderophile but also volatile, they offer potential constraints on the timing of core formation as well as volatile addition [2]. Initial modelling has shown that the Ag isotopic composition of the bulk silicate Earth (BSE) can be explained if accretion occurs with late volatile addition [2]. These arguments were tested for sensitivity for pre-cursor Pd/Ag contents, and for a fixed Pd/Ag ratio of the BSE of 0.1. New Ag and Pd partitioning data [3-7] has allowed a better understanding of the partitioning behavior of Pd and Ag during core formation. The effects of S, C and Si, and the effect of high temperature and pressure has been evaluated. We can now calculate D(Ag) and D(Pd) over the wide range of PT conditions and variable metallic liquid compositions that are known during accretion. We then use this new partitioning information to revisit the Ag isotopic composition of the BSE during accretion.

**Partitioning:** Metal/silicate partitioning can be predicted for siderophile elements using the expression which has been derived elsewhere [8]:

$$\ln D(i) = a \ln fO_2 + b/T + cP/T + \ln \gamma_i + g[nbo/t] + h \quad (1)$$

where $\gamma_i$ is the activity of element i in Fe metallic liquid, nbo/t is the ratio of non-bridging oxygens to tetrahedrally coordinated cations and is a gauge of silicate melt compositional variation, and the coefficients a, b, c, g, and h are derived by multiple linear regression of various datasets. $\gamma_i$ for Ag and Pd are calculated using an activity model based on interaction parameters [9,10]. Pd partitioning data compiled by [8] was combined with the activity model to derive new regression coefficients for Pd [9]. Ag partitioning data [3-6; 11,12] have been combined with Ag activities [10] to derive new regression coefficients for Ag [10]. Both Pd and Ag partition less into FeSi alloys than pure Fe, while Ag is more and Pd less siderophile in FeS alloys. Both elements have low valence in silicate melts and thus are only weakly dependent on $fO_2$ and silicate melt composition. With increasing temperature and pressure, D(Ag) and D(Pd) become less siderophile. All these effects are captured with the regression coefficients that can be used to model the Pd and Ag content of an evolving magma ocean.

**Model calculations and results:** The $^{107}$Ag/$^{109}$Ag isotope composition of the mantle is calculated using pre-cursor Pd/Ag = 2.81, 5.6, and 11.2, $[^{107}$Pd/$^{108}$Pd]$^0$ = $5.9 \times 10^{-5}$ and $\lambda = 1.06638 \times 10^{-7}$ [2]. The $^{107}$Ag/$^{109}$Ag ratio is usually normalized to the value of a standard using the epsilon notation where $\varepsilon^{107}$Ag = $[(^{107}$Ag/$^{109}$Ag$)_{sample}$ /$(^{107}$Ag/$^{109}$Ag$)_{standard}) - 1]$ x 10, 000. Using our partitioning expressions and a simple model of continuous core formation and core-mantle equilibration, we calculate the $\varepsilon^{107}$Ag in the mantle during Earth accretion. The Pd/Ag ratio of the mantle changes from 0.001 to ~ 100 during accretion. The low Pd/Ag ratio during early accretion reflects high D(Pd) and relatively low D(Ag) metal/silicate. As accretion proceeds and PT conditions of metal-silicate equilibrium increase (and core Si content increases), D(Pd) decreases, while D(Ag) increases, thus causing an overall increase in mantle Pd/Ag. If the Earth grows in a 70 Ma timeframe, the model yields a peak of $\varepsilon^{107}$Ag ~ 8 near 18 Ma, which decays down to values near $\varepsilon^{107}$Ag = -1.4 by 70 Ma (for Pd/Ag=5.6). Because the $\varepsilon^{107}$Ag of BSE is -2.2 ± 0.7 [2] and Earth likely accreted on a time frame of 70 to 100 Ma, these calculations show that with the variable Pd/Ag ratios, the BSE Ag isotopic composition can be almost achieved with core formation and the presence of Ag during accretion. Later accretion of low $\varepsilon^{107}$Ag chondritic material would further decrease the $\varepsilon^{107}$Ag values within BSE range [2].

An aspect of our modelling may justify further exploration. The BSE $\varepsilon^{107}$Ag value intermittently becomes high during accretion with the variable Pd/Ag ratios. This peak occurs early for Earth and has time to decrease by the end of accretion through extensive Ag sequestration into the core. For Mars, however, the timescale of accretion and differentiation is much shorter than for Earth [13,14], and martian meteorites may thus have preserved this high Ag signal, which is distinct from BSE by more than +0.5 $\varepsilon^{107}$Ag.

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