

PALLADIUM ISOTOPIC COMPOSITION OF THE EARTH: LATE VENEER VS. MAGMA OCEANS. B. Mayer¹ and M. Humayun¹, ¹National High Magnetic Field Laboratory & Dept. of Earth, Ocean & Atmospheric Science, Florida State University, Tallahassee, FL 32310, USA (mayer@magnet.fsu.edu)

Introduction: The chondritic-relative abundances of the siderophile elements in planetary mantles are often interpreted to be evidence of a late addition, post-core formation, of chondritic material [e.g. 1-3]. Alternative models propose that highly siderophile elements (HSE) are less siderophile than thought under the conditions (high P-T, sulfur core with Si, e.g. [4,5]) of terrestrial core formation. Palladium is important here, since $D(\text{Pd})^{\text{liquid metal-silicate}}$ decreases sufficiently to explain the mantle's higher than chondritic Pd/Ir ratio by equilibration in a terrestrial magma ocean [4,5]. Another important clue is provided by the isotopic compositions of the elements Mo, Ru and Pd, which exhibit an s-process deficit in meteorites relative to the Earth, with the most extreme difference observed in carbonaceous chondrites [6-10]. A late chondritic veneer could potentially be fingerprinted with Ru [9, 10] and Pd isotopes. The Ru and Pd isotopic compositions of the Earth have been determined on reagents [6,7,9], the provenance of which is limited to a few major ore sources, particularly the Noril'sk deposit associated with the Siberian traps. Based on radiogenic excesses of ^{186}Os , the Noril'sk deposit has been interpreted to indicate possible evidence of core-mantle interaction [11]. It is, therefore, necessary to evaluate the internal isotopic variability of Pd (and Ru) in the Earth to ensure that signals from core-mantle interaction do not obfuscate interpretations of the sources of the late veneer. At present, this is analytically challenging since Pd (and Ru) are present at low-ppb concentrations in basalts and peridotites. However, ore-forming processes concentrate Pd to form Pd-minerals in multiple localities, including the Bushveld (South Africa), Stillwater (MT, USA), Wellgreen (Canada), the Urals and Noril'sk (Russia).

Here, we present high-precision Pd isotopic compositions of terrestrial Pd minerals. One set (WMS-1, hollingworthite) is thought to originate from the upper mantle while the other set (cabriite, taimyrite, arsenopalladinite) from the Noril'sk intrusion is arguably the product of core-mantle interaction [11]. In the context of a late veneer scenario, the Noril'sk Pd should be less affected from such a late chondritic addition, while Pd from WMS-1 and hollingworthite should be primarily derived from the late veneer.

Analytical Methodology: Three samples from Noril'sk, Russia have been analyzed: taimyrite, (Pd, Cu, Pt)₃Sn; arsenopalladinite, Pd₈(As, Sb)₃, within a silicate matrix; cabriite, Pd₂SnCu, associated with other Pd-Pt minerals in a sulfide matrix. The massive sulfide ore,

WMS-1, is from the Wellgreen intrusion, Yukon, Canada, a mineralized mafic-ultramafic intrusive body. Hollingworthite, (Rh, Pt, Pd)AsS, is from the Pt placer deposit from Fox Gulch, Alaska, ultimately sourced from the Red Mountain dunite.

All samples were dissolved using aqua regia and HF:HNO₃ digestion in Savillex™ PFA vessels at 160°C for several days until completely dissolved. The matrix and elements that create isobaric interferences (Zn, Zr, Mo, Ru, Cd etc.) were removed with cation and anion exchange column chemistry [5]. All Pd-isotopic compositions were analyzed on a Thermo Neptune™ MC-ICP-MS in medium resolution and static mode in 100 ng/mL up to 500 ng/mL Pd aliquots in 2% HCl introduced with a CETAC Aridus II™ desolvating system. Thermo SuperJet8.2 Ni and Spectron T1001 Ni-X skimmer cones were used. Mass bias correction was performed with the exponential law with ratios normalized to $^{108}\text{Pd}/^{105}\text{Pd} = 1.18899$. All data are given in epsilon notation as deviation from the reference material, an Alfa Aesar® Specpure® Pd standard (APS). To establish their purity, all Pd cuts were analyzed with an ICP-MS (Thermo Element 2™) prior to measurement on the MC-ICP-MS. While collecting Pd isotope compositions, isobaric interferences from Ru (^{101}Ru) and Cd (^{111}Cd) were simultaneously monitored on the MC-ICP-MS.

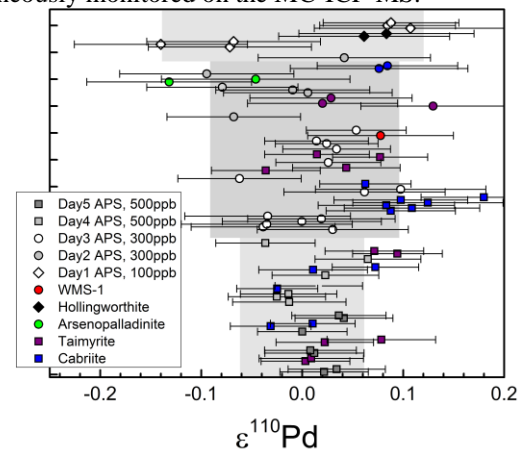


Fig. 1: Pd isotopic composition of the five terrestrial Pd ores compared with the Alfa Aesar Pd standard (at concentration levels of either 100 ppb, top, 300 ppb, middle, or 500 ppb, bottom) and with their in-run $2\sigma_{\text{mean}}$ errors. The gray band represents the reproducibility of the repeated measurements of the Alfa Aesar Pd Standard (APS).

Results: Data of the five terrestrial samples together with their bracketed Alfa Aesar Pd standard are shown for $\epsilon^{110}\text{Pd}$ (the r-process only isotope) in Fig. 1. Here, at the bottom the analytical runs at 500 ppb show smaller uncertainties (light grey area) versus the samples run at

300 ppb (middle, dark grey area) or 100 ppb (top). Overall, the precision can be estimated to be $\pm 0.06 \text{ } \epsilon$ for runs with 500 ppb and $\pm 0.08 \text{ } \epsilon$ for 300 ppb runs. Similar accuracy and precision is observed for $\epsilon^{104}\text{Pd}$ (Fig. 2). The deviation in $\epsilon^{106}\text{Pd}$ is not resolved ($\pm 0.03\epsilon$). Initial runs at 300 ppb analyte concentration for the cabriite provided a hint of a correlated anomaly in $\epsilon^{110}\text{Pd}$ and $\epsilon^{104}\text{Pd}$ (Fig. 2). Hence, measurements at higher analyte concentrations (500 ppb) for both samples and standards were performed. The cabriite was determined to be identical to other terrestrial samples. The measurements of all five terrestrial samples showed no resolvable anomalies (Fig. 2).

Discussion: The content of moderately siderophile elements (MSE) like W and Mo in Earth's mantle are generally agreed to represent equilibrium in a deep magma ocean [e.g., 12]. Thus, the isotopic composition of terrestrial Mo is representative of that of the bulk Earth (core). In contrast, the mantle inventory of Ru and Pd are thought to be derived mainly from chondritic impactors during the late veneer [e.g. 1,4]. Both Ru/Ir and Pd/Ir ratios are higher than chondritic values in the Earth's mantle [1], implying either an unusual type of impactor [1] or a hybrid scenario with contributions from both impactors and from partitioning with the Earth's core [3]. A prediction from the late veneer hypothesis is that the isotopic composition of Pd from the mantle and that of the core (main accretion phase of the Earth) are isotopically distinct due to their provenance within the inner ($\sim 1 \text{ AU}$) vs. outer ($\sim 3\text{-}5 \text{ AU}$) portions of the terrestrial planet region. In this case, core-mantle interaction is expected to change the Pd isotopic composition. Russia is the largest supplier of global Pd, mainly from the Noril'sk ores. If the Earth contained isotopically distinct Pd and Ru in the core and mantle it is conceivable that reagent Pd (and Ru) potentially derived from the Noril'sk sources are not representative of the upper mantle.

The existence of a nucleosynthetic Mo-Ru-Pd isotope correlation [e.g. 6-10] implies that any chondritic contribution would be expected to disturb this correlation, unless the impactors had the same isotopic composition as that of the Earth's mantle. Carbonaceous chondrites show the largest deviation from the terrestrial Mo-Ru-Pd isotopic composition (Fig. 2). The observed Mo-Ru-Pd isotopic correlation [6,7] implies that both the MSE- (e.g. Mo) and the HSE-budget on Earth are not decoupled and all three elements originated from the same source. However, if a late accretion was significant the isotopic composition of Mo should be dominated by the main accretion phase (from inner solar material), while the HSE should be dominated by the late accretion, i.e., by outer solar system material.

The two different sources of the HSE sampled in this study do not exhibit resolvable isotopic differences at $\pm 0.06 \text{ } \epsilon$ (Fig. 1 & 2). If, during core segregation, a K_d of $>10^4$ (e.g. Pd [13]) is applicable, Pd abundances as low as $\sim 0.06 \text{ ppb}$, or lower, would be expected in the mantle. Then 99% or more of today's Pd in the mantle ($\sim 7 \text{ ppb}$ [1]) would originate from the late veneer. However, 99% of a true late veneer (outer solar system; CV like $\epsilon^{110}\epsilon$: 0.6 [6]) would translate to $\epsilon^{110}\text{Pd}$ in the mantle of $+0.59$, a factor of ten higher than allowed by the error bars. This establishes a limit of $<0.001\%$ by mass of CV-like chondritic material to the mantle, an order of magnitude lower than expected from the late veneer. Recent modeling of experimental studies with a sulfur-bearing core and Si as a light element within the core [4,5,14], find that Pd behaves much less siderophile ($K_d \sim <10^3$) that would explain the observed concentration without the need of a late exogenous contribution. The Pd isotopic data presented here support these latter models.

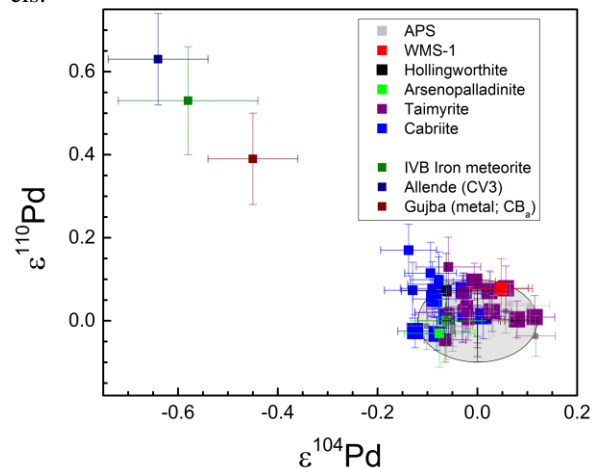


Fig. 2: Palladium isotopic composition ($\epsilon^{104}\text{Pd}$ vs $\epsilon^{110}\text{Pd}$) of terrestrial ores (this study), C chondrites (Allende, CV3 and metal of Gujba, CBa) and the IVB iron meteorites [6,7].

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