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Tracing metal–silicate segregation and late veneer in the Earth and the ureilite parent body with palladium stable isotopes

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Abstract

Stable isotope studies of highly siderophile elements (HSE) have the potential to yield valuable insights into a range of geological processes. In particular, the strong partitioning of these elements into metal over silicates may lead to stable isotope fractionation during metal–silicate segregation, making them sensitive tracers of planetary differentiation processes. We present the first techniques for the precise determination of palladium stable isotopes by MC-ICPMS using a ^{106}Pd–^{110}Pd double-spike to correct for instrumental mass fractionation. Results are expressed as the per mil (‰) difference in the ^{106}Pd/^{105}Pd ratio (δ^{106}Pd) relative to an in-house solution standard (Pd_IPGP) in the absence of a certified Pd isotopic standard. Repeated analyses of the Pd isotopic composition of the chondrite Allende demonstrate the external reproducibility of the technique of ±0.032‰ on δ^{106}Pd. Using these techniques, we have analysed Pd stable isotopes from a range of terrestrial and extraterrestrial samples. We find that chondrites define a mean $\delta^{106}\text{Pd}_{\text{chondrite}} = -0.19 \pm 0.05$‰. Ureilites reveal a weak trend towards heavier δ^{106}Pd with decreasing Pd content, similar to recent findings based on Pt stable isotopes (Creech et al., 2017), although fractionation of Pd isotopes is significantly less than for Pt, possibly related to its weaker metal–silicate partitioning behaviour and the limited field shift effect. Terrestrial mantle samples have a mean $\delta^{106}\text{Pd}_{\text{mantle}} = -0.182 \pm 0.130$‰, which is consistent with a late-veneer of chondritic material after core formation.

Keywords: Palladium; Stable isotopes; Terrestrial planet accretion; Late-veneer; Meteorites

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1. INTRODUCTION

The platinum group elements (PGE; Rh, Ru, Pd, Os, Ir and Pt) all exhibit highly siderophile behaviour, with the bulk of Earth's highly siderophile element (HSE; i.e., PGE + Re, Au) budget concentrated into the core. As such, the HSE have played a key role in constraining models of Earth's accretion and differentiation. Combined with their extreme depletion in the bulk silicate Earth, changes in oxidation state and bonding environment between mantle silicates and the Fe–Ni metallic core may lead to significant fractionation in HSE stable isotopes in the silicate mantles of terrestrial planets. This has led to considerable interest in stable isotope measurements of HSE, and stable isotope data for various sample types have recently been documented for Pt (Creech et al., 2014, 2017), Ru (Hopp et al., 2016) and Os (Nanne et al., 2017). Palladium represents a natural addition to this suite of stable isotope tracers, with potential to complement and contrast with these other HSE stable isotope systems.

Palladium is a transition metal with six naturally occurring stable isotopes—^{102}Pd, ^{104}Pd, ^{105}Pd, ^{106}Pd, ^{108}Pd,

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^{110}Pd—with relative abundances of 1.02%, 11.14%, 22.33%, 27.33%, 26.46% and 11.72%, respectively (Meija et al., 2016; Fig. 1). Palladium can occur in a number of oxidation states, although principally occurs in nature as Pd(0) and Pd(II) (Dennen, 1954; Borisov et al., 1994). Palladium shares the highly siderophile nature of the PGEs, as evidenced by its relative depletion in the mantle as compared with chondritic meteorites (chondrites: ~1 μg g^{-1} Pd; bulk silicate Earth: 4 ng g^{-1} Pd; McDonough, 2014). However, reported metal–silicate partition coefficients for Pd at conditions relevant to core formation are around an order of magnitude lower than those for the other PGE, including Pt ($D_{Pd}^{met/sil} \sim 10^3$–$10^4$; $D_{Pt}^{met/sil} \sim 10^4$–$10^5$; Holzheid et al., 2000; Mann et al., 2012). The PGE also exhibit chalcophile behaviour and in the conditions found in the mantle and crust they are most commonly found in sulphide components of ultramafic complexes. In addition to its weaker metal–silicate partitioning, Pd has the lowest density (11,995 kg m^{-3}; Kaye and Laby, 1995), melting point (1555 °C; Kaye and Laby, 1995), and 50% condensation temperature (1324 K; Lodders, 2003) of the PGE. Previous isotopic studies of Pd have been limited to searches for cosmogenic and nucleosynthetic effects in iron meteorites (Mayer et al., 2015), and as part of an experimental and theoretical study of nuclear volume effects Fujii et al. (2011). However, stable isotope variations of Pd in nature remain unexplored. The properties of Pd, in particular the relatively low condensation temperature, combined with subtle differences in the geochemistry of Pd as compared with Pt, its closest associate amongst the PGE, could lead to differences in stable isotopic compositions in nature.

Stable isotopic fractionations at temperatures relevant to metal–silicate differentiation have now been reported in several stable isotope systems, (e.g., Si (e.g., Young et al., 2015), Mo (Hin et al., 2013; Burkhardt et al., 2014), Zn (Mahan et al., 2017) and Fe (Elardo and Shahar, 2017)). The metal–silicate partitioning of Pd is significantly greater than for these elements, and combined with the differences in oxidation state and bonding environment between mantle silicates and the Fe–Ni metallic core, as well as evidence for Pt stable isotope fractionation related to metal–silicate partitioning (Creech et al., 2017), significant Pd stable isotopic fractionation could occur during planetary core formation. Stable isotopic studies of Pd, especially where contrasted with similar data for Pt, may provide useful insights into a variety of planetary and geological processes.

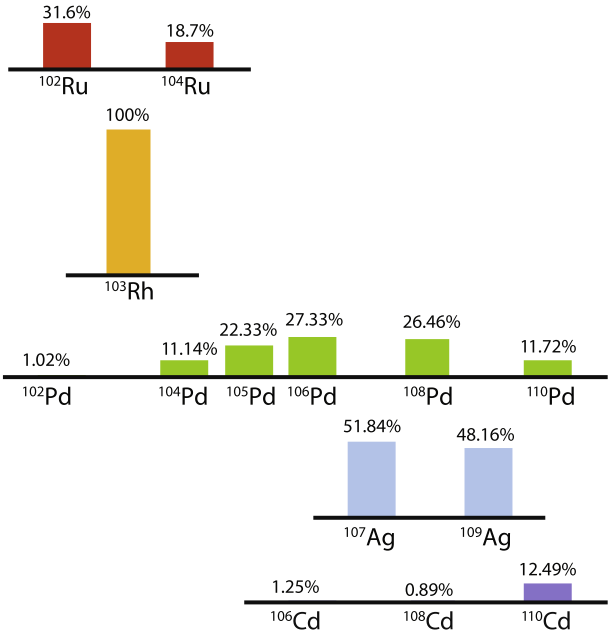

Fig. 1. Relative abundances of isotopes in the mass range of Pd from Meija et al. (2016).

In this paper, we present the first high-precision method to analyse the stable isotopic composition of Pd. We apply this technique to estimate the Pd isotopic composition of a wide range of chondrites and some modern terrestrial samples in order to provide a reference for the Pd isotopic composition of Solar System materials. We compare this solar system Pd isotopic composition to terrestrial Archean samples from Isua and South Africa to investigate the potential preservation of Pd isotopic signatures from prior to the late arrival of chondritic material, similar to those recently observed for Pt (Creech et al., 2017). We further analysed the Pd isotopic composition of a series of ureilite meteorites. Ureilites have a complex petrogenesis, but are considered to be mantle restites formed on a parent body that never totally melted (e.g., Scott et al., 1993; Barrat et al., 2015; Greenwood et al., 2016). The ureilites have HSE contents ranging from approximately chondritic to depletions of several orders of magnitude relative to chondrites (Warren et al., 2006; Rankenburg et al., 2008), which have been interpreted to reflect the early stages of core formation (Warren et al., 2006). These depletions have also been recently shown to have correlated stable isotope fractionations for the element Pt (Creech et al., 2017). These factors, combined with ureilites being among the most common achondrites in our meteorite collections (~400 ureilites are currently reported in the Meteoritical Bulletin Database) make these meteorites some of the best available samples to test the effects of metal–silicate or metal–sulphide segregation on the Pd isotopic composition.

2. DESIGN AND PREPARATION OF THE PALLADIUM DOUBLE-SPIKE

The double-spike method is a well established approach for precise determination of isotope ratios, and has been applied to a broad range of isotope systems using both TIMS and MC-ICPMS analysis (e.g., Pb, Cr, Zn, Fe, Ni, Ti, Mo, Ca, Pt, W; Compston and Oversby, 1969; Eugster et al., 1969; Hamelin et al., 1985; Beard et al., 1999; Beard and Johnson, 1999; Anbar et al., 2001; Siebert et al., 2001; Baker et al., 2004; Dideriksen et al., 2006; Gopalan et al., 2006; Schoenberg et al., 2008; Arnold et al., 2010; Gall et al., 2012; Creech et al., 2013; Hin et al., 2013; Burkhardt et al., 2014; Abraham et al., 2015; Bonnand et al., 2016; Millet et al., 2016; Bezard et al., 2016; Krabbe et al., 2017). These include several recent applications to studying mass-dependent fractionation of PGEs (Creech et al., 2014, 2017; Hopp et al.,