Extreme fractionation of selenium isotopes and possible deep biospheric origin of platinum nuggets from Minas Gerais, Brazil

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ABSTRACT

Platinum-rich nuggets offer an opportunity for understanding how precious metals accumulate. We analyzed the selenium (Se) isotopic composition of Se-rich (10−100 μg g−1) platinum-palladium (Pt-Pd) nuggets from a recent placer deposit in Minas Gerais, Brazil, for which a biogenic origin has been inferred. We obtained Se isotopic values with a relatively narrow range (δ34SeleniteSeSeleniteNIST3149 = −17.4‰ to −15.4‰ ± 0.2‰, two standard deviations [2 SD]). The Pt-Os age of the nuggets is 181 ± 6 Ma (2 SD). The data indicate that the nuggets did not form in the recent placer deposit, but by replacement of hydrothermal vein minerals at ~70 °C and at least 800 m below the surface. The high abundance and extreme isotopic composition of Se as well as the presence of other biophilic elements like iodine, organic carbon, and nitrogen within the nugget matrix are consistent with a microbial origin. Although abiogenic reduction of Se oxynions cannot be ruled out, the nuggets plausibly record Se-supported microbial activity in the deep biosphere.

INTRODUCTION

The origin of platinum (Pt) nuggets in placer deposits and lateritic profiles worldwide remains debated, with two contrasting origins being proposed: (1) magmatic, formed in ultramafic rocks (Hattori and Cabri, 1992; Oberthür et al., 2017); and (2) neoformation under supergene conditions (Cousins and Kinoch, 1976; Bowles and Suárez, 2021). The former is based on the mechanical resistance of Pt-rich alloys and their low solubility, essential in causing residual concentrations in placer deposits, whereas the latter requires dissolution and precipitation processes, with or without biogenic interactions. Biofilms covering Pt-rich nuggets could indicate biogenic supergene formation (Reith et al., 2016), but biofilms are surface coatings that postdate the nugget formation and, therefore, may not necessarily reflect the nugget-forming process. The isotopic composition of within-nugget elements, such as selenium (Se), may help in discriminating between abiogenic versus biogenic origins.

Selenium is an essential nutrient for microorganisms, and Se isotopes have been used to reconstruct redox conditions and to identify microbial processes in ancient and modern environments (Stüeken, 2017; Schilling et al., 2020). Selenium- and selenite-reducing bacteria produce Se8 that is isotopically lighter than the starting Se-oxynion pool (Herbel et al., 2000; Schilling et al., 2020). Elemental Se has a large Eh-pH (Eh—activity of electrons) stability field and coexists with metallic Pt, whereas sulfur (S) occurs as soluble sulfate (Fig. 1 in the Supplemental Material). It is thus expected that supergene Pt and other native metals, such as silver and copper, incorporate Se6. We report Se isotopic compositions and Pt-Os ages for Pt-rich nuggets recovered from a placer deposit in Brazil. Our data provide evidence that the neoformation of Pt-rich nuggets did not occur in the surface environment. Instead, they likely record biogenic metal fixation at depth, ~800 m below the surface or even deeper, in response to groundwater dissolution of Se-bearing, Pt-rich vein minerals.

SAMPLES AND GEOLOGICAL SETTING

Platinum-palladium (Pt-Pd) nuggets were sampled from the placer deposit of Córrego Bom Sucesso, Diamantina-Serro region, in the platiferous Au-Pd belt of Minas Gerais, Brazil (Cabral et al., 2009). Cambrian quartz veins, hosted in Paleoproterozoic quartzite (Fig. 1A), contain specular hematite, palladiferous gold, and Pt-Pd minerals such as arseno-antimonides and selenides (e.g., jactungaitite, Pt3HgSe5). The Bom Sucesso deposit is the locality where Pd was originally identified (Wollaston, 1809;...
Cassedanne and Alves, 1992). The platiniferous deposit is located between a pitted bedrock of quartzite and boulders fallen from a quartzite precipice along which the stream runs (Figs. 1B and 1C; Cassedanne et al., 1996; Cabral et al., 2011a). A north-northwest–trending mafic dike just east of the placer deposit (Fig. 1A) has the preferential direction of the Triassic–Jurassic Transminas mafic swarm, which marks the onset of the breakup of West Gondwana (Chaves and Correia Neves, 2005). During the emplacement of the dike swarm, veins and supracrustal rocks of the Diamantina region were fractured. After the Jurassic, denudation exhumed veins and their quartzite host rock (Barreto et al., 2013; Amaral-Santos et al., 2019). Following the collapse of the precipice in the Holocene, the Pt-Pd nuggets that had formed within the Cambrian...
quartz veins in the Jurassic, as determined in this study, were released to the placer deposit. Mineralized veins have not been found in the study area, and consequently no vein selenide minerals have been sampled. That such a mineralized vein system existed is deduced from abundant specular hematite and, particularly, arborescent palladiferous gold in the placer deposit (Cabral et al., 2008a).

The Pt-Pd nuggets typically have a Pt-rich and Pd-depleted rim (Cassendeane et al., 1996), and are botryoidal (Fig. 1D; Hussak, 1904; Cassendeane and Alves, 1992; Cabral et al., 2009). The Pt-Pd nugget matrix is seleniferous (10^{-2}–10^{-1} µg g^{-1} Se) and contains minor mercury (10^{-3}–10^{-2} µg g^{-1} Hg), but lacks iron (Fe), which identifies magmatic Pt-Fe alloys (Cabral et al., 2019). A within-placer origin for the Pt-Pd nuggets has been proposed (Hussak, 1904; Cabral et al., 2009), given that their botryoidal and arborescent morphologies would not have resisted alluvial abrasion. In addition, high abundances of iodine in the Pt-Pd matrix (10^{2} µg g^{-1} I; Cabral et al., 2011b), where organic carbon and nitrogen are heterogeneously distributed (Reith et al., 2016), as well as nugget-covering biofilms (Fig. 1E; Reith et al., 2016), suggest a biogenic origin.

**METHODS AND RESULTS**

Given the Se distribution as an alloying component of the Pt-Pd matrix (Cabral et al., 2019), we investigated eight nuggets for their Se isotopic compositions using a ^{186}Se/~^{76}Se double-spike, hydride-generation, multicollector–inductively coupled plasma–mass spectrometry (MC-ICP-MS) analytical method at the Isotope Geochemistry laboratory of the University of Tübingen (Germany; Kurzawa et al., 2017; Yierpan et al., 2018; see the Methods section of the Supplemental Material). Another sample set of five Pt-Pd nuggets, which are from the same collection used for Se isotopes, were individually measured to calculate ^{190}Pt/~^{186}Os ages (Table S1 in the Supplemental Material). The ages are, within error, indistinguishable from each other at 181 ± 6 Ma (2 SD). Their contents of radiogenic Os are in the range from 23 to 26 ng g^{-1}, while their ^{187}Os/~^{188}Os ratios are between 0.90 and 1.30 (Table S1).

The Pt-Pd nuggets yielded a narrow distribution of negative ^{82/76}Se values—i.e., deviation of sample ^{82}Se/~^{76}Se relative to reference solution NIST3149 (U.S. National Institute of Science and Technology; see the Supplemental Material)—between −17.4‰ and −15.4‰ (±0.2‰, 2 SD; Fig. 2; Table S2). The ^{82/76}Se values show positive covariances with Se (115–1278 µg g^{-1}), Pd (5–24 wt%), and thallium (Tl,1–33 µg g^{-1}) concentrations and a negative covariation with Os/Ir ratios, but are unrelated to size and mass of the nuggets. Measured Se isotopic compositions are even lighter than the lightest Se isotopes reported from weathered seleniferous and organic-rich shales of the Permian Maokou Formation in China (^{82/76}Se = −14.2‰ to +11.4‰; Zhu et al., 2014; Fig. 2), which have hitherto been regarded as the lowest ^{82/76}Se values in natural deposits and the largest ^{82/76}Se range. Such a large range, or an isotopically heavier complementary reservoir, is entirely absent in our nuggets.

**DISCUSSION**

Combined with the ^{190}Pt/~^{186}Os ages, the ^{82/76}Se values of the Pt-Pd nuggets point to a unidirectional formation process during which Se, derived from Se-bearing vein minerals, was incorporated in the Jurassic. Assuming that the initial aqueous fluid had a ^{82/76}Se value of 0‰, reflecting water equilibrated with the upper continental crust (Fig. 2A; Stüeken, 2017; and crustal ^{187}Os/~^{188}Os ratios between 0.90 and 1.30; Table S1), the highly negative ^{82/76}Se values in the nuggets require a large isotopic fractionation process and a small extent of Se-oxyanion reduction—e.g., <30‰, for which ^{82/76}Se values are still low. Larger extents of Se-oxyanion reduction would have tended to drive the aqueous fluid to higher ^{82/76}Se values, which in turn would have led the Se precipitated in the nuggets to higher and likely more variable ^{82/76}Se values similar to those found in metamorphic sulfides (König et al., 2021). As for hydrothermal sulfides with ^{82/76}Se values of ∼−3‰ (König et al., 2019), even the lowest ^{82/76}Se values may also be explained by abiogenic reduction of high Se-oxyanion concentrations. Indeed, a wide range of ^{82/76}Se values, from +11‰ to −14‰ (average ^{82/76}Se of ∼0‰; Fig. 2A), is recorded in seleniferous black shales of the Maokou Formation (Zhu et al., 2014). This range has been attributed to multiple cycles of oxidation, fluid mobilization, and reduction of Se-oxyanion species (Zhu et al., 2014). However, multiple redox cycles at Córrego Bom Sucesso can be excluded because substantial ^{82/76}Se variability, such as recorded in the Maokou Formation, would be expected. An analogous ^{82/76}Se variability, with isotopically heavier and lighter signatures, is entirely absent in our nuggets. Experimentally, the fractionation factor for abiogenic selenite reduction with green rust was found to be −11.0‰ ± 0.4‰ (^{82/76}Se; Johnson and Bullen, 2003), while the maximum fractionation factor for microbial selenite reduction is −11.8‰ ± 0.6‰ (Schilling et al., 2020). Given that the nuggets are not experimental products, but represent the lightest Se isotopic signatures of natural origin, neither a biogenic nor
The heterogeneous distribution of organic carbon and nitrogen in some Pt-Pd nuggets (Reith et al., 2016), together with high iodine abundances (Cabral et al., 2011b) and the close association of Se and phosphorus (Reith et al., 2019), all indicate that the δ^{82/76}Se values reflect a biogenic pathway. Consequently, we infer that the formation of the Pt-Pd nuggets was microbiologically mediated. Such a process is analogous to the formation of framboidal pyrite, which has highly negative δ^{34}S values and organic carbon and nitrogen in the pyrite matrix, identifying microbial sulfate reduction (Wacey et al., 2015).

The Pt-Pd nuggets show a δ^{82/76}Se variability of only 1.7‰, regardless of their size and mass (4.33–18.38 mg). Subtle covariances of δ^{82/76}Se values with selected trace metals, which are disseminated in our Pt-Pd nuggets (Figs. 2B–2D), support a single incorporation mechanism rather than a two-step process. For example, the correlation between δ^{82/76}Se and Os/Ir ratios implies that Se-oxyanion reduction involved Os release to the fluid phase relative to less-mobile Ir and δ^{82/76}Se. Rather than complex, multiple-stage Se redox events in the weathering zone, as expected from the seasonal variation of the near-surface water table, the 189/187Os age of ca. 180 Ma obtained for the Pt-Pd nuggets indicates that they formed at ~800 m below the surface, assuming a constant average denudation rate of 4.4 m m.y.^{-1}, as estimated by cosmogenic beryllium for the Diamantina region (Barreto et al., 2013). This assumption is supported by thermochronological modeling using apatite fission-track (AFT) data from basement granitic-gneissic rocks (Amaral-Santos et al., 2019).

**Nugget Formation in the Deep Biosphere**

Microstructural and compositional evidence from the southern part of the belt indicates that vein Pt-Pd minerals, including jacutingaite (Pt,HgSe), and hongsuite (Pt,Cu), are the precursors of Pt-Pd concentrations engendered by the removal of less-noble metals; e.g., Se and Cu (Cabral et al., 2008b). It is thus likely that the dissolution of precursor vein minerals produced Pt-Pd nuggets within the veins at ~800 m or even deeper (Fig. 3A). Conditions of relatively low fluid-rock ratio would be compatible with the unusually high Se concentrations in the nuggets; i.e., little dilution of dissolved vein Pt-Pd minerals and Pt-Pd reprecipitation either in situ or close to the veins (Fig. 3B). A local source of metals, concentrated in veins, seems to have been crucial for nugget formation. This is deduced by comparison with nickel (Ni) and iron (Fe), metals dispersed in serpentine, where nanosized particles of Ni-Fe alloy are reported to occur with organic matter in the deep biosphere (~10,000 m below the seafloor; Plümper et al., 2017). Relatively high Se-oxyanion abundances in a nutrient-poor, quartz-rich environment would provide a suitable source of energy for microbial life (Schilling et al., 2020). This would have occurred at ~70 °C, as estimated by AFT thermal modeling for the basement rocks of the Diamantina region, at ca. 180 Ma (Amaral-Santos et al., 2019).

At ca. 180 Ma, we infer that the Jurassic breakup of West Gondwana led to the formation of deep-seated fractures, which facilitated the groundwater flow to the environment of the Pt-Pd nugget formation. A similar scenario is known from the Driefontein consolidated gold mine in South Africa, situated at 3200 m depth, where sulfate-reducing bacteria were isolated from heated groundwater at 50 °C (Moser et al., 2003). Supporting evidence for the presence of microbial activity in a terrestrial deep biosphere, related to fracture-controlled groundwater flow, has been found at 2400 m depth in 2.7 Ga rocks of the Canadian Shield (Li et al., 2016). It is therefore reasonable that metal-tolerant, Se-oxyanion-reducing bacteria were thriving in metal-liferous solutions in deep-seated groundwater.

The covariation between nugget δ^{82/76}Se values and concentrations of Ti (Fig. 2C), a highly toxic element, further suggests that the Ti concentrations were critical and eventually reached a lethal level for the Se-oxyanion-reducing bacteria in this niche environment.

Denudation since the Jurassic brought the Pt-Pd nuggets to the near surface where the precipice collapsed. The collapse-triggering rupture followed the fractured vein system in the country-rock quartzite. Subsequently, the Pt-Pd nuggets were liberated from friable material, quartz vein and immediate host-rock quartzite, and redistributed in the nearby placer deposit (Fig. 3C). Contrary to supergene neoformation within alluvial sediments (Cabral et al., 2011b; Reith et al., 2016, 2019), our data suggest that the Pt-Pd nuggets resulted from deep microbial activity.

**CONCLUSION**

The Pt-Pd nuggets of Córrego Bom Sucesso were likely microbiologically mediated and not formed by supergene accretion within the placer deposit. In combination with 199Pt-209Os ages and trace elements, Se isotopes can be reconciled with biogenic Se fixation. Taken together, our data can further be interpreted as indicative of Se-sustaining microbial life in the deep biosphere.

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