190Pt-186Os geochronometer reveals open system behaviour of 190Pt-4He isotope system

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Abstract

Platinum Group Minerals are typically dated using the 187Re-187Os and 190Pt-186Os isotope systems and more recently using the 190Pt-4He geochronometer. The 187Re-187Os and 190Pt-186Os compositions of Pt-alkyls from the Kondyor Zoned Ultramafic Complex (ZUC) analysed here reveal overprinting for both geochronometers except in one alloy exhibiting the most unradiogenic 187Os/186Os and most radiogenic 188Os/186Os signatures. These signatures argue for an Early Triassic mineralisation, when silicate melts/fluids derived from the partial melting of an Archean mantle crystallised to form the Kondyor ZUC while the 190Pt-4He chronometer supports an Early Cretaceous mineralisation. We propose that Kondyor ZUC represents the root of an alkaline picritic volcano that constitutes the remnants of an Early Triassic island arc formed during the subduction of the Mongol-Okhotsk ocean seafloor under the Siberia craton. After the Early Cretaceous collision of Siberia with the Mongolia-North China continent, the exhumation of deep-seated structures – such as the Kondyor ZUC - allowed these massifs to cool down below the closure temperatures of the Pt-He and K-Ar, Rb-Sr isotope systems, explaining their Early to Late Cretaceous ages for the Kondyor ZUC.

Introduction

Platinum group minerals (PGM, e.g., Os-alloys, Pt-alkyls, Pt-arsenides) are critical host phases of the Highly Siderophile Elements (HSE; Os, Ir, Ru, Pt, Pd, Re) in the Earth’s mantle and crust. They are typically dated with the 187Re-187Os and/or 190Pt-186Os isotope systems (e.g., Walker et al., 1997; Melbom and Frei, 2002; Pearson et al., 2007; Coggon et al., 2012).

Recently, the 190Pt-4He isotopic system has emerged as an alternative geochronometer for Pt-rich PGM. The 190Pt-4He and 190Pt-186Os geochronometers are both measuring the alpha decay of 190Pt, with the only difference being that one measures the accumulation of the daughter product 186Os and the other the accumulation of the decay particle 4He. The Pt-He geochronometer was so far used to date the Pt-alkyls from the Kondyor Zoned Ultramafic Complex (ZUC), which is located in the Aldan Shield on the South-East margin of the Siberian Craton (Fig. S-1 and Supplementary Information) (Shukolyukov et al., 2012a; Mochalov et al., 2016, 2018). The Early Cretaceous Pt-He isochron ages (112 ± 7 Ma and 129 ± 6 Ma, calculated using a 190Pt half-life of 469 Gyr: Begemann et al., 2001) agree well with the Rb-Sr, Sm-Nd and K-Ar ages obtained on the main lithologies (whole rock and mineral phases) but conflict with the Re-Os TDM model ages obtained on erlichmanite (OsS2), sperrylite (PtAs2), Os-alloys and Pt-alkyls (Cabri et al., 1997; Malitch and Thalhammer, 2002) that vary from Neoproterozoic (658-603 Ma) to future ages, when back calculated to the present-day primitive mantle (PM) 187Os/186Os estimate (Meisel et al., 2001).

The combination of multiple isotope systems for dating single mineral phases offers the opportunity to resolve “open system behaviour” and to assess which isotopic signatures provide geologically meaningful information on the age and origin of minerals. Here we report the coupled 190Pt-186Os and 187Re-187Os signatures obtained by Laser Ablation Multi Collector Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) (Supplementary Information) on 13 sub-millimetric Pt-alkyls separated from a chromitite schlieren (sample 1265; Pushkarev et al., 2001) hosted in the dunite core of the Kondyor ZUC. Our Pt-alkyls are a different subset from those investigated for the 190Pt-4He isotope system. Shukolyukov et al. (2012a) and Mochalov et al. (2016, 2018) dated (i) Pt-alkyls from different lithologies of the Kondyor ZUC, including the chromitite lenses of the dunite core and

Received 19 May 2019 | Accepted 28 August 2019 | Published 22 October 2019

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(ii) alluvial Pt-Pd PGM. The FIB-TEM investigations on a few of our Pt-alloys revealed a very complex nanoscale exsolution pattern consisting of spinodal exsolutions of Pt-Fe alloys (e.g., Pt3Fe, PtFe) and pure Os exsolution lamellae (Fig. 1).

**Results**

The Kondyor Pt-alloys display radiogenic $^{186}\text{Os}/^{188}\text{Os}$ and unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions (Fig. 2 a,b). The most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ signatures (0.1246; alloys L-S2 and E-S2, Table S-2) agree well with those previously obtained on five Kondyor Os-rich alloys (0.1248-0.1252; Malitch and Thalhammer, 2002). Conversely, the least radiogenic $^{187}\text{Os}/^{188}\text{Os}$ (0.110096 ± 2136; alloy D-S2) is close to the composition of Re-free, least metasomatized peridotite xenoliths of the Tok locality (0.109; estimated for $\text{Al}_2\text{O}_3=0$ wt. % on the $^{187}\text{Os}/^{188}\text{Os}$ vs. $\text{Al}_2\text{O}_3$ “aluminochron”; Ionov et al., 2006), which like the Kondyor ZUC is located in the East Aldan Shield (Fig. S-1). Overall, the $^{187}\text{Os}/^{188}\text{Os}$ compositions are decoupled from both $^{187}\text{Re}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ signatures (Fig. 2a). In contrast, the $^{186}\text{Os}/^{188}\text{Os}$ composition defines a positive trend with $^{190}\text{Pt}/^{188}\text{Os}$, which - if considered to represent an isochronous relationship - yields an age of 249.8 ± 12 Ma (Fig. 2b). The $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ signatures are negatively correlated despite the sympathetic variation of both parent/daughter elemental ratios (Fig. 2c).

**Robustness of the Re-Os and Pt-Os Isotope Systematics**

The decoupling of the $^{187}\text{Os}/^{188}\text{Os}$ from both $^{187}\text{Re}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ signatures demonstrate the open system behaviour of the Re-Os isotope system in the Kondyor Pt-alloys. This is best explained by the overprinting of the Os-poor, least radiogenic $^{187}\text{Os}/^{188}\text{Os}$ of the Pt-alloy D-S2 by an Os-rich (ca. 700 times richer) contaminant with a $^{187}\text{Os}/^{188}\text{Os}$ of 0.1246 (Fig. 3a), similar to the most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ of our Kondyor alloys (e.g., points E-S2) and very close to the least radiogenic $^{187}\text{Os}/^{188}\text{Os}$ compositions previously reported by Malitch and Thalhammer (2002) and Cabri et al. (1998) for Kondyor PGM (Fig. 2a). Both the $^{186}\text{Os}/^{188}\text{Os}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ vs. $^{187}\text{Re}/^{188}\text{Os}$ relationships (Fig. 3b) can be reproduced with such a mixing scenario. Importantly, the negative $^{187}\text{Os}/^{188}\text{Os}$ vs. $^{187}\text{Re}/^{188}\text{Os}$ and the relationships between the $^{187}\text{Os}/^{188}\text{Os}$ and the abundance of Os exsolution lamellae (monitored by the $^{188}\text{Os}$ signal) in the Pt-alloys likely suggest that this mixing scenario reflects a gradual overprinting of the mantle source of the Kondyor mineralisation by subduction-related fluids (Supplementary Information).

The Pt-alloy D-S2 is then the least overprinted of our Kondyor subset (Fig. 3a,b). This view is further supported by the closeness of its $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ ratios (0.001196 and 0.00541; Table S-2) to those of the Re-free, least metasomatised Tok peridotite xenoliths (0.109 and 0; Ionov et al., 2006),...
implying that the $^{187}\text{Os}/^{188}\text{Os}$ composition of alloy D-S2 may still hold geologically meaningful constraints. Its Re-Os $T_{\text{DM}}$ model age points at a 2630 Ma old PUM-like mantle source for the Kondyor Pt-mineralisation (the Re-Os $T_{\text{DM}}$ model age is 2664 Ma). Occurrence of Archean mantle underlying the Aldan Shield is also supported by the $T_{\text{DM}}$ model ages of the Tok peridotites (2770 Ma) and by Pb-Pb isotope systematics of the Mesozoic lamproitic magmatism (~3 Ga; Davies et al., 2006). Considering that the present-day PM has a $^{186}\text{Os}/^{188}\text{Os}$ of 0.1198388 and a $^{190}\text{Pt}/^{188}\text{Os}$ of 0.0022 (Day et al., 2017), the 2630 Ma PUM-like mantle source of the Kondyor Pt-mineralisation then had a maximum $^{186}\text{Os}/^{188}\text{Os}$ of 0.1198303. If we consider such an initial $^{186}\text{Os}/^{188}\text{Os}$ composition, the D-S2 Pt-alloy would require 242.6 Myr to evolve to its present day $^{186}\text{Os}/^{188}\text{Os}$ signature. This age is similar within error to that extrapolated from the multi-grain Pt-Os isochron-like trend defined by our Kondyor Pt-alloys (249.8 ± 12 Ma; Fig. 2b).

Ages of ~250-250 Ma are recognised regionally within the Aldan Shield (Lena and Aldan (Palaeo) Rivers: Wang et al., 2011; Miller et al., 2013), the Baikal Lake Region (e.g. Gladkochub et al., 2010) and within basins (e.g. Onon and Mobe-Upo Amur), located South of the Aldan Shield and adjacent to the Mongol-Okhotsk Fold belt (Guo et al., 2017). The Mongol-Okhotsk fold belt (Fig. S-1), which rims the Siberian Craton on its South Margin over ca. 3000 km, represents the suture zone left after the closure of the Mongolia-Okhotsk Ocean - as its seafloor was subducted under the Siberian craton and under the Mongolia-North China continent (Amur plate), and, the subsequent collision of the Siberian craton with the Mongolia-North China continent (e.g. Zorin, 1999; Guo et al., 2017). The age distribution along the Mongol-Okhtoks fold belt demonstrates an eastward zip-like closure of the Mongol-Okhtoks ocean (Zorin, 1999) initiated in the Late Palaeozoic in NE Mongolia (Zhao et al., 2017) and in the Early Triassic in the eastern part of the Mongol-Okhtoks belt, south of Aldan Shield Region (Guo et al., 2017). The age of the subsequent collision between the Mongolia-North China continent and Siberia craton also evolves eastwards from Middle Jurassic to Early Cretaceous (Zorin, 1999).

### Why are the $^{190}\text{Pt-}{^{186}\text{Os}}$ and the $^{190}\text{Pt-}{^{4}\text{He}}$ “Ages” of the Kondyor Pt-alloys Different?

Both the $^{190}\text{Pt-}{^{4}\text{He}}$ and $^{190}\text{Pt-}{^{186}\text{Os}}$ isotopic systems are based on the radioactive alpha decay of the $^{190}\text{Pt}$ so they should yield identical ages. However, for the Kondyor Pt-alloys, the Pt-He isochronal ages (Shukolyukov et al., 2012a; Mochalov et al., 2016, 2018) are ~110-140 Myr younger than the Pt-Os ages.

Several lines of evidence suggest that the age inconsistency may reflect an open system behaviour of the Pt-He isotopic system. First, Shukolyukov et al. (2012a,b) and Mochalov et al. (2016) argued that radiogenic $^{4}\text{He}$ is retained in the structure of native metals as vesicles that are only released upon melting of the native metals (>1000 ºC). However, the only $^{4}\text{He}$ thermal desorption experiment conducted on Pt-alloys by Shukolyukov et al. (2012a) revealed $^{4}\text{He}$ loss ($[^{4}\text{He}] \neq 0$) for temperatures as low as ~700 ºC (see Fig. 4 in Shukolyukov et al., 2012a). While the $^{4}\text{He}$ loss appears marginal during their experiment, it will be significant if Pt-alloys reside in the lithospheric mantle (with an equilibration temperature >700 ºC) for 10s-100s of Myr. It is thus possible that the $^{4}\text{He}$ is not fully trapped in the structure of the Pt-alloys until the $^{4}\text{He}$ closure temperature in these minerals is attained. One can additionally consider how the nanoscale exsolution patterns within the Kondyor Pt-alloys will affect the $^{4}\text{He}$ loss/retention. The grain boundaries proposed as a preferential sink for $^{4}\text{He}$ (Shukolyukov et al., 2012b) may turn out to be preferential $^{4}\text{He}$

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**Figure 2.** (a) Variations of $^{187}\text{Os}/^{188}\text{Os}$ vs. $^{187}\text{Re}/^{188}\text{Os}$, (b) of $^{186}\text{Os}/^{188}\text{Os}$ vs. $^{190}\text{Pt}/^{188}\text{Os}$ and (c) of $^{190}\text{Pt}/^{188}\text{Os}$ vs. $^{187}\text{Re}/^{188}\text{Os}$. The primitive mantle (PM) $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ values are respectively from Day et al. (2017) and Meisel et al. (2001). If the positive correlation between $^{186}\text{Os}/^{188}\text{Os}$ vs. $^{190}\text{Pt}/^{188}\text{Os}$ is considered to be an isochronous relationship, it yields an age of 249.8 ± 12 Ma and an intercept of 0.119821 ± 0.000024 (2 sigma) (MSWD = 0.81).
Implication for the Origin and Evolution of the Kondyor ZUC

The combined LA-MC-ICPMS investigation of the Re-Os and Pt-Os isotope signatures demonstrates that the Pt-mineralisation, contemporaneous to the formation of the Kondyor ZUC, originates ~250-240 Myr ago from the melts and fluids produced by partial melting of possibly an Archean PUM-like mantle source, which could be the Siberian cratonic mantle. Considering the orthopyroxene-poor, olivine- and clinopyroxene-rich nature of Kondyor ZUC (Orlova, 1992; Malitch and Thalhammer, 2002) and its extreme Pt-mineralisation, we argue that, rather than being a metasomatised mantle diapir (Burg et al., 2009), Kondyor ZUC represents the root of a ~250-240 Ma old alkaline picritic volcano (Simonov et al., 2011), which together with other Aldan ZUC (e.g., Chad) likely formed part of an Early Triassic island arc at the southeast margin of the Aldan shield due to the subduction of the Mongol-Okhotsk ocean seafloor northwards under the Siberian Craton (see Zorin, 1999; Guo et al., 2017). The uplift associated with the Early Cretaceous collision of the Siberian craton with the Mongolia-North China continent (after the closure of the Mongol-Okhotsk ocean) combined with the subsequent major extensional phase evidenced by the development of Early Cretaceous rift systems may have contributed to the unroofing and exhumation of deep-seated structures such as metamorphic core complexes (Zorin, 1999). In such an unroofing and exhumation scenario, the Kondyor ZUC would attain sub-surface conditions and cool down below the closure temperatures of the K-Ar, Rb-Sr and Pt-He isotope systems, explaining why these geochronometers yield almost exclusively Early to Late Cretaceous ages for the Kondyor ZUC.

Acknowledgements

AL and CB thank the Deutsche Forschungsgemeinschaft for supporting this project (LU 1603/5-1, CB 964/36-1) and EP acknowledges the Russian State Scientific programme No AAAA-A18-118051190022-4. We gratefully thank two anonymous reviewers and our editor, Cin-Ty Lee, for their insightful comments and suggestions.

Editor: Cin-Ty Lee

Additional Information

Supplementary Information accompanies this letter at http://www.geochemicalperspectivesletters.org/article1924.

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