Comment on “190Pt-186Os geochronometer reveals open system behaviour of 190Pt-4He isotope system” by Luguet et al. (2019)

O.V. Yakubovich1,2*, A.G. Mochalov2, V.M. Savatenkov1,2, F.M. Stuart3

Comment

Accurate and precise chronology of ore forming processes is critical for the development of genetic models for ore formation. New methods (190Pt-186Os and 190Pt-4He) have been developed recently for determining the timing and complexity of platinum group metal (PGM) mineralisation (e.g., Coggon et al., 2012; Shukolyukov et al., 2012a, Yakubovich et al., 2015). Although these methods are fraternal, both based on the alpha particle decay of 190Pt, the geochemical behaviour of the daughter products (186Os and 4He) contrasts significantly. The combination of these isotope systems for dating single ore mineral phases offers a great opportunity to resolve the timing of ore formation.

The first combined study of 190Pt-186Os and 190Pt-4He systems in Pt mineralisation - the Kondyor zoned ultramafic complex in the Aldan shield, Russia – has generated a controversial result. Mochalov et al. (2016) obtained 190Pt-4He ages of multiple individual Pt alloy grains to be 112–129 Ma, that was consistent with regional geology, sequence of mineral formation and independent age estimations. Subsequently Luguet et al. (2019) reported a 190Pt-186Os isochron age of 240–250 Ma. This age discrepancy led Luguet et al. (2019) to conclude that the 190Pt-4He ages of the Pt grains reflected “open system” behaviour, essentially arguing that the radiogenic 4He generated by Pt decay had diffused out of the grains since their formation. This explanation is extremely difficult to reconcile with the experimental low diffusion rate of radiogenic 4He in Pt-Fe alloys (Shukolyukov et al., 2012a,b), the retention of extremely high concentrations of cosmogenic 4He by Pt-Fe alloys (Yakubovich et al., 2019) and with the theory of helium behaviour in metals in general (Trinkaus and Singh, 2003). Herein we provide an alternative point of view on the discrepancy between 190Pt-4He and 190Pt-186Os systems in Pt alloys of the Kondyor alkaline-ultramafic complex.

There is abundant independent radiometric geochronological age that the Kondyor ultramafic massif and the associated PGM mineralisation has an Early Cretaceous age; Sm-Nd, Rb-Sr, 40Ar-39Ar, baddeleyite U-Pb ages are in the range 120–132 Ma (Table S-1). These ages are essentially consistent within measurement uncertainty. These isotope systems have closure temperatures that range from ~300 °C (biotite Ar-Ar; Harrison et al., 1985) to over 1150 °C (clinopyroxene Sm-Nd; Van Orman et al., 2001), implying that Pt mineralisation was simultaneous with intrusion, and that post-intrusion cooling of the complex was instantaneous, within our ability to resolve it.

Luguet et al. (2019) have ignored the evidence for the Cretaceous age of alkaline magmatic complexes, and associated ore deposits, in the Aldan shield region (Yarmolyuk et al., 2019 and references therein). In support of the Early Triassic age of the Kondyor ultramafic complex they remark on the similarity with detrital zircon grains from the Lena river and Mobe-Upper Amur basin. These rivers are 800–1500 km from the Kondyor ultramafic massif, and the detrital zircons are generally accepted to originate in the Angaro-Vitim batholiths and the China craton (Wang et al., 2011; Miller et al., 2013; Guo et al., 2017) rather than the Aldan shield.

The Luguet et al. (2019) study failed to put the study material into context. The formation of platinum mineralisation within the Kondyor massif was poly cyclic (Mochalov, 2019). Cumulate dunites, the earliest rocks of the massif, underwent syn-magmatic recrystallisation and metasomatic transformation under the influence of ultramafic, mafic, alkaline, and granitoid intrusions. This resulted in the formation of five genetically distinct types of PGMs. The Pt alloys analysed by Luguet et al. (2019) belong to the later generations of PGM that were formed due to the recrystallisation and remobilisation of earlier PGM at temperatures not higher than 650–850 °C (see Supplementary Information; Table S-2). This indicates that the PGE chemistry of fluids that were responsible for the formation of these Pt alloys evolved with time. It also indicates that the age of Pt alloys is coeval with the emplacement of Kondyor massif. Thus, there is no evidence for the crystallisation of these Pt alloys in a root of an Early Triassic volcano that was exhumed in Early Cretaceous time, as proposed by Luguet et al. (2019).

Figure 1 shows the Pt-Os data sample 1265 obtained by Luguet et al. (2019; Table S-2, part 2). There is significant variation in 188Os/186Os and 186Os/188Os ratios. Based on 188Os/186Os ratio the samples studied by Luguet et al. (2019) fall into several mineral types; native osmium (Os, Os+), aggregates and crypto-aggregates of native osmium with isoferroplatinum (Pt + Os) and isoferroplatinum (Pt, Pt+) (Fig. 1b). The regression line in 190Pt/188Os and 186Os/188Os space for each of these mineral types have different and distinct slopes (Fig. 1a). Ontogeny of the minerals show that native osmium crystallised before the Pt alloys...
eralogy of the PGE and geochemistry of HSE in general. will surely provide a number of significant additions to the min-
in the other ultramafic massifs (mantle, island arc, shield) they
grains. If such phenomena are present in other ore occurrences
able features of the behaviour of the Pt and Os isotopes in PGM
ance of 187Re-187Os isotope system within the same grains
and therefore provides no age information. The obvious disturb-
all the data (Fig. 2b in Luguet et al., 2019) directly confirms this.

In summary, the data provided by Luguet et al. (2019) do not show any evidence for open 190Pt-4He system behaviour. Nor does it provide any support for an Early Triassic age of the Kondyor massif. The discrepancy between 190Pt-4He and 190Pt-186Os ages of the Pt alloys of the Kondyor massif reflect contrasting geochemical behaviour of daughter isotopes during the polycyclic formation of platinum mineralisation. 190Pt-4He age reflects the age of mineral formation itself, while the 190Pt-186Os isotope system fingerprints earlier redistribution of PGE. Luguet et al. (2019) have established a number of remarkable features of the behaviour of the Pt and Os isotopes in PGM grains. If such phenomena are present in other ore occurrences in the other ultramafic massifs (mantle, island arc, shield) they will surely provide a number of significant additions to the mineralogy of the PGE and geochemistry of HSE in general.

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Additional Information

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Comment on “$^{190}$Pt-$^{186}$Os geochronometer reveals open system behaviour of $^{190}$Pt-$^4$He isotope system” by Luguet et al. (2019)

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Supplementary Information

The Supplementary Information includes:

➢ 1. General Remarks on Retentivity of Radiogenic Helium in Pt-alloys
➢ 2. Summary of Previous Geochronology for the Kondyor Massif
➢ 3. General Remarks on Pt Mineralisation of the Kondyor Massif
➢ Tables S-1 and S-2
➢ Supplementary Information References

1. General Remarks on Retentivity of Radiogenic Helium in Pt-alloys

The thermal retentivity of $^4$He in Pt-alloys is high. Numerous studies have shown that helium has an extremely low solubility in metals and at temperatures below half of the melt temperature (0.5 $T_m$) it tends to be trapped by vacancies with the formation of He-V clusters (e.g. Trinkaus and Singh, 2003). Consequently, the diffusion of single helium atoms in metal cannot be significantly faster than self-diffusion (Sciani and Jung, 1983). The activation energy of self-diffusion of Pt metal is ~ 64 kcal/mol (Cattaneo et al., 1962). This is comparable with the activation energy of hetero-diffusion of Pt in Fe-Pt alloys (~ 70 kcal/mol; Kučera and Million, 1975). The same range of values can be expected for hetero-diffusion of radiogenic Os in Pt-Fe alloys. The high retentivity of He in native metals has been empirically confirmed by extensive diffusion experiments (Shukolyukov et al., 2012a,b). Thus, the discrepancy between the $^{190}$Pt-$^4$He and $^{190}$Pt-$^{186}$Os ages cannot be explained by diffusive loss of $^4$He. The $^{190}$Pt-$^4$He dating method has been successfully applied to platinum mineralisation from a wide variety of deposits (e.g., Yakubovich et al., 2015a). In all these studies the $^{190}$Pt-$^4$He age is consistent with independent geochronological age estimates and regional geology.

2. Summary of Previous Geochronology for the Kondyor Massif

A lot of work was done to understand the timeframes of the formation of alkaline ultramafic massif Kondyor (Table S-1). Sm-Nd, Rb-Sr, $^{40}$Ar-$^{39}$Ar, baddeleyite U-Pb and Pt-He dating of the Kondyor ultramafic massif and the associated PGM mineralisation all yield essentially Early Cretaceous ages which are more or less consistent within measurement uncertainty.
<table>
<thead>
<tr>
<th>Dated material</th>
<th>Age, Ma</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroxenite (isochron)</td>
<td>132 ± 8</td>
<td>Rb-Sr</td>
<td>Pushkarev et al., 2002</td>
</tr>
<tr>
<td>Biotite in magnetite peridotite and from veins in dunites</td>
<td>120 ± 1</td>
<td>Ar-Ar</td>
<td>Cabri et al., 1998</td>
</tr>
<tr>
<td>Apatite–phlogopite clinopyroxenites (isochron)</td>
<td>128 ± 2</td>
<td>Rb-Sr</td>
<td>Efimov et al., 2012</td>
</tr>
<tr>
<td>Apatite–phlogopite clinopyroxenites (isochron)</td>
<td>131 ± 35</td>
<td>Sm-Nd</td>
<td>Efimov et al., 2012</td>
</tr>
<tr>
<td>Clinopyroxene from dunite (isochron)</td>
<td>128 ± 40</td>
<td>Sm-Nd</td>
<td>Savatenkov and Mochalov, 2018</td>
</tr>
<tr>
<td>Detrital and lode isoferroplatinum</td>
<td>129 ± 6</td>
<td>Pt-He</td>
<td>Mochalov et al., 2016</td>
</tr>
<tr>
<td>Detrital and lode sperrylite (PtAs₂)</td>
<td>122 ± 6</td>
<td>Pt-He</td>
<td>Yakubovich et al., 2015b</td>
</tr>
<tr>
<td>Baddeleyite in dunite</td>
<td>125 ± 2</td>
<td>U-Pb</td>
<td>Ronkin et al., 2013</td>
</tr>
<tr>
<td>Zircon from dunite</td>
<td>2477 ± 18</td>
<td>U-Pb</td>
<td>Ronkin et al., 2013</td>
</tr>
<tr>
<td></td>
<td>1895 ± 50</td>
<td></td>
<td>Malitch et al., 2012</td>
</tr>
<tr>
<td></td>
<td>1885± 52</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1016 ± 22</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>390 ± 12</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>176 ± 1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>125.8 ± 3.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

U-Pb ages of zircon from dunites sometimes reflect the age of magmatic event, although zircon cannot crystallise from ultramafic melts (Heaman, 2009; Borisov and Aranovich, 2019). Typically, zircon grains are xenocrysts (Bea et al., 2001) or crystallised during later metasomatic processes (e.g. Rudnick and Walker, 2009). Crystallisation event with the age of 240–250 Ma is not observed in the zircon U-Pb population (Table S-1). However, the youngest zircon U-Pb age is fully consistent with the Early Cretaceous formation of the Kondyor ultramafic complex suggested by other methods.

To explain the discrepancy between $^{190}\text{Pt}^{186}\text{Os}$ and $^{190}\text{Pt}^{4}\text{He}$ ages Luguet et al. (2019) proposed that Kondyor massif represents the root of an Early Triassic volcano that was exhumed in the Early Cretaceous. According to Luguet et al. (2019) the rapid exhumation of Kondyor massif occurred in response to extension followed by the exhumation of deep-seated structures, such as metamorphic core complexes. This requires a cooling rate for Kondyor massif of ~ 160 °C/Myr. For metamorphic core complexes cooling of 80 °C/Myr is considered to be rapid (e.g., Kargaranbaqghi et al. 2015). There are no metamorphic core complexes so far documented within the Aldan shield. The nearest metamorphic core complexes are located approximately 1,000 km to the south-west of Kondyor (Wang et al., 2011).

### 3. General Remarks on Pt Mineralisation of the Kondyor Massif

The prevailing view of the sequence of platinum group element (PGE) ore formation in the Kondyor massif has been developed from studies of the ontogeny of PGM aggregates with silicates, oxides and sulfides (Mochalov, 2019). The massif is composed of alkaline mafic-ultramafic rocks: dunites, wherlites, pyroxenites, kosvites, hornblendites, gabbros, alkaline pegmatites, alkaline syenites, monzodiorites, and sub-alkaline granites. It was intruded into basement composed.
of Archean crystalline rocks and Proterozoic meta-sediments (Nekrasov et al., 2005; Mochalov, 2019). Cumulate dunites, the earliest rocks of the massif, underwent syn-magmatic recrystallisation and metasomatic transformation under the influence of ultramafic, mafic, alkaline, and granitoid intrusions. Five genetically-distinct types of PGMs can be distinguished on the basis of mineralogy and geochemistry: (1) Magmatogenic platinum grains in cumulates of alkaline ultramafic (picritic) magma; (2) Magmatogenic-fluid-metasomatic Pt grains in metasomatic dunites that underwent high-temperature recrystallisation under the influence of picritic magmas; (3) Magmatogenic-fluid-metasomatic osmium-platinum grains (Pt>Os) in veins and schlieren of clinopyroxenites; (4) Fluid-metamorphic iridium-platinum grains (Pt>Ir) that formed as a result of syn-magmatic recrystallisation of dunite cumulates and the conversion of PGMs from the Pt- to Pt>Ir-type and is developed in dunites and chromitites; (5) Magmatogenic-fluid-metasomatic palladium-platinum grains (Pt>Pd) that formed due to remobilisation of all early types of PGMs and is present in a series of metasomatites within dunites, chromitites, clinopyroxenites and amphibolites. Currently 91 PGM species have been identified in the Kondyor massif and the related alluvial deposits. Native minerals of platinum (NMP), mainly isoferroplatinum, are the main type of PGM within the massif. Based on the $^{187}$Os/$^{188}$Os ratios and sample description (Luguet et al., 2019) we can conclude that PGM from sample 1265 are Pt>Ir or Pt>Pd type grains of chromitites (Table S-2). The general discerption of sample 1265 provided by Pushkarev et al. (2015) is consistent with this conclusion.

**Table S-2** Average chemical composition of the different isoferroplatinum grains types from Kondyor deposit and placer deposit of the Kondyor-Uorgalan rivers.

<table>
<thead>
<tr>
<th>Type</th>
<th>n</th>
<th>Pt</th>
<th>Ir</th>
<th>Os</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-</td>
<td>16</td>
<td>87.75</td>
<td>0.37</td>
<td>0.24</td>
<td>0.04</td>
<td>1.08</td>
<td>0.70</td>
<td>8.43</td>
<td>0.07</td>
<td>0.74</td>
<td>99.42</td>
</tr>
<tr>
<td>Pt&gt; Os-</td>
<td>21</td>
<td>89.27</td>
<td>0.35</td>
<td>0.37</td>
<td>0.04</td>
<td>1.12</td>
<td>0.97</td>
<td>6.70</td>
<td>0.06</td>
<td>0.81</td>
<td>99.69</td>
</tr>
<tr>
<td>Pt&gt; Ir-</td>
<td>37</td>
<td>86.66</td>
<td>2.25</td>
<td>0.29</td>
<td>0.05</td>
<td>0.48</td>
<td>0.22</td>
<td>8.89</td>
<td>0.16</td>
<td>0.70</td>
<td>99.70</td>
</tr>
<tr>
<td>Pt&gt; Pd¹</td>
<td>47</td>
<td>89.47</td>
<td>0.00</td>
<td>0.01</td>
<td>0.03</td>
<td>0.60</td>
<td>0.76</td>
<td>8.38</td>
<td>0.01</td>
<td>0.74</td>
<td>100.00</td>
</tr>
<tr>
<td>Pt&gt; Pd²</td>
<td>27</td>
<td>88.89</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
<td>0.63</td>
<td>1.13</td>
<td>8.59</td>
<td>0.09</td>
<td>0.62</td>
<td>99.98</td>
</tr>
<tr>
<td>Pt&gt; Pd³</td>
<td>12</td>
<td>88.07</td>
<td>0.00</td>
<td>0.02</td>
<td>0.01</td>
<td>0.67</td>
<td>0.90</td>
<td>9.14</td>
<td>0.49</td>
<td>0.69</td>
<td>99.99</td>
</tr>
<tr>
<td>Placer</td>
<td>765</td>
<td>87.03</td>
<td>1.84</td>
<td>0.24</td>
<td>0.08</td>
<td>0.54</td>
<td>0.40</td>
<td>9.02</td>
<td>0.14</td>
<td>0.71</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Comment: For Pt> Pd type grains: 1 - crystals, 2 – twin crystals, 3 – chromitites; n is the number of the chemical analyses; element concentrations in weight %.

The structural state of the NMP corresponds to the relatively low-temperature region of the phase diagram of the Pt-Fe system. Formation of PGM occurred during crystallisation of picrite, monzonite, alkaline and granitoid melts and metasomatic transformations of dunites in shallow areas of the Aldan shield (Simonov et al., 2011; Mochalov, 2019). Oxygen fugacity in NMP of the Pt>Ir-, Pt>Os, Pt>Pd-types and in syngenetic clinopyroxene, chromespinelide and olivine are between the buffer equilibria of quartz-fayalite-magnetite and wustite-magnetite. At temperatures in excess of 1000 °C this indicator is similar to the oxygen fugacity of the redox state of the mafic magmas in near-surface environments in which Pt and Pt>Os PGMs are formed. At temperatures below 800–850 °C, the volatility of all these minerals is close to or below the buffer equilibrium of iron-wustite, which corresponds to the release of iron from silicates and indicates the conditions for the formation of NMP of Pt>Ir and Pt>Pd types (Kadik et al., 1998). The oxygen isotopic composition ($\delta^{18}$O = 3.1–5.2 ‰) of chromium spinels, clinopyroxenes, olivine in intergrowths with NMP of Pt>Ir, Pt>Pd PGM indicates that the formation of the minerals occurred in subsurface conditions from magmatic fluid in association with a water vapour that was ultimately of meteoric origin (Ukhanov et al., 1997).
Supplementary Information References


