Platinum group elements in Kostomuksha komatiites and basalts: Implications for oceanic crust recycling and core-mantle interaction

IGOR PUCHTEL* and MUNIR HUMAYUN
Department of the Geophysical Sciences, The University of Chicago, 5734 S. Ellis Avenue, Chicago, IL 60637, USA

(Received January 7, 2000; accepted in revised form June 27, 2000)

Abstract—We report precise PGE (Os, Ir, Ru, Pt, and Pd) concentrations for komatiite-basalt lava sequences of the Kostomuksha greenstone belt, and for the komatiite standards KAL-1 (Abitibi) and WITS-1 (Barberton). The flowtop breccia komatiites (MgO = 27.5%) from the Kostomuksha sequence, which represent the composition of the primary komatiite liquid, have Os = 1.5 ± 0.1 ppb, chondritic (Os/Ir)$_N$ = 1.06 ± 0.05, and moderately fractionated PGE patterns, (Pd/Os)$_N$ = 6.5 ± 0.4. Based on the KAL-1 standard, the Alexo primary liquid had Os = 1.8 ± 0.1 ppb, (Os/Ir)$_N$ = 1.05 ± 0.05, and (Pd/Os)$_N$ = 8.5 ± 1.0. PGEs in the Kostomuksha komatiites exhibit incompatible behavior during magmatic differentiation, with bulk D values of Os, Ir = 0.75, Pt = 0.52 and Pd = 0.

PGE abundances from Kostomuksha komatiites and basalts were used to calculate the Pt/Os and Re/Os composition of a magnesian Archean oceanic crust. The Pt-Re-Os isotopic evolution of this crust was modeled, indicating that coupled $^{186,187}$Os enrichments observed in some modern plumes require a non-crustal source. A previously proposed model for core-mantle interaction by physical admixture was evaluated and was shown to produce mantle sources with high PGE abundances (Os = 6 to 14 ppb, Pd = 140 ppb for 1% outer core addition) and (Os/Ir)$_N$ = 1, depending on the assumptions made. These features were not observed in the Kostomuksha komatiites ($\gamma^{^{187}}$Os(T) = +3.6), shown here to be derived from a reservoir with ~25% lower absolute PGE abundances than primitive mantle. If the radiogenic initial $^{187}$Os/$^{188}$Os in the Kostomuksha komatiite is an outer core signature, then core-mantle interaction cannot have involved physical admixture of outer core material into mantle plume sources. Instead, it must have occurred in the form of isotopic equilibration between liquid outer core and solid mantle at the core-mantle boundary.

1. INTRODUCTION

Due to their highly siderophile and generally compatible nature, platinum group elements (PGE = Ru, Rh, Pd, Os, Ir, Pt) are a powerful tool for studying processes of the Earth’s accretion, core-mantle differentiation, mantle evolution and magma genesis. In addition, the development and application of the siderophile element radiogenic systems, $^{187}$Re-$^{187}$Os and $^{190}$Pt-$^{186}$Os (see review in Shirey and Walker, 1998 and Walker et al., 1997; Rehkämper et al., 1999a; Rehkämper et al., 1999b) provide both tracer and chronological information on differentiation processes affecting these elements. However, high-quality studies of PGE concentrations still cover a limited range of mantle samples (e.g., Pattou et al., 1996; Rehkämper et al., 1997; Rehkämper et al., 1999a; Rehkämper et al., 1999b) and do not report Os abundances.

The behavior of PGEs during partial melting and crystal fractionation can be studied from PGE compositions of mantle-derived lavas such as basalts and komatiites. Rehkämper et al. (1999b) showed that PGE abundances in basalts were drastically modified by extensive PGE fractionation in these sulfide-saturated magmas, rendering basalts unsuitable for determining source PGE compositions. We used komatiites as indicators of mantle source PGE composition since these lavas are sulfide-unsaturated primary melts.

Komatiites formed as a result of extensive melting in hot mantle plumes (e.g., Campbell and Griffiths, 1990; Storey et al., 1991). The degrees of melting during komatiite formation were very substantial (30 to 50%) enabling the melts to extract large proportions of compatible elements (e.g., PGE). Komatiites are low-viscosity melts, rapidly erupted, at temperatures well in excess of their liquidus temperatures, assuring that basically no differentiation occurred before eruption (Arndt, 1976; Herzberg, 1995). Differentiation that occurs in individual flows during emplacement can be assessed by thorough sampling from representative sections, such as afforded by drill cores.

In this study, we report precise PGE data for komatiites from the 2.8 Ga Kostomuksha and 2.7 Ga Abitibi greenstone belts. Data for Kostomuksha basalts associated with the komatiites are also presented. On the basis of field relationships, and lithophile trace element and Nd-Pb isotope characteristics, the submarine lava sequences of these greenstone belts have been proposed to be remnants of upper crustal portions of Archean plume-derived oceanic plateaux (Desrochers et al., 1993; Puchtel et al., 1997), though both contain thick sequences of well-preserved komatiites free of crustal contamination. Kostomuksha and Abitibi komatiites were derived from mantle sources with distinct $^{186}$Os/$^{188}$Os isotope compositions. While the source of the Abitibi komatiite was characterized by a chondritic initial $^{187}$Os/$^{188}$Os (Walker et al., 1988; Shirey, 1997), Os data for the Kostomuksha komatiites indicate that the source of these lavas had a supachondritic initial $^{187}$Os of +3.6 ± 1.0 (Puchtel et al., 2000a). This radiogenic signature, though extremely rare in the Archean (the only other occurrence being the 3.3 Ga Nondweni greenstone belt in South Africa, Shirey et al., 1998), is...
ubiquitous in modern and recent plumes (Pegram and Allègre, 1992; Hauri and Hart, 1993; Marcantonio et al., 1995; Widom and Shirey, 1996; Lasister and Hauri, 1998). The enriched $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition of the Kostomuksha plume has been recently interpreted (Puchtel et al., 2000a) in terms of the core-mantle interaction model of Walker et al. (1995).

Two major mechanisms have been proposed to explain the enriched $^{187}\text{Os}/^{188}\text{Os}$ isotopic compositions of mantle plume sources. These include (1) recycling of oceanic crust (Walker et al., 1991; Hauri and Hart, 1993; Marcantonio et al., 1995; Roy-Barman and Allègre, 1995) and (2) entrainment of small amounts of outer core material by rising mantle plumes (Walk-er et al., 1995; Walker et al., 1997a). Recently, efforts have been made to distinguish the effects of the two processes by examining the Pt-Re-Os isotope systematics of modern and recent plume-derived lavas (Walker et al., 1997a; Brandon et al., 1998). The crucial test of the two hypotheses lies in obtaining a correlation between the $^{186}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ initial ratios. Due to a substantially higher Pt/Re ratio in the model outer core (Walker et al., 1995; Morgan et al., 1995; Smoliar et al., 1996) compared to the oceanic crust (90 to 100 vs. ~7), melts derived from the sources that experienced core-mantle interaction plot along a much steeper trend in $^{187}\text{Os}$ vs. $^{186}\text{Os}$ space (Brandon et al., 1999).

One consequence of such physical addition of outer core to mantle sources is a very significant increase in PGE abundances. For example, Widom and Shirey (1996) showed that OIB that experienced physical addition of small amounts (0.3%) of outer core would have elevated Os, and especially Re, abundances, but pointed out that this effect would be difficult to recognize as compatible Os (and Ir) can be severely depleted in even relatively primitive basaltic magmas. The absence of a correlation between Os abundances and $^{187}\text{Os}/^{188}\text{Os}$ ratios was not regarded as conclusive evidence against such physical addition by Shirey and Walker (1998) because of petrogenetic complexities in relating OIB Os abundances to their source compositions. Hauri and Hart (1997) compared Re/Yb ratios of OIB and MORB and argued for less than 0.3% outer core addition in most plumes, with a maximum limit of 1.2% for all OIB lavas in their study. Rehkämper et al. (1999b) in their study of PGE abundances in OIB and MORB found evidence of substantial PGE fractionation, limiting the reconstructions of mantle source PGE compositions. In this paper, we determine the PGE abundances in Kostomuksha and Abitibi komatiites and basalts and show how to reconstruct PGE compositions of mantle sources. This work addresses the question of PGE fractionation during mantle melting and differentiation; tests the hypothesis that subducted Archean oceanic crust could be the source of coupled radiogenic $^{186,187}\text{Os}$ in the mantle; and evaluates the potential effects of core-mantle interaction on the PGE abundances in plume-derived magmas.

2. GEOLOGICAL BACKGROUND AND PREVIOUS ISOTOPE AND TRACE ELEMENT STUDIES

The geological setting of the Gimola-Kostomuksha greenstone belt in the NW part of the Karelian granite-greenstone terrane has been described in detail elsewhere (e.g., Puchtel et al., 1997; Puchtel et al., 1998, and references therein) and is only briefly summarized here. The belt consists of several conjugate synforms that can be traced over a distance of >400 km (Fig. 1) with the Kostomuksha synform being the largest of these. The latter includes at least two distinct lithotectonic terranes, one mafic igneous and the other sedimentary, separated by a major structural unconformity. The mafic terrane contains submarine-erupted komatiite and basalt lavas, volcaniclastic mafic and ultramafic sediments and numerous gabbro and peridotite sills. The sedimentary terrane is composed of shelf-type rocks and banded iron formations (BIF). The komatiites and basalts from the mafic terrane have Sm-Nd and Pb-Pb isochron ages of 2843 ± 39 and 2813 ± 78 Ma, respectively, and are intruded and overlain by felsic subvolcanic, volcanic and volcaniclastic rocks of dacite-rhyolite composition with a U-Pb zircon age of 2821 ± 1 Ma. Trace element characteristics and Nd-Pb isotope compositions of the source reservoirs of the komatiites and basalts resemble those of recent Pacific oceanic flood basalts (see review in Puchtel et al., 1998) at their respective time of eruption. Based on these lines of evidence, the authors argued that the Kostomuksha lava sequences represent remnants of the upper crustal part of an Archean oceanic plateau derived from partial melting in a mantle plume head. Similar conclusions were reached by Des-rochers et al. (1993) for the Abitibi greenstone belt.

From the Kostomuksha belt, samples of flowtop breccias, and olivine spinifex-textured and cumulate komatiites from a number of differentiated lava flows recovered from a 300 m deep diamond drill hole (#15) were selected. In addition, samples of pillow and massive basalts from this and two other drill holes (#79 and #124), and from surface outcrops, were studied. Most of these samples have been previously analyzed for major and trace elements and Pb-Nd isotopes. Sample location and more detailed geological information can be found in Puchtel et al. (1998). For a selected set of komatiite samples, Puchtel et al. (2000a) obtained a Re-Os isochron with an age of 2795 ± 40 Ma and a radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition ($^{187}\text{Os(T)}/^{188}\text{Os} = +3.6 ± 1.0$). From the Abitibi belt, we studied an olivine spinifex-textured komatiite sample, KAL-1, from a single Alexo lava flow (Arndt 1986) developed as a standard by N. T. Arndt, C. M. Lesher, and S. B. Shirey (personal communication). This sample is stratigraphically equivalent to sample M663 from the same flow.

3. ANALYTICAL TECHNIQUE

The NiS fusion procedure (Robert et al., 1971; Hoffman et al., 1978) employed here was modified from that used by Hauri and Hart (1993) for Os-isotope analysis, by the substitution of Li-tetraborate as the flux. Ravizza and Pyle (1997) developed a NiS fusion procedure similar to that employed here, to analyze Os isotopes. For a selected set of komatiite samples, Puchtel et al. (2000a) obtained a Re-Os isochron with an age of 2795 ± 40 Ma and a radiogenic initial $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition ($^{187}\text{Os(T)}/^{188}\text{Os} = +3.6 ± 1.0$). From the Abitibi belt, we studied an olivine spinifex-textured komatiite sample, KAL-1, from a single Alexo lava flow (Arndt 1986) developed as a standard by N. T. Arndt, C. M. Lesher, and S. B. Shirey (personal communication). This sample is stratigraphically equivalent to sample M663 from the same flow.
the NiS beads were extracted and dissolved in 6N HCl. Double-distilled acids from Seastar™, and 18.2 MΩ deionized water, were used throughout the chemical procedures. Upon dissolution, Ni forms a NiCl₂ solution and the PGEs react with the released H₂S gas to form insoluble PGE sulfides. The solutions were filtered through a cellulose membrane to recover the precipitates and to remove most of the Ni. The cellulose membrane was then dissolved in 2 mL of hot (~100°C) aqua regia.

Fig. 1. Geological sketch map of the Karelian granite-greenstone terrane, Baltic Shield (after Sokolov; 1987, with some modifications). The study area in the inset map includes the Kostomuksha synform of the Gimola-Kostomuksha greenstone belt.
Table 1. PGE abundances in the analytical blank.

<table>
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<tr>
<th>Sample</th>
<th>Sample wt. (g)</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Pt</th>
<th>Pd</th>
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<tr>
<td>9436</td>
<td>0.5576</td>
<td>29.3</td>
<td>40.8</td>
<td>170.7</td>
<td>1018</td>
<td>1441</td>
</tr>
<tr>
<td></td>
<td>1.4920</td>
<td>58.6</td>
<td>99.1</td>
<td>412.3</td>
<td>2145</td>
<td>3186</td>
</tr>
<tr>
<td></td>
<td>2.0037</td>
<td>81.8</td>
<td>130.2</td>
<td>538.3</td>
<td>3119</td>
<td>3110</td>
</tr>
<tr>
<td></td>
<td>4.4032</td>
<td>155.0</td>
<td>258.4</td>
<td>1229</td>
<td>6041</td>
<td>6931</td>
</tr>
<tr>
<td>Blank (pg)</td>
<td></td>
<td>11</td>
<td>14</td>
<td>310</td>
<td>704</td>
<td></td>
</tr>
<tr>
<td>9443</td>
<td>0.5648</td>
<td>38.6</td>
<td>323.6</td>
<td>696.8</td>
<td>761.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.9181</td>
<td>59.6</td>
<td>434.0</td>
<td>879.9</td>
<td>1028</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5500</td>
<td>88.8</td>
<td>504.6</td>
<td>1179</td>
<td>1224</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.2140</td>
<td>133.1</td>
<td>743.3</td>
<td>1929</td>
<td>1713</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.5049</td>
<td>201.5</td>
<td>1074</td>
<td>2429</td>
<td>1997</td>
<td></td>
</tr>
<tr>
<td>Blank (pg)</td>
<td></td>
<td>7.0</td>
<td>170</td>
<td>339</td>
<td>606</td>
<td></td>
</tr>
<tr>
<td>Average (pg)</td>
<td></td>
<td>11</td>
<td>11</td>
<td>170</td>
<td>325</td>
<td>655</td>
</tr>
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</table>

for 3 to 4 h to ensure the complete digestion of the PGE sulfides. This oxidation proved insufficient to completely remove the dissolved cellulose nitrate, which tended to clog the nebulizer during sample introduction. Like Ravizza and Pyle (1997), we found that Os was only partially lost during the aqua regia digestion, so an aliquot of this liquid was taken up in 1 N HCl and used for Os, Ir and Pt abundance determinations. The remaining solution was dried down and the residue was subjected to aggressive oxidation, including a 5-h perchloric acid attack in sealed Savillex™ vials at 160°C, followed by dry-down at −200°C, to remove the cellulose nitrate. The residue was processed through a cation exchange column to separate anionic PGEs from cationic impurities such as residual Ni, and Mo and Cd, which were probably concentrated from the sample during the NiS fusion. A procedure modified from Jarvis et al. (1997) was followed. The sample was loaded in 0.5 mL of 0.15N HCl on a quartz glass column filled with 2.0 mL of cleaned, equilibrated AG 50WX8 (100 to 200 mesh) cation exchange resin. Anionic PGE chlorocomplexes were eluted in the first 1.5 mL of 0.15N HCl, while Ni, Cd and Mo were retained on the column. The column yield was 97% for all PGEs. From this aliquot, Ru, Pd, Ir and Pt were determined. Isotopic compositions of Ir and Pt were found to be identical within mass-spectrometric error to those determined from the first aliquot, but significant improvements were obtained for Ru (interfered at masses 98, 100, 101 and 102 by Mo⁺ and NiAr⁺) and Pd (¹¹⁰Cd interference on ¹¹⁰Pd spike isotope). Separation of the PGEs employed in several published procedures (Rehkämper and Halliday, 1997; Pearson and Woodland, 2000) was not found to be essential.

Isotopic measurements were performed on a single-collector, magnetic sector, high-resolution ICP-MS, the Finnigan Element™. Sample solutions were introduced with a CETAC MCN6000 nebulizer. Three sets of scans were carried out for each analysis: an initial set of 20 scans of the masses: 7, 64, 97, 98, 99, 100, 101, 102, 105, 106, 108, 110, 112, 190, 191, 192, 193, 195, 198, 200, to assess the Ni signal, and to drive the magnet through the mass range used in the centering routine. The magnet was then parked at mass 97, and the Mo-Ru-Pd-Cd peaks (97, 98, 99, 100, 101, 102, 105, 106, 108, 110, 112) were scanned 200 times by varying the accelerating potential (EScan). Isobaric interferences from ¹⁰⁷Pd on ¹⁰⁸Ru were corrected, and those from NiAr⁺ and Cd were monitored at masses 98 and 112. These corrections were generally <1%. The magnet was then moved to mass 190, and 200 scans of the Os-Ir-Pt-Hg peaks (190, 191, 192, 193, 194, 195, 198, 200) were obtained. Isobaric corrections of the minor Pt isotopes (190 and 192) on both measured Os isotopes, and of ¹⁹⁸Hg (<1000 cps) on ¹⁹⁸Pt, were performed. Although the Hg corrections were minor (<1%), the Pt interferences on Os isotopes were substantial (30 to 100%) because of high Pt/Os ratios in the solutions. The use of separate EScan routines for each of the PGE mass ranges allowed rapid scanning with 1 ms settling times facilitating the collection of precise isotope ratios. Typical count rates were 10⁵ – 10⁶ cps (except for Os ~5 to 9 × 10⁴ cps), internal precisions were ~0.2 to 0.5%, and external reproducibility of the ratios was comparable.

Total procedural blanks were determined using a reverse standard addition technique by analyzing two sets of low-PGE basalts, 4 to 5 aliquots in each set (Table 1, Fig. 2). Blanks were determined from the intercepts of the linear regressions of each set and were (average for the standard mass of reagents, in pg): Os, Ir 11, Ru 170, Pt 325, Pd 655 (Table 1). Blank corrections applied were estimated as <5% for the komatiites and 10 to 20% for the basalts. Precision of the procedure, determined by duplicate analyses of 10 samples from this study, and by quadruplicate analyses of two komatiite standards KAL-1 and WITS-1 (Tables 2 and 4), was 2 to 5% (except for WITS-1), which included uncertainties from both analytical errors and sample powder heterogeneity. A few Ru analyses were irreproducibly high, and are not considered further. Our data for the KAL-1 standard agree within ~10% with those reported by Rehkämper et al. (1999b), although we note that their Ru, Pd, and Pt abundances are systematically up to 12% higher. The Barberton komatiite standard, WITS-1, shows poorer reproducibility and substantial interlaboratory biases (Pearson and Woodland 2000; Tredoux and Mcdonald 1996). Hoffman et al. (1978) obtained yields for the NiS procedure that were 95% for each of the PGEs. No attempt was made here to determine fusion yields. The accuracy of the analysis is guaranteed by spiking of the sample before fusion, attaining complete sample-
spike equilibrium, and accurate calibration of the separated isotope spikes using high-purity metals as standards.

4. RESULTS

PGE data for the komatiites and basalts are listed in Tables 3 and 4 and are shown in Figures 3 and 4. Initial results were reported by Puchtel and Humayun (1999), and since that time we have significantly improved the Ru and Pd results by cation column clean-up.

4.1. Komatiites

The PGE abundances in the chilled samples (flowtop breccias and spinifex-textured komatiites) with MgO = 24 to 28% vary in a narrow range (by ~10% about the mean). Relative to the primitive mantle, they are depleted in Os-Ir and enriched in Pt and Pd (Fig. 3). The olivine cumulates (MgO = 33 to 40%) are distinct in having slightly lower (except for sample 9490) Os and Ir abundances and substantially lower Pt and Pd concentrations compared to the chilled samples. Both chilled samples and the cumulates show unfractionated (Os/Ir)$_N$.

Table 2. PGE abundances in komatiite standards (ppb).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Pt</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAL-1a</td>
<td>1.86</td>
<td>1.65</td>
<td>4.33</td>
<td>13.5</td>
<td>20.2</td>
</tr>
<tr>
<td>KAL-1b</td>
<td>1.73</td>
<td>1.68</td>
<td>3.89</td>
<td>12.5</td>
<td>17.6</td>
</tr>
<tr>
<td>KAL-1c</td>
<td>1.81</td>
<td>1.79</td>
<td>5.41</td>
<td>12.1</td>
<td>18.2</td>
</tr>
<tr>
<td>KAL-1d*</td>
<td>1.87</td>
<td>1.71</td>
<td>4.73</td>
<td>12.1</td>
<td>15.1</td>
</tr>
<tr>
<td>KAL-1 average</td>
<td>1.82</td>
<td>1.71</td>
<td>4.59</td>
<td>12.5</td>
<td>17.8</td>
</tr>
<tr>
<td>±1 σ</td>
<td>0.07</td>
<td>0.06</td>
<td>0.65</td>
<td>0.69</td>
<td>2.1</td>
</tr>
<tr>
<td>KAL-1 [1]</td>
<td>1.71</td>
<td>5.10</td>
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<td></td>
</tr>
<tr>
<td>±1 σ</td>
<td>0.03</td>
<td>0.37</td>
<td>0.60</td>
<td>0.60</td>
<td>0.40</td>
</tr>
<tr>
<td>WITS-1a</td>
<td>0.846</td>
<td>1.21</td>
<td>3.79</td>
<td>6.31</td>
<td>6.51</td>
</tr>
<tr>
<td>WITS-1b</td>
<td>0.718</td>
<td>1.14</td>
<td>2.96</td>
<td>5.12</td>
<td>4.97</td>
</tr>
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<td>WITS-1c*</td>
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<td>6.00</td>
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<td>WITS-1d*</td>
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<td>1.31</td>
<td>5.40</td>
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<td>5.21</td>
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<td>WITS-1 average</td>
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<td>±1 σ</td>
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<td>0.07</td>
<td>1.12</td>
<td>0.51</td>
<td>0.68</td>
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<td>WITS-1 [2]</td>
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<tr>
<td>±1 σ</td>
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<tr>
<td>±1 σ</td>
<td>0.04</td>
<td>0.09</td>
<td>0.23</td>
<td>0.61</td>
<td>1.18</td>
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* Samples not processed through ion exchange columns.
1.00 ± 0.05 and 0.98 ± 0.05 and, with the exception of the cumulate sample 9490, are depleted in Os relative to Pd \((\text{Pd/Os})_N = 6.4 ± 0.6\) and 4.2 ± 0.4, respectively). The Alexo komatiite, KAL-1, has higher PGE abundances than the Kostomuksha chilled samples, with higher \((\text{Pd/Os})_N = 8.5 ± 1.0\), and chondritic \((\text{Os/Ir})_N = 1.05 ± 0.05\) (Table 2). The Barberton komatiite, WITS-1, has a distinctly non-chondritic \((\text{Os/Ir})_N = 0.65 ± 0.04\), the origin of which is unclear. The lack of reproducibility for WITS-1 indicates the presence of PGE nuggets. The loss of iridosmine nuggets would explain the subchondritic Os/Ir ratio, and the lower Os and Ir abundances in our batch of powder relative to the consensus WITS-1 composition of Tredoux and Mcdonald (1996).

### Basalts

The basalts analyzed have MgO abundances varying between 6.5 to 8.4%, a range typical of Archean tholeiites. They are strongly depleted in Os-Ir relative to the primitive mantle \((\text{B/PM}) = 0.01 \text{ to } 0.03\), are characterized by highly fractionated PGE patterns, \((\text{Pd/Os})_N = 61 \pm 10\), and variable but basically subchondritic \((\text{Os/Ir})_N = 0.69 \pm 0.17\). One sample (#9443) has

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>MgO</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Pt</th>
<th>Pd</th>
<th>Ni</th>
<th>Cr</th>
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<tr>
<td>9450</td>
<td>15/264.0</td>
<td>26.4</td>
<td>1.50</td>
<td>1.43</td>
<td>4.70</td>
<td>9.94</td>
<td>11.5</td>
<td>1244</td>
<td>3120</td>
</tr>
<tr>
<td>9451</td>
<td>15/261.2</td>
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<td>1.65</td>
<td>1.46</td>
<td>4.49</td>
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<tr>
<td>9499</td>
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Note: Here, and in Table 4, analyses were recalculated on an anhydrous basis; MgO in wt%, Cr and Ni in ppm. For sample location, numerator corresponds to the drill hole number, and denominator—the depth. SW—surface outcrops in the SW part of the synform. For drill hole and outcrop locations see Figure 1 in Puchtel et al. (1998). Location of the drill hole #15 corresponds to the SK tick (Southern Komatiite section) in the same figure.

### Olivine-cumulate komatiite:

<table>
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<th>Sample</th>
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<td>1254</td>
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</table>

* Different fusions of the same sample.

Table 3. PGE abundances in Kostomuksha basalts (ppb).

Table 4. PGE abundances in Kostomuksha komatiites (ppb).
Os and Ir abundances ∼50% lower, and Pt and Pd concentrations about an order of magnitude lower compared to the majority of the basalt samples.

5. DISCUSSION

5.1. Assessing PGE Mobility During Postmagmatic Processes

PGE mobility can potentially be an important issue in studies of metamorphosed Precambrian rocks. Kostomuksha sequences were subjected to seafloor alteration and greenschist facies metamorphism, which resulted in almost complete replacement of igneous mineralogy by serpentine + chlorite assemblages, though primary volcanic textures and structures remained well preserved. To assess the potential PGE mobility in the Kostomuksha lavas, the approach developed for lithophile elements by Arndt (1986) and Barnes et al. (1988) was utilized here. These workers recognized that komatiite samples containing magmatic elemental abundances must follow olivine control lines. The latter are mixing lines for suites of samples derived from a single liquid containing variable proportions of olivine. Figure 4 shows PGE, Ni and Cr abundances plotted against MgO, with olivine control lines drawn for comparison. Note that even olivine-rich, and hence highly serpentinitized, cumulate samples follow the olivine control lines for MgO, Ni, and Cr, indicating that these elements were immobile during secondary alteration. In Figure 4, the PGEs exhibit regular trends relative to MgO, that are interpreted here as being magmatic in origin and representing olivine control lines for these elements. It is noteworthy that the application of this approach to lithophile elements in Kostomuksha had indicated that only the alkalis, Sr, Ba, Pb and U, were mobilized during alteration (Puchtel et al., 1998).

5.2. PGE Fractionation During Magmatic Differentiation and Partial Melting

The hosts of PGEs in the mantle are most likely not silicates, but sulfides and PGE minerals and alloys (Mitchell and Keays, 1981; Hart and Ravizza, 1996; Humayun, 1998; Burton et al., 1999; Handler and Bennett, 1999; Rehkämper et al., 1999b). Oceanic basaltic magmas are thought to be sulfide-saturated (McGoldrick et al., 1979; Hertogen et al., 1980; Wallace and Carmichael, 1992), and experimentally determined Ni-Cu sulfide melt-silicate melt partition coefficients for PGEs are on the order of 10^4 (Peach et al., 1990; Fleet et al., 1996). This suggests that Ni-Cu sulfide fractionation is the main cause of PGE depletion in basaltic magmas during differentiation, though this latter process cannot be responsible for fractionation of Os from Pd as both have very similar sulfide melt-silicate melt partition coefficients (Peach et al., 1994). However, since differentiation of basaltic magmas is usually accompanied by olivine and chromite fractionation, it has been assumed that these phases controlled PGE fractionation in basals and, by analogy, in komatiites (Crocket and MacRae, 1986; Brügmann et al., 1987; Barnes and Picard, 1993). The available PGE data for olivines and chromites are quite ambiguous. Ross and Keays (1979) observed elevated concentrations of Ir in Kambalda olivines (5.7 ppb vs. 1.3 ppb in host lava) and Brügmann et al. (1987) estimated a bulk D_{Os} of ∼1.8 for the olivines from Gorgona and Alexo komatiites. Similar results were reported by Barnes and Picard (1993) for Cape Smith Fold Belt lavas and by Crocket and MacRae (1986) for Pyke Hill komatiites. This is in contrast with direct measurements of Os concentrations in komatiitic and picritic olivines from Gorgona Island (Walker et al., 1999), Pechenga (Walker et al., 1997b) and Vetreny belt (Puchtel et al., 2000b), indicating that Os was incompatible with olivine.

Chromite is usually substantially enriched in Os and depleted in Pd relative to the melt from which it crystallized. For instance, several workers obtained Os concentrations of 6 to 51 ppb in komatiitic chromites from Gorgona (Walker et al., 1999)
and Kostomuksha and Vetreny belt (Puchtel et al., 2000a; Puchtel et al., 2000b), compared to 0.2 to 2 ppb in respective primary magmas. Direct measurements of PGE abundances in chromites from ultramafic residues also indicate that the former are about two orders of magnitude lower in Pd compared to Os or Ir (Page and Talkington 1984; Walker et al., 1996), though it is not yet clear if the IPGEs are incorporated into the spinel crystal lattice or are carried by the mineral species that are included into spinel (e.g., sulfide or Os-Ir alloy). Therefore, it is possible that chromite under some circumstances (e.g., when the amount of the fractionating phase exceeds 1 to 2%) may cause IPGE depletions and fractionation of Os from Pd during differentiation of basaltic magmas.

In the Kostomuksha basalts, there is a strong positive correlation between MgO, Ni, Cr, and PGE, which attests to the compatible behavior of these components in the whole range of basaltic compositions (Fig. 4). However, due to the advanced differentiation that these basaltic melts have undergone under conditions of sulfide saturation, it is difficult to draw any definite conclusions as to the ultimate cause of the PGE fractionation. A similar problem has been recently addressed by Rehkämper et al. (1999b), who concluded that “the PGE are not well suited as geochemical tracers of basalt source compositions, because the PGE systematics of melts are so readily modified during petrogenesis.” Though the Kostomuksha basalts plot within the upper end of the concentration range for the basalt samples studied by Rehkämper et al. (1999b), i.e., have PGE abundances similar to those of plume-derived Icelandic tholeiites, yet these by no means represent primary mantle melts. We will, therefore, concentrate our efforts mostly...
on the studies of PGE abundances in the komatiites, which apparently do not show sulfide saturation.

In the Kostomuksha komatiites, the flowtop breccias formed during magma emplacement and did not experience flow differentiation. Therefore, the erupted Kostomuksha komatiite magma PGE composition is constrained by the average composition of the flowtop breccias collected from three flows (Table 4). In the spinifex-textured and cumulate komatiite samples, the variations in major and trace element compositions during differentiation were controlled by a single major mineral phase, olivine (Puchtel et al., 1998). Indeed, on the variation diagrams in Figure 4, a positive correlation between MgO and Ni and a negative correlation between MgO and Cr indicates that the low-pressure fractionating assemblage included only olivine; no chromite was precipitated over the entire compositional range of the komatiite lavas. From lithophile trace element variations, Puchtel et al. (1998) estimated the MgO content of the liquidus olivine and the erupted komatiite liquid to be 51 and 27%, respectively. Furthermore, from the regressions in Figure 4, the Ni and Cr contents of this olivine were estimated to be 3210 and 1715 ppm, respectively. These estimates are very close to direct microprobe analyses of olivine compositions from komatiites with a similar MgO range (e.g., Arndt et al., 1977; Arndt, 1986). Thus, the Ni-MgO variations in Figure 4 can be accounted for solely by olivine fractionation, and no Ni-Cu sulfide liquid fractionation is required.

Figure 4 shows that a reverse correlation exists between PGEs and MgO for both cumulate (excluding Os and Ir data for #9490, which on both plots is well above the regression lines) and noncumulate komatiites indicating incompatible behavior of PGEs during olivine fractionation. From these correlations, apparent bulk partition coefficients between the fractionating assemblage (Oi ± PGE-phases) and komatiitic melt were calculated to be $D_{Os} = 0.70$, $D_{Ir} = 0.75$, $D_{Pt} = 0.52$ and $D_{Pd} \approx 0$. Thus, the degree of incompatibility varies substantially from Os to Pd, the latter behaving as a highly incompatible element during olivine fractionation. These calculations show that crystall fractionation during differentiation of the Kostomuksha komatiite magma tends to concentrate PGEs in the residual liquid (represented by the spinifex-textured lavas), though the effect is relatively small. From the MgO vs. Pd and Ni correlations in Figure 4, it is also evident that no Ni-Cu sulfide fractionated during differentiation, implying that the initial komatiite magma was sulfide-unsaturated, and remained so during olivine fractionation. Note from Table 4 that the average composition of the flowtop breccias and the average composition of the spinifex-textured komatiites are practically identical.

One cumulate sample (#9490) is substantially enriched in Os and Ir compared to the primary komatiite melt, and this enrichment is not supported by variations in either Pt-Pd or Ni-Cr-MgO concentrations. We attribute this enrichment to the presence of tiny Os-Ir nuggets as an additional cumulate phase in this komatiite. However, as this enrichment was only found in a single cumulate sample, we conclude that the effect of Os-Ir nugget fractionation in the Kostomuksha komatiites was very sporadic.

5.3. PGE Fractionation During Mantle Melting and PGE Compositions of Mantle Sources

To estimate the PGE composition of a mantle source, the following are required: (1) the composition of a primary liquid derived from this source; and (2) the relationships between the composition of the primary liquid and the source composition (degree of melting $F$, partition coefficients $D$, and melting model). There are no experimentally determined PGE partition coefficients for melt extraction from the mantle. The PGE host phases in the mantle, the melting reactions of which determine the amounts of PGE entering the melt, are also not well known. Some workers have adopted the assumption that PGEs reside in sulfide (Os, Ir, Ru, Pt, Pd) and/or in alloy (Os, Ir, Ru), and that the relative fractions of these phases involved in the melting can be modeled to describe PGE behavior during melting (Barnes et al., 1985; Barnes and Picard 1993; Rehkämper et al., 1999b). We will assume for the sake of simplicity that the carrier phases of PGEs in the mantle were non-silicates, that these were the same for all komatiite source regions, and that these phases were not affected by phase transformations in the pressure range of interest, i.e., constant D values during partial melting were assumed. The approach adopted here involved the derivation of mantle-melt apparent partition coefficients for a reference komatiite primary liquid, followed by the application of these apparent partition coefficients to other komatiite suites. The composition of the Alexo komatiite was chosen as a reference since arguably both its primary liquid composition and its source composition can be constrained.

The primary melt PGE composition of the Alexo komatiite was estimated from the mean of four measurements of KAL-1 (Table 2), an olivine spinifex-textured komatiite from a single Alexo lava flow, the major element composition of which closely approximates the Alexo liquid composition estimated by Arndt (1986). The Munro Township komatiites have a chondritic initial $^{187}$Os/$^{188}$Os implying derivation from a source with a long-term chondritic Re/Os ratio (Walker et al., 1988; Shirey, 1997). We assume that this is also true for the Alexo komatiite (for which Os-isotope data are presently not available), since both come from spatially closely associated parts of the Abitibi greenstone belt. As Re is one of the most incompatible highly siderophile elements, and Os is one of the most compatible ones, the chondritic Re/Os ratio implies that the Munro-Alexo source was also characterized by chondritic relative abundances of other PGEs. For the absolute PGE abundances in this source, we then assume a primitive mantle (PM) composition (Table 5), and will examine the ramifications of that assumption later.

The relationship between source composition and melt composition is given by the batch melting equation which requires knowledge of a set of partition coefficients for the PGEs and an estimate of the degree of melting. From the relative abundances of moderately incompatible lithophile trace elements Ti, Zr, Gd, Y, and Yb compiled from Arndt (1986), the degree of partial melting for the Alexo komatiite was estimated to be 45%, which is only slightly higher than that calculated in the same manner for the Kostomuksha komatiite (40%) from the data of Puchtel et al. (1998). The apparent partition coefficients for the PGEs applicable to extraction of the Alexo komatiite from a PM source were obtained using a batch partial melting
model. The observed Pd enrichment in the Alexo komatiite is too large for a single-stage batch melting model, i.e., the Pd abundance implies a much lower degree of melting than other trace elements. This discrepancy, typical of highly incompatible elements, was resolved here by applying a multistage batch melting model, in which the melt fraction, \( F(z_i) \), is specified as an exponential function of depth:

\[
F(z_i) = F(0)e^{-kz_i} \ldots \tag{1}
\]

where 0 < \( z_i < 100 \) km was used for Alexo, \( F(0) \) is the melt fraction near the surface, and \( k \) is the reciprocal e-folding distance. The batch partial melting equation is solved for a single set of partition coefficients (Table 5) for each depth, in 1 km increments,

\[
C_i = \frac{C_L}{\left[F(z_i) + D(1 - F(z_i))\right]} \tag{1a}
\]

where \( C_i \) is the concentration of the element in the melt at depth \( z_i \) and \( C_L \) is the concentration of the element in the source (assumed to be uniform before melting). The melts are averaged according to Eqn. 2:

\[
C_L = \frac{\Sigma F(z_i)C_i}{\Sigma F(z_i)} \tag{2}
\]

where \( C_L \) is the concentration of the element in the aggregated melt. The functional dependence of melt fraction on depth was taken as a tunable parameter and the net melt composition derived from this procedure was matched with the average melt composition of the Alexo liquid. The calculated melting curve for the Alexo komatiite is shown in Figure 5.

The resulting partition coefficients for Os, Ir and Ru are relatively insensitive to the assumptions of the model, with the exception that \( D_{Ru} \sim 1 \) because of the choice of PM as the source composition. The partition coefficient for Pd is highly sensitive to the multistage-stage melting model, but the behavior of Pd as a highly incompatible element with \( D_{Pd} \) < 0.1 appears to be certain. This model was then applied as a pedagogical tool to examine which features of the Kostomuksha komatiite liquid composition.

The outer core is specified as 1% of the outer core-III (OC-III) to the primitive mantle source (PM), calculated as a physical admixture of 1% of the outer core-I to the primitive mantle source (PM), calculated as a physical admixture of 1% of the outer core-II to the primitive mantle source (PM), 12 Partition coefficients calculated from the multistage batch melting model for the Alexo komatiite.

13 Calculated as a multistage batch melt from the hybrid source-I using the partition coefficients (12).

14 Calculated as a batch melt from the hybrid source-II using the partition coefficients (12).

15 Calculated as a batch melt from the hybrid source-III using the partition coefficients (12).

16 Average of four KAL-1 analyses.

17 Average of three flowtop breccia samples representing the best estimate of the Kostomuksha komatiite liquid composition.

18 Calculated as 10% Kostomuksha komatiite primary melt and 90% average basalt (from Table 3).

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|c|}
\hline
Parameter & Os & Ir & Ru & Pt & Pd \\
\hline
Primitive mantle (PM) & 3.33 & 3.30 & 4.88 & 6.79 & 3.84 \\
CI-chondrite & 486 & 481 & 712 & 990 & 560 \\
D (solid metal-liquid metal) & 12.0 & 7.50 & 2.10 & 2.24 & 0.68 \\
D (solid metal-liquid metal) & 19.0 & 14.0 & 4.20 & 3.80 & 0.49 \\
Bulk core & 2280 & 2260 & 3340 & 4640 & 2630 \\
Outer core-I (OC-I) & 2280 & 2260 & 3340 & 4640 & 2630 \\
Outer core-II (OC-II) & 1490 & 1560 & 3140 & 4330 & 2670 \\
Outer core-III (OC-III) & 823 & 1080 & 2790 & 3960 & 2700 \\
Hybrid source-I (PM+1%OC-I) & 26.1 & 25.8 & 38.2 & 53.1 & 30.1 \\
Hybrid source-II (PM+1%OC-II) & 18.1 & 18.8 & 36.1 & 49.8 & 30.4 \\
Hybrid source-III (PM+1%OC-III) & 11.4 & 14.0 & 32.5 & 46.1 & 30.7 \\
D (silicate liquid-mantle residue) & 2.12 & 2.25 & 1.09 & 0.41 & 0.04 \\
Komatiite melt from hybrid source-I & 14.2 & 13.4 & 35.8 & 97.3 & 138 \\
Komatiite melt from hybrid source-II & 9.86 & 9.73 & 33.8 & 91.2 & 140 \\
Komatiite melt from hybrid source-III & 6.23 & 7.24 & 30.5 & 84.5 & 141 \\
Alexo primary melt & 1.82 & 1.71 & 4.59 & 12.5 & 17.8 \\
Calculated Alexo batch melt & 1.82 & 1.71 & 4.59 & 12.5 & 17.8 \\
Kostomuksha primary melt & 1.45 & 1.38 & 3.86 & 8.22 & 10.6 \\
Calculated Kostomuksha batch melt & 1.41 & 1.38 & 3.45 & 8.81 & 10.5 \\
Archean oceanic crust (I) & 0.197 & 0.204 & 0.627 & 3.06 & 4.24 \\
\hline
\end{tabular}
\caption{Parameters Used in Modeling, and Model Results for Hybrid Sources (ppb).}
\end{table}
dances were dependent on the validity of the choice of PM as the Alexo source.

Compared to the Alexo komatiite melt, the Kostomuksha primary komatiite liquid was distinct in having lower abundances of all PGE, lower Pd/Ir ratio (Fig. 3), and in having formed at a slightly lower degree of partial melting. Furthermore, the petrological data indicate that the Kostomuksha komatiite primary melt is distinct from its Alexo counterpart in that it was separated from the melting source region at far greater depths in the mantle, while still in the garnet peridotite stability field, thus acquiring the HREE- and Al-depleted signature. Using a constant set of partition coefficients, an $F(0) = 40\%$ (based on lithophile trace elements), and allowing $F(z_i)$ to be a tunable parameter, we applied the melting model to calculate the source of the Kostomuksha primary komatiite liquid. Using PM as the source, the model produces solutions that yield lower Os and Ir only at lower degrees of melting, giving much higher Pd/Ir ratios than observed. To produce the observed Os, Ir and Ru abundances, the use of a source with absolute abundances of $0.75 \times$ PM (or 25% lower than the Alexo source, regardless of its assumed composition), is required. The Kostomuksha PGE pattern could then be fitted with the $F(z)$ curve shown in Figure 5. Two specific features of this curve require further comment. Firstly, the presence of a region of melting where $F(z) = F(0)$ is required by the lower Pd/Ir and Pd/Ir of the Kostomuksha komatiite relative to the Alexo komatiite. Such a feature could also be produced by depleting the Kostomuksha source in Pt and Pd before the melt extraction. There is presently no way of distinguishing between these alternatives. Secondly, the Al-depleted nature of the Kostomuksha komatiite was interpreted to require melt removal at depths corresponding to the majorite stability field (Puchtel et al., 1998). Thus, the curve was modified by starting the melting at a depth of 500 km (Fig. 5) and proceeding all the way up to the ~260 km level until the degree of melting attains 40%, after which it remains constant till the melt separates from the source as the plume reaches the 180 km level. This corresponds approximately to the depth where garnet becomes unstable and Al-depleted komatiitic melts are replaced by Al-undepleted liquids (e.g., Herzberg, 1995).

Because of the strong fractionation of Pt and Pd from Ir by melting, variations in the Pt/Ir and Pd/Ir ratios of partial melts can always be accounted for by manipulation of the parameters of the melting model. Factors that determine the composition of the source, such as the nature of accreted chondritic material or addition of outer core, produce source compositions that have Pd/Ir ratios varying within only 10 to 20% of PM (although different absolute abundances of Pd and Ir). Thus, the large and correlated variations in Pt/Ir and Pd/Ir seen both in our data and in those of others (Fig. 6) can be attributed to the effects of partial melting. If the partition coefficients derived here are approximately correct, the PGE composition of residual mantle can also be determined. In Figure 6, the calculated residue compositions are compared with the data on mantle peridotites and xenoliths. Most of the published data clusters near the chondritic value, partly because of a concerted effort by most workers to analyze “fertile” samples, and partly because of metasomatic processes in the upper portion of any melting column which act to enrich residual peridotites in Pd and Pt, an effect seen most strikingly in abyssal peridotites (Rehkämper et al., 1999a). A group of very depleted samples from the studies of both Lorand et al. (1999) and Handler and Bennett (1999) fall along the calculated melt depletion trend. Samples from the Olmani harzburgite and two E. African xenoliths plot along a depletion trend featuring constant P/Pd ratios (Rehkämper et al., 1997). The complementary melts of such residues have not been observed.

5.4. Subducted Archean Oceanic Crust as the Source of Coupled Radiogenic $^{186,187}$Os in the Mantle

Lithophile trace element and isotope studies (e.g., Hofmann and White, 1982; Galer and Goldstein, 1991; Hofmann, 1997) have established recycled oceanic crust to be an important component of certain plume sources, and this conclusion has been extended to explain the systematically radiogenic $^{187}$Os/$^{188}$Os isotopic compositions observed in many plumes (e.g., Walker et al., 1991; Hauri and Hart, 1993; Roy-Barman and Allegre, 1995; Lassiter and Hauri, 1998; Widom et al., 1999).

Some plumes, in addition to high $^{187}$Os/$^{188}$Os ratios, are also characterized by elevated $^{186}$Os/$^{188}$Os ratios (Walker et al., 1997a; Brandon et al., 1998). Brandon et al. (1999) found a positive correlation ($r^2 = 0.94$) between $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os isotopic ratios in Hawaiian picrites and interpreted this to be the result of incorporation of outer core material into these plume sources. To account for the observed correlation, Brandon et al. (1999) showed that the recycled oceanic crust

![Fig. 5. The $F(z)$ vs. depth used in the melting models. Note the difference in melting initiation depths and distinct melting curves for the two plumes.](image-url)
must have had Pt/Re $\sim$80 to 100, while most modern crustal materials are characterized by a Pt/Re of <30, generally \(~7.
However, crustal materials recycled into the sources of modern plumes, have been derived from the mantle billions of years ago and might have included more magnesian lavas (e.g., komatiites). Therefore, the evolution of the Pt-Re-Os system in such ancient crust could also be distinct from that of its modern counterpart. Here, the Pt-Re-Os evolution of a model Archean oceanic crust is evaluated using the PGE abundances determined for basalts and komatiites from Kostomuksha (Table 5); Re concentrations were from Puchtel et al. (2000a).

Such oceanic crust consisting of komatiite and basalt in the proportion 1:10 (the proportion typical of the majority of late Archean greenstone belts, DeWit and Ashwal, 1997, including Gimola-Kostomuksha), had the following parameters: Re = 1.0 ppb, Pt = 3.1 ppb, Os = 0.20 ppb, $^{187}\text{Re}/^{188}\text{Os} = 23$, $^{190}\text{Pt}/^{188}\text{Os} = 0.014$, and Pt/Re = 3. The results of the model calculations, illustrated in Figure 7, show that 80 to 100% of such crust with a residence time of 2.0 Ga are needed to account for the $^{186}\text{Os}(T)$ values of $\sim$1.0 to $\sim$1.3, typical of the majority of picrites from Mauna Loa, Loihi and Hualalai, where,

$$^{186}\text{Os}(T) = 10,000 \times \left[ \frac{^{186}\text{Os}_{\text{sample}}}{^{188}\text{Os}_{\text{cura}}} \right]^{188}\text{Os}_{\text{PM}} - 1$$

There are major element constraints arguing against such a possibility. A large amount of basaltic crust in the mantle source of the Hawaiian plume (at that depth converted into eclogite) is unlikely as its melting products will mostly consist of tonalite-trondhjemite magmas (Drummond et al., 1996; Rapp et al., 1991) and not picrites as observed (Norman and Garcia, 1999). Moreover, such a crust will develop very radiogenic $^{187}\text{Os}(T)$ values of $>700$, while the most radiogenic Hawaiian picrites have $^{187}\text{Os}(T)$ of $\sim$9 (Brandon et al., 1999).

We conclude that although recycled Archean oceanic crust is a viable source of radiogenic $^{187}\text{Os}/^{188}\text{Os}$ in the mantle, the origin of the coupled $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ enrichments observed by Brandon et al. (1999) still requires a non-crustal source. Such a source should have low lithophile element concentrations in order not to destroy the observed trace element and Pb-Nd-Sr isotope relationships (Hofmann, 1997). It should also have suprachondritic Pt/Os ratios, and Os abundances substantially exceeding those of the oceanic crust and the primitive mantle. The only known major terrestrial reservoir which meets these requirements is the outer core.

5.5. The Effect of Core Metal Addition on the PGE Budget of Plume Magmas and the Mechanisms of Core-Mantle Interaction

The introduction of radiogenic Os derived from the differentiated outer core into silicate mantle at the core-mantle boundary (CMB) was first proposed by Walker et al. (1995). These authors suggested that the crystallization of the outer core to produce the solid inner core, which accounts for 5.5% of the total mass of the bulk core, will fractionate both Pt and Re from Os assuming that apparent D$^{\text{vin-iron}}$ derived from the
magmatic Group IIAB iron meteorites (Morgan et al., 1995; Smoliar et al., 1996) are applicable to the Earth's core. The partitioning behavior during iron solidification is $D_{\text{Re}} > D_{\text{Os}} > D_{\text{Pt}}$, with Os preferentially entering the solid metal of the inner core, and Pt/Os, Re/Os and Pt/Re thus increasing to suprachondritic values during differentiation of the liquid outer core. As a result, with time the latter develops radiogenic $^{186}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os ratios. Walker et al. (1995) also argued that, because Os abundances are more than two orders of magnitude higher in the core compared to the primitive mantle, physical addition of even small amounts (1 to 2%) of outer core material to the plume source will dominate its Os isotopic composition, as is evident from Figure 7. It should be emphasized that the magnitude of $^{186,187}$Os-enrichment in the resulting outer core strongly depends on the choice of $D_{\text{sm-alm}}$ for Re, Os and Pt, and the timing of differentiation. Using partition coefficients from Morgan et al. (1995), Smoliar et al. (1996) and Walker et al. (1997a), and assuming (as did Walker et al., 1997a) for the convenience of this calculation that core differentiation was completed within the first 100 Ma of Earth's history, the present-day $^{186}$Os of the outer core can be shown to attain the value of +1.7 (Fig. 7). We have recently carried out siderophile element analyses of the Group IIAB irons and have derived a refined set of internally consistent apparent partition coefficients (Campbell and Humayun, 2000), which are smaller than those of previous workers. Calculations using the $D_{\text{sm-alm}}$ values of Campbell and Humayun (2000) produce a present-day $^{186}$Os in the outer core of +0.6. Most Hawaiian picrites with radiogenic $^{186}$Os/$^{188}$Os plot between these two outer core estimates (Fig. 7). It appears that Group IIAB irons are at best imperfect analogues for the Earth's outer core and that appropriate $D_{\text{Os}}/D_{\text{Re}}$ and $D_{\text{Os}}/D_{\text{Pt}}$ at the inner core-outer core boundary must be larger than values derived from magmatic iron meteorites if this hypothesis is to be viable.

The mechanism proposed by Walker et al. (1995) for core-mantle interaction is that of physical admixture of outer core material into primitive mantle to form hybrid mantle sources, with the metal getting entrained into the mantle as the plume starts its ascent from the CMB. This process must have a profound effect on the PGE abundances in the plume source, raising these by about an order of magnitude relative to mantle source regions not affected by core addition. Below, we quantitatively model the potential effect of this physical admixture on the PGE abundances in hybrid sources and, therefore, on the plume magmas derived from such sources.

Three outer core model compositions were used here: un-fractionated [Outer Core-I] and after 5.5% crystallization with $D_{\text{sm-alm}}$ from Campbell and Humayun (2000) [Outer Core-II] and Smoliar et al. (1996) [Outer Core-III]. The effects of physical admixture of 1% of the outer core material into a mantle plume source, here taken as the primitive mantle (Table 5), are shown in Figure 8. The multistage batch melting model, described above, was used to calculate the composition of hypothetical komatiite melts derived from hybrid mantle sources, which were then compared with the Kostomuksha and Alexo komatiite liquid compositions (Fig. 8).

The first conclusion is that independent of which set of $D_{\text{sm-alm}}$ is used to estimate the outer core composition, the resulting komatiite melts derived from such hybrid sources would have had PGE abundances substantially higher than komatiites derived from mantle sources not affected by core addition (e.g., Pd = 140 ppb vs. 10 to 20 ppb). As can be seen
in Figure 8, the Kostomuksha komatiite does not show such elevated PGE concentrations. The second conclusion concerns the fractionated Os/Ir ratio in the model komatiite magmas derived from hybrid sources, most obvious for those mixtures with outer core-III composition (Fig. 8). This, too, is not observed in the Kostomuksha komatiites, which have a chondritic Os/Ir ratio. A chondritic Os/Ir ratio is typical of mantle peridotites (Humayun et al., 1997), komatiites (e.g., this study; Brügmann et al., 1987; Humayun et al., 1997), and some basalts (Ravizza and Pyle, 1997), indicative of the similarity of Os and Ir partitioning into mantle melts.

From the discussion above, our data do not support physical admixture of any substantial amount (>0.01%) of outer core material into the Kostomuksha source, as this would increase the PGE abundances in the resulting partial melts to levels not seen in this komatiite. We conclude that if the enriched Os-isotope signature in the Kostomuksha komatiite was indeed derived from the outer core, then core-mantle interaction cannot involve simple physical admixture of the outer core material into the plume source. A reconciliation of these facts would be that the enriched 187Os iso- tope signature in the Kostomuksha komatiite was acquired from the base of the lower mantle, which had experienced isotopic equilibration with the liquid outer core at the CMB. Small, but distinct, changes in the PGE relative abundances are expected to accompany the Os-isotopic exchange, which would include the development of suprachondritic Re/Os and Pt/Os ratios, and slightly subchondritic Os/Ir ratios and fractionated PGE patterns (Pd>Pt = Ru>Ir>Os). These patterns resemble those resulting from the effects of partial melting (Pd>Pt>Ru>Ir = Os), but the differences should be resolvable by precise analyses of PGEs in high-degree partial melts from mantle plumes.

6. CONCLUDING REMARKS

The following conclusions were drawn from this study:

1. Platinum group elements (Os, Ir, Ru, Pt and Pd) were found to be immobile during seafloor alteration and upper greenschist facies metamorphism of the Kostomuksha komatiites and basalts.

2. During high-degree partial melting, Os and Ir are compatible and mostly retained in the mantle residue. Platinum and Pd concentrate in the melt, Pt being moderately and Pd highly incompatible with the mantle residue. During komatiite low-pressure differentiation, the PGEs are incompatible with olivine. The calculated bulk partition coefficients range from ~0.70 for Os and Ir to 0.50 for Pt and nearly zero for Pd.

3. Unlike most basalts, komatiites are primary mantle melts that faithfully retain their original PGE compositions. These compositions were used to determine relative PGE abundances between the Alexo and Kostomuksha sources, which were shown to differ by 25%.

4. Substantial Pt/Os enrichments combined with the relatively high Os abundances estimated for Archean komatiite-basalt crust, which could potentially become subducted and incorporated into the source of mantle plumes, are insufficient to account for the coupled radiogenic 186,187Os signature observed in some modern plume magmas. The origin of this signature requires a non-crustal source.

5. If the radiogenic initial 187Os/188Os in the Kostomuksha komatiite is an outer core signature, then core-mantle interaction cannot involve physical admixture of the outer core material into mantle plume sources. Instead, this type of interaction must occur in the form of Os-isotope exchange at the core-mantle boundary.
This study demonstrates that komatiites are important probes of possible chemical exchange processes at the core-mantle boundary and that PGE abundances in high-degree, sulfide-unsaturated mantle melts provide information on mantle source PGE compositions, that is complementary to that derived from $^{186,187}$Os isotopic studies.

Acknowledgments—Komatiite standards, KAL-1 and WITS-1, were generously provided by Steve Shirey. Comments from Alan Brandon, Kevin Righter, Andy Davis, and Larry Grossman were appreciated. Very constructive comments from an anonymous but identified reviewer helped to substantially improve the original draft of the ms. We thank Horton Newsom for his efforts as Associate Editor, and discussions on core-mantle interaction. We thank Andy Campbell for assistance with the ICP-MS measurements and many discussions on PGE partitioning in metallic systems. The acquisition of the Elemento™ was supported by NSF EAR 9601478 to MH. This study was also made possible by funding from the Block Fund at The University of Chicago.

Associate editor: H. E. Newsom

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