Highly siderophile element geochemistry of $^{187}$Os-enriched 2.8 Ga Kostomuksha komatiites, Baltic Shield

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Abstract—New analyses of highly siderophile elements (HSE; Re, Os, Ir, Ru, Pt, and Pd) obtained by Carius tube digestion isotope dilution inductively coupled plasma mass-spectrometry (ID-ICPMS) technique are reported for $^{187}$Os-enriched 2.8 Ga komatiites from the Kostomuksha greenstone belt. As a result of a significant improvement in the yield over our previous digestions by the NiS fire-assay technique, these komatiites have now been shown to contain 22 to 25% more Os, Ir, and Pt and 34% more Ru. The emplaced komatiite lavas at Kostomuksha thus had siderophile element abundances comparable to those of the Abitibi belt. The discrepancies observed between the two techniques are interpreted to be the result of incomplete digestion of HSE carriers (particularly chromite) during the NiS fire-assay procedure. Our results for UB-N peridote reference material agree well with those obtained by the high-pressure ashing digestion ID-ICPMS technique reported in the literature. Two types of komatiite lavas have been distinguished in this study based on the IPGE (Os, Ir, and Ru) behavior during lava differentiation. The Kostomuksha type is unique and is characterized by an incompatible behavior of IPGEs, with bulk solid-liquid partition coefficients for IPGEs being close to those for olivine. Cumulate zones in this type of komatiite lava occupy <20% of the total thickness of the flows. The Munro type exhibits a compatible behavior of IPGEs during lava differentiation. The cumulative zone in this type of komatiite occupies >20% of the total thickness of the flows. The calculated bulk partition coefficients indicate that, as with the other Munro-type komatiite lavas, the bulk cumulate contained an IPGE-rich minor phase(s) in addition to olivine. The non-CI chondritic HSE pattern for the source of the Kostomuksha komatiites calculated here is similar to that of Abitibi komatiites and to average depleted spinel hertzolite (ADSL) and supports the hypothesis of a non-CI chondritic HSE composition of the Earth’s mantle. The absolute HSE abundances in the source of the Kostomuksha komatiite have been demonstrated to be comparable to those of the source of Abitibi komatiites, even though the two komatiites contrast in their Os isotopic compositions. This supports the earlier hypothesis that if core-mantle interaction produced the $^{187}$Os/$^{188}$Os radiogenic signature in the Kostomuksha source, it must have occurred in the form of isotope exchange at the core-mantle boundary. Other explanations of the radiogenic Os signature are similarly constrained to conserve the elemental abundance pattern in the mantle source of Kostomuksha komatiites. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

The 2.8 Ga Kostomuksha greenstone belt is one of the few Archean komatiitic lava suites on Earth that were shown to have been derived from a mantle source with radiogenic initial $^{187}$Os/$^{188}$Os isotopic composition (Puchtel et al., 2001; Walker and Nisbet, 2002). These lavas provide the type of material that can be used to test models of core-mantle interaction and oceanic crust recycling through studying variations in highly siderophile element (HSE; Re, Os, Ir, Ru, Pt, and Pd) abundances in mantle sources of these lavas, and of those that exhibit near-chondritic initial $^{187}$Os/$^{188}$Os isotopic compositions, such as Alexo (Gangopadhayay and Walker, 2003) and Pyke Hill komatiites (Puchtel et al., 2004a) in Canada. These tests require an accurate determination of HSE abundances in the emplaced lavas.

Puchtel and Humayun (2000) reported platinum group element (PGE) abundances in komatiitic and basaltic lavas from the Kostomuksha greenstone belt analyzed by the NiS fire-assay digestion isotope dilution inductively coupled plasma mass-spectrometry (ID-ICPMS) technique. These PGE data were used to infer the PGE abundances in the mantle source of the lavas to test models of ocean crust recycling and core-mantle interaction. Subsequently, the NiS fire-assay technique was shown to be inefficient at digesting some PGE carriers in komatiitic samples (Puchtel et al., 2004b). Due to these shortcomings, abundances of some PGEs in the lavas were shown to be underestimated by as much as 50%. This, in turn, results in underestimation of PGE abundances in the mantle source of the lavas and may have broader impact on several important conclusions in that study, including the incompatible behavior of Os and Ir during lava differentiation.

The Carius tube (CT) digestion technique (Shirey and Walker, 1995) has been recently demonstrated to be superior to the NiS fire-assay method in digesting PGE carriers in komatiites (Puchtel et al., 2004b). In this paper, we present new CT digestion, ID-ICPMS analyses of PGEs and Re in the complete set of eighteen drill core samples from seven komatiite lava flows from the Puchtel and Humayun (2000) study, as well as in nine additional samples from the same lava flows, including...
six samples from Flow 13, from which only one sample (9490) was previously analyzed. A much lower blank of the CT digestion procedure compared to the NiS fire-assay technique made it possible to obtain Re abundances. In this study, we have also obtained HSE abundances for a peridotite reference material UB-N, previously analyzed by high-pressure ashing (HPA) digestion ID-ICPMS technique (Meisel and Moser, 2004). On the basis of the new data, we revised values for the PGE compositions of the Kostomuksha emplaced komatiite lava, and for its mantle source. These data, when combined with the results for komatiites from the Abitibi greenstone belt (Puchtel et al., 2004b), provide new constraints on the possible nature of HSE abundances in mantle sources with both supra-chondritic and chondritic $^{187}\text{Os}/^{188}\text{Os}$ isotopic compositions.

2. GEOLOGICAL-GECHRONOLOGICAL BACKGROUND AND SAMPLING

The details of geology, petrology, and mineralogy, as well as trace element and Pb, Nd, and Os isotope systematics of mafic and ultramafic lavas from the Kostomuksha greenstone belt have been previously reported by Puchtel et al. (1998, 2001). The mafic terrane of the Kostomuksha synform is part of the Gimola-Kostomuksha greenstone belt in NW Karelia, Baltic Shield. The terrane contains submarine-erupted komatiite and basalt lavas, mafic and ultramafic volcanioclastic sediments, and numerous gabbro and peridotite sills. The komatiites and basalts have Sm-Nd and Pb-Pb whole rock isochron ages of 2843 ± 39 and 2813 ± 78 Ma, respectively. The whole sequence is intruded and overlain by mafic and felsic subvolcanic, volcanic, and volcanioclastic rocks with a U-Pb zircon age of 2821 ± 1 Ma (Puchtel et al., 1998). As a result of seafloor alteration and/or greenschist facies metamorphism, the igneous mineralogy of the lavas was almost completely replaced by serpentine-chlorite-magnetite assemblages at 2757 ± 113 Ma (Puchtel et al., 1998). However, primary volcanic textures, structures, and most chemical features remained intact. For a selected set of komatiite samples and a chromite separate, Puchtel et al. (2001) obtained a Re-Os isochron corresponding to the age of 2795 ± 40 Ma and a radiogenic initial $^{187}\text{Os} = +3.6 ± 1.0$. The lithophile trace element and isotope characteristics of the komatiites (e.g., $(\text{Nb/Th})_n = 1.5 - 2.1$, $\varepsilon\text{Nd(T)} = +2.8 ± 0.2$, $\mu_i = 8.77 ± 0.02$) resemble those of the contemporary oceanic mantle (Puchtel et al., 1998). On the basis of geological evidence and isotope and geochemical data, Puchtel et al. (1998) argued that the mafic terrane represented remnants of the upper crustal part of an Archean oceanic plateau derived from partial melting in a starting mantle plume head.

Twenty-seven drill core samples from seven differentiated komatiite lava flows have been analyzed in this study for PGEs and Re. Out of these, six new samples from Flow 13, for which major element data were not available, were also analyzed for major elements. Samples 9487–94126 (except for 94104) come from the four flows (13, 17, 19, and 26) shown in Figure 1. Samples 9469, 9479, and 94104 are from three other flows (#8, 10, and 18). The flows consist of an upper spinifex zone (A) and a lower cumulate zone (B). The spinifex zone contains an up to 1 m thick chilled margin at the top, which grades downward into a subzone of random, and then oriented, platy olivine spinifex. A distinct feature of all komatiite flows studied at Kostomuksha compared to those we examined at Alexo and Pyke Hill (Puchtel et al., 2004b) is a very small thickness of cumulate zones in the former, normally <20% of the total.
3. ANALYTICAL TECHNIQUES

3.1. Major and Minor Element Analysis

Major and minor (Cr, Ni) element abundances in the six whole rock samples from Flow 13, not previously reported by Puchtel et al. (1998), were determined on pressed powder pellets by wavelength-dispersive X-ray fluorescence spectrometry using a VRA-20R spectrometer at the Institute of Geology and Geophysics in Novosibirsk. The accuracy and reproducibility of the analyses were ~1% and ~3% (relative) for major and minor elements, respectively. Major element abundances in all other samples, reported in the Puchtel et al. (1998) study, and for the sake of completeness presented here, were also determined at the Institute of Geology and Geophysics in Novosibirsk using the same technique. The abundances of Cr and Ni in these samples were measured on fused glass disks by wavelength-dispersive X-ray fluorescence spectrometry using an automated Philips PW-1404 spectrometer at the Johannes-Gutenberg-Universität in Mainz, with an accuracy and reproducibility of ~1% (relative).

3.2. HSE Analysis

In this study, we used a mixed komatiite spike #000531, also utilized by Puchtel et al. (2004a, 2004b) in their study of Abitibi komatiites. By contrast, the multielement spike used by Puchtel and Humayun (2000) had been optimized for primitive mantle abundances.

3.2. HSE geochemistry of Kostomuksha komatiites

Table 1. HSE data (ppb) for the UB-N peridotite standard.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T, °C</th>
<th>Time, h</th>
<th>Re (ppb)</th>
<th>Os (ppb)</th>
<th>Ir (ppb)</th>
<th>Ru (ppb)</th>
<th>Pt (ppb)</th>
<th>Pd (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB-N (1)</td>
<td>240</td>
<td>24</td>
<td>0.188</td>
<td>3.16</td>
<td>2.91</td>
<td>6.15</td>
<td>7.23</td>
<td>6.05</td>
</tr>
<tr>
<td>UB-N (2)</td>
<td>240</td>
<td>48</td>
<td>0.255</td>
<td>4.41</td>
<td>3.51</td>
<td>8.45</td>
<td>8.09</td>
<td>6.00</td>
</tr>
<tr>
<td>UB-N (3)</td>
<td>240</td>
<td>96</td>
<td>0.186</td>
<td>3.67</td>
<td>3.54</td>
<td>7.38</td>
<td>7.43</td>
<td>6.35</td>
</tr>
<tr>
<td>UB-N (4)</td>
<td>270</td>
<td>24</td>
<td>0.187</td>
<td>4.03</td>
<td>4.10</td>
<td>7.71</td>
<td>7.07</td>
<td>5.80</td>
</tr>
<tr>
<td>UB-N (5)</td>
<td>270</td>
<td>48</td>
<td>0.185</td>
<td>3.31</td>
<td>3.47</td>
<td>6.88</td>
<td>7.55</td>
<td>5.93</td>
</tr>
<tr>
<td>UB-N (6)</td>
<td>270</td>
<td>72</td>
<td>0.190</td>
<td>3.37</td>
<td>3.34</td>
<td>6.65</td>
<td>7.55</td>
<td>6.54</td>
</tr>
<tr>
<td>UB-N (7)</td>
<td>270</td>
<td>96</td>
<td>0.188</td>
<td>3.51</td>
<td>3.74</td>
<td>7.46</td>
<td>7.43</td>
<td>6.02</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>0.197</td>
<td>3.64</td>
<td>3.52</td>
<td>7.24</td>
<td>7.48</td>
<td>6.10</td>
</tr>
<tr>
<td>UB-N</td>
<td></td>
<td></td>
<td>0.206</td>
<td>3.71</td>
<td>3.38</td>
<td>6.30</td>
<td>7.42</td>
<td>6.11</td>
</tr>
</tbody>
</table>

Before digestion at 270°C, aliquots (4) to (7) were preheated at 240°C for 24 h.

1 Data of Meisel and Moser (2004) obtained by the HPA digestion ID-ICPMS technique.
4. RESULTS

4.1. Major and Minor Element Data and the MgO Content of the Emplaced Komatiite Lava

Major and minor (Cr, Ni) element data for all samples analyzed for HSE in this study are presented in Table 2, and the abundances of Al, Ti, Cr, and Ni are plotted against MgO on the variation diagrams in Figure 2. Samples from Flow 13, including two chilled margin samples, plot on the same olivine fractionation trends as samples from the other flows, and thus, show no evidence of postmagmatic disturbance of these elements, as concluded by Puchtel et al. (1998). The average MgO content of the chilled margin samples from the four complete lava flows studied is 27.4 ± 0.4% and is considered here to reflect the MgO content of the emplaced komatiite lavas. This value is identical to 27 ± 1% MgO calculated by Puchtel et al. (1998) for a larger number of komatiite lava flows using several independent approaches.

Both compatible (MgO, Ni) and incompatible elements (Al, Ti, Cr) exhibit variations across the lava flows, typical of those reported for other differentiated komatiite lava units worldwide with a comparable MgO content (e.g., see recent review by Puchtel et al., 2004b). The MgO content varies between 24 and 28% in the A zone, generally decreasing towards the lowermost part of it, and between 29 and 40% in the B zone. The highest MgO content (40%) is observed in the cumulate portion of Flow 19, whereas in the cumulate zone of Flow 13, the MgO content does not exceed ~37%.

4.2. PGE and Re Abundances in the Emplaced Komatiite Lava

PGE and Re data for the analyzed samples are listed in Table 3 and are plotted on the variation diagrams in Figure 3. PGE data are also plotted as CI chondrite-normalized abundances in Figure 4. The PGE abundances in the emplaced komatiite lava were calculated from an average PGE content of the chilled margin samples, which have been shown to represent the composition of the emplaced komatiite lava at Kostomuksha (Puchtel et al., 1998). These samples plot on the bulk differentiation trends for PGEs (Fig. 3) and do not show any evidence of postmagmatic PGE mobility. Nine analyses of five samples indicate that the emplaced komatiite lava contained 1.9 ppb Os and was characterized by a slightly supra-chondritic (Os/Ir)N = 1.07 and a moderately fractionated PGE pattern with (Pd/Ir)N = 5.2 (Table 3; Fig. 4).

Unlike PGEs, the Re abundances display a totally irregular behavior on the MgO vs. Re plot due to a Re mobility during seafloor alteration and/or subsequent greenschist facies metamorphism, as was also concluded by Puchtel et al. (2001).
makes it impossible to estimate the Re content of the emplaced komatiite lava with any degree of confidence.

4.3. Comparison of PGE and Re Abundances Obtained by Different Methods

To compare the results obtained using two different digestion techniques, also presented in Figure 3 and Table 3 are PGE data from the Puchtel and Humayun (2000) study. The abundances of Os, Ir, and Pt in the emplaced komatiite lava obtained here are, on average, 22 to 25% higher, and abundances of Ru are ~34% higher, compared to those reported by Puchtel and Humayun (2000). We attribute the discrepancies between the results from the NiS fire-assay and Carius tube digestion techniques to incomplete dissolution of PGE carriers, mostly chromite, during the NiS fire-assay procedure. A similar interpretation has been put forward by Puchtel et al. (2004b), who have digested a large set of samples of Abitibi komatiites using both the Carius tube and NiS fire-assay techniques. In their study, the observed discrepancies between the results from the two digestion techniques were even larger, likely due to a better state of preservation of mineral phases in the Abitibi samples. The Pd contents are identical between the two techniques, indicating that Pd is not hosted by a phase that is resistant in the NiS fire-assay digestion procedure.

4.4. PGE Fractionation During Magmatic Differentiation

In the variation diagrams (Fig. 3), Pt and Pd abundances in all samples show a strong ($r = 0.97–0.98$) inverse correlation with MgO, indicating that these PGEs behaved incompatibly during lava differentiation. The bulk $D_{\text{Pt-Liq}}$ of $<0.1$ was calculated from the MgO vs. Pt and Pd differentiation trends in Figure 3, using the MgO content of the emplaced komatiite lava of ~27% and assuming that the MgO content of the bulk cumulate was determined by olivine and was ~51% (Puchtel et al., 1998). The bulk $D_{\text{Pt-Liq}}$ from this study (0.09) is much lower than that obtained by Puchtel and Humayun (2000) (0.52), whereas $D_{\text{Pd-Liq}}$ is similar.

According to the IPGE (IPGEs: Os, Ir, and Ru; Barnes et al., 1985) behavior during lava differentiation, all lava flows ana...
Samples from the first, dominant type, which we term the Kostomuksha type, in the MgO vs. Os, Ir, and Ru diagrams plot on the trend lines with negative slopes indicating an incompatible behavior. In this type of lavas, spinifex-textured samples with the lowest MgO content have the highest PGE abundances (Fig. 4). This was the only type recognized in the Puchtel and Humayun (2000) study. The bulk D_Sol-Liq calculated in this study are 0.37, 0.41, and 0.81 for Os, Ir, and Ru, respectively. The bulk D_Sol-Liq are two times lower than those obtained by Puchtel and Humayun (2000) for this type of lavas (0.70 and 0.75). Also plotted in Figure 3 are average PGE and Re abundances in olivine from Abitibi komatiites (Puchtel et al., 2004b), which have compositions of emplaced lava similar to that at Kostomuksha.

### Table 3. PGE and Re abundances (in ppb) in Kostomuksha komatiites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Pt</th>
<th>(Os/Ir)_N</th>
<th>(Pd/Ir)_N</th>
<th>Pt/Ti</th>
<th>Pd/Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>9469</td>
<td>1.75</td>
<td>1.65</td>
<td>5.69</td>
<td>10.7</td>
<td>11.5</td>
<td>1.05</td>
<td>5.99</td>
<td>3.57</td>
<td>1.07</td>
</tr>
<tr>
<td>9469*</td>
<td>1.53</td>
<td>1.59</td>
<td>3.97</td>
<td>9.19</td>
<td>12.0</td>
<td>0.95</td>
<td>6.48</td>
<td>3.05</td>
<td>1.31</td>
</tr>
<tr>
<td>9479</td>
<td>0.939</td>
<td>2.01</td>
<td>1.88</td>
<td>5.59</td>
<td>10.5</td>
<td>11.0</td>
<td>1.06</td>
<td>5.03</td>
<td>4.05</td>
</tr>
<tr>
<td>9479</td>
<td>1.77</td>
<td>1.71</td>
<td>4.04</td>
<td>8.51</td>
<td>11.2</td>
<td>1.03</td>
<td>5.62</td>
<td>3.30</td>
<td>1.31</td>
</tr>
<tr>
<td>9487</td>
<td>0.684</td>
<td>1.83</td>
<td>1.70</td>
<td>5.84</td>
<td>10.5</td>
<td>11.0</td>
<td>1.06</td>
<td>5.55</td>
<td>4.13</td>
</tr>
<tr>
<td>9488</td>
<td>0.559</td>
<td>0.742</td>
<td>0.878</td>
<td>5.60</td>
<td>11.6</td>
<td>11.5</td>
<td>0.84</td>
<td>11.3</td>
<td>3.92</td>
</tr>
<tr>
<td>9489</td>
<td>2.44</td>
<td>0.774</td>
<td>0.889</td>
<td>5.92</td>
<td>9.78</td>
<td>8.80</td>
<td>0.86</td>
<td>8.50</td>
<td>4.16</td>
</tr>
<tr>
<td>9490</td>
<td>0.040</td>
<td>5.11</td>
<td>4.15</td>
<td>5.75</td>
<td>6.24</td>
<td>4.97</td>
<td>1.22</td>
<td>1.03</td>
<td>3.99</td>
</tr>
<tr>
<td>9490*</td>
<td>0.045</td>
<td>5.26</td>
<td>4.26</td>
<td>7.12</td>
<td>6.60</td>
<td>1.22</td>
<td>1.33</td>
<td>4.56</td>
<td>0.93</td>
</tr>
<tr>
<td>9490</td>
<td>6.19</td>
<td>6.15</td>
<td>4.93</td>
<td>6.82</td>
<td>5.37</td>
<td>1.00</td>
<td>0.75</td>
<td>4.36</td>
<td>0.79</td>
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<td>9490A</td>
<td>0.051</td>
<td>4.55</td>
<td>3.79</td>
<td>5.96</td>
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<td>5.95</td>
<td>1.19</td>
<td>1.35</td>
<td>4.32</td>
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<tr>
<td>9491</td>
<td>0.739</td>
<td>2.94</td>
<td>2.47</td>
<td>5.93</td>
<td>8.03</td>
<td>8.26</td>
<td>1.18</td>
<td>2.88</td>
<td>4.10</td>
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<tr>
<td>9492</td>
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<td>1.87</td>
<td>1.69</td>
<td>5.86</td>
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<td>11.0</td>
<td>1.09</td>
<td>5.57</td>
<td>4.07</td>
</tr>
<tr>
<td>9493*</td>
<td>2.02</td>
<td>1.85</td>
<td>5.98</td>
<td>11.3</td>
<td>10.7</td>
<td>1.08</td>
<td>4.98</td>
<td>4.12</td>
<td>0.95</td>
</tr>
<tr>
<td>9493*</td>
<td>0.546</td>
<td>1.96</td>
<td>1.77</td>
<td>5.93</td>
<td>11.2</td>
<td>10.1</td>
<td>1.10</td>
<td>4.90</td>
<td>4.10</td>
</tr>
<tr>
<td>9493*</td>
<td>0.604</td>
<td>2.22</td>
<td>1.98</td>
<td>5.97</td>
<td>11.0</td>
<td>0.97</td>
<td>1.11</td>
<td>4.27</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Normalizing values (N) from Anders and Grevesse (1989). Plain text and boldfaced values (this study) samples digested at 240°C and 270°C for 48–72 h, respectively; italicized values - data from Puchtel and Humayun (2000). * Separate CT digestions of aliquots from the same batches of sample powder.

Lavas in this study were subdivided into two types. Samples from the first, dominant type, which we term the Kostomuksha type, in the MgO vs. Os, Ir, and Ru diagrams plot on the trend lines with negative slopes indicating an incompatible behavior. In this type of lavas, spinifex-textured samples with the lowest MgO content have the highest PGE abundances (Fig. 4). This was the only type recognized in the Puchtel and Humayun (2000) study.
muksha. The olivine composition plots on or close to the regression lines for all PGEs except Ru, thus confirming the conclusion of Puchtel and Humayun (2000) that PGE variations in this type of lava were controlled by a single phase, olivine.

In contrast to the Kostomuksha-type flows, Os, Ir, and Ru data for samples from the second type, represented by Flow 13 and which we term the Munro type, plot along trends with positive slopes, indicating a compatible behavior during lava differentiation. In this type of lava, spinifex-textured samples and B1 cumulates have the lowest IPGE content, and B2–4 cumulates have the highest IPGE abundances (Fig. 4). This is something that was not completely realized by Puchtel and Humayun (2000), who at that time analyzed only one cumulate sample from this flow (9490). This type of compatible behav-

Fig. 3. Variation diagrams of HSE (ppb) vs. MgO (wt%) for Kostomuksha komatiites. The trends represent best fit lines drawn through the komatiite analytical data points. Note that the IPGE data for samples from Flow 13 plot on trends (dashed lines) with positive slopes, indicating compatible (Munro type) behavior during lava differentiation, whereas the IPGE data for the other flows plot on trends (solid lines) with negative slopes, indicating an incompatible (Kostomuksha type) behavior during lava differentiation. The latter trends also pass through or close to the composition of Abitibi olivine. Platinum and Pd data for both Kostomuksha- and Munro-type komatiites plot on the olivine control lines, and the calculated compositions of bulk cumulates are similar to that of olivine. Rhenium data exhibit a totally irregular behavior as a result of Re mobility during postmagmatic processes. The data from Puchtel and Humayun (2000) obtained by the NiS fire-assay ID-ICPMS technique are shown for comparison. See also legend for Figure 2 and text for explanation.
ior, with the bulk D^Sod-Liq of 4.8, 4.1, and 1.1 for Os, Ir, and Ru, respectively, is similar to that found in Pyke Hill and Alexo komatiites (Puchtel et al., 2004b).

5. DISCUSSION

5.1. Thickness of Cumulate Zone and IPGE Behavior During Lava Differentiation

The Kostomuksha-type komatiite lavas are quite unique in their IPGE fractionation pattern as a function of lava differentiation. Indeed, many previous studies have demonstrated a strong positive correlation between Os, Ir, and MgO in lavas in which olivine was shown to be the major liquidus phase (Barnes et al., 1985; Crocket and MacRae, 1986; Brügmann et al., 1987; Zhou, 1994; Barnes et al., 1995; Keays, 1995; Lesher and Stone, 1996; Rehkämper et al., 1999b; Puchtel and Humayun, 2001; Puchtel et al., 2004b). At the same time, it becomes increasingly clear that olivine alone played only a minor role in controlling the IPGE budget of mantle derived rocks. In their study of Alexo and Pyke Hill komatiites, Puchtel et al. (2004b) have established that there was a minor IPGE-rich phase present on the liquidus of the differentiated lava flows studied, which fractionated separately from olivine and concentrated mostly in the lowermost cumulate part of the flows. However, the identity of this phase, and whether it was already present in the lava upon eruption or crystallized after emplacement, could not be established conclusively. In contrast, the IPGEs were incompatible during differentiation of the majority of komatiite lavas at Kostomuksha. The only other example known to the authors, where IPGEs are characterized by a similarly incompatible behavior, are komatiites from the Komati formation in the Barberton Mountain Land (Maier et al., 2003), although these komatiites have relatively low PGE abundances overall.

One feature that distinguishes the Kostomuksha-type flows is very small thicknesses of cumulate zones, which constitute 1/3 of the total thicknesses of the flows. The only exception is Flow 13, in which cumulate zone occupies 2/3 of its thickness, and this flow does display the commonly observed Munro-type positive correlation between IPGEs and MgO.

Komatiite lava flows with thick spinifex zone and thin cumulate zone are less common than their counterparts, which are either massive throughout or contain a thick cumulate zone. The extent to which a spinifex zone is developed in any particular lava flow depends on the initial concentration of olivine phenocrysts, the temperature of the lava upon emplacement, and the thickness of the lava unit (Pyke et al., 1973;
The radiogenic $^{187}\text{Os}^{188}\text{Os}$ isotopic composition of the Kostomuksha komatiite source established by Puchtel et al. (2001) indicates that, whatever its origin, this source evolved with a time-integrated supra-chondritic Re/Os ratio. Here, we determine the PGE abundances in the source of the Kostomuksha komatiites at the time of komatiite formation. These were calculated on the basis of several techniques and assumptions outlined in detail by Puchtel et al. (2004a, 2004b), which are only briefly summarized here. First, it was assumed that the abundances of moderately incompatible and compatible lithophile elements in the Kostomuksha source can be approximated by those in an average depleted spinel lherzolite (ADSL; Puchtel et al., 2004b), as both are similarly depleted in large ion lithophile elements (LILE) such as LREE, Th, and U. As such, the degree of partial melting of the Kostomuksha source was calculated to be 48% using a batch partial melting model (Shaw, 1970), and the abundances of moderately incompatible elements (e.g., Al, Ti, Gd; $D_{\text{Sol-Liq}}^{\text{Al-Ti-Gd}} <$0.1; Green, 1994) in ADSL and in the Kostomuksha emplaced komatiite lava. At such high degrees of partial melting in the spinel to garnet peridotite stability field, all interstitial sulfide, which is the main host of Pt and Pd, is completely consumed (Barnes et al., 1985; Keays, 1995), and the only major phase that is left behind in the residue is olivine and possibly small amounts of majorite garnet (Arndt, 1976), as indicated by a slight depletion of heavy rare earth elements (HREE) in the Kostomuksha lavas (Puchtel et al., 2004a). Hence, the abundances of moderately incompatible elements, including Pt and Pd, in the lava and in the source, must plot on olivine control lines in the MgO variation diagrams. Using 38.3% MgO in ADSL as an estimate of MgO content is 15% lower, and Pd content is 10% higher in the

### 5.2. PGE Composition of the Kostomuksha Mantle Source

The radiogenic $^{187}\text{Os}^{188}\text{Os}$ isotopic composition of the Kostomuksha komatiite source established by Puchtel et al. (2001) indicates that, whatever its origin, this source evolved with a time-integrated supra-chondritic Re/Os ratio. Here, we determine the PGE abundances in the source of the Kostomuksha komatiites at the time of komatiite formation. These were calculated on the basis of several techniques and assumptions outlined in detail by Puchtel et al. (2004a, 2004b), which are only briefly summarized here. First, it was assumed that the abundances of moderately incompatible and compatible lithophile elements in the Kostomuksha source can be approximated by those in an average depleted spinel lherzolite (ADSL; Puchtel et al., 2004b), as both are similarly depleted in large ion lithophile elements (LILE) such as LREE, Th, and U. As such, the degree of partial melting of the Kostomuksha source was calculated to be 48% using a batch partial melting model (Shaw, 1970), and the abundances of moderately incompatible elements (e.g., Al, Ti, Gd; $D_{\text{Sol-Liq}}^{\text{Al-Ti-Gd}} <$0.1; Green, 1994) in ADSL and in the Kostomuksha emplaced komatiite lava. At such high degrees of partial melting in the spinel to garnet peridotite stability field, all interstitial sulfide, which is the main host of Pt and Pd, is completely consumed (Barnes et al., 1985; Keays, 1995), and the only major phase that is left behind in the residue is olivine and possibly small amounts of majorite garnet (Arndt, 1976), as indicated by a slight depletion of heavy rare earth elements (HREE) in the Kostomuksha lavas (Puchtel et al., 1998). Hence, the abundances of moderately incompatible elements, including Pt and Pd, in the lava and in the source, must plot on olivine control lines in the MgO variation diagrams. Using 38.3% MgO in ADSL as an estimate of MgO content is 15% lower, and Pd content is 10% higher in the

### Table 4. Results of modeling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Os</th>
<th>Ir</th>
<th>Ru</th>
<th>Pt</th>
<th>Pd</th>
<th>MgO</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>1.90</td>
<td>1.75</td>
<td>5.81</td>
<td>10.7</td>
<td>10.6</td>
<td>27.4</td>
<td>0.432</td>
<td>7.39</td>
</tr>
<tr>
<td>[2]</td>
<td>1.45</td>
<td>1.38</td>
<td>3.86</td>
<td>8.22</td>
<td>10.6</td>
<td>27.5</td>
<td>0.431</td>
<td>7.41</td>
</tr>
</tbody>
</table>

The bulk $D_{\text{Sol-Liq}}^{\text{Pt-Pd}}$ were calculated from the bulk differentiation trends in Fig. 3 assuming an MgO content of the bulk cumulate of 51% (i.e., its MgO content was determined by that of olivine) and using the PGE abundances in the emplaced lava [1]. Bulk D1 and D2 for PGEs were calculated from data for the Kostomuksha- and Munro-type lavas, respectively; bulk Ds for Pt and Pd were calculated using data for both types of lavas.

$D_{\text{Os-Liq}}^{\text{Pt-Pd}}$ are from Puchtel et al. (2004b). These apparent Ds were calculated using the average measured composition of Abitibi olivine and the average composition of the emplaced komatiite lava from which this olivine has crystallized.

[1] PGE data from this study; major element data from Puchtel et al. (1998).
[3] Calculated source for Kostomuksha komatiites from this study.
the emplaced komatiite lavas is 5.8 ppb, so we assume that the Ru abundance in the komatiite source was also 5.8 ppb. This is slightly higher than that in ADSL (5.4 ppb) with an overall uncertainty of 2% (2σ_mean). The average (Os/Ir)_{3.4} ratio in the emplaced Kostomuksha komatiite lava is close to CI-chondritic (1.07), is identical to that in the Abitibi emplaced komatiite lava (1.07), and is taken to be also such in the Kostomuksha mantle source, as Os/Ir ratios fractionate very little during partial melting. We assume that the Ru/Ir in the Kostomuksha source was CI-chondritic (1.48), which then yields the Os and Ir abundances in the source of 4.3 and 3.9 ppb, respectively (Table 4). These IPGE abundances are \( \sim 10\% \) higher than those in ADSL and in the source of the Abitibi komatiites (Fig. 5).

Both the Kostomuksha and Abitibi sources are depleted in Pt and enriched in Pd with Pd/Pt of 0.90 and 1.0, respectively, thus revealing non-CI chondritic PGE patterns. This is a significant departure from the approach of Puchtel and Humayun (2000), who assumed a CI-chondritic source, and then assumed that “excess Pd” was present in the Kostomuksha emplaced lava due to melt-focusing of low-degree melt fractions from variable depths. It can be seen that there is no “excess” of Al, Ti, or Pt, which are equally incompatible during high degrees of partial melting, so that interpretation is abandoned here. The Pd/Pt ratio of the Kostomuksha komatiite source (0.90) is similar to that of the Abitibi komatiite source (1.00) obtained by Puchtel et al. (2004b), i.e., 60% higher than in a CI-chondritic mantle (0.57), indicating that “excess” Pd relative to a CI-chondritic mantle is a feature of komatiite mantle source regions which exhibit both radiogenic and chondritic long-term Re/Os ratios. Pattou et al. (1996) argued that the supra-chondritic Pd/Ir ratios observed in some upper mantle peridotites were evidence of a non-chondritic mantle PGE composition. However, Alard et al. (2000) observed high Pd/Ir- and low Pd/Ir-bearing sulfides by laser ablation ICPMS in the same set of xenoliths studied by Pattou et al. (1996) and argued that the PGE patterns observed by these authors could be explained by the presence of these two sulfide phases in different proportions. Thus, supra-chondritic Pd/Ir ratios have been attributed to magmatic modifications of the upper mantle source regions of mantle xenoliths. Similarly, Rehkämper et al. (1999a) explained supra-chondritic Pd/Ir ratios of some abyssal peridotites in terms of melt percolation. Our results indicate that one must either accept that melt percolation has significantly enriched the Pd/Ir ratios of two independent komatiite source regions to almost exactly the same degree, or that such high Pd/Ir ratios are genuine characteristics of the Earth’s mantle.

Although the mantle sources of the Kostomuksha and Abitibi komatiites had very similar lithophile trace element, Pb- and Nd-isotope characteristics, and HSE compositions, they had distinct \( ^{187}\text{Os}/^{188}\text{Os} \) isotopic compositions. The source of the Kostomuksha komatiites had a radiogenic \( ^{187}\text{Os}/^{188}\text{Os} \) ratio (Puchtel et al., 2001), whereas the source of the Abitibi komatiites had a nearly chondritic \( ^{187}\text{Os}/^{188}\text{Os} \) ratio (Gangopadhyay and Walker, 2003; Puchtel et al., 2004a). Puchtel et al. (2001) proposed that the enriched \( ^{187}\text{Os}/^{188}\text{Os} \) signature in the Kostomuksha komatiites was derived from the outer core. If this was indeed the case, the results obtained in this study have an important bearing on our understanding of the core-mantle interaction mechanism. Walker et al. (1995) postulated that core-mantle exchange occurred by physical mixing of outer core material into mantle plume sources. Although this process should have substantially enriched mantle sources of the lavas in Os, the fact that such an enrichment was not observed was later explained by difficulties in deducing the exact abundances of Os in the mantle sources from those in lavas (Shirey and Walker, 1998). Puchtel and Humayun (2000) demonstrated the potential of PGE studies on komatiites for resolving these issues. They estimated that, to account for the Os isotopic enrichment in the Kostomuksha komatiites, the amount of core material required by the physical mixing model is on the order of 1%, but noted that physical addition of such amount of outer core material would have increased the PGE abundances in the Kostomuksha source by about an order of magnitude. They compared the abundances of PGEs in their estimate of the Kostomuksha komatiite source with those in the source of the Alexo komatiites derived from KAL-1 and concluded that there was no evidence of PGE addition to the Kostomuksha source.

Using the new PGE data for the Abitibi and Kostomuksha komatiites (Table 4), it is now possible to refine the conclusions of Puchtel and Humayun (2000) and to show that both sources contained essentially identical abundances of PGEs. This observation supports the conclusion of Puchtel and Humayun (2000) that if core-mantle interaction produced the supra-chondritic initial \( ^{187}\text{Os}/^{188}\text{Os} \) in the Kostomuksha komatiites, then some kind of isotopic exchange rather than physical mixing is required. Importantly, this conclusion is independent of any melting model. This means that the similarity in Ru contents of the Kostomuksha and Abitibi magmas can be used to compare PGE abundances in their respective mantle sources, and can then be applied to other komatiites to determine whether they were derived from mantle sources with enhanced PGE abundances.
1. PGE analysis by the Carius tube digestion ID-ICPMS technique produces data comparable to those obtained by the HPA digestion ID-ICPMS technique, provided Carius tubes are heated at T ≥ 240°C for ≥ 48 h.

2. Incomplete digestion of chromite, and possibly some other PGE carriers, in samples of Kostomuksha komatiites during the NiS fire-assay procedure used by Puchtel and Humayun (2000) led to underestimation of Os, Ir, and Pt abundances by 22 to 25% and Ru abundances by 34% in the emplaced komatiite lava.

3. Two types of komatiite lavas have been distinguished in this study based on the IPGE behavior during lava differentiation. The first type, which we term the Kostomuksha-type, is characterized by an incompatible behavior of IPGEs during the lava differentiation. This type is quite unique, the only other known example being komatiites from the Komati Formation in the Barberton greenstone belt (Maier et al., 2003). The bulk partition coefficients for IPGEs calculated from the bulk differentiation trends in the Kostomuksha-type komatiite are similar to those for olivine. Cumulate zone in this type of komatiite lava occupies <20% of the total thickness of the flows. The second type, which we named the Munro type, exhibits a compatible behavior of IPGEs during the lava differentiation, with bulk partition coefficients similar to those obtained for Abitibi komatiites by Puchtel et al. (2004b). These bulk partition coefficients indicate that, as with the other Munro-type komatiite lavas, the bulk cumulate contained an IPGE-rich minor phase in addition to olivine. The cumulate zone in this type of komatiite occupies >20% of the total thickness of lava flows.

4. A non-CI chondritic PGE pattern has been established for the source of the Kostomuksha komatiites. This pattern is very similar to that calculated for Abitibi komatiites (Puchtel et al., 2004a, 2004b). The new results indicate that the non-CI chondritic HSE patterns are a genuine characteristic of the Earth’s mantle.

5. The absolute PGE abundances in the source of the Kostomuksha komatiites are calculated to be identical to those in the source of the Abitibi komatiites to within ~10%.

6. The conclusion of Puchtel and Humayun (2000) that core-mantle interaction must have occurred in the form of isotopic exchange at the core-mantle boundary was confirmed in this study. However, any other mechanism proposed to be responsible for creating radiogenic $^{187}\text{Os}^{188}\text{Os}$ in ancient komatiite mantle source regions must not affect the PGE abundances in the sources by a measurable amount, either. Studies of the Pt-Os systematics in Kostomuksha komatiites are required to further test this hypothesis.

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