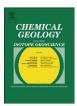
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Research paper

The concentration of platinum-group elements and gold in southern African and Karelian kimberlite-hosted mantle xenoliths: Implications for the noble metal content of the Earth's mantle

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ABSTRACT

We have determined the concentrations of the platinum-group elements and gold in 111 mantle xenoliths from more than 20 kimberlite pipes in southern Africa and the Karelian craton, Fennoscandian Shield, with the aim to constrain the composition of the Archean- early Proterozoic primitive mantle. Average noble metal contents of the southern African peridotite xenoliths (in ppb) are 3.67 Ir, 6.54 Ru, 0.93 Rh, 4.3 Pt, 1.84 Pd, and 1.09 Au, and for the Karelian xenoliths 3.75 Ir, 6.58 Ru, 0.79 Rh, 4.84 Pt, 2.28 Pd, and 1.46 Au. The distribution of PGE-bearing phases is heterogenous, as in previously published datasets of lithospheric mantle from the Kaapvaal and other cratons. We argue that the heterogenous noble metal content of the cratonic lithospheric mantle is partly due to sluggish equilibration of the Archean mantle with late veneer (Maier et al., 2009, Nature, v. 460, 620–623). As a result, the noble metal content of the primitive mantle cannot be accurately determined using cratonic mantle samples. Younger mantle rocks (e.g., orogenic and oceanic peridotites) show more homogenous noble metal contents, but since they formed after the onset of crust formation it is debatable whether their composition accurately defines the noble metal content of PUM.

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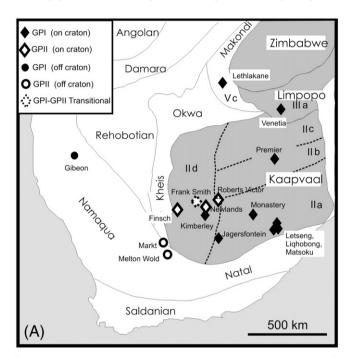
1. Introduction

The Kaapvaal craton represents the most comprehensively studied craton on Earth, in part owing to an abundance of mantle xenoliths derived from kimberlites. Study of mantle xenoliths from the Karelian craton, on the Fennoscandian Shield, has begun only relatively recently, after the discovery of several diamondiferous kimberlites (Peltonen et al., 1999). Many mantle xenoliths derived from both the Kaapvaal and Karelian cratonic sub-continental lithospheric mantle (SCLM) are depleted in basaltic components (e.g. Al₂O₃, CaO, Sc) relative to primitive mantle (Nixon et al., 1981; Boyd and Mertzman, 1987; Peltonen et al., 1999; Pearson et al., 2003). These characteristics have been modeled by extraction of large-degree mantle melts of basaltic and komatiitic composition (Boyd and Mertzman, 1987; Boyd, 1989; Walker et al., 1989; Canil, 1991, 1992; Herzberg, 1993; Pearson et al., 2004; Griffin et al., 2008), followed by multiple episodes of refertilisation and metasomatism with fluids and/or melts of alkaline basaltic, kimberlitic,

* Corresponding author. E-mail address: wolfgang.maier@oulu.fi (W.D. Maier). komatiitic, or siliceous composition of asthenospheric and lithospheric derivation (Erlank et al., 1987; Kelemen et al., 1998; Peltonen et al., 1999; Gregoire et al., 2003; Wittig et al., 2010) that affected different portions of the SCLM to variable degrees (Simon et al., 2007; Griffin et al., 2008; Kobussen et al., 2008; Lehtonen and O'Brien, 2009). It is likely that the complex interaction of melting and refertilization also modified the noble metal distribution in the cratonic mantle. As a result, the unraveling of the petrogenesis of the SCLM via small-scale studies has proved to be challenging, particularly since our knowledge of the composition of the Archean SCLM is almost entirely based on xenoliths brought to surface by kimberlites. Whether such xenoliths are representative of the cratonic lithospheric mantle as a whole remains uncertain (Griffin et al., 2008).

In the present study we aim to constrain the petrogenesis of the SCLM by using large databases containing geochemical data for mantle-derived magmas and their melt residues with the aim to test whether the reservoirs are complimentary. We have thus determined the concentrations of the PGE and gold in 89 southern African peridotite xenoliths from 12 on-craton and 2 off-craton kimberlite pipes, plus the Bultfontein dumps that contain material from the Kimberley mines (Bultfontein, Du Toits Pan, Wesselton) (Fig. 1a). Our

samples are from both Group I and Group II pipes. In order to further constrain variation between on-craton and off-craton SCLM, we also analysed 4 peridotite xenoliths from the Gibeon kimberlite field in Namibia. Into the database, we integrated our previously published data on 10 Premier xenoliths (Maier et al., 2005), and we consider the PGE data on Lesotho xenoliths published by Pearson et al. (2004) and Becker et al. (2006). In order to evaluate inter-cratonic PGE variability we have also determined PGE in 18 xenoliths from four Group I kimberlite pipes on the Karelian craton (Fig. 1B), the first of such data to be published. We have placed particular emphasis on sampling the complete spectrum of rock types present in the xenolith suites, including garnet-lherzolites, garnet- and spinel-harzburgites, garnet-



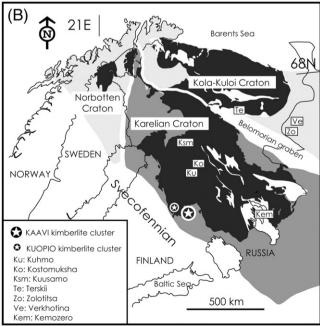


Fig. 1. (A) Simplified geological map, showing sample localities and tectonic units of southern Africa (modified after Griffin et al., 2004). (B) Generalized geological map of north-eastern Fennoscandia. Present samples are from craton-margin KAAVI cluster (Pipes #2, #5, #9, #14). Other Finnish and NW Russian kimberlites are also shown. Modified from Peltonen and Bruegmann (2006).

free harzburgites, pyroxenites, dunites, and several MARIDs. Finally, we also analysed PGE in two kimberlite-hosted olivine and clinopyroxene megacrysts, to evaluate partitioning of PGE with regard to some of the main mantle phases.

2. PGE contents of mantle reservoirs

PGE contents of the Earth's mantle are believed to be controlled by two main processes (Palme and O'Neill, 2004). (i) Formation of the Earth's metal core <30 Ma after the beginning of the solar system largely depleted the Earth's mantle in the siderophile PGE and Au. (ii) Subsequent accretion of a small component (<1%) of chondritic meteoritic late veneer, culminating during the late heavy meteoritic bombardment, led to reintroduction of PGE and Au to the mantle. Thus, the primitive mantle (PM) is defined as the mantle after accretion of the late veneer, but before crust formation (Palme and O'Neill, 2004).

Several studies have estimated the HSE content of PM. The most common method is by compiling the large database on Ir contents of what are believed to be the most fertile mantle rocks, and then assuming carbonaceous-, ordinary-, or enstatite-chondritic ratios between Ir and the other HSE (Morgan et al., 2001; Palme and O'Neill, 2004). Because mantle rocks available for study are exclusively derived from the lithospheric mantle, and the most fertile, least metasomatised ones are from the shallow, post-Archean, non-cratonic mantle, instead of PM, many authors prefer the term PUM, referring to a hypothetical primitive upper mantle reservoir (Meisel et al., 1996; Morgan et al., 2001; Becker et al., 2006). Pristine lithospheric mantle rocks that have not undergone any refertilization/metasomatism are rare, therefore the PGE content of PUM has been calculated by extrapolation from what were considered to be relatively fertile lherzolites. There are various PUM estimates, with the most recent (Becker et al., 2006) yielding markedly higher Ru, Pt, and Pd contents than previous estimates of PM and PUM, resulting in non-chondritic Pt/Pd, Pd/Ir, and Ru/Ir. Becker et al. (2006) have proposed that the origin of the non-chondritic ratios are due to either an unknown crustal fractionation process or an exotic meteorite component, not yet identified amongst the meteorites collected on Earth. Lorand et al. (2008a, c) have recently questioned the validity of PUM. They pointed out that seemingly fertile lherzolitic mantle rocks may be the result of multiple melt depletion and metasomatic events that could have altered the lithophile and siderophile element contents.

3. Petrography and P-T data

Most of our Kaapvaal samples have been collected from the "mantle room" at the University of Cape Town, including the samples from Jagersfontein, Monastery, Frank Smith, Newlands, and the Kimberley cluster (Bultfontein, DuToits Pan and Wesselton mines), as well as the off-craton Markt and Melton Wold samples. "The Letlhakane, Venetia, Finsch and Premier samples were provided by De Beers Group Exploration", whereas the Lesotho samples were provided by Dr A Woodland from Frankfurt University. Rocktypes, textural information, modal proportions and olivine and orthopyroxene compositions of most samples are provided in Supplementary Tables 1-3. The bulk of the samples are coarse grained or porphyroclastic garnet-bearing lherzolites and harzburgites containing predominantly olivine and orthopyroxene as well as variable proportions of garnet (up to 20%) and clinopyroxene (up to 11.5%). Primary phlogopite occurs in several of the samples which may be classified as GPP xenoliths following Erlank et al. (1987), but phlogopite is notably absent from the Venetia and Finsch suites (Skinner, 1989; Stieffenhofer et al., 1999). Dunites are relatively rare, but two dunitic samples were collected from Jagersfontein, and several samples from Monastery and Lethlakane may also be dunitic, based on MgO contents >45 wt.% and olivine modes in thin section approaching 90%. The degree of alteration is mostly very low, but xenoliths from Finsch tend to be extensively serpentinized, mainly around the rims. We also collected several MARID's (alkali rich, coarse grained mica-amphibole-

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