Silica and carbon deposition in the Kimberley peridotites.

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INTRODUCTION

Our goal is to reconstruct the geological history of the mantle root to the Kaapvaal Craton in order to understand how ancient continental lithosphere was stabilized and has evolved. Here we report on work aimed at isolating features of ancient mantle petrogenesis beneath Kimberley, South Africa, focusing on the origin of silica enrichment, ancient trace element enrichment, and carbon deposition, including diamond formation. These processes are discussed with reference to large scale geologic processes specific to the region, and their consequences for craton stabilization.

SAMPLING

In order to construct useful models for the early petrogenesis and associated tectonic context of ancient mantle lithosphere formation, an understanding of the complex, multi-stage evolutionary history of this region of the mantle is required. Recent studies have shown that Mesozoic metasomatism connected with kimberlite and orangeite genesis, and their precursory or associated mantle upwellings, has resulted in substantial chemical (Griffin et al 1999, Grégoire et al 2003, Simon et al 2003) and thermal (Brown et al 1998, Bell 2002) modification of Kaapvaal craton low-temperature lithospheric peridotites. These effects include the growth of minerals such as diopside and in some cases garnet, that might normally be considered part of the primary assemblage residual from Archean melting. In an attempt to minimize these complicating effects, a large collection of nominally clinopyroxene-free, but petrographically diverse harzburgites was assembled from the Boshof Road Dump derived from the Bultfontein kimberlite. Highly deformed xenoliths were avoided. A special attempt was made to collect samples with extreme modal characteristics, and those with internal modal heterogeneities. Such samples, rather than more common or "typical" peridotites, were considered likely to provide the most unambiguous information about petrogenetic process. This strategy produced a collection of some two hundred refractory peridotites that included several dozen dunites and opx-poor harzburgites, harzburgites with veins or blobs of garnet orthopyroxenite or garnet websterite.

METHODS

The strategy adopted is to base all studies on samples carefully selected for their petrographic characteristics. Macroscopic textures and mineral assemblages were described from natural and sawn surfaces of the xenoliths, examined by low-power stereomicroscope. The major element chemical affinities of the peridotites were surveyed by electron microprobe analysis of grain mounts. Garnet and phlogopite from a representative sampling of textural types were analyzed by LA-ICP-MS. Chemical maps that permitted the spatial analysis of phases were prepared from large (5 X7 cm) thin sections of selected samples on the electron microprobe. These samples were subjected to detailed mineralogical and geochemical analysis.

OBSERVATIONS

Correlations of chemistry and petrography

Harzburgites are refractory with Mg# in olivine from 93 to 95.6. The highest Mg# (>94) samples are orthopyroxene-poor harzburgites with non-symplectic, Cr-rich spinels and relatively sparse, strongly subcalcic garnets. Diamond was identified in one sample of this type and probable magnesite pseudomorphs in several. Many of these refractory dunitic harzburgites have large clusters of texturally primary phlogopite. Most olivines contain 0.34-0.37 wt. % NiO (Fig. 1). In contrast, orthopyroxene-rich harzburgites are typically less refractory (93.1 < Fo < 93.5), rarely contain spinel and have garnets that are Ca-saturated or mildly Ca-undersaturated. Olivine NiO contents are higher, ranging up to 0.42 wt % (Fig. 1). A few samples of this latter group contain graphite and many contain inferred carbonate pseudomorphs (Berg 1986). Rare samples of a third group are intermediate between these two groups and have diffuse veins up to 5 cm wide transgressing subcalcic garnet harzburgite. The veins consist of garnet orthopyroxenite with high concentrations of phlogopite.

Sulfide is common and graphite and probable magnesite pseudomorphs are observed (Fig. 2). Some of these minerals also occur in the surrounding wall rock. The highest olivine NiO content of 0.46 wt. % (Fig. 1) is found in a sulfide-bearing garnet orthopyroxenite that appears to be a vein in a coarse-grained dunite.
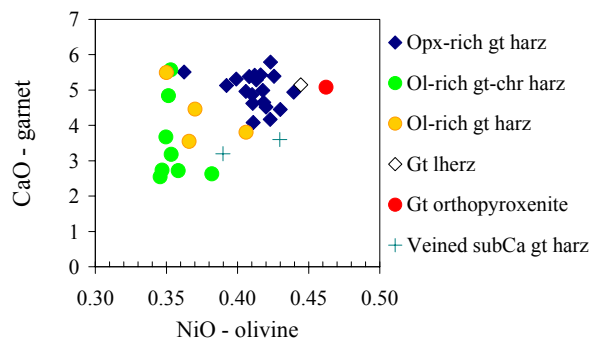

Figure 1. CaO in garnet vs. NiO in olivine for Bultfontein garnet harzburgites

In all xenoliths, alteration due to emplacement-related hydrothermal solutions is common along grain boundaries and internal fractures, resulting in widespread partial serpentinization of olivine and the replacement of inferred primary carbonate by a fine grained intergrowth of serpentine and subordinate brucite (Fig. 2). Depending upon degree of exposure to fluids, sulfides are partially oxidized to magnetite, barite and secondary Ni sulfides with incorporation of kimberlitic Pb. Phlogopite is chloritized and leached of K, Rb and Ba along zones parallel to cleavage planes.
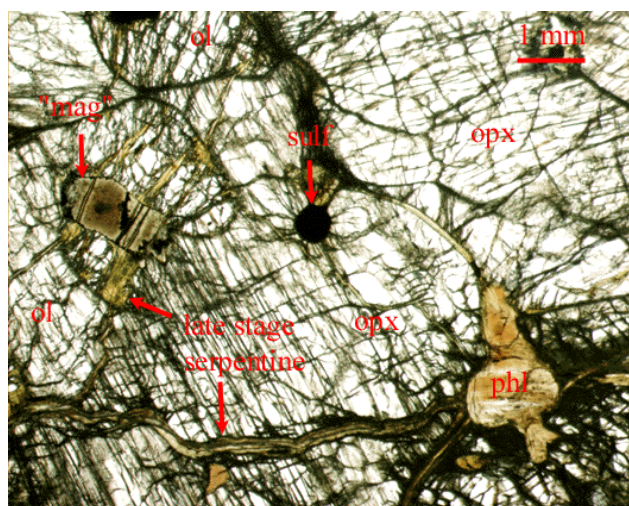

Figure 2. Volatile-rich minerals in orthopyroxenite vein in subcalcic garnet harzburgite BFT137. Abbreviations: ol-olivine, opx-orthopyroxene, sulf-sulfide, phl-phlogopite, "mag"-serpentine-brucite pseudomorph after probable magnesite.

Evidence of metasomatic reaction

In order to test proposals for silicification of Archean mantle by fluids or melts (Kesson and Ringwood, 1989; Rudnick et al., 1994; Kelemen et al., 1998) we analyzed in detail rare samples with pyroxene-rich veins in an olivine-rich matrix. A subcalcic garnet harzburgite containing a vein of phlogopite garnet orthopyroxenite was mapped chemically using 5 X 7.5 cm thin sections (e.g., Fig. 3). Apart from alteration effects, primary minerals are generally unzoned and compositionally homogeneous throughout the xenolith (Fig. 4), consistent with an ancient origin.
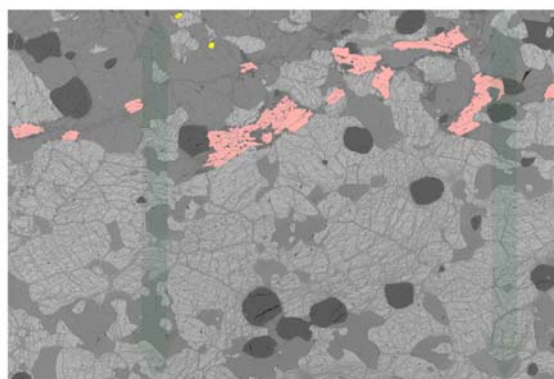

Figure 3. Mg map of harzburgite BFT137 showing vein of orthopyroxene (medium grey) along upper margin, with phlogopite (pink) and sulfide (yellow). Smaller poikilitic grains of orthopyroxene occur in the olivine (pale grey) matrix. Dark grey = garnet. Chemical traverses of Fig. 4 are denoted by the arrows. Field of view 4 X 6 cm.
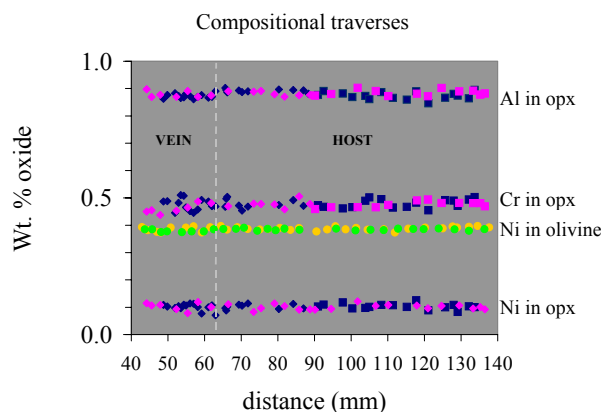

Figure 4. Minor element compositions of olivine and orthopyroxene in traverses across vein and host (Fig 3) of veined harzburgite BFT137.

The composition of the introduced component was calculated by comparing the composition of vein and wall rock, subject to certain assumptions about the initial

composition of the substrate. The introduced component represents about 16 mole % of the original rock and is dominated by SiO_2, with minor quantities of Al, K, H, Na, S, Ba, Rb, and Cl. Trace element characteristics of vein and host are typical "bell-shaped" REE patterns in garnet (Fig. 5), low HFSE and high LIL concentrations, that are quite distinct from those of Mesozoic kimberlite-associated metasomatism (Gregoire et al 2002, 2003) (Fig. 6). The Ni contents of olivines from opx-poor and opx-rich peridotites are consistent with replacement of olivine in the former by enstatite in the latter (Kelemen et al 1998).
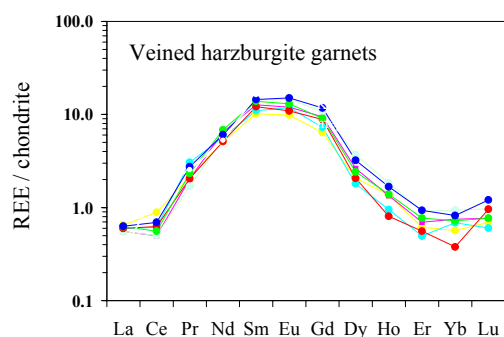

Figure 5. REE in six garnet grains from veined subcalcic garnet harzburgite BFT137
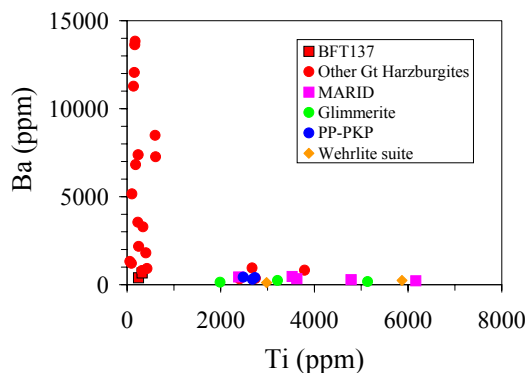

Figure 6. Ba vs. Ti in phlogopite from Kimberley harzburgites compared with other Kimberley xenolith rock types that are the products of Mesozoic metasomatism.

DISCUSSION

Suturing of a proto-continental fragment constituting the present western Kaapvaal craton with the eastern Kaapvaal shield occurred in a collisional event between 2.93 and 2.88 Ga (Schmitz et al 2003). The associated processes of subduction and orogenesis resulted in modification of the mantle of this region, including growth of eclogite paragenesis diamonds (Richardson et al 2001). We suggest that the observations reported above are consistent with modification of the Archean mantle by fluids ascending from subducted oceanic lithosphere (Kesson and Ringwood, 1989).

Fluid-mediated silicification of cratonic mantle

It is proposed here that a dominantly hydrous fluid with substantial dissolved Si and Mg (Stalder et al 2001, Mibe et al 2002), ascending from subducting oceanic lithosphere, infiltrated the subcontinental mantle, locally in narrow channels to form veins, but mainly by grain-boundary porous flow (Mibe et al 1998), and deposited silica pervasively by the reaction of olivine to orthopyroxene. Beginning with a refractory substrate of olivine-rich peridotite containing high-Cr spinels and subcalcic Cr-rich garnets, variable P, T and fluid/rock ratios resulted in a compositionally variable mantle dominated by orthopyroxene-rich garnet harzburgite, but in which residual pockets of olivine-rich mantle remained. The latter may be more prevalent in the deeper layers, where fluid reaction was less due to dominantly shallow dehydration of the descending slab. In addition to Si, minor quantities of Al were introduced, resulting in garnet growth and conversion of chromite to Cr-rich garnet and Cr-Al enstatite. Minor Ca addition, coupled to increased buffering of Ca due to increased orthopyroxene content resulted in muting and destruction of the subcalcic "G10" garnet signature in common lithospheric peridotites.

Formation of carbonate, graphite and diamond

The association of probable magnesite pseudomorphs and graphite with phlogopite and orthopyroxene-rich veins leads to a model for carbon deposition, linked to the infiltration of an oxidized, subduction-derived fluid into a reduced, refractory olivine rich peridotite substrate, highly depleted in Fe^{3+} by magmatic processes. We propose that metasomatism created, among other chemical potential gradients, a gradient in fO_2 between orthopyroxene-rich, fluid-dominated mantle, and olivine rich, rock-dominated substrate. Carbon introduced along with water in the subduction-derived fluid was precipitated mostly as magnesite in the former, and graphite and diamond in the least reacted latter environments in response to the fO_2 gradient. Percolation of the fluid and its reaction-differentiation products (hydrous alkali carbonate melt or fluid) resulted in the characteristic cryptic trace element enrichment and growth of trace element-enriched metasomatic minerals such as phlogopite. Extreme enrichments in incompatible elements, including unusually high LREE/HREE (e.g., Shimizu and Richardson 1987) are expected at the most distal sites that host diamond precipitation.. Carbonate reduction from the fluids to form diamond may have led to residual KCl-rich brines such as those observed as inclusions in some diamonds (e.g., Izraeli et al 2001).

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