Source regions for oxides, sulfides and metals in the upper mantle: Clues to the stability of diamonds, and the origin of kimberlites and lamproites.

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Although oxides, sulfides and metals are minor components in the upper mantle, these mineral groups provide information on redox conditions, mineral complexing and compositions of metasomatic fluids, liquid immiscibility and diamond genesis, and serve as prospecting and evaluation guides to diamond resource potential. New mineral data from kimberlites, lamproites, metasomatised harzburgites, carbonatites, melilitites, and discrete nocules has broadened the scope for genetic models of these rock types.

Oxides: Lithosphere-derived ultramafic diamonds contain magnesiochromite (Cr.0.260 wtp) with estimated P-40-50 Kb and T-1100-1400°C. Similar compositions are now shown to be present in depleted spinel harzburgites from kimberlites. Metasomatism followed by lindsleyite (AM₂₁0₃₉), where A = large cations Ba, Ca, Sr, K, Na, and M = small cations, Fe, Ti, Cr, Mg, Zr, REE, in association with Ca-Cr-Zr armalcolite at estimated P-20-25 kb and T-900-1100 C. Priderite and jeppeite are the Crdepleted, low pressure analogues in lamproites. These minerals imply a continuum between kimberlites and lamproites, differing only in the degree of metasomatic assimilation. Low pressure, high T melt-derived spinels in kimberlites and lamproites are members of the Mg-titanomagnetite series, nucleated on Mg-Al-Cr spinels, underscoring a genetic relationship. Spinels in carbonatites and carbonated kimberlites have higher magnetite components and are, therefore, more oxidized. WUstite is present as a diamond inclusion and in some kimberlite dikes and sills indicative of low redox conditions. From a global compilation of upper mantle-derived ilmenites (Fig. 1) it is concluded: that ilmenites having ≤ 10 wt% MgO and \$0.5 wt% Cr₀, are either of low P origin or are derived from the asthenosphere; correspondingly higher values are of lithosphere origin; carbonated ilmenites have high MnO (≥5wt%) contents; and lamproites are depleted in ilmenite because of the high alkali affinity for Ti, hence priderite, jeppeite, Ti-phlogopite and titanian-richterite. Rutiles in eclogites and diamond inclusions are close to end-member compositions, whereas metasomatic rutiles and rutiles in MARID suite nodules are typically Nb 0 (>2wt%), and Cr 0 (>2wt%) enriched. High Ti contents and large concentrations of silicate-incompatible elements are, therefore, characteristic of metasomatic fluids; high Cr values derive from depleted lithosphere. A single ovoid grain (3 x 2 mm) from heavy mineral concentrates of the Argyle olivine lamproite is an unusual K-Cr-priderite. The grain has an inclusion of Cr-armalcolite, minor Mnilmenite along cracks and MnCrMg spinel along grain boundaries in association with talc, phlogopite and titanite (sphene). This priderite is similar in composition to one of two unidentified minerals described as an alteration fringe to picroilmenite in a metasomite from Bultfontein. Mineral compositions similar to mannardite-redledgeite series minerals, (Ba.OH) Ti $_{\rm 0}$ V $_{\rm 010}$ - (Ba.OH) Ti $_{\rm 0}$ Cr $_{\rm 016}$ are recorded for discrete opaque crystals present in an ultramafic clast from an autobrecciated olivine lamproite at Argyle. Dolomite is an associated mineral and both are enclosed in talc, probably after xenocrystic olivine. Analytical data for an unidentified mineral from the Benfontein kimberlite-carbonate sills is similar in large cation Ba concentrations $^{\circ}$ is the dominant small cation replacing Cr and V in the inferred mannarditebut Feredlegeite series. The relationship between BaO and TiO for a variety of LIL-titanates show that two distinct groupings are present, both having negative slopes (Fig. 2). LIMA minerals, K-Cr-priderite from Bultfontein and Argyle, and the possible mannardite-redledgeite minerals from Argyle (dolomite association) and Benfontein (calcite and baddeleyite associated), are Cr + LREE-bearing and form one group. The second mineral grouping is composed of a variety of priderites and these are demonstrably melt-derived. It is tentatively concluded that the K-Ba-titanate field, in which LIMA is present, is typical of metasomatic association.

<u>Sulfides</u>: Low temperature equilibrated assemblages in diamonds, eclogites, and in discrete nodules of olivine, garnet, pyroxene, ilmenite and ilmenite-pyroxene intergrowths, are troilite, pyrrhotite, pyrite, pentlandite and chalcopyrite, with accessory polydymite and hazelwoodite. Bulk compositions conform to monosulfide solid solutions and liquid immiscibility (900-1100°C) is inevitable at upper mantle P-T conditions; carbon solubility may be enhanced and carbon reduction catalytically accelerated, thus accounting for the abundance of sulfides in diamonds. A new sulfide signature is apparent based on Fe/Fe+Ni ratios: eclogitic suite diamonds have the highest values (0.88-0.99), discrete nodules are intermediate (0.77-0.82), and depleted ultramafic diamonds are the lowest (0.59-0.64). Discrete nodules are geochemically fertile and intermediate Fe:Ni ratios are, therefore, asthenospheric. Complex alkali phyllosulfides, in association with pyrrhotite, are present in metasomites, indicating that the fluids were sulfur bearing.

Metals: Increasing recognition of Fe metal in diamonds supports the proposition for growth in a highly reduced lower lithospheric environment. Metallic Fe from the lower erust implies that the upper lithosphere is also highly reduced. However, metasomatism at 75-100 km, and the source regions inferred for carbonatites (-50-70 km) are more oxidizing, suggesting that the lithosphere has an alternating redox potential, more complex than previously modelled.

It is concluded that a genetic relationship exists between kimberlites and lamproites, and between kimberlites and carbonatites; metasomatism is the critical keystone. Oxide, sulfide and metal mineralogies are a reflection of rock types and processes in the upper mantle. Compositional signatures are specific and a more accurate definition of sub-cratonic environments is becoming possible. Opaque mineral stratigraphy for the upper mantle (Fig. 3) establishes the inferred presence of two metasomatic horizons: a phlogopite, K-richterite peridotite (PKP) metasome; and a phlogopite, amphibole, carbonate, zircon metasome. Experimental mineral equilibria place the zones at depths of ~ 60-100 km. Metasomatism is induced from melt stagnation in cool lithosphere and volatile liberation following thermal trauma of asthenospheric proto-melts. Maximum intensities of metasomatism, and development of metasomes, arises at ~ 100 km depth because this lithospheric region is coincident with the thermal blip in the C-O-H peridotite solidus. Rapidly ascending proto-melts from the astnenosphere, intersect the metasomes (which are hydrous and carbonated minimum melts) and lateral flash melting results (Fig. 4). Kinetic energy for alkali explosive volcanism, and the acquisition of silicate incompatible element signatures and high redox states, results directly from metasome assimilation. Geophysical implications for metasomes relate to the seismic low velocity zone and to electrical conductivity anomalies in the upper mantle (Fig. 4). These properties may not be due to partial melting but to attenuations caused by hydrous and carbonated mineralogies.

Evidence for metasomatism in the Kaapvaal craton of southern Africa is unequivocal. The presence of LIMA and magnetoplumbite minerals in China and Africa suggests a comparable metasomatic style, and preliminary data for an equally exotic array of LL-titanates in olivine lamproites from NW Australia, in association with Tiphlogopite and K-Ti richterite as essential components, logically implies that all three provinces have undergone similar upper mantle processes of metasomatism. Lamproites are an ultrametasomatic progression from metasomatic kimberlites. Thermal crisis of proto-melts ascending from the asthenosphere into old and cooler lithosphere assures that subcratonic metasomatism is the rule rather than the exception.



