Review of diamond indicator mineralogy and major element chemistry

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Introduction

Indicator minerals are powerful tools for diamond exploration because they provide hard evidence that a kimberlite or closely related rock type is in the area. (For simplicity in this review, the term "kimberlite" will include archetypal group 1 kimberlite, micaceous group 2 kimberlite, and olivine lamproite, although it should be recognized that indicator abundance is likely to be much lower in the latter 2 rock types.) Because indicator minerals are fragments of the kimberlite, and because some are derived from the same mantle rocks that host diamonds, their recovery from sediment samples can reveal much more than simply pointing the way to a kimberlite source. The mineralogy and chemistry of mantle phases can give insight into the potential of the kimberlite to carry diamonds, while the magmatic phenocrysts can be used to infer oxidation conditions of the intruding kimberlite. In addition, surface textures on indicator grains record evidence of their transport history, which can be used to infer distance to source.

Previous reviews of indicator minerals and their chemistry in kimberlite exploration that explain the methods in detail include Gurney *et al*. (1993), Lee (1993), Schulze (1995), and Fipke *et al*. (1995). This review incorporates concepts from these earlier reviews, as well as recent ideas and observations.

Indicator minerals – what are they?

Kimberlite indicator minerals are phases relatively common in kimberlites, but rare in most other crustal rock types. The classic indicators minerals are high pressure phases Cr-pyrope, eclogitic garnet, chrome diopside, Mg-ilmenite (picroilmenite), chromite, enstatite, olivine, and diamond. Grains of these minerals derived from kimberlite share characteristics, including moderately high density (s.g. 3.2 to 4.5), distinctive appearance, and some degree of paramagnetism (except for diamond), which allow them to be separated effectively from non-kimberlitic grains in sediment samples, even when present in less than parts per million concentrations. The density and

paramagnetic characteristics make the indicators suitable for concentration, and their distinctive color, crystal habits, and surface textures makes them suitable to recovery by visual identification through binocular microscopes. Once recovered, estimates of transport distance can be made from recovered indicators, due to the variable susceptibility of the different phases to chemical and mechanical weathering, which leads to changing surface textures and indicator ratios downstream (or down ice) from the source.

In addition to their utility in locating kimberlites, most of these indicator minerals (Cr-pyrope, eclogitic garnet, chrome diopside, chromite, enstatite, olivine, and diamond) are useful for evaluating the chemistry and composition of the mantle sampled by a particular kimberlite, because they have been passively transported to the surface in the kimberlite magma. Some of these xenocrystic indicators have compositional signatures similar to inclusions in diamond, indicating that the kimberlite masgma sampled the diamond stablity field. Others can be used as single phase geothermometers and/or geobarometers to determine if suitable mantle pressures and temperatures were sampled by a magma source.

In contrast, Mg-ilmenite, as well as a portion of the olivine and chromite grains, may be derived from the kimberlite magma itself and thus can provide chemical information specific to a particular kimberlite magma. Mg-ilmenite is especially useful in this regard, because its major and trace element chemistry varies significantly during evolution of the kimberlite magma, providing a potential fingerprint for individual pipes, clusters or fields.

Recovery techniques – creation of a heavy mineral concentrate followed by hand-sorting for indicator minerals

Kimberlite indicator minerals are separated from sediment samples using a variety of density and magnetic based procedures. These separation techniques are applied to sieved fractions of medium to coarse sand grains usually between 0.25 and 1.0 mm. The most commonly applied separation tools include pans, jigs, heavy liquids, shaking (wilfley-type) tables, various permanent or electromagnets, and dense media (cyclone) separators. Another tool that is being used increasingly combines aspects of dense media and magnetic separators by using a magnetite suspension rotating in an adjustable

electromagnetic field to make separations (e.g. the Magstream™). The separation is thus based on an adjustable combination of density and magnetic properties (Walker and Devernoe, 1991). Each laboratory or exploration team develops their own set of procedures using some combination of the available tools, all trying to produce the smallest concentrate possible for hand sorting under a microscope.

As examples of possible routines, a classical approach to separation (Fig. 1) of kimberlite indicators would be to sieve a 25 to 40 kg sediment sample (whether from stream or till) to produce a 0.25 to 1.0 mm sand fraction, which would then run through bromoform or tetrabromide at a density of 2.98, and methylene iodide at a density of 3.32. The heavy liquid concentrate then might be run through electromagnetic separators such as a Frantz separator. Prior to heavy liquid separation, samples may have been run through some sort of pan, jig, or shaking table to remove some of the less dense grains. Alternatively, some programs rely on only jigs or pans to produce a concentrate suitable for sorting in the field.

A more recently developed approach used in some laboratories essentially replaces the heavy liquid step with the Magstream™, resulting in an entirely water based separation routine.

Figure 1: simplified heavy liquid separation routine; alternative replaces heavy liquids with Magstream™
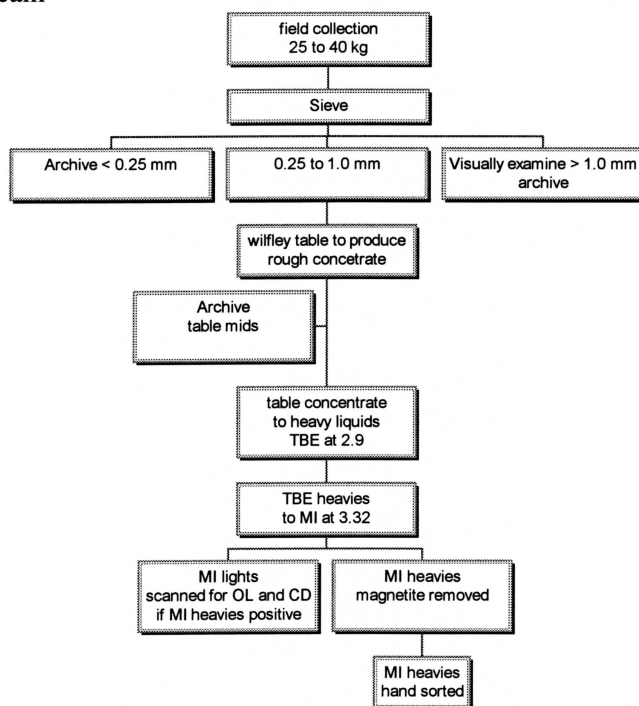
The heavy mineral concentrates are hand sorted for indicators with each grain examined individually, usually using a reflected light binocular microscope. Sorters look for the distinctive colors, surface textures, and (in some cases) cleavages that reveal grains of kimberlitic origin, as described in more detail later. Any grains that appear to be likely candidates are pulled out and examined in more detail after completion of each concentrate, usually by a mineralogist or more experienced supervisor. Use of a transmitted light petrographic microscope by the supervisor helps to distinguish some of the silicate indicator minerals. A transmitted light microscope with crossed Nicols is especially useful for eliminating birefringent staurolite from isotropic orange garnet that may be derived from eclogite, as well as distinguishing between olivine with its high birefringence and enstatite with birefringence closer to quartz. Some exploration programs send all of their probable indicators for chemical determination, either by electron microprobe or scanning electron microscope. Although such complete analysis provides high levels of confidence as to a kimberlitic origin for individual grains, it also is destructive to the surface texture features that may help determine transport distance. Care must be taken, therefore, to completely describe surface textures during sorting operations.

Appearance and chemistry of the most important indicators

Most of the important kimberlite indicator minerals share some common morphologic and chemical characteristics. The most pervasive morphological feature among different indicator mineral phases is some sign of resorption, such as rounded grain shapes, reaction rims, or cockscomb and finely matte textures. Exceptions to this general trend of resorption occur most commonly in those indicators closely related to the kimberlite magma, including tablet shaped olivine crystals, and polycrystalline aggregates of ilmenite. Although diamonds are also usually partially resorbed, microdiamonds occasionally have sharp euhedral crystal shapes that are not obviously resorbed. The silicate indicator minerals also commonly lack visible inclusions, with the exception of black oxides in occurring in some chrome diospside (usually ilmenite) and olivine (usually chromite). Chemical characteristics common to most indicators (excepting diamond, of course) include elevated MgO, Cr_2O_3 (excepting eclogitic garnet), and less commonly TiO_2, compared to the same minerals derived from crustal sources.

More detailed descriptions of indicators (excepting diamond) are provided below. Caution is advised because there are exceptions to almost every generalization provided.

Cr-pyrope

Cr-pyropes are the purple garnets that comprise the most widely recognized indicator mineral for kimberlite. The Cr-pyropes, like all garnets, are mechanically and chemically resistant to erosion, which favors their preservation during sediment transport. Cr-pyropes from kimberlite occur in shades of purple ranging from rose pink to dark purple. Blue and purple shades are associated with generally increased CaO and Cr_2O_3 content. Elevated TiO_2 also is associated with noticeably darker crystals. Some Cr-pyropes preserve thick kelyphite reaction rims with a radially oriented fibrous habit on their rounded surfaces. A matte or slightly bumpy (orange-peel texture; McCandless, 1990) texture on rounded outer surfaces forms beneath the kelyphite (Garvie and Robinson, 1984). This sub-kelyphitic texture helps distinguish kimberlitic pyropes when the kelyphite has been removed either in the kimberlite or during sediment transport. In addition, kimberlitic grains are distinguished by lack of crystal faces and inclusions.

The chemical composition of Cr-pyropes from sediment samples can be used to confirm a kimberlitic origin, and predict more or less precisely the diamond potential of the source. Cr-pyrope indicators are Mg-rich and contain variable Cr_2O_3, CaO, and TiO_2. Dawson and Stephens (1975) divided 352 kimberlitic garnets into 12 groups based on clustering of 5 oxide concentrations: MgO, FeO, CaO, Cr_2O_3, and TiO_2. Most of the Cr-rich kimberlitic garnets split mostly into groups 9 (G9) and 10 (G10). Cr-rich group 11 (G11) is basically a Ti-enriched population otherwise similar to G9. Gurney (1984, Fipke *et al*, 1995) showed that the G9 garnets are lherzolitic, and the G10 garnets are calcium depleted (sub-calcic) and harzburgitic. Most of the Cr-pyrope inclusions in diamond are G10 rather than G9, and therefore indicator mineral suites with G10s point to diamond potential in the source kimberlite (Fig. 2). Comparisons between populations can be quantified using simple graphical systems such as Gurney's J factor (Lee, 1993), which values most highly sub-calcic Cr-pyropes with > 4.0 % Cr_2O_3 and < 4.0 % CaO (Fig. 3).

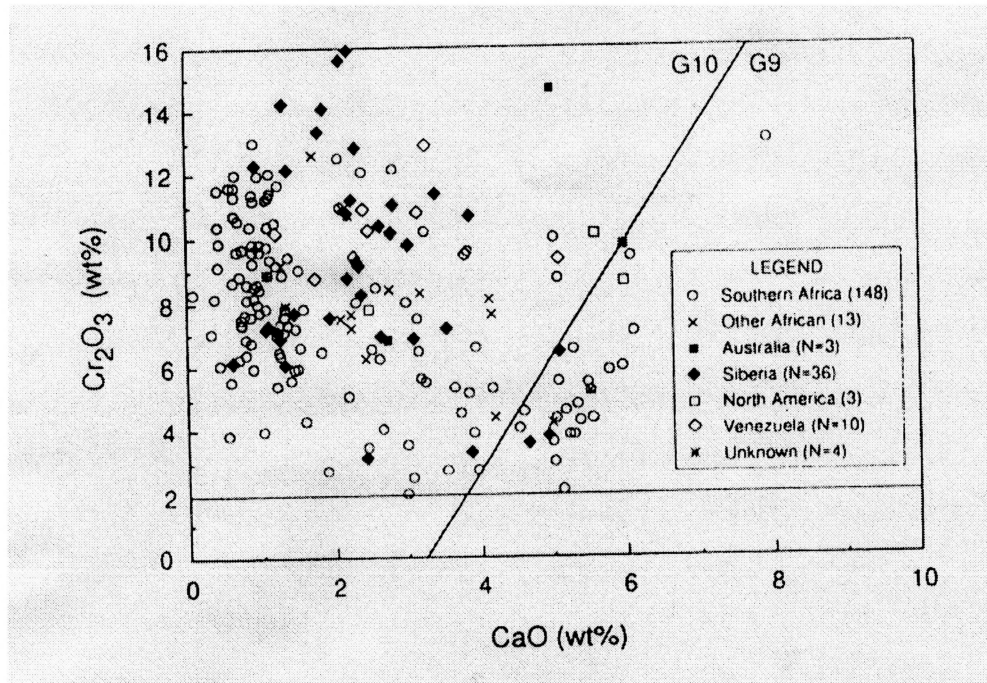Figure 2: Diamond inlcusion Cr-pyrope compositions after Fipke et al., 1995.

Figure 3: Gurney's J factor for quantifying comparisons between suites of Cr-pyropes, after Lee (1993).
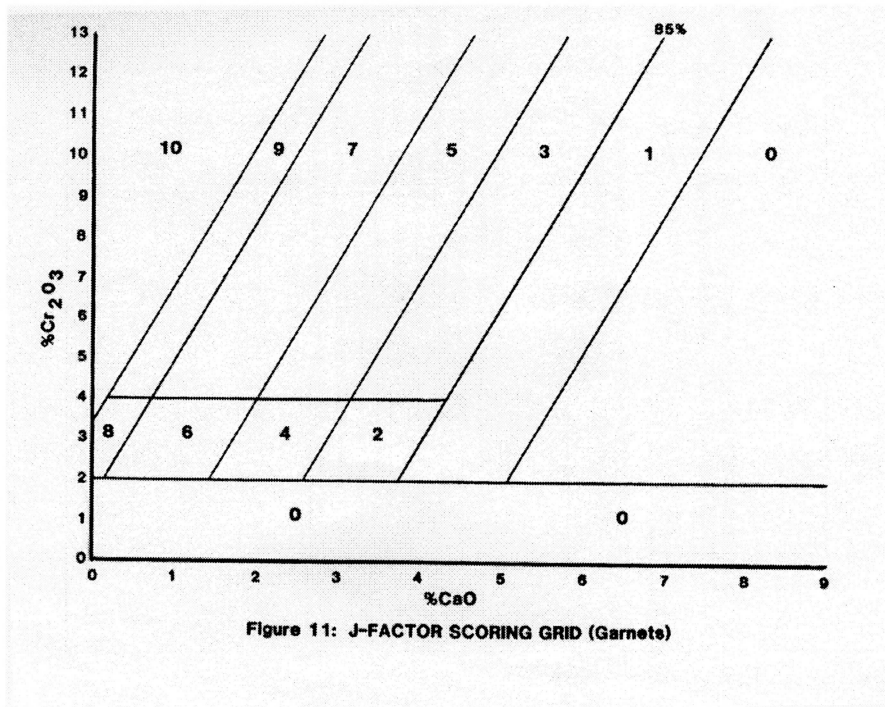

Figure 11: J-FACTOR SCORING GRID (Garnets)

Distance of transport can be gauged by the increase of chipping along edges and pits on conchoidal fracture surfaces. Such mechanical abrasion is especially rapid in alluvial environments, the rate depends strongly on the coarseness of the transport media (McCandless, 1990). Progressive wear on kelyphitic rims can help identify proximal sources in alluvial transport systems (Mosig, 1980). In glacial environments, ratios of grains with well preserved kelyphite to those with their kelyphite removed can help determine distance of transport.

Eclogitic garnet

Eclogitic garnets are bright to reddish orange and have matte surface textures on rounded surfaces similar to the Cr-pyropes. The orange garnets lack crystal faces and inclusions, also like the Cr-pyropes. Kelyphite, if present at all, does not form thick radial rims as in Cr-pyropes, but rather tends to be thin plates of phlogopite. Because eclogitic garnets are isotropic, they can be easily distinguished from superficially similar staurolite in heavy mineral concentrates by use of the petrographic microscope.

Eclogitic garnets have highly variable compositions, but always contain significant MgO (3.0 to 20.0%), FeO, and CaO reflecting varying amounts of pyrope, almandine, and grossular components. Mantle derived eclogite garnets also lack significant manganese, with most analyses < 1.0 % MnO.

Eclogitic garnets generally lack Cr, although rarely some may contain up to 2.0% Cr_2O_3. Most eclogite garnets belong to Dawson and Stephens (1975) group 3 (G3), which is characterized by high FeO and CaO concentrations, or group 5 (G5) which has higher FeO but lower CaO than G3. Very CaO enriched eclogitic garnets classify as group 8 (G8) from grosspydites.

Most orange garnet inclusions in diamond have elevated sodium contents (Sobolev and Lavrent'yev, 1971) > 0.07 % Na_2O, and thus eclogitic garnets in sediment samples with > 0.07 % Na_2O are considered especially significant (Fig. 4). Comparable Na_2O concentrations occur in orange garnet megacrysts from kimberlite, but these garnets have higher TiO_2, and thus can be distinguished using Na_2O-TiO_2 plots (Fipke *et al.*, 1995). However, orange garnets from diamondiferous eclogite may have lower Na_2O concentrations, as in the Jericho kimberlite of northern Canada, where

diamondiferous eclogite garnets contain between 0.03 and 0.06% Na_2O (Cookenboo *et al.*, 1998).

Figure 4: Orange (eclogitic) garnet inclusions in diamond after Fipke et al., (1995).
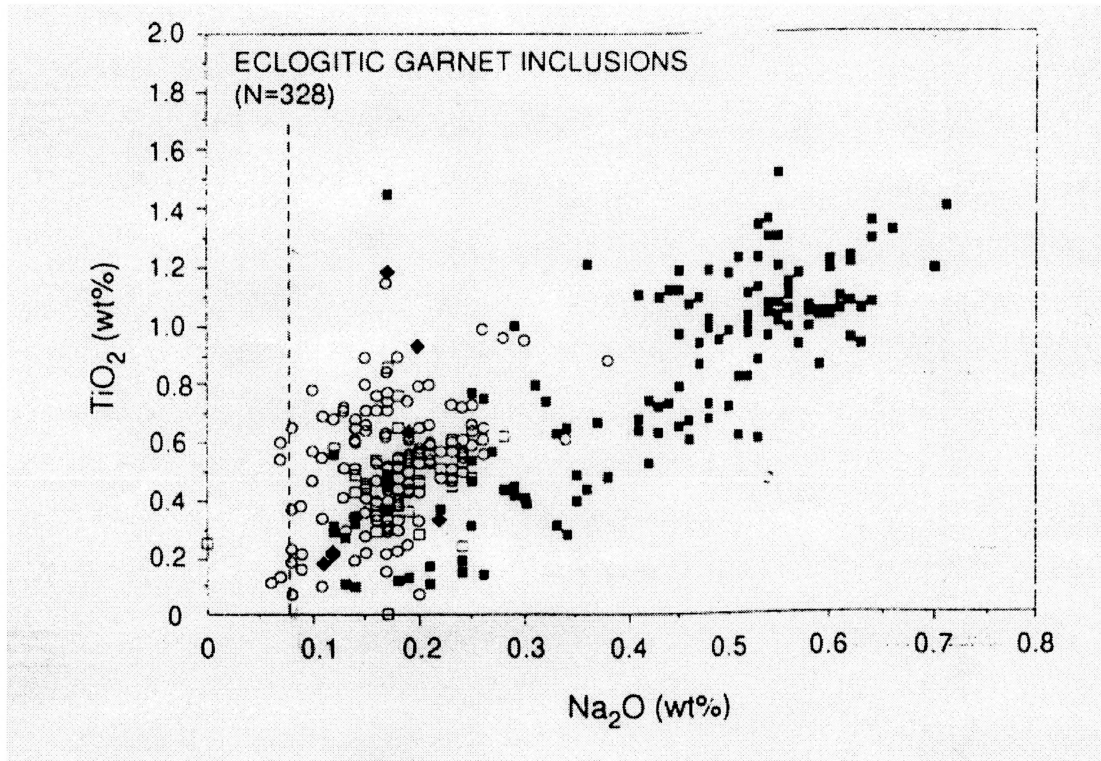
Chrome diopside

Chrome diopside from kimberlite is bright emerald green, and commonly exhibits distinctive surface features, including cockscomb points, shiny unblemished cleavage planes, rounded surfaces, and finely matte textures due to resorption. Usually, the chrome diopside lack inclusions, although black oxide inclusions (typically ilmenite) occur in some grains. The distinctive color and surface features make chrome diopside one of easiest indicators to recognize, although bright uvaroite garnet can be confused visually unless birefringence is confirmed.

Low chrome diopside (< 0.80% Cr_2O_3) from kimberlite is less distinctive both visually and chemically, than common crustal clinopyroxene (CPX). Such low Cr-diopside is pale green, but may have similar surface features to chrome diopside. Among the pale green CPX may occur omphacitic CPX derived from eclogite, which lacks Cr and is Na-rich. Recovery of eclogitic CPX in an exploration program is especially important due to the potential for eclogite to be rich in diamonds (Schulze, 1995).

Most chrome diopside (> 1.0 % Cr_2O_3) in kimberlite is derived from peridotite. Populations of chrome diopside from peridotite are characterized by elevated Na_2O at concentrations similar to Cr_2O_3. Until recently, chrome diopside chemistry was not considered particularly useful for assessing diamond potential (Schulze, 1995), but Cr exchange in lherzolitic CPX has been proposed recently as a single phase geothermobarometer (Taylor, 1998), which should help assess mantle P/T conditions. Elevated K indicates a high pressure origin (Harlowe, 1998), and concentrations of K_2O greater than 0.07% commonly occur in CPX associated with diamond and thus such trace concentrations are significant to exploration programs (Fipke, *et al.*, 1995).

Chrome diopside is more susceptible to mechanical and chemical weathering than garnet and its presence in sediment samples in tropical or subtropical environments is reported to imply the sample was collected within 2 to 3 km of source (Fipke *et al*, 1995). In glacial till from colder environments, chrome diopside may persist much farther during transport. However, cleaving and signs of wear such as chipping and etch pits accumulate rapidly and can be used to assess transport distance.

Olivine

Olivine from kimberlite is Mg-rich, usually pale yellow, and commonly displays cockscomb shapes and matte textures similar to those describe earlier for chrome diopside. Recovered grains are commonly rounded, and may have curved fracture surfaces. Euhedral, tablet shaped grains (or fragments thereof) may also occur in some concentrates. Olivine is the most abundant mineral in kimberlite magmas, although serpentinization and weathering following emplacement usually destroys crystal forms prior to entrainment in sediment transport systems. Furthermore, olivine is susceptible to chemical and mechanical weathering during transport. However, in areas where olivine survives the emplacement and enters the transport system, it may be the most important indicator mineral due to its initial abundance in the kimberlite.

Olivine from kimberlite includes a wide range of Mg-rich compositions (Fo 82 to 96), with the most magnesian (FO $_{90.2. to 96.6}$) being equivalent to inclusions in diamond (Fipke, *et al.*, 1995). The less magnesian compostions may be phenocrysts from the kimberlite magma usually including the tablet shaped grains,. The compositional range

overlaps olivine from other crustal sources, making the chemistry of individual grains ambiguous in regards to a kimberlitic origin.

Olivine can be very helpful in assessing the distance to source, especially of proximal kimberlites, due to its susceptibility to weathering. Etch pits appear on previously glassy surfaces within 1 to 3 km of transport in till, and probably less in warmer environments.

Orthopyroxene (Enstatite)

Orthopyroxene from kimberlite is pale green, Mg-rich (usually enstatite), and displays the same cockscomb and matte surface features due to resorption that characterize kimberlitic olivine and chrome diopside. Enstatite can be distinguished from kimberlitic olivine by its lower birefringence, 90° cleavage, and slightly greener tinge. Enstatite is subject to breakage by cleaving and thus is less robust in most sediment transport environments than garnet. However, enstatite is less subject to chemical weathering than olivine, and thus appears fresher at greater distance from source.

Enstatite in kimberlite is derived from peridotite, and can yield important information regarding depth of sampling. Most of the widely used two phase geobarometers are based on Al in OPX, with concentrations of Al decreasing at higher pressures of formation. Reflecting their high pressure origin, most enstatite inclusions in diamond have less than 1.2% Al_2O_3, and many less than 0.6% Al_2O_3 (data from Fipke, *et al*, 1995). Single grains with such low Al contents can be used to estimate mantle depths sampled by a kimberlite source, assuming they formed in equilibrium with CPX and garnet.

Chromite

Chromite in kimberlite occurs both as small phenocrysts in the groundmass and xenocrysts derived from mantle peridotite. The mantle derived chromites tend to be larger, and may be the only grains recovered in sediment sampling. They are black and opaque, although thin broken edges may be trnaslucent brown in transmitted light. Chromites from kimberlite tend to be rounded on their octahedral edges due to resoprtion, and may have matte textures on curved fractured surfaces. Chromite phenocrysts may be euhedral, or have resorbed textures, including atoll morphologies.

Chromite compositions vary widely wihtin a single kimberlite, reflecting their multiple origins. Very Cr- and Mg-rich chromite (> 60% Cr_2O_3 and 12% MgO) is similar to most inclusions diamond, with similarly Cr-rich spinels intergrown with diamonds extending to slightly lower MgO concentrations (e.g. Fipke *et al*., 1995). These chromites also have very low TiO_2 and Fe^{3+} (calculated by stoichiometry) contents. Their recovery in sediment samples suggests that a kimberlite source sampled the diamond stability field. However, such compositions are not exclusive to rocks likely to carry diamonds. Such high Cr and Mg chromites (with low Ti and Fe^{3+}) have also been reported from podiform chromites in alpine-type ophiolites from British Columbia (Whittaker and Wadkinson, 1984), alkali minettes from Alberta (Kjarsgaard, 1998), and presumed phenocrysts in lamproites and kimberlites (Grütter and Apter, 1998).

Other chromites from kimberlite with distinctive compositions belong to Mitchell's (1986) magmatic trend 1. These chromites are Ti-enriched (> 0.6% TiO_2), with between 50 and 62% Cr_2O_3 (Grütter and Apter, 1998).

Trace elements in chromite can be used to both support a kimberlitic or lamproitic origin, and to infer crystalizatuion temperatures in the mantle (Griffin and Ryan, 1993). Exposure of the chromite to a kimberlite or lamproite magma is supported by detection of elevated Zr and Nb, especially towards the grains margins (Griffin and Ryan, 1993). Griffin and Ryan (1993) also show that Zn concentrations in chromite decrease with increasing temperature of formation, and can be used as a single phase geothermometer.

Mg-ilmenite (picroilmentite)

Ilmenite from kimberlite is Mg-rich picroilmenite, and is distinguished from common crustal ilmenite by its high concentrations of MgO (> 3.0%) and Cr_2O_3 (> 0.3%). Visually, Mg-ilmenite appears blacker and slightly less metallic than crustal Fe-ilmenite, and typically occurs in rounded grains with conchoidal fracture surfaces. Other kimberlitic grains of Mg-ilmenite form polycrystalline aggregates, and coatings of light brown perovskite, reddish brown rutile or whitish leucoxene are distinctive (Schulze, 1995).

Mg-ilmenite is a mantle crystallization product of the kimberlite or proto-kimberlite magma in which Cr, Mg, Fe^{3+}, Ti, Nb, and Zr concentrations vary broadly during evolution of the magma. Differences major and trace element evolution patterns

are manifest in Cr_2O_3-MgO and Nb-Zr plots for 20 South African kimberlites (Griffin *et al.*, 1995). These differences comprise a chemical signature for each batch of magma, and may be useful in determining the number of separate sources contributing to an ilmenite-rich sediment sample.

The major elements evolve from Mg- and Cr-rich with low Fe^{3+} (calculated from stoichiometry) to Mg-poor compositions, with elevated Fe^{3+} concentrations. The elevated Fe^{3+} suggests more oxidizing conditions in the kimberlite magma, and thus greater probabilities of resorption of diamond during kimberlite emplacement. Such an association between low diamond contents and high Fe^{3+}/Fe^{2+} ratios (and commensurate low MgO concentrations) occurs in many southern African kimberlites (Fipke *et al.*, 1995; Griffin *et al*, 1995).

Exploration implications

The economic incentives of diamond exploration have pushed indicator minerals techniques in diamond exploration beyond being simply a tool for pointing the direction to a kimberlite. Detailed surface texture analysis permits estimation of transport distance, and detailed chemical analyses reveal information regarding the mantle, including potentially detailed estimations of pressure, temperature and diamond potential. Revealing methods of estimating whether a kimberlite source has sampled the diamond stability field are available using either direct comparison to diamond inclusions, or by single phase geothermometry, from Cr-pyropes, eclogitic garnets, chromite, chrome diopside, and enstatite. Each of these geochemical techniques is permissive of diamond accumulations, but none are genetically tied to diamond occurrence. Given the heterogeneous distribution of both indicator minerals and diamonds in the mantle, it seems prudent to accept any of the geochemical indications of the diamond stability field as justification for following an indicator mineral train back its source. If numerous such trains are available for follow-up, then exploration priorities can be based on the presumption that those suites of indicators with the most diamond stability field signatures should have the best chance of leading back to a diamondiferous kimberlite.

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