Paper 9

Mantle-Derived Indicator Mineral Compositions as Applied to Diamond Exploration

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ABSTRACT

Diamond exploration and mantle studies have pushed geochemical methods to very high resolution which is useful both in evaluating kimberlites and in describing the subcontinental lithosphere. Developing these methods initiated with direct comparisons of distinctive indicator minerals from kimberlite and sediment concentrates to unusual compositions of the same minerals included in diamond. More recently, single grain thermobarometer methods have been developed based on simplifications of equilibrium phase studies of mantle xenoliths and high pressure experiments. These single grain methods have enhanced evaluation of indicator mineral concentrates for diamond potential by greatly increasing the proportion of each suite that provides useful data on mantle conditions. Concurrently, these methods have broadened studies of the subcontinental lithosphere by permitting detailed evaluations beyond the occurrence of kimberlites with well studied mantle xenoliths. This review provides description of these indicator methods and their underlying principles. Simple comparison of diamond inclusion compositions for Cr-pyropes, eclogitic garnets, chromite, chrome diopside and enstatite is followed by a review of the concepts behind equilibrium phase thermobarometry, because these concepts are the underlying foundations for the increasingly widely applied single grain thermobarometry methods. Descriptions of such single grain methods based on peridotitic chrome diopside, pyrope garnet saturated with chromium, and Ni in Cr-pyrope are followed by brief examples of the power of these methods to describe the subcontinental lithospheric mantle. This review is presented both to summarize high resolution geochemical methods being widely applied in diamond exploration and mantle studies, and hopefully to inspire development of analogous methodologies applicable to other rock types.

INTRODUCTION

Indicator mineral chemistry methods used in diamond exploration are some of the most advanced and sensitive of geochemical applications. These methods developed from detailed studies of kimberlite concentrates in order to evaluate diamond potential in known bodies, as well as sediment samples collected to explore for new diamond-bearing sources. Typically, exploration for diamonds begins with detection of a few indicator sand grains out of an alluvial or glacial sediment sample comprising hundreds of millions or billions of grains. These recovered grains may then be examined for major and minor element chemistry using the electron microprobe, and more recently trace elements using laser ablation ICP-MS or PIXIE proton microprobe, yielding useful data at concentrations of a few 10s of ppm. Thus indicator mineral methods can produce important inferences about diamond potential from the sedimentary environment at parts per 10^{-14} or 10^{-15} concentrations, largely as a result of the initial sampling for specific indicator mineral grains.

Indicator minerals targeted in diamond exploration include visually distinct types of pyrope garnet, chromite, picroilmenite, forsteritic olivine, chrome diopside, enstatite, and of course diamond. These minerals are derived from kimberlite or closely related rock types. Diamond potential was first inferred from these kimberlite indicator minerals based on comparison to inclusions of the same minerals in diamond, with similar compositions implying derivation from mantle rocks in the diamond stability field. These simple compositional comparisons to diamond inclusions emphasize Ca and Cr concentrations in Cr-pyrope garnets, Na in eclogitic garnets, Cr-rich chromites, Al in enstatite, as well as trace elements in chrome diopside and olivine. Because of the unusual composition of these minerals included in diamond as compared to lower pressure sources, these simple comparisons have been quite effective in identifying indicator mineral concentrates associated with diamond-bearing sources. However, these diamond inclusion compositions are not exclusive to the high pressure and temperature regime suitable for diamonds. Although effective in many cases, numerous examples are known where the simple comparisons fail, either due to lack of some of the diamond inclusion indicators, or due to lack of predicted diamonds.

More recently, assessment of diamond potential is evolving to calculations of mantle pressure and temperature conditions using newly developed methods of single grain mantle thermobarometry. Widely used methods include Cr-saturation arrays on Cr-Ca plots from pyrope garnets, Ni and other trace elements in Cr-pyropes as well as temperature and pressures calculated from peridotitic chrome diopside compositions. Further insight into mantle metasomatism has been derived from trace element concentrations in Cr-pyrope. These methods can take advantage of the entire sample of recovered indicators and yield much more precise estimates of the pressures and temperatures of mantle sampled by any particular source.

Researchers are using these single grain methods to describe mantle stratigraphy in remarkable detail, starting with simple indicator mineral concentrates. These data provide a basis for interpreting mantle stratigraphy and history. Examples from the Kaapvaal Craton in southern Africa and the Slave Craton in northern Canada demonstrate the power of these techniques, and suggest analogous methodologies could be used exploring for other minerals as well as in sandstone provenance studies.

REVIEW OF DIAMOND INDICATOR MINERAL CHEMISTRY

Distinctive upper mantle minerals (kimberlite indicator minerals or "KIMs") from sediment samples such as purple pyrope garnets and emerald green chrome diopside have been used as indicators to discover kimberlite since shortly after the discovery of the first diamond pipes in the 1870s. By the 1970s, electron microprobe analyses became widely available and the first important steps were taken to predict diamond potential of kimberlites from indicator minerals (diamond indicator minerals or "DIMs"). These first steps made direct comparisons of the long-followed KIMs pyrope garnet and chromite to the unusual compositions of the same minerals included in diamond. Where an abundance of the KIMS proved to be DIMs, the kimberlite source was concluded to have a strong potential to carry diamonds.

Recognition of these unusual diamond inclusion compositions began with Cr-rich and Ca-poor pyrope garnets (Meyer, 1968). Similar diamond inclusion composition garnets were also found to occur in concentrates from diamondiferous kimberlites in Russia (Sobolev, 1971, Sobolev et al., 1973) and South Africa (Gurney and Switzer, 1973). Such sub-calcic Cr-pyropes (loosely referred to as G10s) are rare from rock types not associated with diamonds, and thus were concluded to be a good indicator of diamond potential. Distinctive diamond inclusion compositions were subsequently recognized for other important indicator minerals: eclogitic garnet and omphacite, as well as less distinctive types of chrome diopside and enstatite.

The electron microprobe diamond-inclusion comparisons remain a robust tool for locating prospective kimberlites and are a foundation of diamond exploration today. However, examples where such comparisons do not hold, or are difficult to evaluate due to the rarity of the important DIM eclogite garnet, have spurred development of more subtle methods based on equilibrium phase thermobarometry as applied to mantle xenolith and high-pressure experiments. These

equilibrium phase methods have recently been adapted to work with single mineral phases such as recovered in sediment or kimberlite concentrates. These single phase methods extract information on the entire suite of recovered indicator minerals providing insight into a wide range of mantle conditions. Starting with surface sediment samples, these single phase methods permit mapping of the subcontinental lithospheric mantle as shown in examples from several cratons later.

This paper reviews the diamond indicator methods, starting with the distinctive diamond inclusions compositions, followed by a summary of the equilibrium thermobarometric methods applicable to upper mantle conditions, and culminating with description of the most widely used single phase methods. After this review of methods, we present some examples from various authors, who starting with surface sediment samples or kimberlite concentrates put it all together into lithospheric cross sections that show the mantle evolving through time. Necessarily, this review of methods is founded on the works of many authors which our discussions merely summarize.

Limitations to this review include the lack of consideration of single grain radiometric dating methods, as well as the lack of any description of the many methods of direct study of diamonds. These methods are not excluded for any reason of merit, but simply to keep this review to a manageable size.

DIAMOND INCLUSION COMPOSITIONS

Cr-pyrope garnets

Cr-pyrope garnets derived from peridotite occur in most kimberlite heavy mineral concentrates and are probably the most informative of the diamond indicator minerals, due to wide range of substitution that can occur in the garnet structure. Calcium and Cr exhibit the broadest compositional ranges among the major elements in kimberlitic garnets. Plotted against each other, they define fields suggestive of derivation from different mantle peridotite types including lherzolite, harzburgite and websterite (Figure 1). Sub-calcic (G10) compositions are associated with clinopyroxene-free harzburgites and dunites (Sobolev, 1974).

Most Cr-pyrope inclusions in diamond plot in the sub-calcic field to the left of the lherzolite field in Figure 1. The Cr-rich sub-calcic grains with >5.0% Cr_2O_3 are most distinctly associated with diamond (Sobolev, 1974), although less Cr-rich inclusions may dominate populations from some locales (an example being Letseng (McDade and Harris, 1999). The Ca-poor boundary of the lherzolite field approximately coincides with the line enclosing 85% of Cr-pyrope inclusions in diamond (Gurney, 1984). Ca-rich garnets plotting to the right of the lherzolite trend in the wehrlite field also occur included in diamond occasionally.

Chromium pyrope diamond inclusions are consistently Mg-rich, Mn-poor, and usually nearly devoid of TiO2. Some exceptional compositions, including majoritic garnet with excess silica, and Cr- Ca-rich varieties from wehrlite also occur occasionally (Sobolev et al., 2004), but are less useful than the typical diamond inclusion compositions for predictions due to their rarity.
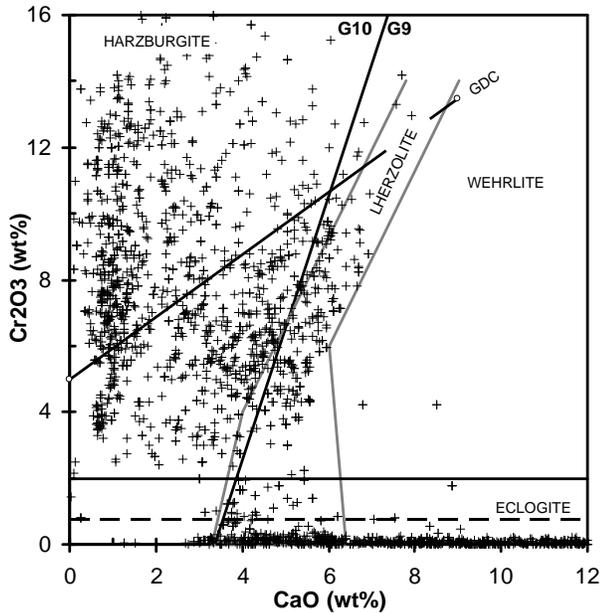
Figure 1: Cr_2O_3-CaO plot for diamond inclusion garnets showing compositional fields for wehrlite, lherzolite, and harzburgite, as well as G9 and G10 pyropes. The eclogite field is commonly reported as >2.0% Cr_2O_3, but the vast majority of eclogitic garnets in diamond contain < 0.75% Cr_2O_3 (After Sobolev et al., 1992; Gurney, 1984). Graphite-Diamond Constraint (GDC) after Grütter et al., 2006.

The simplest interpretation assumes that the higher the proportion of garnets that plot within the Cr-rich, sub-calcic field (harzburgite-dunite), the greater the potential for diamonds whether from a kimberlite concentrate or indicator mineral anomaly.

Cr-poor (eclogitic) garnets

Chromium-poor magnesian orange garnets (typically <0.75% Cr_2O_3) in kimberlite are derived from two upper mantle sources: eclogite and the Cr-poor megacryst suite. Eclogite garnet inclusions occur in diamond and are characterized by a wide range of compositions which largely overlap garnets from non-diamondiferous eclogite, as well as orange garnets from the Cr-poor megacryst suite. Notably, eclogite garnets from diamond inclusions contain elevated Na_2O (>0.07% Na_2O) which distinguishes them from many lower pressure mantle eclogites; Sobolev and Lavrent'ev, 1971; Gurney and Moore, 1993). The Na:Ti ratio is close to unity (Reid, et al., 1976) which helps distinguish eclogite diamond inclusions from those in Cr-poor megacrysts. The latter are markedly more enriched in Ti (Figure 2).
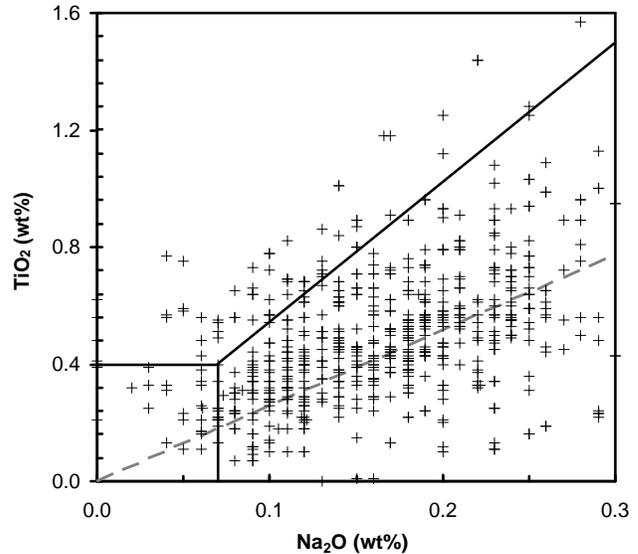

Figure 2: Na_2O-TiO_2 plot for eclogite garnet included in diamond (< 0.75% Cr_2O_3); dashed line atomic ratio of Na:Ti = 1.

The recovery of eclogite garnets with such diamond inclusion compositions from either sediment samples or kimberlite heavy mineral concentrates suggests possible sampling of the diamond stability field in the mantle. Grütter and Quadling (1999), however, have demonstrated that elevated Na in eclogitic garnet is an imperfect indicator of diamond association, because garnets from many graphite-bearing eclogite xenoliths significantly overlap the diamond-inclusion compositions. This suggests that Na enrichment in eclogitic garnets occurs above the depth of the graphite-diamond transition.

Chromite

Typical diamond inclusion chromites contain exceptionally high concentrations of Cr and Mg while being Al- and Ti-poor containing >62.0 Cr_2O_3: >11% MgO; and <0.50%TiO_2; Sobolev et al., 2004) (Figure 3). Chromites intergrown with diamond are less enriched in MgO. Although these Cr-rich, Ti-poor compositions are rare from non-kimberlitic rocks, they occur in some non-diamondiferous kimberlites as well as diamond-bearing examples, implying they can be phenocrysts from high pressure mantle magmas not necessarily sourced from depths below the graphite-diamond transition (Grütter and Apter, 1998). Trace elements Zn and Ni show respectively distinct negative and positive correlations to temperature in mantle chromites. Typical diamond inclusion Zn concentrations occur in the range of 200 to 750 ppm (Griffin et al.1994, 1993; Lavrent'ev et al., 2005). Nickel concentrations in diamond inclusion chromites range from 500 to 1000 ppm (Griffin et al., 1994).
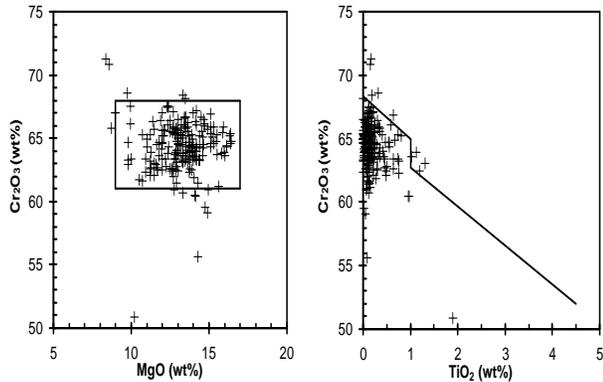
Figure 3: Cr_2O_3-MgO and Cr_2O_3-TiO_2 plots for diamond inclusion chromites with MAXCR line which all primary chromites plot beneath, from (Grutter and Apter, 1998)

Chrome diopside

Clinopyroxene (Cpx) inclusions in diamond occur in two common types: ones that derive from peridotite, and others that derive from eclogite. The clinopyroxenes derived from peridotite are chrome diopside, with a dominance of Tschermaks component ($CaAlAlSiO_6$), which as shown in Figure 4 is distinguished by proportional substitution of Al+Cr and Na+Ti (Harlow, 1999; Sobolev, 1977; Sobolev et al., 1992). Chrome diopside inclusions in diamond typically contain between 0.5 and 4.5% Cr_2O_3, and <4.0% Al_2O_3 (Nimis, 2002). As expected, such grains classify as being derived from on-craton garnet peridotites as opposed to off-craton peridotites using Ramsay and Tompkins (1994) Cr_2O_3-Al_2O_3 plot. However, the diamond-inclusion compositions are not markedly distinct from non-diamond associated grains (Stephens and Dawson, 1977).

Chromium-poor and Na-rich clinopyroxene inclusions in diamonds are derived from eclogite (Figure 4). This omphacitic Cpx is characterized by approximately 1:1 Tschermaks and Eskola ($Ca0.5AlSiO6$) components and a distinctive enrichment in potassium (0.6 to 1.3% K2O; McCandless and Gurney, 1989; Harlow, 1999).

Orthopyroxene

Orthopyroxene (Opx) inclusions in diamond are Mg-rich (enstatite), with Mg# (Mg/Mg+Fe) typically near 93 (Figure 5). Enstatite inclusions in diamond typically contain trace Cr_2O_3, and very low concentrations of Al (typically <<1.0% Al_2O_3; Sobolev, 1974). The Al-poor compositions reflect high pressure during crystallization, as shown by two-phase equilibrium experiments, in which Al in enstatite is inversely related to pressure (Perkins and Newton, 1980; Finnerty and Boyd, 1984). Thus Al-poor enstatites comparable to diamond inclusion are suggestive of high-pressure origin within the diamond stability field.
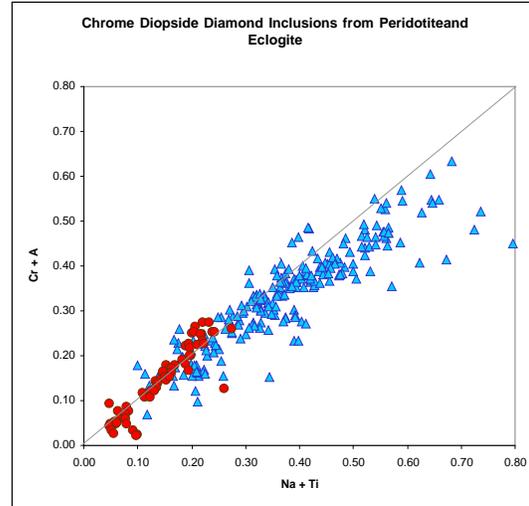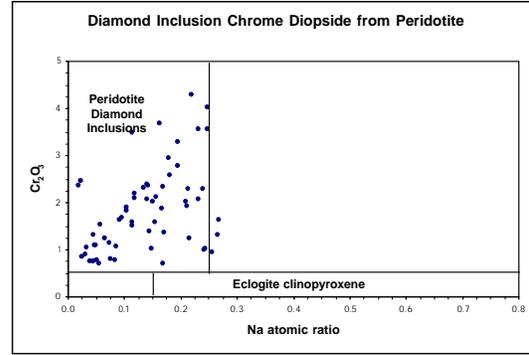

Figure 4: Chrome diopsides from diamond inclusions. Peridotitic (circles) inclusions are more Cr-rich and less aluminous than eclogitic (blue diamonds).
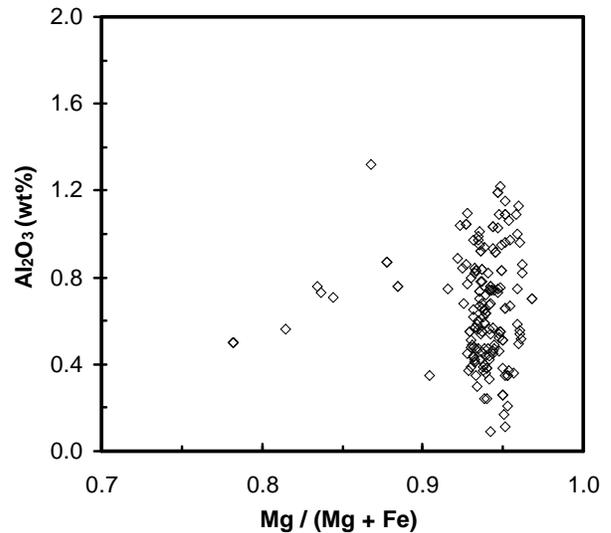

Figure 5: Orthopyroxene inclusions in diamond show the low Al compositions associated with high-pressure origin.

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EQUILIBRIUM PHASE THERMOBAROMETRY METHODS

The hunt for diamond-inclusion compositions of indicator minerals remains an important component of diamond exploration programs world-wide. However, exceptions to the expectation that an abundance of sub-calcic (G10) Cr-pyrope and Cr-rich chromite in a concentrate points to a diamondiferous kimberlite are numerous. Partly, this results from some of the distinctive diamond inclusion compositions for Cr-pyrope and chromite being derived from above the graphite-diamond transition. This imperfect correlation between distinctive diamond-inclusion compositions (including eclogite garnet) means abundant G10s or Cr-rich chromite do not necessarily equate with sampling diamondiferous mantle. For example, some non-economic kimberlites in the central Slave Craton contain even more abundant G10 populations than the nearby Ekati and Diavik mines (Griffin and O'Reilly, 2005). Relative rarity of eclogite garnets provides further 'exceptions' to abundant diamond inclusion compositions pointing to prolific diamonds, including some of the most important diamond mines in the world. For example, Orapa, Jwaneng and Letlhakane in Botswana, Argyle in Australia, plus the Jericho Mine in Nunavut, and the Victor Mine (under construction) in Ontario, contain very few sub-calcic G10 pyropes and yet eclogitic mantle is the apparent source for most of their diamonds (Gurney, 1984; Sage, 1996, Cookenboo, 1999; Kopylova et al., 1999; Giffin and Ryan, 1993; and Griffin and O'Reilly, 2005). Although eclogitic garnets of diamond inclusion compositions occur in these bodies, their relative rarity makes evaluation of sediment samples difficult. In light of these significant complications, efforts have focused on deriving pressure (P) and temperature (T) from individual indicator mineral grains, regardless of whether or not they have diamond inclusion characteristics. These efforts have led to adaptations of equilibrium multi-phase thermobarometry to individual grain analyses. These P/T methods can then be applied to the entire indicator mineral population recovered from sediment samples, greatly enhancing the detail in predictions of diamond potential from yet undiscovered or unevaluated kimberlites. This enhanced detail, in turn, has become a powerful tool for mapping the sub-continental lithospheric mantle through time using indicator minerals in sediment samples.

Equilibrium phase methods and simplifications for single grains applications

Pressure, temperature, and bulk chemistry control the composition of mantle phases. Multi-phase thermobarometry calculates P and T for minerals from mantle xenoliths presumed to be in equilibrium, which provides control on bulk mantle composition. The calculations are heavily dependent on high-pressure experiments. In these experiments, mineral compositions of simple systems measured at varying controlled temperatures and pressures are expanded to formulate mantle thermobarometers that can be applied to actual grains from the mantle, assuming they formed under

similar compositional conditions. Such high-pressure experiments are necessarily limited by their use of simple systems to approximate mantle conditions. For example, the spinel peridotite to garnet peridotite transition deepens by 5.5 to 6.5 Kbars when changing from Ca-Mg-Al-Si systems to Ca-Mg-Cr-Si systems (Klemme and ONeill, 2000; Klemme, 2004). Added to limitations from simplified compositional systems are inherent difficulties in high-pressure experiments such as achieving equilibrium and reversibility of reactions.

The applicability of these formulations are commonly tested in part by comparison to mineral compositions associated with phase changes, including the change from graphite-facies to diamond inclusion compositions for indicator minerals described earlier. Applicability is furthered tested by comparison with other existing thermobarometers.

Presented below are details of equilibrium phase determinations for temperature and pressure, because these methods are the foundations upon which the single grain methods are built, as discussed later. Understanding the equilibrium phase methods is important to understanding the limitations of the single grain methods. However, the reader more focused on the practical uses of single grain methods can skim quickly trough, or skip entirely, the following sections on temperature and pressure determination below, if they prefer.

Temperature

The most reliable mantle thermometers are based on the mutual solubility of Opx and Cpx because this relationship is relatively insensitive to changes in pressure or fO_2 (Smith, 1999). However, bulk compositional variability in Al, Cr, Na, Fe and Ti exert non-trivial compositional effects on Cpx-based thermometers (Brey et al., 1999; Taylor, 1998; Nimis and Taylor, 2000). Bulk compositional effects are possibly less important for diopside-in-Opx thermometers (Figure 6), suggesting that the simple Ca-in-Opx thermometer of Brey and Kohler (1990) could be applied to single enstatite xenocrysts at high (diamond associated) mantle temperatures. Smith (1999) suggests that Ca-in-Opx thermometry may form the basis for fairly accurate temperature determinations in low temperature (graphite-facies) peridotites. The requirement of Opx-Cpx coexistence limits pyroxene-based thermometers to lherzolitic and pyroxenitic bulk compositions.
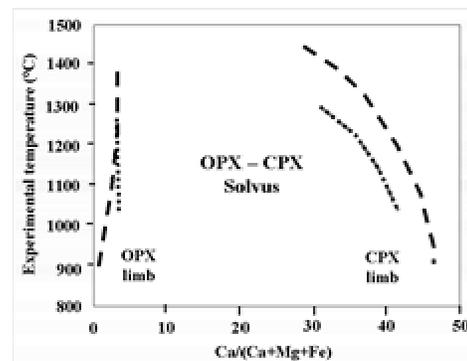

Figure 6: Divalent cation substitution in OPX varies little over a broad experimental temperature range, compared to CPX. After Taylor (1998) (heavy dashed lines) and Brey et al. (1990) (light dashed lines).

The Nimis and Taylor (2000) enstatite-in-CPX thermometer formulation (NT00) corrects for bulk compositional effects, reproduces calibration experiments in simple and complex bulk compositional systems to within +/- 30°C (1   ), satisfies the graphite-diamond phase change constraint, and should be preferred to simpler formulations as presented in Finnerty and Boyd (1984). NT00 is also readily applied to single diopside xenocrysts, as discussed later (Figure 7).

Iron-Mg exchange reactions in garnet (Grt) are applicable to thermometry for a broad range of mantle assemblages. The Fe-Mg exchange thermometer for Grt-Cpx is most useful for lherzolites, being twice as sensitive to temperature changes as the Grt-Ol, Grt-Opx or Opx-Cpx exchange reactions (Brey et al., 1990; Grütter, 2001). However, application of garnet-based Fe-Mg exchange thermometers to peridotite xenoliths suffers from a long list of ills. These include significant scatter of results in calibration experiments, unresolved apparent differences of fO_2 between various experimental calibrations and natural xenoliths, lack of correction for Cr or Ti effects, and partial re-equilibration of Fe and Mg along mineral rims during transient thermal events.
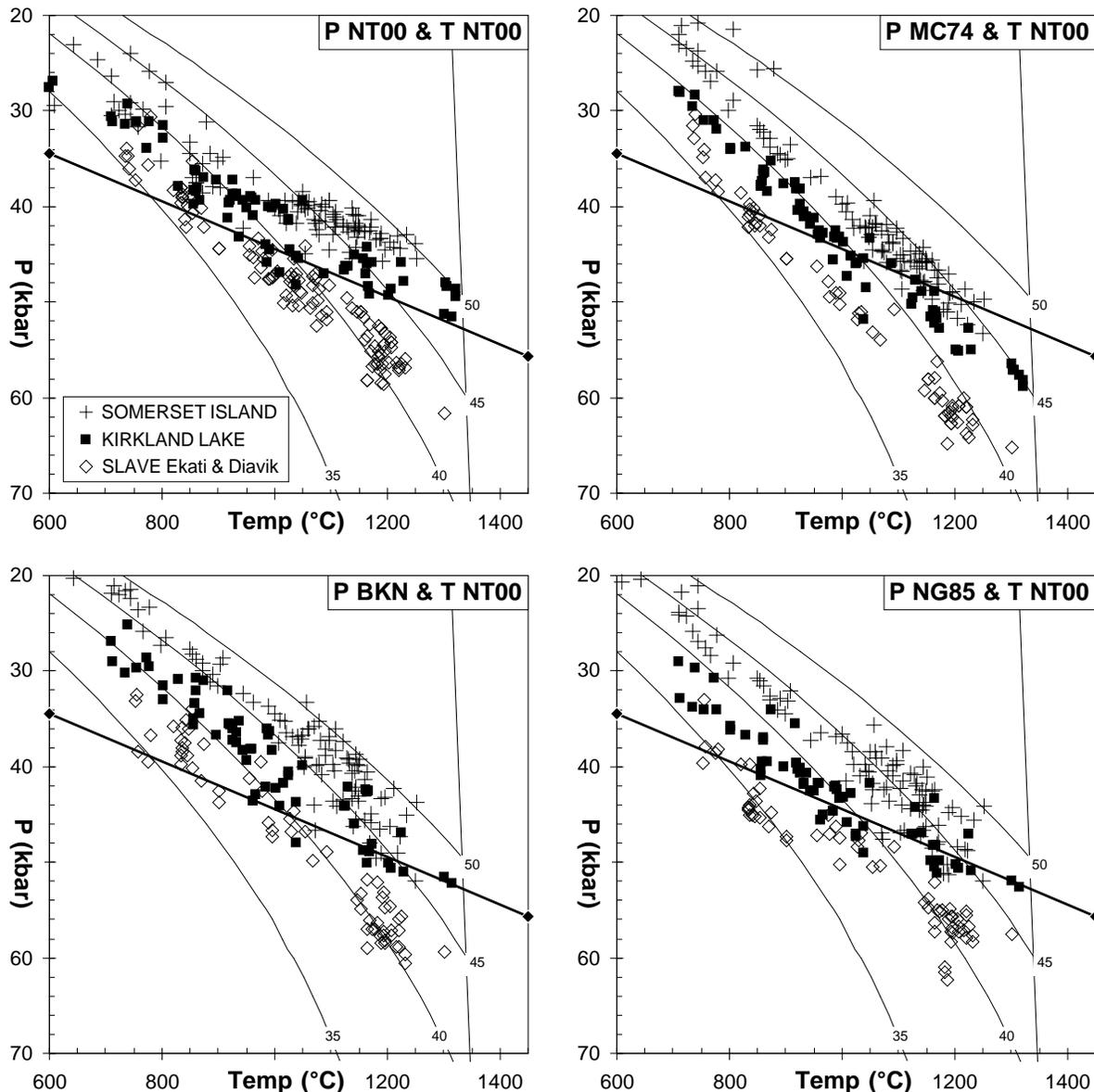

Figure 7: Comparison of P-T results for garnet lherzolite xenoliths from Canadian kimberlites in three geothermal settings. P and T calculated for four barometers (P NT00, P MC74, P BKN and P NG85) in combination with the clinopyroxene-solvus thermometer of Nimis and Taylor (2000, T NT00), as in Grütter and Moore (2003). The graphite/diamond transition is after Kennedy and Kennedy (1976) and conductive geotherms are after Pollack and Chapman (1977). Note specific application of the Nimis and Taylor (2000) method is discussed in more detail later under the heading of single grain methods.

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Taylor (1998) has tabulated relative precisions ranging from +/-45°C to +/- 65°C (1 sigma) for at least 7 common Fe-Mg exchange thermometer formulations as measured against experiments assuming in each case all Fe is ferrous. However, the accuracy of each formulation remains poorly constrained when applied to natural xenoliths. Comparisons to Cpx-based thermometers for xenoliths yield divergent results for different Fe-Mg thermometers, as well as significant scatter (e.g. Brey and Kolher, 1990; Canil and O'Neill, 1996; Smith, 1999).

Pressure

All commonly used mantle barometers represent slightly different formulations of the solubility of Al_2O_3 in orthopyroxene coexisting with garnet. P-T conditions for calibration experiments overlap those recorded in arguably equilibrated peridotite xenoliths over the temperature range 900-1100°C and where Opx in garnet lherzolite contains $Al_2O_3 > 0.9$ wt%. These conditions are recorded by 30 lherzolite xenoliths from the Kirkland Lake kimberlites (Meyer et al., 1994) and 17 xenoliths from kimberlite on Somerset Island (Kjarsgaard and Peterson, 1992). Application of four mutually consistent thermobarometers (as in Grütter and Moore, 2003) to these xenoliths illustrates the approach to equilibrium for mantle peridotite and the typical precision of current mantle thermobarometers.

All four combinations are consistent with each other at +/- one sigma in P or T. Nominal relative errors of +/- 11% in pressure and +/- 8% in temperature (1 sigma) are considered normal for peridotite "equilibrated" at about 40 kbar and 1000°C. It is also observed that P-T errors are strongly correlated: a +100°C error in T induces a +4 kbar shift in P, and vice versa. Since this error envelope occurs sub-parallel to conductive cratonic geotherms, the precision of current thermobarometers is probably best assessed by measurement relative to a geotherm, not relative to one another. A linear geotherm was accordingly fit to the P-T segments defined by the Kirkland Lake and Somerset Island xenoliths and the P-T scatter found relative to the geotherm is denoted by σT or σP in Table 1.

One-sigma precisions of +/-2.0 to 2.5 kbar and +/-50°C are hence derived and are largely independent of correlations amongst thermobarometer components. The values are quite similar to one-sigma fit statistics for calibration experiments (+/- 2.3 kbar and +/-15 to 30°C; Brey and Kohler, 1990; Nimis and Taylor, 2000), implying the precisions outlined in Table 1 are typical of the resolution to be expected for current thermobarometers. Their mutual concordance with calibration experiments also indicates that Ca, Mg, Fe, Al (and probably Cr and Ti) must be in diffusive equilibrium in coarse grained peridotites at about 1000°C. This latter inference is supported by the work of Smith and Wilson (1985), Smith and Barron (1991) and Smith and Boyd (1992) as well as Grütter and Sweeney (2000); diffusive equilibrium is a critical assumption in the single-grained techniques discussed below.

Accuracy of thermobarometry methods

Accuracy of thermobarometry is constrained by the diamond-graphite transition. Pearson et al (1994) demonstrated relative accuracy of common thermobarometers by showing that P-T conditions calculated for graphite-bearing peridotites are consistently lower than those of diamond-bearing perdidotites (Figure 8). Given the likely precision of P-T calculations, as discussed above, absolute accuracy is best shown by the thermomobarometric combinations shown in Fig 8A and Fig 8C, which are consistent with the diamond stability curve of Kennedy and Kennedy (1976). Discrepant formulations are shown in Fig 8B and 8D, where graphite xenoliths plot deep into the diamond stability field. In summary, it would appear that the thermobarometric techniques discussed above are consistent with the occurrence of graphite or diamond in xenoliths at P = 44 +/- 2.5 kbar and T = 1000° +/- 50°C (1).

Table 1: P-T precision of mantle thermobarometers (at 1σ), relative to a conductive geotherm, and compared to equilibrated experiments.

Thermobarometer Combination 1	Kirkland Lake (n=30)		Somerset Island (n=17)		Calibration experiments	
	σP (kbar)	σT (ºC)	σP (kbar)	σT (ºC)	σP (kbar)	σT (ºC)
PNT00 / TNT00	2	46	2.1	63	2.3	30
PBKN / TNT00	2.4	47	0.8	20	2.2	30
PNG85 / TNT00	1.8	43	0.9	22	3.0?	30
PMC74 / TNT00	1.2	21	0.8	15	3.0?	30
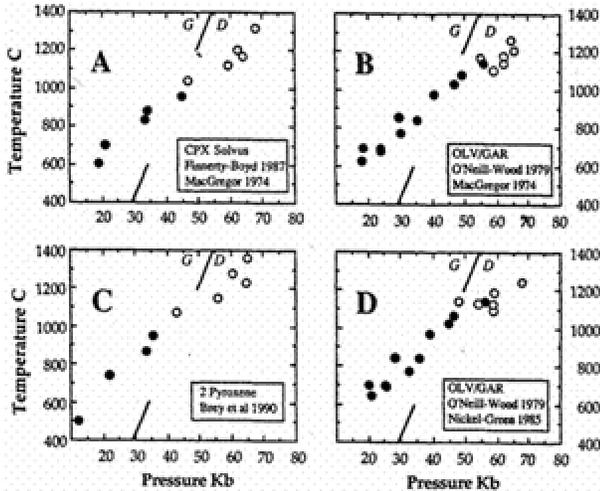
Figure 8: Temperature and pressure of equilibration for graphite-(solid circles) and diamond- (open circles) bearing peridotites calculated using a variety of thermobarometer combinations

SINGLE GRAIN THERMOBAROMETRIC METHODS

Single grain methods are increasingly important to mantle investigations because of their applicability to sediment sampling results.

The first of these methods widely applied was developed by Griffin et al. (1989) based on Ni and other trace element concentrations in Cr-pyrope. By assuming diffusive equilibrium in a mantle-wide compositional reservoir for certain elements, the 2 phase thermobarometric methods discussed above have been simplified for single grain application. Three single grain methods with broad applicability to diamond exploration are described below. Two of these methods work with Cr-pyropes, one focusing on the major elements Cr and Ca, and the other based on Ni and other trace elements. The third widely used single grain method uses chrome diopside.

Chromium-saturation arrays for PT determinations from Cr-pyropes

Determining pressure and temperatures of origin for Cr-pyropes requires only electron microprobe results for major elements, especially calcium and chromium. The oxides CaO and Cr_2O_3 are commonly plotted against each other because they record at least partially the substitution occurring in the divalent and trivalent sites, and because they typically have the most variability among major elements in Cr-pyropes. As noted earlier, the distinctive sub-calcic compositions typifying most Cr-pyrope diamond inclusions have long been the target of exploration programs. A simple method of applying thermobarometry to the entire suite of Cr-pyropes recovered in sediment samples (or kimberlite concentrates) enhances understanding of diamond potential and the mantle.

Deriving P-T information from CaO and Cr_2O_3 concentrations in Cr-pyropes was pioneered by Malinovsky and Doroshev (1975 and 1977), and refined during the 1990s by Grütter and colleagues at Anglo American Research Laboratories (Pty.).

The Cr-in-pyrope barometer is founded on the increase in Cr concentration with increasing pressure for both Cr-pyrope and chromite, in a spinel saturated mantle (Klemme, 2004). Assuming spinel saturation, a regular increase of approximately 0.01Cr/(Cr+Al) per kbar is predicted by laboratory experiments for conductive mantle geotherms relevant to diamond exploration (Girnis and Brey, 1999; Girnis et al., 2003). By explicitly selecting a particular conductive geotherm as applicable to the Cr-pyropes being examined, both a pressure and temperature can be derived (Figure 9). For most cratonic geotherms between 36 and 42 milliwatts per square meter (mW/m^2) the graphite-diamond stability field boundary should be crossed between Cr/(Cr+Al) values of 0.10 and 0.14, always assuming Cr-saturated mantle. Temperatures implied for these minimal Cr concentrations for entering the diamond stability field range from approximately 850°C to 1000°C for conductive geotherms spanning 36 to 42 mW/m^2, respectively.

Independent constraint for this Cr-Ca in Cr-pyrope diamond window is provided by the distribution of garnet compositions from diamond or graphite bearing spinel-garnet peridotite xenoliths (Fig 10). Because they carry spinel, these xenoliths are assumed to be Cr-saturated. Diamond-bearing spinel-garnet peridotites plot above the 'diamond- in-out' line in Figure 10, and graphite bearing spinel-garnet xenoliths plot below this line. Only one exception, from more than 30 diamond-bearing examples violates this empirical rule. (A-90a in Figure 10). Notably, diamond-bearing garnet peridotites lacking spinel are not constrained by the 'diamond in-out' line presumably due to a lack of Cr-saturation.
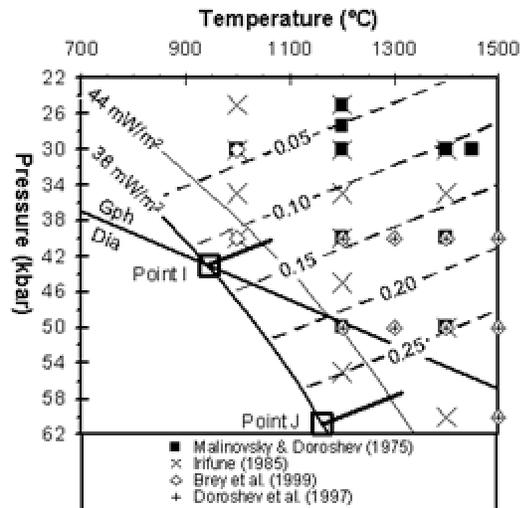

Figure 9: Isopleths of increasing Cr/Cr+Al with depth, in relation to the diamond stability field and model conductive geotherms (Pollack and Chapman, 1977).
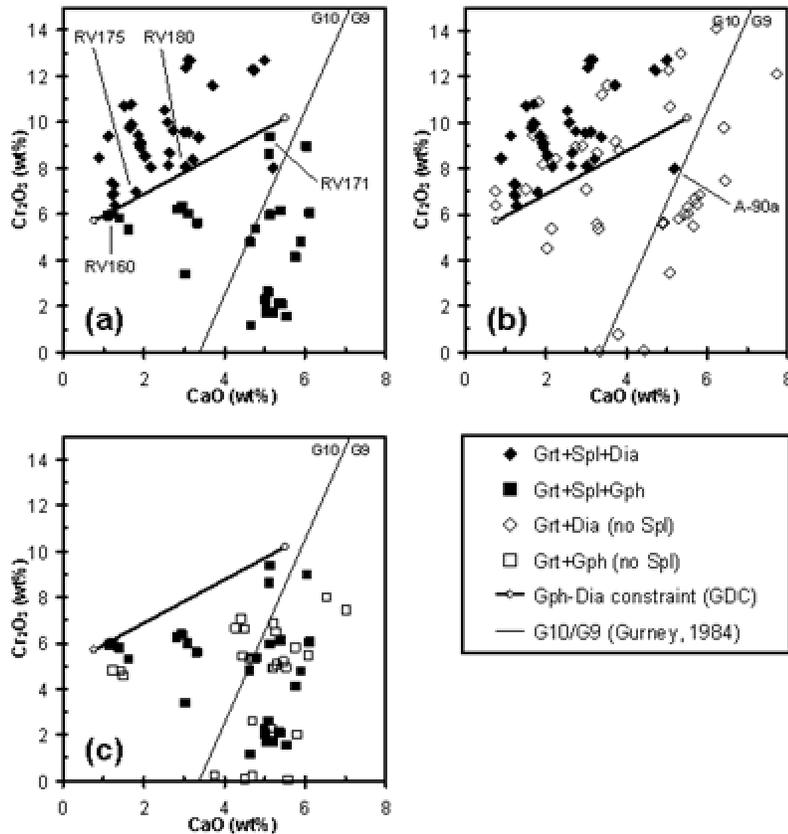
Figure 10: Pyropes from Cr-saturated (spinel-garnet) diamond bearing peridotites plot above the graphite-diamond constraint, and r-saturated graphite bearing peridotites occur below the line. Garnet peritite xenoliths with diamond but lacking chromite can occur above or below the line.

The entire dataset of such diamond-bearing peridotite xenoliths from the spinel-garnet facies is rather limited, both numerically, and in terms of geographical distribution. Some of the most significant samples are from the Roberts Victor kimberlite in South Africa (Viljoen, et al., 1994) where graphite in two xenoliths and diamond in two others effectively pin the position of the graphite-diamond constraint (GDC) line. These peridotites tightly constrain the diamond-graphite transition at Roberts Victor to T=941°C +/-50°C and P=42.9+/-1.3 kbar on the 38mW/m2 conductive geotherm deduced for the area (Grütter, et al, 2006). Although no evidence exists suggesting these data are not robust reflections of the mantle, some Roberts Victor peridotites carry zoned pyropes and veins of eclogite recording transient heating events (Viljoen, et al., 1994). Expansion of the dataset of diamond and graphite bearing xenoliths will further test the robustness of the GDC constraint.

The most Cr-rich sub-calcic garnets provide another constraint. For a large number of analyses, the most Cr-rich grains are assumed to be from Cr-saturated mantle. Empirically, these most Cr-rich grains form linear arrays parallel to the GDC line from some prolifically diamond-bearing kimberlites (Figure 11). For both the Venetia K1 and Udachnaya kimberlites, the maximum Cr limit projects to about 10% Cr2O3, which equates to Cr/(Cr+Al) of 0.28 or approximately 60 kbar on the 38mW/m^{2} geotherm from Figure 9. Numerous sub-calcic grains plot between the GDC and this maximum Cr limit, implying both pipes sampled a thick section of high-pressure mantle, consistent with their prolifically diamond-bearing character.

In contrast, the Finsch kimberlite sample projects to approximately 8% Cr_2O_3, suggesting that it may have sampled a less thick section of potentially diamond-bearing mantle down to approximately 50 kbars (Figure 12). By similar reasoning, the Koffiefontein kimberlite sampled an even thinner section of potentially diamond-bearing mantle, with the lower limit projected to 6% Cr_2O_3, or approximately 47 kbar on the 38 mW/m^{2} conductive geotherm (Figure 12). Each Cr-saturation array is very nearly parallel from the GDC to the highest pressures for which this thermobarometer is calibrated, such as encountered in Venetia K1 and Udachnaya.
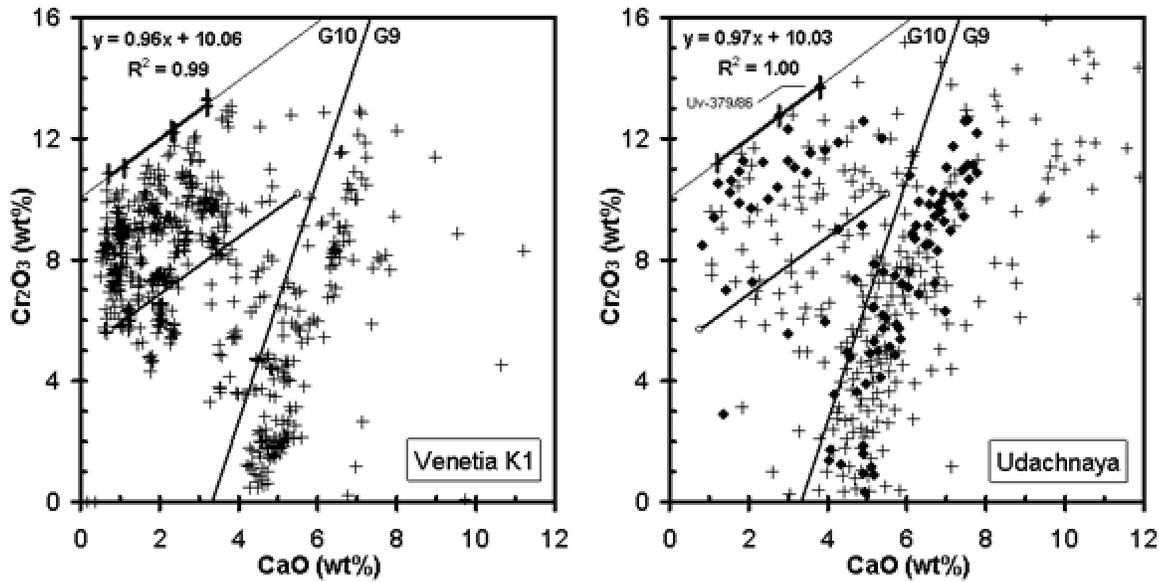
Figure 11: Garnet concentrates from prolific diamond mines in South Africa (Venetia) and Siberia (Udachnaya), showing the abundance of Cr-rich sub-calcic pyropes plotting above the graphite-diamond constraint line (data from Sobolev et al., 1973 and 1992). The parallel "Cr-saturation array" at higher Cr_2O_3 projects to about 10% for both kimberlites, equating to 60 kbars pressure and consistent with sampling a thick diamond-bearing section of mantle lithosphere.
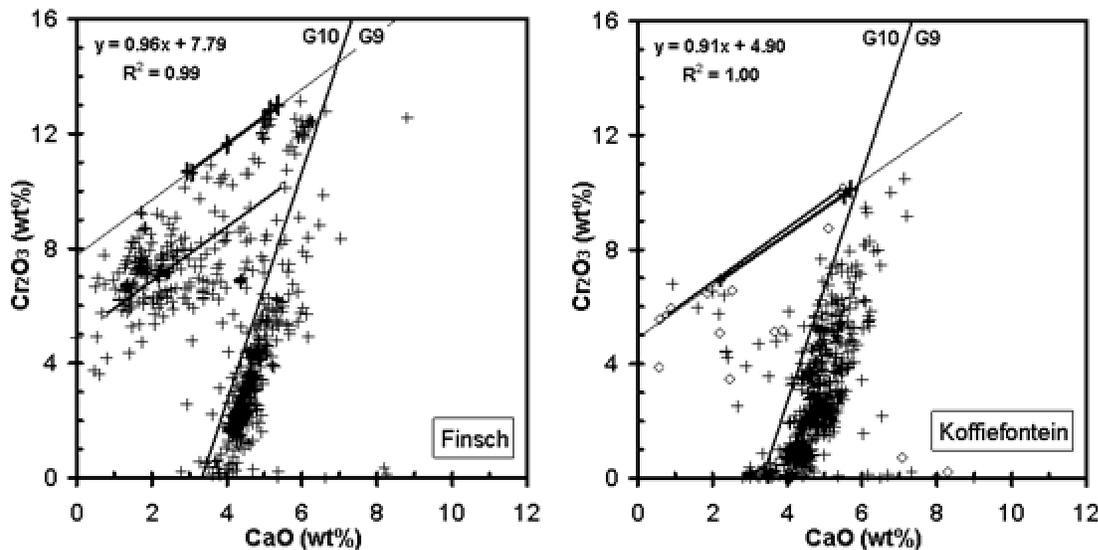

Figure 12: Garnet concentrate from Finsch and Koffiefontein kimberlites in South Africa. The upper Cr-saturation array for Finsch projects to 8% Cr_2O_3 consistent with sampling a mantle lithosphere section to 50 kbars, whereas Koffiefontein's upper Cr-saturation array suggests a much thinner diamond prospective lithosphere.

Extrapolating the parallelism between the empirical GDC and Cr-rich pyrope limits permits construction of Cr-saturation pressure arrays covering the harzburgite and lherzolite fields of the Cr-Ca plot (Figure 13). These arrays record the maximum pressure harzburgite or lherzolite sampled by any particular kimberlite if the analyses are sufficiently numerous to include Cr-saturated grains from all sampled depths and thus to be representative. By assuming representative sampling, and further assuming a reasonable conductive geotherm, these pressure arrays can be used to determine maximum temperature in addition to pressure for each mantle-derived peridotitic garnet suite. Concentrates lacking sufficient analyses can still be interpreted as providing minimum mantle sampling depth estimates. Depths shallower than the GDC are also empirically calibrated on sub-parallel arrays. In lower pressure regimes than the GDC, the Cr-saturation arrays become markedly more shallow, reflecting the decreased separation between spinel and spinel-garnet peridotite in curves from experimental data (Klemme, 2004). The arrays have been calibrated to as shallow as 20 kbar, based

on lherzolite xenoliths from Pali-Aike alkali basalts in Chile (Fig. 14).

Theses arrays formulate into:

If $Cr_2O_3 >$ or $= 0.94*CaO +5$, then $P38 = 26.9 + 3.22*Cr_2O_3 – 3.03*CaO$

<div align="center">or</div>

If $Cr_2O_3 < 0.94*CaO +5$, then $P38 = 9.2 + 36[(Cr_2O_3 + 1.6)/CaO + 7.02]$

Notes: P38 = Pressure for 38mW/m2 conductive geotherm; valid for harzburgite and lherzolite field pyropes.

For conductive geotherms hotter than 38 mW/m^2, calculated pressures need to be reduced. A simple correction for hotter geotherms has been formulated empirically (Grütter et al., 2004):

$$Pcg= 0.997*P38 – 0.3888*CG + 14.9$$

This works out to a small correction of roughly 0.5 kbar increase in pressure for a 1 milliwatt decrease in conductive geotherm.

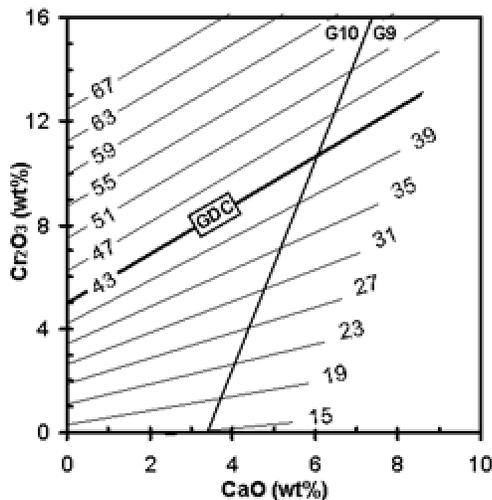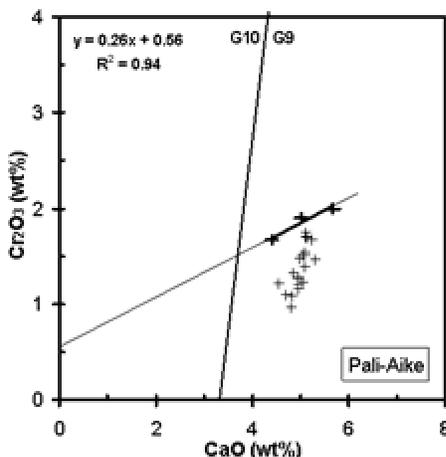**Figure 13:** Graphical projection of Cr-saturation arrays for Cr-pyrope concentrates.

Figure 14: Shallow calibration of Cr-saturation array based on Pali-Aike alkali basalts, southern Chile.

Single clinopyroxene thermobarometry

Thermobarometry of single chrome diopside grains (Taylor and Nimis, 1998; Nimis, 1998) derived from garnet peridotite (lherzolite) has been developed by Nimis and Taylor (2000) into a robust and independent technique to augment Cr-pyrope methods. Single grain chrome diopside thermobarometry employs a Cr-in-CPX barometer and an enstatite-in-CPX thermometer. Both the thermometer and barometer were calibrated with experiment between 850-1500°C and 0-60 kbar and satisfies important physical constraints such as the graphite-diamond transition (Nimis and Taylor, 2000).

The Cr-in-CPX barometer depends on Cr exchange between CPX and garnet. As reported by Nimis and Taylor (2000), temperature dependence is a relatively low 1.2 to 2.4°C/kbar which is weaker than widely used Al-in-OPX barometers (Brey and Kolher, 1990; Nimis, 2002). Furthermore, only Al, Cr, and Na in CPX need to be measured to determine pressure and the pressure determined is independent of co-existing garnet composition. The formulation has been tested against a variety of experimental clinopyroxenes representing fertile to refractory lherzolite (Nimis and Taylor, 2000).

The single grain CPX thermometer is based on the exchange of enstatite between CPX and OPX, simplified under the observation that in natural peridotitic rocks the activity of enstatite in OPX is near unity, and largely insensitive to temperature and compositional variation, permitting Nimis and Taylor (2000) to formulate a thermometer based on CPX composition alone. Their formulation includes empirical corrections for Fe, Ti, Al and Cr and reportedly reproduces experimental conditions to ± 30°C at the 1 level.

The single grain chrome diopside thermobarometer satisfies the graphite-diamond constraint. Application of the thermobarometer to a world-wide data-set separates graphite-bearing garnet-peridotite xenoliths above from diamond-bearing xenoliths and inclusions in diamond below, with only a small proportion of diamond-associated examples plotting slightly (<3 kbar) into the graphite stability field (Nimis and Taylor, 2000). The fit is remarkably robust given the wide variety of potential errors in such a world-wide data set, including analytical errors, possible re-equilibration or lack of complete equilibration, and potential occurrence of some Fe as Fe^{3+}. A similar consistency with the diamond-graphite constraint was demonstrated by calculating P and T for more than 100 chrome diopsides included in diamond inclusions (Nimis, 2002). This data set shows inclusion trapping pressures over a broad span up to 70 kbar, closely following expected conductive geotherms. Again, only a few analyses plot slightly above the graphite-diamond transition (Nimis, 2002).

Meaningful application of the method requires that all analyzed CPX grains are derived from garnet lherzolite because the barometer assumes equilibration with garnet and the thermometer assumes equilibration with orthopyroxene. Only clinopyroxenes with >0.5% Cr_2O_3 and <4.0% Al_2O_3 (<4.5 Al_2O_3 for Cr_2O_3> 2.25%) are selected as suitable "on-craton garnet peridotites" (Ramsay and Tompkins, 1994). Chrome diopsides with CaO >23%

are eliminated as being derived from a wehrlitic source and thus lacking orthopyroxene (Taylor et al., 1998). Furthermore, chrome diopside with high Tsermaks component (distinguished by Al+Cr-Na-K >0.05 for 6 oxygen formula) is eliminated from P-T calculations as likely to be derived from spinel peridotite (Read et al., 2004). However, realistic temperatures may be calculated for such spinel peridotite grains using an assumed constant pressure, due to the insensitivity of the thermometer to pressure (e.g. Read et al., 2004). Peridotitic chrome diopside from kimberlite also displays increasing Cr with Na, at approximately 1Cr:2Na ratio (e.g. data from Quirts, 2004), which provides a useful check of the selected data set.

Additionally, the effect of analytical errors must be minimized. Nimis and Taylor (2000) accept analyses where cation sums on both the T and M1+ M2 sites >1.990 for 6 oxygen basis, and reject analyses where:

$$Cr- 0.81(Cr/Cr+Al)*(Na+K) < 0.003.$$

The composition of chrome diopside overlaps widely from many different source rocks (Stephens and Dawson, 1977). Due to this broad compositional overlap, regionally specific steps may be required to remove all inappropriate chrome diopside grains before calculation of temperatures and pressures. For example, voluminous kamafugitic volcanism in central Minas Gerais, Brazil, yields phenocrystic or groundmass grains similar to basaltic clinopyroxene which should be eliminated (Read et al., 2004). Elsewhere, extremely Al-poor grains can be derived from low-P metasomatized peridotite, and thus may be eliminated or treated carefully (Figure 15 upper sloped line from Nimis 2002, lower sloped line includes most diamond inclusions).
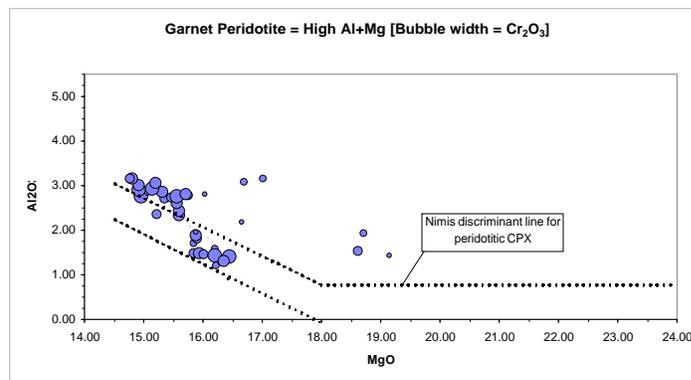

Figure 15: Discriminant diagram for excluding low Al chrome diopside beneath sloped line using example kimberlite data set (upper line adapted from Nimis, 2002; lower line suggested herein as more inclusive).

Nickel-in-Cr-pyrope thermobarometry and trace element analysis

Ni-in-Cr-pyrope Temperature (NiT)

High-precision trace element analyses of Cr-pyrope garnet started becoming available in the late 1980s using the proton microprobe. Pioneering work led by W. Griffin and colleagues noted important relations between temperature, mantle metasomatism and depletion (Griffin et al, 1989; Griffin et al., 1992). From this work, Griffin et al. (1989) developed a Ni-in-Cr-pyrope geothermometer, and refined their methods to semi-quantitatively estimate diamond potential (Griffin et al.,1992; Griffin and Ryan, 1995; and Ryan et al. 1996). Further refinements continued, including introduction of an experimentally calibrated Ni-in-Cr-pyrope thermometer (Canil, 1994), incorporation of Zn temperatures from chromite, and descriptions of mantle lithospheric stratigraphy through time. New technologies such as laser ablation ICP-MS and secondary ion mass spectrometry are being used more widely.

Under each of the three formulations, Ni content increases with mantle temperatures for garnet from peridotite xenoliths using equilibrium phase thermometry with which the first version of the Ni-in-cr-pyrope thermometer was calibrated. Nickel in olivine also increases with increasing Ni content of the reservoir, but Griffin et al (1989) make the important assumption that mantle olivine tends to have a nearly constant Ni content of approximately 3000 ppm. By assuming a constant Ni content in olivine, increase of Ni in garnet becomes directly related to increasing temperature formation by the formulation:

$$T, °C = \{1000/[-0.435 \log_{10}(Ni_{gnt}/30)+0.83]\} – 273$$

As a check of their new Ni-in-Cr-pyrope, Griffin et al. (1989b) analyzed >50 Cr-pyrope inclusions in diamond, with >90% of the calculated temperatures >1000°C, and only 5 grains yielding temperatures below 900°C. This suggests reasonable accuracy of the thermometer.

Canil (1994) produced an independent experimental calibration of the Ni-in-Cr-pyrope thermometer using high-pressure apparatus. The experiment used unnaturally high Ni concentrations (1.1% NiO in Cr-pyrope; 10.1% NiO in olivine) so that the results could be measured with an electron microprobe. Based on runs between 5 and 8 GPa and 1100°C to 1700°C, Canil (1994) confirmed a strong temperature dependence of Ni in Cr-pyrope and formulated:

$$T°K = -10210/[\ln(Ni \text{ in Garnet})/(Ni \text{ in Olivine})-3.59]$$

Canil's experimental formulation generally agrees with Griffiin et al. (1989) between 900 and 1100C. Compared to Griffin et al. (1989) , this experimental thermometer yields somewhat lower values at temperatures hotter than 1100°C, and higher values at temperatures cooler than 900° (Figure 16).

Ryan et al. (1996) re-equilibrated the original Ni-in-Cr-pyrope thermometer using an extended xenolith database as well as additional equilibrium phase thermometers to cover more rigorously sub-calcic pyropes and low temperature grains. This new xenolith based formulation assumes a constant mantle Ni content in peridotitic olivine of 2900 ±360 ppm:

$$TNi°C = \{1000/(1.506 – 0.19 \ln(Ni\ ppm) – 273$$

Temperatures are lowered by approximately 30°C at low temperatures (approaching Canil 1994), and elevated by about 85°C at high temperatures (diverging further from Canil 1994) compared to the original thermometer (Griffin et al., 1989; see Figure 16).

Metasomatism related trace elements Zr, Y, Ga and Ti

Mantle stratigraphy can be constrained by correlating these trace element signatures with Ni temperatures and Ca-Cr contents in the same garnets. In Siberia for example, Griffin et al. (1996) used concentrates from kimberlites to show that the temperature at the base of lithosphere is approximately 1150°C, based on of a sharp increase in Y-enriched garnets from higher temperatures. Essentially all the garnets with higher NiT (i.e. Ni > 70 ppm) also show elevated Zr and Ti supporting melt-related metasomatism suggestive of athenospheric origin (Griffin et al., 1996).

Pressure from Cr-pyrope – assuming equilibrium

Pressure of origin for Cr-pyrope can be deduced after determination of the NiT. Cr in pyropes increases with increasing pressure, if the pyrope is in equilibrium with chromite. For any suite of pyropes, the most Cr-rich grains at any given NiT are taken to be the highest pressure grains. The line connecting these most Cr-rich grains is termed Crmax, and its slope relates to the local geotherm. Of course, the accuracy of the Crmax is dependent on the garnet suite being sufficiently numerous to include at least a few in equilibrium with chromite throughout the recorded temperature range. However, comparison of each Cr-pyrope to a combination of experimental and empirical data sets allows assignment of pressure, if in equilibrium with chromite, or minimum pressure if not in equilibrium with chromite. Under these assumptions, the highest Cr-in-garnet pressure at any NiT defines the geotherm, but Grutter et al. (2006) have shown that this methodology underestimates the typical geotherm by 2mW/m2.

Similar single grain trace element methods were used to produce a Zn in chromite thermometer, which provides support for the NiT and is described below.

Zinc T in Chromite

Nickel T from Cr-pyropes in spinel-garnet peridotite xenoliths demonstrate an inverse relation between temperature and the Zn concentration in chromite (Griffin et al., 1994). This Zn thermometer (ZnT) is dependent on an assumed constant Zn reservoir in mantle olivine analogous to the Ni in olivine for Cr-pyrope. The original ZnT thermometer of Griffin et al. (1994) was re-formulated approximately 30°C lower (Ryan et al. 1996):

$$TZn\ (°C) = 1000 /(-0.904 + 0.264 \ln(Zn\ in\ ppm) – 273$$

As noted earlier, Zn concentrations in diamond inclusion chromites occur in the range of 200 to 750 ppm (Griffin et al. 1994, 1993; Lavrent'ev et al., 2005) which equates to a temperature range of 1750° to 910°C. These Zn concentration levels can be measured by electron microprobe, using extended count times (Lavrent'ev, et al. 2005). The lower temperature end of this range is consistent with the diamond-graphite constraint. The seemingly unrealistically high temperatures for the low Zn part of the diamond inclusion range may reflect either: (a) equilibration of chromite with olivine more enriched in Zn than assumed in the formulation; (b) limitations to the formulation for high temperatures; or (c) imprecision of measurements at low Zn concentrations, which might be expected to be most significant for electron microprobe analyses.
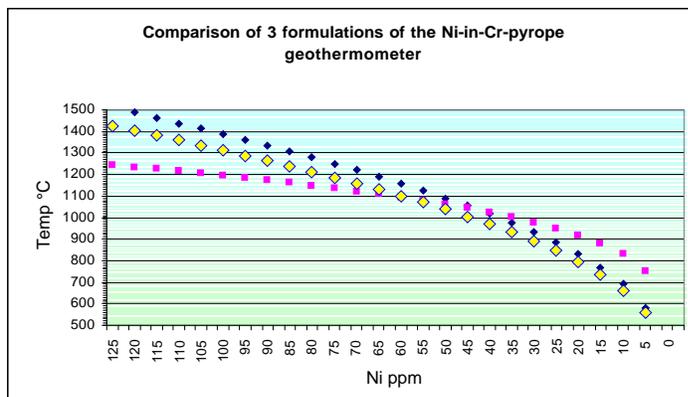

Figure 16: Comparison of different formulations of Ni-in-Cr-pyrope thermometer: Blue = Griffin et al., (1989); Yellow = Canil (1994) and Pink = Ryan et al., (1996). For Griffin et (1989) equilibrating olivine is assumed to be 3000 ppm Ni; for Canil (1994) and Ryan et al., (1996) olivine is assumed at constant 2900 ppm Ni

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Griffin and his co-workers combine NiT, ZnT, and trace element inferences regarding melt and hydrous metasomatism to produce semi-quantitative estimates of diamond potential for sediment or kimberlite concentrates. They define a diamond-window from the intersection of the local geotherm with the graphite-diamond phase boundary, to the base of the lithosphere (as determined by the NiT at which Y-enriched garnets increase in abundance). The local geotherm can be determined from Crmax, or xenolith studies. The proportion of Cr-pyropes from within the diamond-window compared to those from outside increases with diamond grade in most economic kimberlites, and thus is an empirical predictor of grade (Griffin and Ryan, 1995). This predicted grade is further refined by considering the average Zr value for diamond-window pyropes. The higher the Zr content, the more extensive the effects of melt metasomatism which may destroy diamonds in the lithosphere, and thus lowers the predicted grade (Griffin and Ryan, 1995).

Temperature defined by MnO

Manganese in Cr-pyrope provides another useful single grain thermometer (Grütter et al., 1999). Mn concentration in garnets from peridotite xenoliths demonstrates an inverse relation with temperature. As with Ni in pyrope and Zn in chromite, the Mn thermometer is dependent theoretically on a relatively constant Mn concentration in olivine as a stable reservoir. Measurements of olivine from a large sample of peridotites suggest a concentration of 0.104% MnO in olivine is representative of most mantle conditions (Grütter et al., 1999). Calibration by comparison to temperatures derived from equilibrium exchange thermometers gives a formulation (Grütter et al., 1999):

$$T_{Mn} (°C) = 1000/[0.268 + 0.374*ln(MnO\%_{garnet}/MnO\%_{olivine})] - 273$$

Grütter et al. (2004) suggest the graphite diamond phase boundary occurs at approximately 0.36% MnO (±0.1% at 1). This formulation classifies more than 80% of peridotitic diamond inclusions as satisfying the diamond graphite constraint, although there is a large associated error (Grütter et al. (2004). Moreover, many of the diamond inclusions that do not fit might be attributable to problems with the electron microprobe routine. Significant peak overlap causing over estimation of MnO at low concentrations can occur unless a LiF crystal is selected rather than a PET crystal (Grütter et al., 2004).

LITHOSPHERE MAPPING

Single grain thermobarometry combined with metasomatic trace element analyses form the basis of remarkably detailed descriptions of sub-continental lithospheric mantle. Mantle stratigraphic profiles are constructed by linking pressure temperature data to the rock type inferred for each pyrope, chrome diopside or chromite. Rock type is assigned based on major element classification of Cr-

pyropes into harzburgite or lherzolite, and pressure-temperature determination by Ni content. These profiles are enhanced by noting trace abundances of light rare earth elements Y, Ga, Ti and Zr in Cr-pyrope associated with melt or hydrous metasomatism, and can be traced through time based on variations in spatially associated kimberlites of different ages. The stratigraphic picture can be further enhanced by back calculating olivine forsterite content, whole rock Al2O3, and even deducing mantle seismic velocities from the thermobarometry data.

Remarkably, these methods can be applied to kimberlite concentrates, sediment samples, and potentially even grains derived from sedimentary strata. Kimberlites of course are located at a single point and thus give the best spatial resolution,. They also may carry mantle xenoliths, permitting direct comparison with multiphase equilibrium methods, and an emplacement age placing the mantle section in time as well as space. For these reasons most published mantle profiles are based on kimberlite concentrates. However, alluvial or till samples can provide detailed mantle information covering regional areas even before any kimberlites are located, and are commonly addressed within proprietary diamond exploration datasets.

Kaapvaal Craton

The Kaapvaal Craton provides a good example of the detailed subcontinental lithosphere mantle profiles that can be deduced from kimberlite concentrates (O'Reilly and Griffin, 2006). Using kimberlite concentrates from southwest Kaapvaal Craton, O'Reilly and Griffin (2006) define a subcontinental lithospheric mantle stratigraphy dominated by fertile lherzolite above (from 80 to 120 km depths) depleted and metasomatized peridotites below (Figure 17). Harzburgite and significant amounts of depleted lherzolite appear at 110 km, and extend to about 170 kms depth. Melt metasomatized peridotite dominates beneath 170 km as signaled by a sharp increase in Y- and Ti-enriched garnets. O'Reilly and Griffin (2006) use the loss of harzburgite and increase in Y- and Ti-enriched garnets to define a chemical lithosphere-athenosphere boundary (LAB) at roughly 170 km. Zr enriched garnets dominate from 110 to below the LAB at 170 km, suggesting a different and possibly more hydrous metasomatism type affected the lower lithosphere.

Olivine composition can be derived from Ni temperature of garnet by inversion of the olivine Fe-Mg exchange thermometer (Gaul et al., 2000). Assuming an appropriate geotherm, forsterite content of olivine from the Kaapvaal Craton remains between Mg# 92.0 to 93.5 to the LAB depth of roughly 170 km (O'Reilly and Griffin, 2006). Beneath the LAB, forsterite content drops rapidly to between Mg# 89.0 and 91.0 (O'Reilly and Griffin, 2006). Whole rock compositions can also be estimated from Cr-pyrope data. Concentrations of both Cr2O3 and Y show a robust relationship to Al2O3 in co-existing peridotite whole rock compositions (Griffin et al., 1999 and Griffin et al., 2002), and can record stratigraphic changes when assigned position in P/T space from Ni temperatures. For the Kaapvaal, there is a distinct rise in predicted whole rock Al2O3 based on correlation with both Cr2O3 and Y in garnet at the top of the LAB (O'Reilly and Griffin, 2006). The LAB is thus marked by more depleted rocks above and more fertile rocks below. The more depleted rocks,
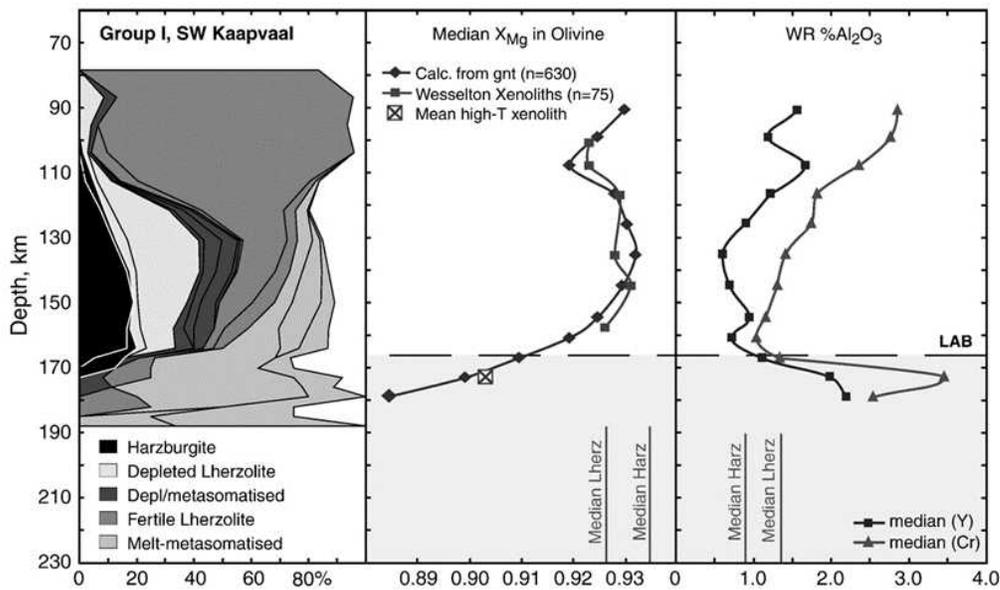
Figure 17: Subcontinental lithospheric mantle and the Lithospere-Athenosphere Boundary beneath the SW Kaapvaal Craton.

comprised of harzburgites and depleted lherzolites, are characterized by Mg-rich forsterite and Al-poor whole rock compositions. The more fertile rocks below comprise less Mg-rich olivine and Al-rich peridotite, with the LAB boundary interpreted as the chemical and mineralogical boundary between the lithosphere and the convecting athenosphere below (O'Reilly and Griffin, 2006).

Kaapvaal Craton

Similar methods applied to kimberlite concentrates of the Lac de Gras region of the Slave Craton in northern Canada

define a LAB at about 200 km depth, but with a very different distribution of rocks types above (O'Reilly and Griffin, 2006). Based on the work of Griffin and co-workers harzburgite and depleted lherzolite extend from roughly 90 km to 150 km defining a shallow ultradepleted layer (O'Reilly and Griffin, 2006). Fertile lherzolite dominates the lithosphere below the ultradepleted layer to the inferred LAB Figure 18). Unfortunately, few garnets have been recovered from below 200 km, leaving the athenosphere beneath the central Slave Craton poorly defined (O'Reilly and Griffin, 2006).
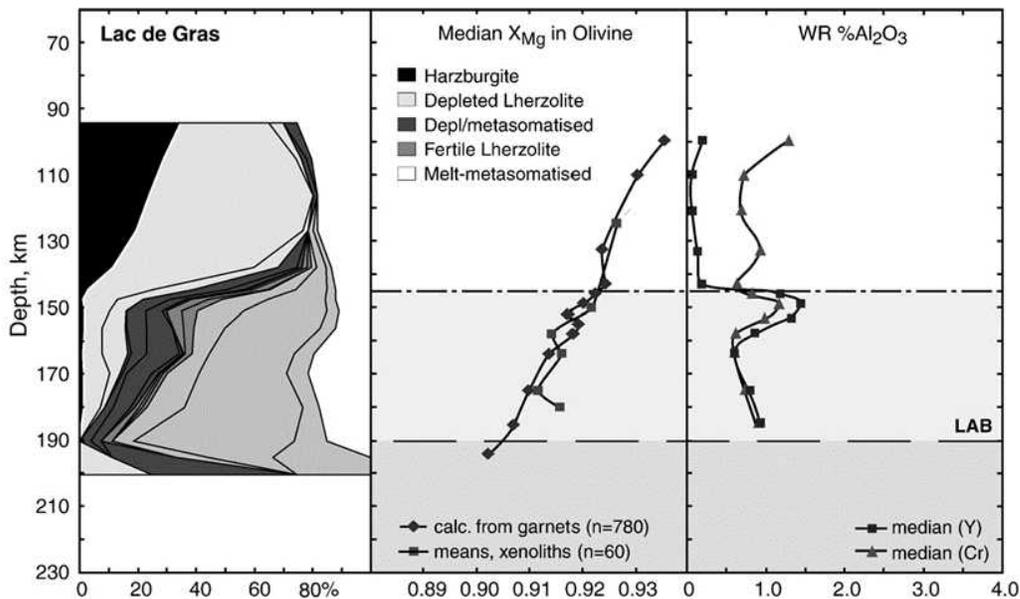

Figure 18: Subcontinental lithospheric mantle and LAB beneath the Lac de Gras region of the Slave Craton.

Regional mapping of the subcontinental lithosphere demonstrates the potential of using sediment samples where kimberlite concentrates may be lacking (Griffin et al, 2004). Griffin and his co-workers used nearly 6000 garnets from more than 85 kimberlites to map the subcontinental lithosphere beneath North America (Griffin et al., 2004). Composition of till samples from the northern Slave Craton closely match that of nearby kimberlites including the Jericho (Kopylova et al., 1999) and Tenacity pipes, showing the potential of extending mapping beyond the limits of sampled pipes. For the Jericho Kimberlite, a dearth of harzburgite is noted from a rarity of sub-calcic garnets. Also, Y- and Zr- depleted garnets dominate the concentrate population at Ni concentrations below about 35 ppm (900C using the 1996 Ni temperature formulation), with Y-, Zr- and Ti-enriched garnets associated with higher NiT (Griffin et al., 2004). These data point to a more fertile lithosphere beneath Jericho than in the Lac de Gras region of the Slave Craton. Further north, garnets from till samples down-ice of the Tenacity Kimberlite again closely reflect the kimberlite populations, and contain harzburgitic (sub-calcic) Cr-pyropes that become increasingly abundant with depth (Griffin et al., 2004).

Concluding Remarks: Wider applicability of concepts?

A coherent methodology for describing the sub-continental lithospheric mantle has developed from geochemical methodologies originally designed for diamond exploration. These methods started with the recognition of unique garnet and chromite compositions that occur in diamond inclusions, subsequently incorporating equilibrium phase P/T formulations and most recently developing from those foundations the single grain geothermometers and barometers increasingly used today. Investigators are continuing to try new ideas. For example, Matveev and Stachel (2007) has recently used micro-Fourier transform Infrared-Spectroscopy (micro-FTIR) to show distinct water contents in in olivines from the mantle, possibly a harbinger of further advances in characterizing mantle phases. A further broad spectrum of methods quite beyond the scope of this review (including micro-FTIR) is also applied to diamonds themselves, whether from sediment samples, or kimberlite concentrates. Additionally, radiometric age dating of individual grains offers the possibility of further describing mantle history, as well as helping to hone in on new kimberlite discoveries. Included in the age dating methods are single zircons (as exploited in many settings) and, more recently, phlogopite from kelyphitic rims on Cr-pyrope garnets.

The continued striving for new, more detailed methods to characterize individual grains associated with the diamond stability field reflects both the value of economic diamond deposits and the rarity of minerals from such deep upper mantle at the surface. The rarity of such minerals motivates extracting from them the most information possible.

The authors hope that this review, incomplete as it necessarily is, will help broaden application of analogous geochemical methods in other realms. When pushed to the limits of modern measuring technology, rare grains can yield remarkably detailed information.

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