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LA-ICP-MS analysis of garnet: Trace-element characterization and single-mineral thermometry applied to diamond exploration.

Par

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SUMMARY

Indicator mineral studies are commonly used in diamond exploration to help locate and characterize kimberlite and other potential diamond-bearing source rocks. Garnet is one such indicator mineral. Garnet is a common metamorphic mineral in the crust and occurs throughout the mantle lithosphere. It is stable over a wide range of pressure and temperature conditions and the major-element chemistry of garnet is widely used to model pressures and temperatures recorded during geological events. Analytical techniques such as laser-ablation linked to an inductively coupled plasma mass spectrometer (LA-ICP-MS) have been developed over the past decade which allow fast, accurate and cost effective trace-element analysis of minerals. Trace-element concentrations in minerals, and garnet in particular, commonly vary by several orders of magnitude, from a few 100 parts per million (g/g), to a few parts per billion (ng/g). Trace-element patterns in mantle-derived garnets can be used to examine the evolution of mantle sources and may preserve a record of pressures and temperatures recorded during and after mineral formation. The most diamond-rich kimberlites tend to have depleted mantle sources, located beneath ancient cratons, where lower than normal geothermal gradients are prevalent. Therefore, the temperatures recorded by mantle garnets which may have come from these sources can used to help locate more diamondiferous deposits. The element Nickel (Ni), which substitutes into garnet, is particularly sensitive to variations in temperature. The major reservoir for Ni in the mantle is the mineral olivine and the variation in Ni-content within mantle olivine is very small (~3100-2700 ppm). Thus, the Ni-content of mantle garnet which has equilibrated with olivine in the mantle can be measured and used as a single-mineral thermometer. LA-ICP-MS is well suited to measuring Ni-contents in mantle garnets (10-150 ppm) which are typically below the detection limits of other methods and the measurement of Ni-contents can be performed at the same time as a full suite of other trace-elements (Ti, Zn, Ga, Y, Zr, rare-earth elements (REE), Hf, etc.) to provide a rapid and comprehensive examination of indicator garnets. A suite of G9 and G10 indicator garnets from the Notre Dame du Nord kimberlite complex, north of Lake Timisskiming, Québec, Canada have been characterized by LA-ICP-MS. The REE-patterns are consistent with depleted mantle sources, including a major, deep lherzolite and possible harzburgite sources. The Cr-contents along with the temperatures recorded by the garnet suite, using the Ni-in-garnet thermometer, suggest a high to normal geothermal gradient. It is likely therefore that the Notre Dame du Nord pipes have sampled only a limited segment of diamond-bearing mantle source rocks. The LA-ICP-MS technique is a cost effective tool for trace-element analysis of indicator garnet suites and can be used in conjunction with other techniques to provide important information, which in turn will help locate and characterize the diamond potential of future exploration targets.

1. INTRODUCTION

The diamond potential of Quebec has recently been recognized and this has led to an increase in exploration for potential diamond sources. The locations of possible diamond bearing rock-types can be traced by delineating indicator mineral occurrences, e.g. Cr and Mg-rich silicates (garnet and pyroxene) and oxides (spinel and illmenite). Of the commonly studied indicator minerals, garnet has the greatest potential to provide single-mineral temperature estimates and a record of source evolution and thermal history based on trace-element (principally REE) concentrations. The trace-element information can be used to better constrain source-rock history and prioritize exploration targets with the highest diamond potential.

This project is designed to develop and test a rapid, multi-element method for trace-element characterization of garnet using the recently established LA-ICP-MS facility at UQAC. Trace-element contents from a well characterized garnet reference material (PN2) and from garnet indicator separates were analysed in order to assess the method and provide a platform for future studies.

1.1 Objectives

The objective of this study was to test the LA-ICP-MS method using reference materials and carry out a study of trace-element variations in indicator garnets from various diamond exploration targets in Québec. It was hoped that we would be able to study at least one diamond-bearing kimberlite; however, due to a lack of access to such samples this was not possible. Instead the study focuses on a simple calibration procedure for the LA-ICP-MS technique and a detailed study of a garnet indicator suite from the Notre Dame du Nord kimberlites.

1.2 Geological outline

Kimberlite intrusions and other potential diamond-bearing rock-types (lamproite, ailikite) have been documented in eastern Ontario, Quebec, and Labrador and a number of these have proven to be diamond bearing. Diamonds form at minimum pressures in excess of 25 kbar, which corresponds to depths of around 90 km (Fig. 1). The temperature recorded in the Earth's interior increases with depth and the rate of increase is called a geothermal gradient. The diamond/graphite transition, is the line in pressure/temperature space where graphite is replaced by diamond. Following typical geothermal gradients this line is crossed at 1200 ^{o}C and 45 kbar,

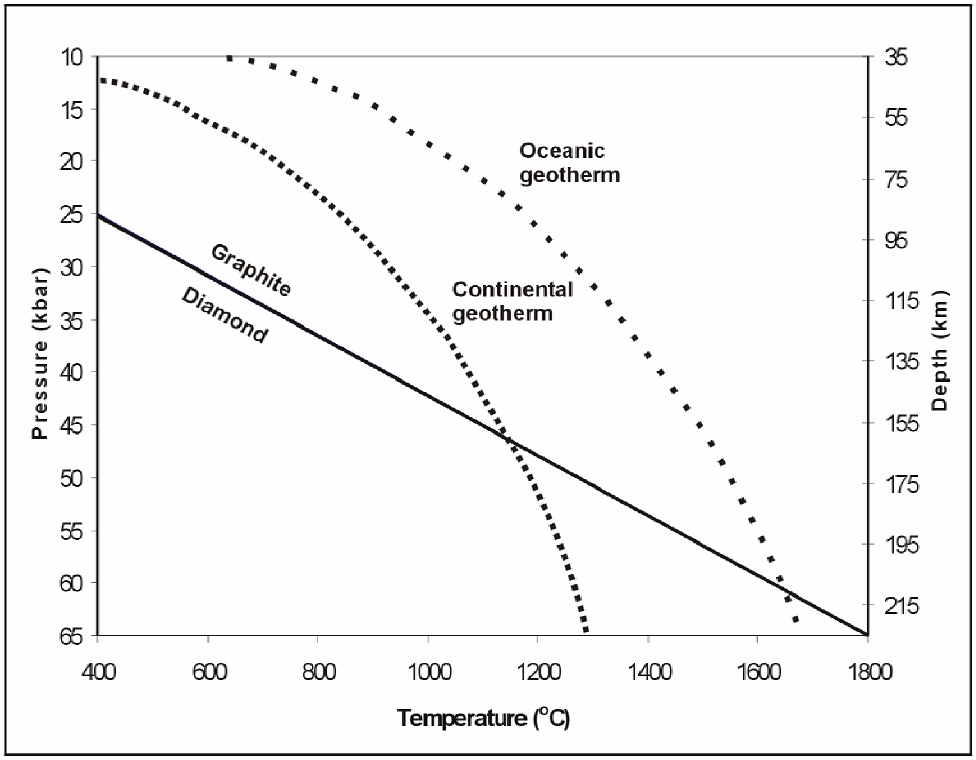

Fig 1. Typical geotherms below continental crust and oceanic crust along with the diamond/graphite stability field. Rocks lying in a tectonic regime with low heat flow (to the right of the continental geotherm) would lie within the diamond stability field at shallower levels.

(160 km) below continental lithosphere, and 1700 ^{o}C and 60 kbar (210 km) below oceanic lithosphere (Fig. 1).

The most favorable conditions for diamond formation/preservation are in regions of low heat flow where the geothermal gradient is low. Areas of lower than average heat flow occur in two tectonic regimes, namely, steep subduction zones where dense, cold, oceanic crust is thrust below orogenic (mountain) chains and, below stable shield areas where the cold, thick continental crust compresses the underlying lithospheric mantle. In both cases the geothermal gardients are deflected downwards to create colder temperature gradients. Kimberlite and other intrusions with very deep magma sources sample material from the underlying rock compositions on their way to the surface (Fig. 2). In Fig. 2, the ascending magma shown in red will travel through a diamond “window” and will sample mantle minerals which record a 900-1200 ^{o}C temperature range. The kimberlite to the right shown in blue will sample indicator minerals with a mantle composition but which will record much higher temperatures, indicating that the magma sampled less, or no material from the diamond stability window. By reconstructing the temperatures recorded by minerals sampled by the ascending kimberlite magma, it is possible to determine the range of temperatures recorded in the segment of the mantle lithosphere through which the intrusion traveled. This information can be used to determine whether the material sampled by the rising intrusion lay within the diamond stability window and therefore can be used to constrain the diamond potential of each intrusion.

1.3 Garnet chemistry and diamond potential

The chemistry of various minerals including Mg-Cr garnet is commonly used to characterize the diamond potential of a particular intrusion. The exchange of trace-quantities of Ni from olivine, the main mantle source of Ni, into the garnet structure is temperature dependant. The T-range over which Ni substitution from olivine into garnet occurs has been both experimentally and empirically determined (Ryan et al. 1996, Canil 1999). Olivine in the mantle has a very restricted range of Ni-contents (~3100-3700 ppm) and therefore the variation in the Ni-content of

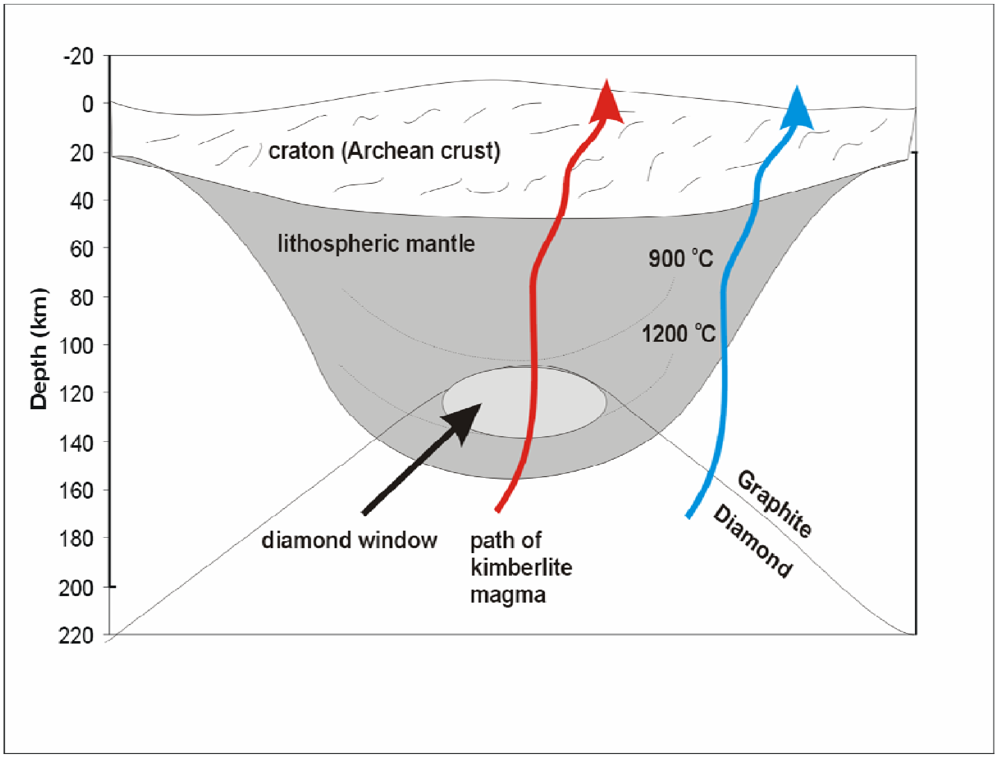

Fig 2. The diamond stability window in the mantle lithosphere produced by the downward deflection of continental geothermal gradients. The path of a kimberlite magma travelling through this window (red) will sample diamonds and diamond indicators from this window as well as units above and below this level on its way to the surface.

garnet can be used alone to determine the temperature at which it equilibrated with olivine in the mantle. In other words the Ni-content of garnet can be used as a single mineral thermometer. The T recorded by the garnet can then be used to determine whether it lay within the diamond window (900-1200 ^{o}C). If it did then the ascending magma will be significantly more likely to have sampled material from this window and therefore be diamond-bearing.

The rare-earth elements (REE) comprise fourteen elements (La-Lu) and are widely used in by geologists to understand magmatic and metamorphic processes. Garnet has a high affinity for the heavy REE (Dy-Lu) and indeed, is regarded as the major reservoir for heavy REE in the lithospheric mantle. Garnet which has grown and resided in the mantle for long periods should have either steep or flat, heavy REE enriched patterns (e.g. Burgess and Harte 2004). If such crystals are undisturbed in the mantle and exhumed quickly, they will preserve this REE pattern. Exhumation of mantle xenocrysts, through a rapidly ascending magma, will greatly enhance the preservation of the sampled material which of course includes diamonds. Garnet crystals which have been partially re-equilibrated by ancient geological events or by slower exhumation will show disrupted REE patterns. Mantle garnet crystals will commonly display sinuous REE patterns if they have been derived from ancient depleted mantle sources (e.g. Stachel et al 1998). By combining the heavy REE data with temperatures recorded using Ni-in-garnet thermometry the range of mantle sources sample by the ascending magma can be better characterized. This information will in turn maximize the understanding of diamond potential for each exploration target.

2. METHODOLOGY

2.1 Samples

A small segment of the garnet reference material, known as PN2, was obtained from Dr. Dante Canil (University of Victoria). The piece comes from a very large single garnet megacryst which has been analyzed by various methods including electron microprobe, ion-microprobe and neutron activation. The PN2 garnet is known to show a restricted but nonetheless significant variation in trace-element concentrations. However, the general shape of the REE pattern is known to be small and invariant and in general other trace-elements are homogenous at the 5-25% level (Canil et al. 2003). Comparing the results of LA-ICP-MS analysis using the UQAC system and the reported values will help validate the results of the LA-ICP-MS analysis for every analytical session. Heavy-mineral separates from the Notre Dame Kimberlite pipes were supplied by Rejean Girard of IOS Geoscientifiques Inc. Mr. Girard's also supplied the results of a electron microprobe analysis which was in part used to calibrate the LA-ICP-MS using the measured Ca-contents in the garnets, and also to compare the results for elements determined by both electron microprobe and LA-ICP-MS (e.g. Cr, Ti). However, as the electron microprobe results are part of a confidential report supplied to a current client of IOS Geoscientifiques Inc. the data is not reproduced in this report.

2.2 Analytical Methods

The UQAC LA-ICP-MS is comprised of a Thermo X7 quadrupole ICP-MS attached to a New Wave Research 213 nm Nd:YAG UV laser probe. Typical detection limits for elements above mass 70 AMU are 1-10 ppb. As the ICP-MS interface is equipped with a Ni cone and Ni skimmer, gas blanks for elemental Ni are high, typically in the 0.5-1 ppm range. The average (3σ) detection limit measured over the course of this study is 4.57 ppm for Ni. The typical range for Ni in mantle garnets is 10-180 ppm and is therefore well above the average detection limit. On the other hand, at this concentration range it is impractical for electron microprobe measurements to be made as extremely long count times would be required and many samples would be below the typical detection limit for the instrument. All LA-ICP-MS were performed with a 40 µm spot size and data was collected by peak jumping with a 10 msec dwell time for each isotopes. Each run consisted of a 30 sec gas blank measurement and a 60 sec laser ablation analysis. Ablation was performed using helium as the carrier gas. Data was reduced after integrating the entire signal and normalizing to the internal standard value. The concentrations were calculated using NIST 610 and NIST 612 reference materials. The results for measurement of the PN2 reference material (Ni and the REE) are listed in

Table 1. Ni and REE contents (in ppm) for the PN2 reference material carried out over 3 separate analytical sessions and in three different segments of the garnet fragment.

								PN2 garnet							
Analysis #	**Ni**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
pn2-1	52.6	0.02	0.149	0.062	0.704	0.852	0.546	2.506	0.622	5.855	1.415	4.427	0.646	4.517	0.603
pn2-2	55.35	0.028	0.162	0.063	0.724	0.923	0.562	2.419	0.637	5.833	1.4	4.471	0.653	4.613	0.605
pn2-3	49.64	0.018	0.184	0.062	0.76	0.929	0.616	2.628	0.685	6.273	1.516	4.727	0.696	5.055	0.662
pn2-4	61.03	0.021	0.174	0.066	0.777	0.958	0.601	2.595	0.675	6.26	1.481	4.69	0.697	4.97	0.643
pn2-5	62.43	0.022	0.179	0.069	0.745	0.91	0.594	2.603	0.676	6.245	1.505	4.721	0.689	4.901	0.643
pn2-6	71.3	0.019	0.188	0.069	0.813	0.953	0.649	2.734	0.726	6.595	1.607	5.035	0.737	5.23	0.693
pn2-2-1	37.24	0.011	0.186	0.069	0.944	1.116	0.744	3.039	0.829	7.219	1.78	5.427	0.784	5.595	0.768
pn2-2-2	40.93	0.018	0.189	0.071	0.903	1.166	0.741	3.116	0.857	7.438	1.821	5.548	0.789	5.785	0.786
pn2-2-3	52.17	0.022	0.172	0.068	0.954	1.239	0.766	3.449	0.927	8.115	2.03	6.18	0.909	6.351	0.87
pn2-2-4	57.7	0.025	0.186	0.068	0.959	1.278	0.777	3.491	0.945	8.3	2.095	6.212	0.892	6.391	0.886
pn2-2-5	50.83	0.018	0.199	0.078	1.019	1.229	0.783	3.308	0.905	8.021	1.953	5.966	0.863	6.267	0.84
pn2-2-6	55.27	0.019	0.195	0.08	0.995	1.299	0.796	3.478	0.939	8.201	2.025	6.174	0.886	6.407	0.871
pn2-LS-1	52.49	0.079	0.156	0.065	0.771	0.859	0.586	2.686	0.761	6.639	1.513	5.149	0.746	4.828	0.748
pn2-LS-2	45.06	0.058	0.227	0.062	0.789	0.887	0.606	2.684	0.764	6.758	1.515	5.155	0.742	4.831	0.762
pn2-LS-3	42.12	0.044	0.163	0.066	0.815	0.882	0.591	2.799	0.778	6.839	1.563	5.248	0.752	4.933	0.777
pn2-LS-4	40.55	0.044	0.153	0.072	0.833	0.949	0.592	2.699	0.773	6.795	1.593	5.37	0.769	4.948	0.778
pn2-LS-5	34.79	0.062	0.205	0.066	0.853	0.927	0.642	2.907	0.787	7.082	1.626	5.524	0.801	5.129	0.803
pn2-LS-6	34.89	0.036	0.164	0.067	0.799	0.897	0.614	2.646	0.752	6.702	1.541	5.174	0.743	4.884	0.755
Mean of Measured	**49.80**	**0.03**	**0.18**	**0.07**	**0.84**	**1.01**	**0.66**	**2.88**	**0.78**	**6.95**	**1.67**	**5.29**	**0.77**	**5.31**	**0.75**
SD	**10.13**	**0.02**	**0.02**	**0.01**	**0.10**	**0.16**	**0.09**	**0.35**	**0.10**	**0.78**	**0.23**	**0.57**	**0.08**	**0.65**	**0.09**
PN2	*47.5*	*0.025*	*0.2*	*0.085*	*1.225*	*1.315*	*0.82*	*3.83*	*1.055*	*9.53*	*2.285*	*7.31*	*0.905*	*6.64*	*1.035*

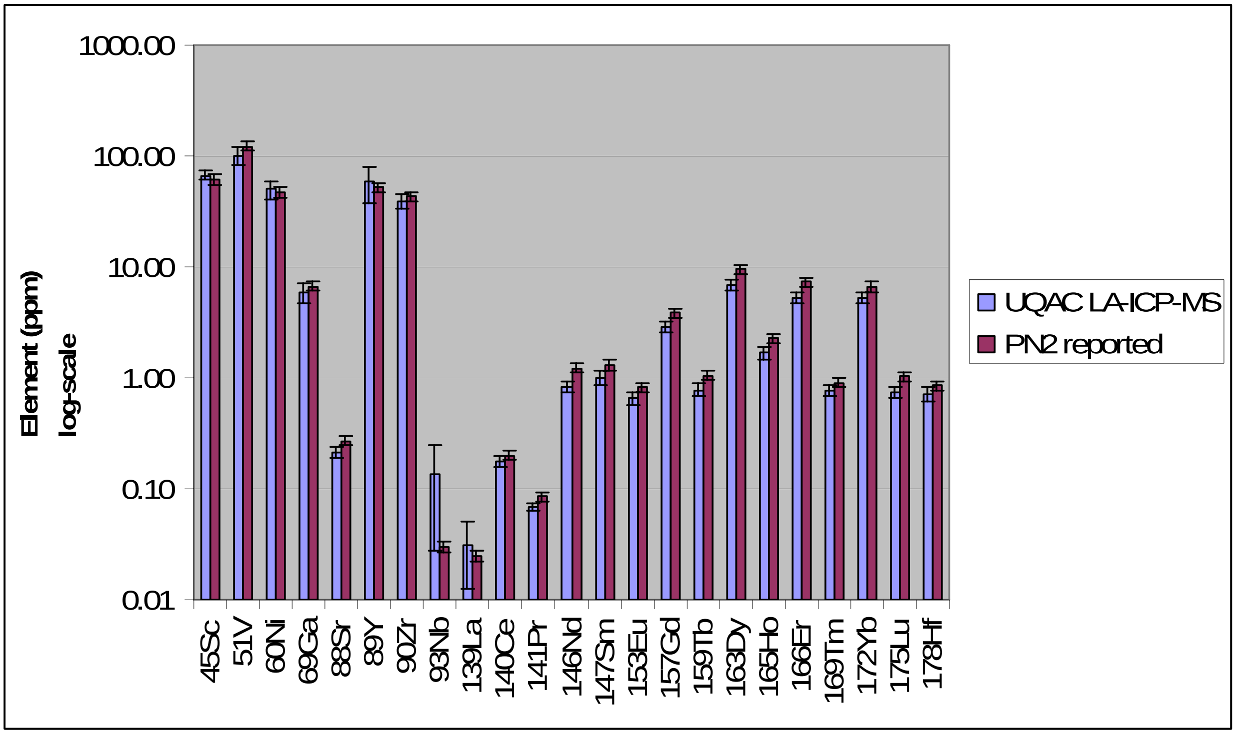

Fig 3. Comparison of reported concentration for PN2 garnet reference material with UQAC LA-ICP-MS results for 23 trace-elements. Ca was used as the internal standard. The error bars are shown at 1 SD.

Table 1. An additional 12 elements (Sc, Ti, V, Cr, Zn, Ga, Sr, Y, Zr, Nb, Hf and Ta) along with Ca, used as an internal standard, were also routinely measured. Of these Sc, Ga, Sr, Y, Zr and Hf are reported for the PN2 reference material and the results of the UQAC LA-ICP-MS measurements are shown in Fig. 3.

The UQAC LA-ICP-MS results illustrated in Table 1 and Fig. 3. show reasonable agreement with the reported values for the PN2 garnet. However, it is clear that in general the REE values reported in Canil et al. 2003 are 10-20% higher than the results obtained in this study, although the shape for the REE patterns obtained are identical. A regression through the UQAC data and the reported PN2 values produces a correlation coefficient of >95%. The variations observed in the UQAC LA-ICP-MS data are also significantly greater than observed for the NIST reference glasses analyzed during the same analytical session. It is therefore assumed that the values for the PN2 chip analyzed in this study are accurate and that there is indeed variation in trace-element concentrations and in general the REE in our chip are slightly lower than average. Encouragingly, the calculated and reported Ni values are identical within error, suggesting the calibration method using Ca as an internal standard is reasonably accurate for Ni and other trace-elements as well as the REE. In summary, The LA-ICP-MS method used in this study can determine 28 trace-elements for each indicator garnet in a 100 sec analysis.

3. NOTRE DAME DU NORD KIMBERLITES

The Cr and REE contents for a representative suite of LA-ICP-MS analysis (N = 68) of indicator garnets from the Notre Dame du Nord kimberlite pipes are shown in Tab. 2. The data were collected using the same method as for the PN2 garnet as described above. The Ni contents along with the calculated temperatures are 1 SD errors are also shown. The Ni-in-garnet temperatures were calculated using the method Ryan et al. (1996), where:

$$\text{Temperature } ^{o}\text{C (Ni-in-garnet)} = 1000 / (1.506 - 0.189 \times \ln(\text{Measured Ni content (ppm)})) - 273$$

The results in Tab 2 are arranged in order from the highest to the lowest recorded temperatures.

Tab 2. Representative Cr, REE and Ni contents (in ppm) for indicator garnets from the Notre Dame du Nord kimberlites.

Notre Dame du Nord								**REE data**									**Ni data**	
Analysis #	Cr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ni-content	Ni-in-grt Temp (°C)	+/-
262-1-5-1	132400	0.004	0.123	0.042	0.588	0.907	0.319	0.685	0.064	0.29	0.052	0.199	0.037	0.456	0.084	*162.80*	*1685.95*	*68.79*
262-1-6-15	37640	0.147	1.288	0.503	4.608	2.422	0.784	1.76	0.18	1.204	0.291	1.138	0.206	1.681	0.29	*126.70*	*1519.63*	*65.74*
262-1-5-2	112900	0.145	1.928	0.578	2.424	0.26	0.054	0.079	0.005	0.051	0.018	0.069	0.02	0.28	0.072	*123.20*	*1502.78*	*65.01*
262-1-6-8	39150	0.049	0.405	0.077	0.621	0.364	0.174	0.791	0.173	1.506	0.397	1.35	0.221	1.779	0.299	*118.90*	*1481.87*	*57.96*
262-1-6-6	35810	0.02	0.163	0.067	0.817	0.691	0.369	1.51	0.327	2.72	0.68	2.27	0.348	2.878	0.48	*108.50*	*1430.18*	*57.87*
262-1-5-6	96740	0.599	11.41	3.21	15.53	1.855	0.275	0.598	0.053	0.237	0.037	0.108	0.012	0.162	0.046	*105.60*	*1415.46*	*57.27*
262-1-5-4	84280	0.17	4.794	1.126	4.93	0.41	0.082	0.154	0.009	0.048	0.011	0.09	0.029	0.382	0.095	*100.30*	*1388.18*	*47.85*
262-1-6-14	49970	2.378	5.941	0.954	5.847	3.038	1.222	3.962	0.692	4.614	0.843	2.359	0.332	2.332	0.337	*100.20*	*1387.66*	*56.62*
262-1-4-15-1	50520	0.095	0.785	0.334	3.821	3.131	1.405	4.86	0.682	3.199	0.448	0.955	0.125	1.022	0.186	*95.19*	*1361.36*	*56.95*
262-1-6-11	29540	0.006	0.234	0.075	0.819	0.835	0.495	2.596	0.664	5.64	1.349	4.357	0.727	5.781	0.962	*95.14*	*1361.09*	*50.78*
262-1-6-12	36240	0.096	2.607	1.598	10.72	1.572	0.388	0.879	0.105	0.46	0.052	0.138	0.028	0.325	0.102	*94.62*	*1358.33*	*56.82*
262-1-6-13	34760	0.016	0.275	0.122	1.531	1.754	0.75	2.026	0.227	1.469	0.397	1.426	0.274	2.498	0.447	*92.21*	*1345.47*	*52.97*
262-1-5-5	82630	0.173	1.359	0.263	1.025	0.086	0.028	0.057	0.008	0.053	0.032	0.195	0.055	0.753	0.163	*89.96*	*1333.33*	*50.08*
262-1-6-7	38760	0.061	0.351	0.092	0.893	0.623	0.298	1.182	0.24	1.793	0.409	1.281	0.206	1.712	0.29	*86.07*	*1312.07*	*50.33*
262-1-6-4	41930	0.042	0.602	0.209	2.647	2.62	1.152	2.988	0.46	3.024	0.68	2.23	0.348	2.603	0.371	*81.55*	*1286.87*	*44.36*
262-1-5-3	91370	0.008	0.252	0.126	1.781	1.629	0.723	2.561	0.406	2.324	0.372	0.861	0.124	1.022	0.171	*80.75*	*1282.35*	*55.09*
262-1-6-9	44770	0.029	0.259	0.103	1.216	1.155	0.493	1.595	0.253	1.931	0.485	1.9	0.36	3.192	0.567	*80.47*	*1280.77*	*52.86*
262-1-6-5	38720	0.066	1.072	0.326	2.455	0.865	0.247	0.486	0.043	0.162	0.027	0.054	0.008	0.118	0.041	*79.97*	*1277.93*	*48.00*
262-1-4-10	38890	0.052	0.11	0.023	0.221	1.348	0.758	2.778	0.379	1.77	0.248	0.496	0.075	0.648	0.128	*77.44*	*1263.46*	*47.16*
262-1-5-8	97150	0.138	1.13	0.322	2.913	1.64	0.592	1.894	0.312	2	0.336	0.928	0.115	0.831	0.129	*77.34*	*1262.88*	*41.80*
262-1-6-2	43840	0.008	0.293	0.199	2.63	1.398	0.567	1.474	0.248	1.635	0.344	0.981	0.147	1.041	0.166	*76.98*	*1260.81*	*54.54*
262-1-6-3	27560	0.009	0.307	0.119	1.067	0.32	0.102	0.146	0.024	0.159	0.049	0.214	0.054	0.576	0.129	*76.47*	*1257.86*	*50.43*
262-1-4-15	51600	0.044	0.605	0.287	3.138	2.514	1.144	3.993	0.548	2.389	0.35	0.759	0.093	0.85	0.137	*74.26*	*1244.98*	*98.22*
262-1-4-14	52840	0.444	6.287	1.799	8.735	1.532	0.366	0.792	0.074	0.307	0.043	0.164	0.047	0.665	0.176	*74.23*	*1244.81*	*46.44*
262-1-6-10	28890	0.04	0.441	0.159	1.473	0.999	0.403	1.491	0.29	2.464	0.624	2.095	0.364	2.913	0.489	*72.05*	*1231.94*	*51.73*
262-1-5-18	43190	0.009	0.59	0.544	5.882	1.867	0.657	2.527	0.385	2.236	0.373	0.991	0.148	1.152	0.187	*71.96*	*1231.41*	*45.94*
262-1-4-15-3	52550	0.048	0.781	0.36	4.117	3.367	1.51	4.775	0.681	3.251	0.439	0.896	0.139	1.055	0.183	*71.59*	*1229.21*	*83.85*
262-1-5-10	64440	0.007	0.214	0.074	0.94	0.747	0.369	1.573	0.28	2.129	0.478	1.454	0.215	1.628	0.258	*68.71*	*1211.90*	*49.18*
262-1-5-7	76770	0.116	1.988	1.529	20.94	5.598	1.184	1.746	0.15	0.693	0.084	0.194	0.026	0.229	0.071	*68.23*	*1208.99*	*46.38*
262-1-4-15-2	52950	0.036	0.767	0.351	3.874	3.183	1.466	4.913	0.681	3.276	0.452	0.954	0.124	0.984	0.172	*67.90*	*1206.98*	*47.52*
262-1-5-13	65790	0.038	0.713	0.185	1.545	0.685	0.247	0.748	0.122	0.871	0.199	0.761	0.133	1.151	0.205	*66.80*	*1200.25*	*49.22*
262-1-4-14	56330	0.241	3.713	1.231	6.478	1.333	0.284	0.628	0.051	0.258	0.03	0.114	0.035	0.503	0.135	*66.20*	*1196.56*	*87.69*
262-1-5-12	65890	0.135	1.051	0.88	14.36	2.505	0.555	1.21	0.127	0.721	0.133	0.333	0.046	0.53	0.096	*66.09*	*1195.88*	*44.64*

								REE data									Ni data	
Analysis #	Cr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ni-content	Ni-in-grt Temp (°C)	+/-
262-1-5-9	57090	0.05	0.623	0.224	1.676	0.162	0.042	0.167	0.029	0.206	0.053	0.263	0.056	0.635	0.15	62.46	1173.21	43.22
262-1-4-13	45360	0.123	0.363	0.103	0.929	1.102	0.706	4.07	1.063	8.111	1.432	2.865	0.302	1.596	0.219	61.87	1169.47	49.11
262-1-5-14	72420	0.139	1.933	0.649	4.524	1.465	0.48	1.252	0.146	0.661	0.123	0.37	0.06	0.661	0.143	59.74	1155.83	46.34
262-1-5-19	44960	0.11	3.655	0.879	4.339	0.957	0.238	0.548	0.057	0.291	0.063	0.208	0.042	0.61	0.131	54.90	1123.97	47.02
262-1-4-9	38550	0.158	1.573	0.687	6.871	3.666	1.405	5.023	0.678	3.804	0.645	1.427	0.177	1.161	0.173	54.53	1121.48	88.58
262-1-5-11	46100	0.147	1.285	0.276	1.524	0.103	0.032	0.044	0.008	0.068	0.033	0.229	0.067	0.793	0.188	53.32	1113.29	46.61
262-1-4-9	51780	0.216	1.48	0.618	6.168	3.212	1.186	4.42	0.616	3.303	0.544	1.254	0.155	0.995	0.151	53.18	1112.33	73.47
262-1-5-16	38920	0.03	1.351	0.324	1.657	0.218	0.053	0.156	0.013	0.059	0.016	0.014	0.002	0.111	0.036	52.34	1106.59	45.67
262-1-4-12-1	47050	0.096	1.03	0.368	3.496	1.553	0.535	1.849	0.313	2.214	0.474	1.442	0.245	1.975	0.35	49.48	1086.67	44.56
262-1-5-17	35840	0.292	4.752	0.792	3.645	0.395	0.075	0.093	0.01	0.058	0.023	0.165	0.048	0.593	0.14	49.00	1083.28	45.49
262-1-5-20	30840	0.071	2.779	1.731	10.46	0.881	0.217	0.494	0.047	0.266	0.033	0.088	0.013	0.245	0.077	47.35	1071.48	42.18
262-1-4-10	51240	0.012	0.038	0.017	0.203	1.003	0.608	2.356	0.311	1.428	0.193	0.423	0.065	0.514	0.108	47.26	1070.83	75.71
262-1-5-15	47890	0.068	0.975	0.497	6.092	2.562	0.837	2.654	0.487	3.402	0.649	1.651	0.214	1.426	0.224	46.41	1064.66	41.64
262-1-4-12-3	49640	0.086	1.049	0.41	3.728	1.86	0.682	2.242	0.38	2.597	0.567	1.653	0.256	2.171	0.369	45.56	1058.44	41.40
262-1-4-12-2	49460	0.094	1.056	0.38	3.593	1.686	0.623	1.994	0.339	2.364	0.5	1.523	0.248	2.021	0.341	43.75	1045.01	41.89
262-1-4-13	49630	0.037	0.211	0.075	0.768	0.859	0.579	3.271	0.829	6.013	1.062	2.143	0.211	1.067	0.142	40.14	1017.34	76.13
262-1-4-12	49580	0.096	0.834	0.323	2.804	1.235	0.445	1.52	0.254	1.702	0.369	1.191	0.194	1.541	0.257	39.83	1014.90	69.23
262-1-4-18	43770	0.228	1.715	0.345	1.962	0.433	0.098	0.212	0.017	0.126	0.04	0.229	0.072	0.782	0.155	39.08	1008.97	96.85
262-1-4-17	38320	0.349	2.196	0.372	1.741	0.52	0.135	0.362	0.027	0.149	0.038	0.265	0.06	0.718	0.159	38.16	1001.62	78.92
262-1-4-16	47800	0.144	2.095	0.692	5.444	3.453	1.139	2.679	0.29	1.643	0.274	0.791	0.111	0.803	0.138	36.12	984.98	77.80
262-1-4-19	39260	0.163	1.656	0.441	3.775	1.681	0.522	1.418	0.183	1.124	0.205	0.461	0.058	0.524	0.106	29.60	928.15	65.85
262-1-4-2	36700	0.084	0.819	0.299	2.487	1.167	0.366	1.184	0.185	1.112	0.194	0.511	0.073	0.731	0.125	28.10	914.14	87.74
262-1-4-20	31480	0.118	1.293	0.627	9.387	6.037	1.872	6.181	0.519	1.301	0.136	0.274	0.039	0.426	0.131	27.44	907.85	55.34
262-1-4-12-4	49890	0.104	1.073	0.421	3.897	1.794	0.665	2.265	0.381	2.607	0.528	1.662	0.277	2.182	0.368	26.97	903.31	37.28
262-1-4-8-2	37850	0.147	0.933	0.184	1.322	1.067	0.441	1.607	0.262	1.753	0.338	0.91	0.128	0.862	0.149	26.41	897.85	65.80
262-1-4-8-1	33490	0.154	0.845	0.169	1.24	0.971	0.405	1.456	0.247	1.66	0.317	0.848	0.122	0.866	0.144	25.85	892.33	66.77
262-1-4-8-3	38320	0.16	0.953	0.181	1.362	1.085	0.433	1.645	0.264	1.796	0.349	0.907	0.119	0.868	0.153	25.26	886.43	69.93
262-1-4-4	31430	0.042	0.48	0.169	1.782	1.856	1.111	4.556	0.809	4.954	0.857	2.015	0.257	1.594	0.233	23.06	863.75	52.65
262-1-4-5-2	33730	0.037	0.477	0.171	1.752	1.874	1.108	4.721	0.812	5.105	0.868	2.086	0.265	1.623	0.236	21.70	849.10	60.04
262-1-4-3	33300	0.065	0.7	0.224	2.215	1.212	0.459	1.432	0.208	0.983	0.128	0.279	0.034	0.318	0.066	21.61	848.11	60.18
262-1-4-7	29010	0.043	0.449	0.161	1.888	1.687	0.668	2.291	0.295	1.577	0.229	0.459	0.047	0.296	0.055	21.22	843.80	35.33
262-1-4-5-1	28690	0.03	0.351	0.119	1.316	1.467	0.892	3.696	0.675	4.193	0.731	1.798	0.228	1.377	0.197	20.86	839.79	55.47

								REE data									Ni data	
Analysis #	Cr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Ni-content	Ni-in-grt Temp (^{o}C)	+/-
262-1-4-1	27460	0.096	1.707	0.563	3.55	0.832	0.326	1.186	0.254	2.042	0.467	1.474	0.235	1.805	0.275	*18.84*	*816.46*	*64.33*
262-1-6-1	30550	0.037	0.684	0.33	4.953	2.463	0.792	1.859	0.226	1.264	0.218	0.579	0.082	0.638	0.1	*18.69*	*814.67*	*33.24*
262-1-4-5-3	34690	0.057	0.524	0.174	1.837	2.123	1.165	4.996	0.937	5.598	0.936	2.327	0.307	1.899	0.244	*18.25*	*809.37*	*55.21*

3.2. Notre Dame du Nord: Ni-in-garnet thermometry

The results of the Ni-in-garnet temperature determinations are shown in a combined histogram and cumulative probably plot below (Fig 4).

The Cr-content of mantle garnet has been used to model recorded pressures, i.e. used as single mineral barometer (Ryan et al. 1996). Coupled with the Ni-in-garnet thermometer the data can be used to determine geothermal gradients (e.g. Stiefenhofer et al. 1999). However, the Cr-in-garnet barometer assumes that garnet is in equilibrium with Cr-spinel or chromite which is not likely in higher pressure (deeper) mantle sources where these oxides are not stable. In addition, with increasing pressure garnet can accommodate large quantities of Cr even when not in equilibrium with Cr-bearing oxides (Girnis et al. 1999). Thus, the pressures calculated using the Cr-content in garnet can be highly misleading. An alternative use for the temperature data and Cr-contents is presented in Fig 5. By plotting the Cr-contents against the recorded temperatures two trends can be seen. One is a horizontal cluster of data with temperatures recorded between 800 and 1600 °C but with a limited range of Cr-contents between 30,000-40,000 ppm. A second trend is also present with the same low-T low Cr end-members and a few points with high-Cr (110,000-130,000 ppm) and temperatures in excess of 1500 °C.

If the Cr-contents in these garnet are indeed representative of pressure (depth) then in an ideal suite of indicator garnets the recorded temperatures would all lies between 900-1200 °C and the Cr-contents would define a near horizontal trend. This would then mean that garnets have been sampled from a wide depth range with a narrow temperature variation. This in turn would suggest colder than average temperatures at depth in the mantle lithosphere, i.e. that the prevailing geothermal gradient was very steep. As show in Fig 1 this is one of the most important requirements for diamond formation and stability. The use of this type of plot to qualitatively define geothermal gradients is

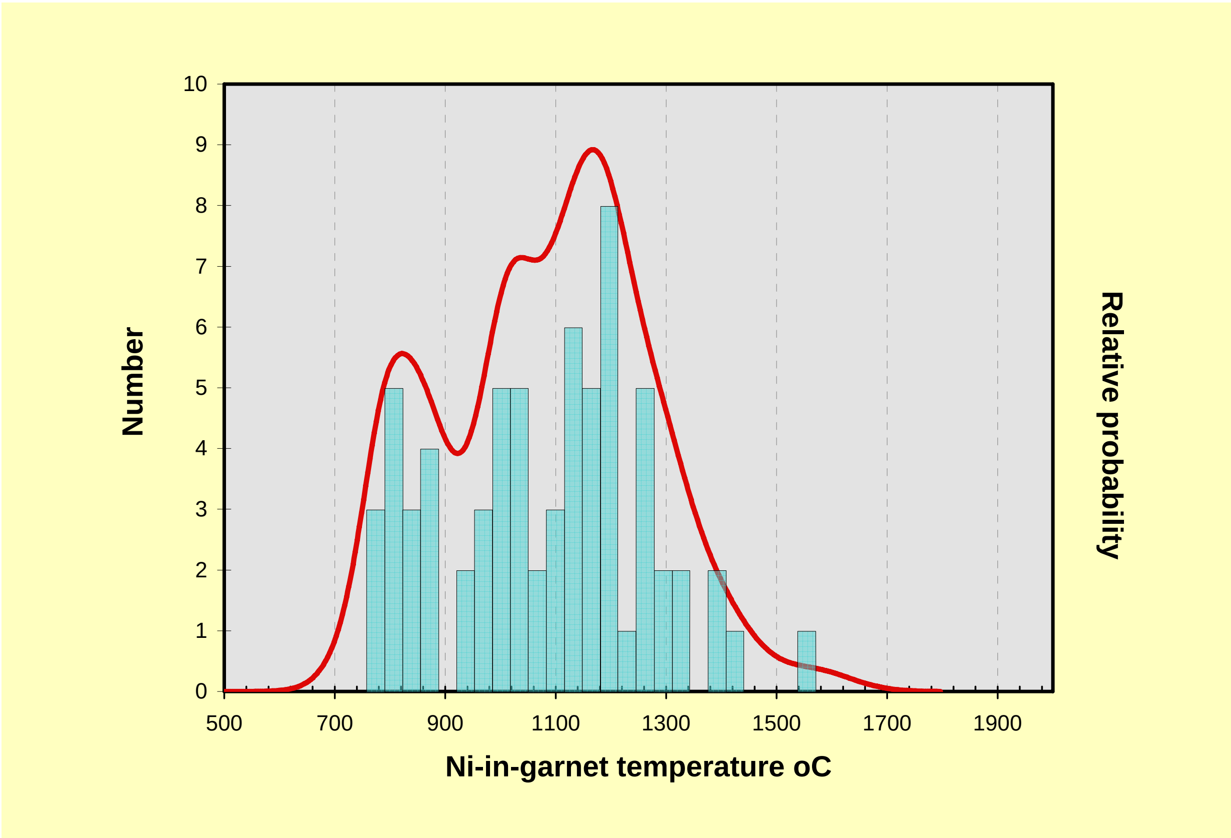

Fig 4. A combined histogram and relative probability curve (red line) for the Ni-in-garnet temperature determinations from the Notre Dame du Nord indicator garnets suites.

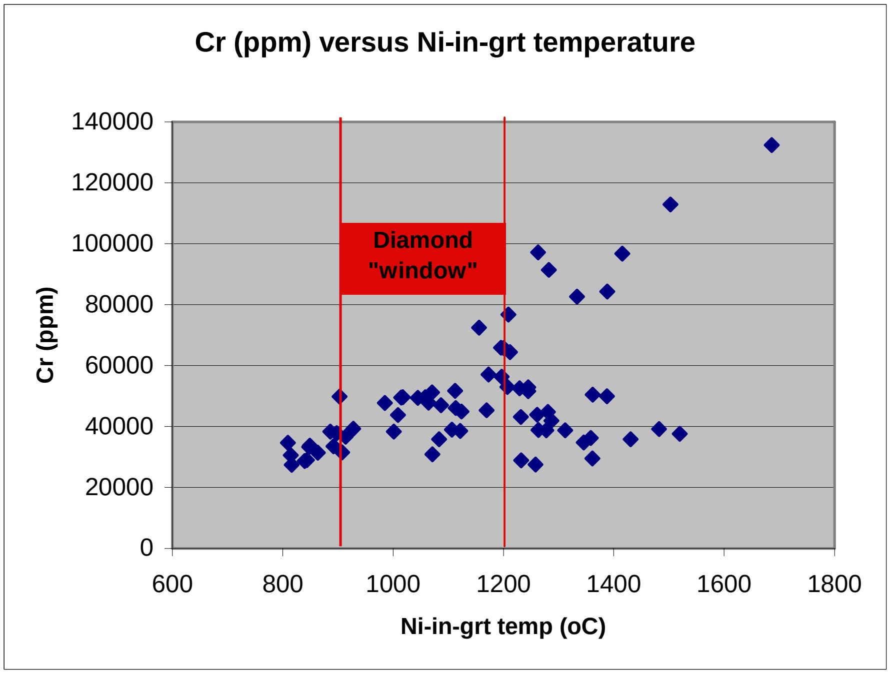

Fig 5. Cr-contents (in ppm) versus Ni-in-garnet temperatures for the Notre Dame du Nord indicator garnet suite. The stability field for the diamond window at typical cool geothermal gradients is shown.

independent of exact calibration of Cr-in-garnet barometry and requires only that at least some of the garnets analyzed in an indicator suite record variations in Cr-contents that are pressure sensitive. Given this approach it is clear that for either trend shown in Fig 5 the data suggest normal to high geothermal gradients for the Notre Dame du Nord kimberlites. Thus, even though a significant portion of the garnets record temperatures from with the diamond window, this particular target is less likely to yield high volumes of diamonds as the inferred geothermal gradients are likely higher that would be desired for a highly diamondiferous target. However, that fact that at least some of the temperatures recorded lie within the diamond window suggests that this particular target cannot be ruled out as a potential diamond source using this method alone.

3.2. Notre Dame du Nord: REE patterns

The garnet indicator suite can be divided into four groups based on recorded temperatures. These can be subdivided based on REE patterns as shown in Table 3. The chondrite normalized REE patterns are shown in Fig 6.

One of the first features is the high quantity of sinuous REE patterns recorded. These can be

Table 3. Indicator garnet suite subdivision based on Ni-temperature ranges and general characteristics of the recorded REE patterns.

Ni-in-grt Temp (°C)	Total number of garnets in group	REE type / number of each type					
		Sinuous low Dy	Sinuous high Dy	Sinuous High MREE	Steep high HREE	Flat high HREE	Flat high LREE
1350-1700	11	5	2	0	3	0	1
1250-1350	11	3	4	0	2	2	0
1100-1250	19	6	3	7	1	1	1
950-1100	12	4	1	1	0	5	1
800-950	15	0	6	6	0	3	0

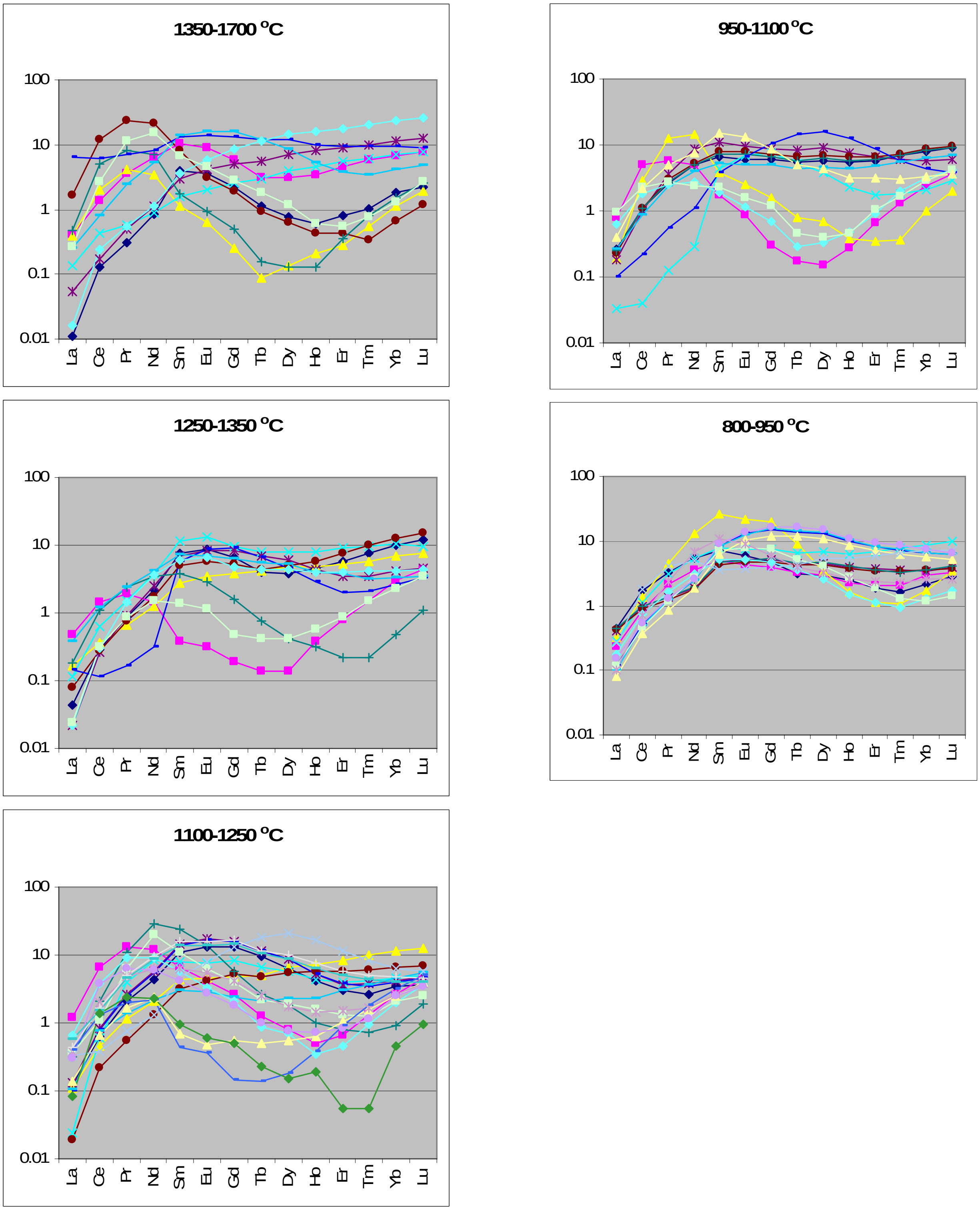

Fig 6. Chondrite nomalized REE-patterns for indicator garnets grouped according to recorded temperatures

grouped into those which display Dy contents below 1 times chondrite, (low Dy), sinuous patterns with the same general shape but with Dy contents above 1 times chondrite (high Dy) and sinuous patterns which have high MREE contents. These latter patterns only occur in garnets with recorded temperatures below 1250 °C. The former two sinuous pattern-types are likely representative of fragments of zoned crystals and are fairly evenly distributed across all the temperature ranges. Mantle garnets with this type of REE-pattern are normally thought to have grown in a depleted mantle environment (e.g. S; Canil et al. 2003). Garnets with steep HREE-enriched patterns only occur in those which record high temperatures and the majority of garnets with flat HREE-enriched patterns are found in those with lower recorded temperatures. The former are most likely formed in a high-P lherzolitic mantle source and the latter in a lower-P lherzolitic mantle source (Burgess and Harte 2004). Only three garnets with flat LREE- enriched patterns were found. These also have relatively low (<50,000 ppm) Cr-contents are therefore likely G10 garnets from a harzburgitic mantle source (Stachel et al. 1998; Burgess and Harte 2004). The REE-patterns can be used in conjunction with the Cr-contents and recorded temperatures in a number of ways to examine diamond potential. Firstly, the presence of a high number of garnets with depleted mantle signatures across wide temperature ranges and Cr-contents suggests that the Notre Dame du Nord pipes samples these garnets from a wide range of depths. This observation supports the qualitative assessment of apparent geothermal gradients indicated in Fig 5.

This is further supported by the fact that garnets with steep HREE-enriched patterns are found at high temperatures whereas MREE-contents and flatter patterns correspond to cooler recorded temperatures. This is consistent with garnets sampled from deep (steep REE-patterns) to shallow (flat REE-patterns) lherzolitic mantle sources (Stachel et al. 1998; Burgess and Harte 2004). In short the REE patterns are consistent with a garnets sampled from a wide range of depths and from predominantly depleted, lherzolitic sources. Only a very small proportion of these garnets have come from harzburgitic sources and thus, the diamond potential is likely limited for the Notre Dame du Nord kimberlites.

4. CONCLUSIONS

The detection limit of the LA-ICP-MS technique for Ni (<5 ppm) is ideal for applying the single mineral, Ni-in-garnet thermometer to indicator garnet suites. The Ni-concentration data can be collected with up to 26 other trace-elements including the full suite of REE in a 100 second ablation analysis. The REE-patterns can be used in conjunction with the recorded temperatures to elucidate mantle sources and determine the range of depths sampled by the ascending intrusion. This information can be combined to determine the diamond potential of an exploration target. The LA-ICP-MS is fast (>100 samples per day) and is the one of the only cost-effective methods for determining Ni and REE in mantle garnets. Although not discussed in this study, other trace elements (V, Cr, Ti, Zn, Ga, etc.) can be determined routinely in a single run. This data can be used to further characterize indicator garnets (e.g. Canil et al. 2003).

Based on Ni-in-garnet thermometry, Cr-contents and REE-patterns it is likely that he Notre Dame du Nord kimberlite magmas sampled depleted mantle source rocks, largely lherzolitic in nature. The inferred geothermal gradients are normal to high. It is unlikely that he Notre Dame du Nord pipes will yield large quantities of diamonds but, may contain small numbers of diamonds largely sampled from deep lherzolitic mantle sources or a very minor component of depleted harzburgitic mantle.

The use of LA-ICP-MS for the analysis of indicator garnets is therefore a powerful addition to the range of tools available to assess diamond potential of kimberlites and other rock types.

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