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Ni in chrome pyrope garnets: a new geothermometer

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Abstract. Proton microprobe analyses of the minerals in garnet-peridotite xenoliths from kimberlites show that the partitioning of Ni between chrome pyrope garnet and olivine is strongly temperature(T)-dependent. The range of Ni contents in olivines is small relative to that in the analyzed garnets; a geothermometer therefore can be derived, based only on the Ni content of garnet. This allows estimation of T for single Cr-pyrope grains, such as the inclusions in diamonds, if these can be assumed to have equilibrated with olivine.

Introduction

The proton microprobe (PMP), equipped with an energy-dispersive X-ray analyzer, allows the in-situ non-destructive microanalysis of a wide range of trace elements at the ppm level in minerals. The HIAF proton microprobe (Sie 1985; Sie and Ryan 1986) is dedicated to geological applications, including trace element analysis of mantle-derived minerals used in exploration for diamond deposits. The application of the HIAF proton microprobe to mineral analysis has been described by Griffin et al. (1988). Most of the analyses reported here were carried out with a 20–30 μm beam spot, 3 μC accumulated charge, and a sample current of 7–10 nA, requiring average analysis times of ca. 7 min/sample. The precision of the data is indicated by the uncertainties quoted for typical analyses in Table 1. The accuracy of the method at similar levels has been established by analysis of standard materials, and is similar to the quoted precisions (Griffin et al. 1988; Ryan et al. 1988). The method is independent of standards, and uses the previously-determined Fe content of the grains as an internal calibration.

Geothermobarometry on olivine-garnet pairs

The samples analyzed here include three general types of xenolithic material, derived from kimberlitic diatremes.

High-temperature (HT) sheared peridotites

The material includes sheared lherzolites and a dunite from the Frank Smith and Thaba Putsoa kimberlites; these are described in detail by Smith and Boyd (1987, 1989) and by Griffin et al. (1989). The garnets typically show strong zoning, with rims enriched in Ti, Zr, Y and Ga relative to their cores; representative ranges are shown in Table 1. However, Ni and Zn are *not* significantly zoned (Table 1) except in PHN5555, where Ni rises from 60 ppm (core) to 79 ppm (rim). Detailed analyses of zoned grains, as well as the interpretation of the Zr – Ti – Y zoning and its petrological significance, are presented elsewhere (Griffin et al. 1989a). Temperatures were estimated using the preferred two-pyroxene thermometer and opx-gnt barometer recommended by Finnerty and Boyd (1987) except for the garnet dunite FBR450, where we have used the olivine-garnet thermometer of O'Neill and Wood (1979, 1980), at an assumed $P = 50$ kb. These two thermometers generally give concordant results for the HT lherzolite xenoliths considered here (Table 1).

Low-temperature (LT) granular peridotites

This group includes five lherzolites from the Matsoku pipe (LBM-; Cox et al. 1973), two from Pipe 200, one from the Bultfontein pipe (BD2454) and one (garnet + spinel-lherzolite) from the Thaba Putsoa pipe (PHN1569). The garnets of these samples are unzoned in trace elements and, with one exception, in major elements. Temperatures calculated by the two methods given above are generally concordant, assuming $P = 40$ kb (the median value derived from the lherzolites by opx-gnt barometry) for the O'Neill and Wood (1979, 1980) thermometer (Table 1).

Very-low temperature (VLT) garnets

These samples consist of garnet grains gathered from anthills on the Garnet Ridge diatreme on the Colorado Plateau, SW USA. The garnets contain inclusions of olivine, pyroxenes, carbonates, amphibole and chlorite. Hunter and Smith (1981) and Smith (1987) describe the Garnet Ridge material and present analyses of the garnets and their inclusions. They show that the garnets have had a long cooling history, recorded as zoning profiles in the inclusions and the surrounding garnets. We have analyzed the cores of these small inclusions, and the garnet within 50 μm of the inclusions. The temperature estimates used here for garnet-olivine pairs are calculated by the thermometer of O'Neill and Wood (1979, 1980) assuming $P = 25$ kb. Hunter and Smith (1981) showed that this thermometer underestimates T by ca. 75° C at c. 6–700° C, and the calculated temperatures have been corrected by this amount.

Analytical data

Representative analyses are given in Table 1. Electron microprobe data for these samples have been provided by sample donors (see references above), except for 10429 which was analyzed at CSIRO, using standard techniques.

Figure 1 shows the temperature dependence of Ni partitioning between garnet and olivine. At high temperatures, the garnet accepts more Ni; the relatioship between log K_D (where $K_D = Ni_{gnt}/Ni_{oliv}$) and $1/T$ is linear over c. 700° C,

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Table 1. Representative analyses of garnets and olivines

	PHN 1611/A RIMS	FRB 450/A CORES	FRB 450/A RIMS	FRB 76/E CORES	FRB 76/E RIMS	PHN 5555 RIMS
TYPE[a]	HT	HT	HT	HT	HT	HT
(Electron microprobe analyses, wt%)						
SiO_2	42.8	42.3	41.7	42.6	41.4	42.6
TiO_2	0.97	0.37	1.11	0.44	1.20	0.25
Al_2O_3	20.4	20.3	20.2	19.7	19.7	20.9
Cr_2O_3	2.54	3.13	1.74	4.40	3.65	3.84
FeO	8.34	8.74	9.02	7.05	7.25	5.90
MnO	–	–	–	0.27	0.31	0.24
MgO	21.2	20.2	20.2	21.1	21.3	21.1
CaO	4.74	4.81	4.86	4.92	5.25	4.91
(Proton microprobe analyses, ppm)						
Ni	126 ±11	86 ±4	96±4	100 ±4	103 ±4	79±12
Zn	23 ± 1	20 ±1	21±1	19 ±0.5	17 ±0.5	12± 0.5
Ga	12 ± 0.6	12 ±0.5	15±0.5	12 ±0.5	13 ±0.5	9± 0.5
Sr	1.6± 0.4	1.2±0.5	3±0.5	2.8±0.3	2.8±0.3	<0.5
Y	25 ± 1	15 ±1	24±1	14 ±1	20 ±1	17± 0.5
Zr	77 ± 2	24 ±1	106±2	28 ±1	103 ±2	19± 0.5
Fo, oliv	88		88		91	92
Ni, oliv	2400		2600		2750	2600
T, °C[b]	1450				1280	1200
T, °C[c]	1460		1250		1240	1340

Quoted uncertainties are 1 standard deviation.
[a] See text
[b] Finnerty and Boyd (1987)
[c] O'Neill and Wood (1979, 1980)

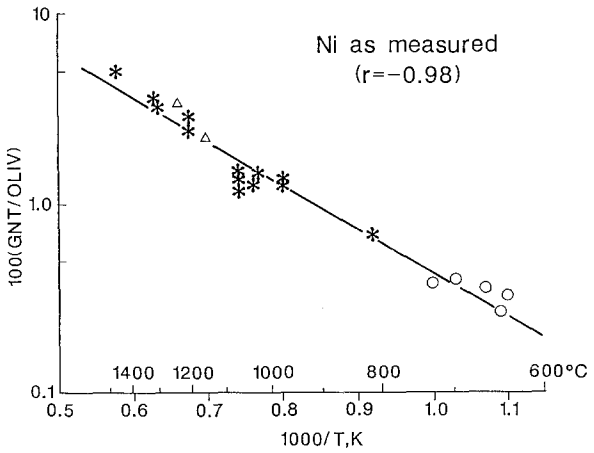

Fig. 1. $100K_D^{Ni}$ ($K_D = Ni_{gnt}/Ni_{oliv}$) vs 1000/T. *Stars*, xenolith garnets; *circles*, Garnet Ridge; *triangles*, garnet-olivine pairs from single Argyle diamonds (Griffin et al. 1988)

despite the relatively wide range in garnet composition (Table 1). Two garnet-olivine pairs from Argyle diamonds (Griffin et al. 1988) also fit this line; these two garnets have 1.8% and 14.6% Cr_2O_3 respectively.

The regression line in Fig. 1 uses all points and is described by the equation

$$1000/T(\mathrm{K}) = -0.428 \log_{10}(100K_D) + 0.84 \quad (r = -0.98) \qquad \text{I}$$

The Ni content of the analyzed garnets ranges from <10 to 120 ppm, while the Ni content of the olivines in the analyzed peridotite xenoliths, and in nearly all other peridotite xenoliths we have analyzed, ranges only from ca. 2400–3200 ppm. The average value for 16 garnet peridotites is 2840±200 ppm (1σ); the average for 76 olivine inclusions in African diamonds is 3140±215 ppm (Griffin and Gurney, in prep). In most garnet peridotites, garnet makes up < 10% of the mode; olivine ranges mainly from 60–80% (Boyd and Mertzman 1987). In terms of Ni, the olivine represents an essentially infinite reservoir of fixed composition relative to the garnet. It should therefore be possible to assume a mean olivine composition, calculate the "mean K_D" for a given garnet, and derive a temperature which is not far from the real temperature of equilibration. If we assume that $Ni_{oliv} = 3000$ ppm, we obtain the regression line in Fig. 2, which has the equation

$$1000/T(\mathrm{K}) = -0.435 \log_{10}(Ni_{gnt}/30) + 0.83 \quad (r = -0.98), \qquad \text{IIa}$$

or

$$T, ^\circ\mathrm{C} = \{1000/[-0.435 \log_{10}(Ni_{gnt}/30) + 0.83]\} - 273 \qquad \text{IIb}$$

This regression omits the values for three Garnet Ridge olivine-garnet pairs in which the olivine inclusions have Ni >4000 ppm. These high Ni contents, which are not typical of mantle olivines, are interpreted as the result of partitioning of Ni from a large volume of garnet into a small volume of olivine, during cooling (cf. Smith and Wilson 1985).

Equation IIb reproduces the estimated temperatures for each of the samples with an average error of ±4%, corresponding to c. ±50° C for the common granular peridotites of the LT group. This is well within the uncertainty of the

LBM 37	LBM 11	P200/1	BD2454	PHN 1569	GR 107	GR 115	10429
LT	LT	LT	LT	LT	VLT	VLT	LOW-P
40.4	42.0	42.7	41.6	42.3	41.8	42.0	42.8
0.18	0.13	0.08	0.05	0.0	0.10	0.14	0.25
20.3	19.7	19.5	19.2	20.7	22.8	22.5	23.0
2.32	5.83	5.72	6.18	4.12	1.99	1.83	1.32
11.1	7.26	6.56	7.28	6.98	8.42	9.23	7.79
0.41	0.35	0.29	0.32	0.38	0.41	0.43	0.32
20.3	20.5	19.9	20.0	20.6	20.5	20.4	21.0
4.68	5.24	5.64	6.02	5.77	5.16	5.22	4.96
37 ±4	43 ±4	32 ±2	44 ±5	25 ±3	12±3	10 ±2.5	44 ±1.5
12.5±0.5	15 ±1	11.5±0.5	13 ±1	11 ±0.5	12±2	9.5±1.5	10.5±0.5
7 ±1	4 ±0.3	3.7±0.4	6 ±0.7	2.7±0.4	5±1	5.5±1	5.4±0.4
<1.5	1.8±0.3	3 ±0.5	<1	<1	<1	<2	<1.5
20 ±1	15.5±0.5	1.4±0.3	3.8±0.4	19.5±0.5	58±2	26 ±3	20 ±2
63 ±2	112 ±3	19 ±1	57 ±2	102 ±2	11±1	23 ±1.5	40 ±2
88	92	93	96	91	94	93	90
3000	3000	2950	3130	3030	4450	2810	2460
1070	1040	1040	975	815			865
1000	1010	1005	1005	860	640	665	1155

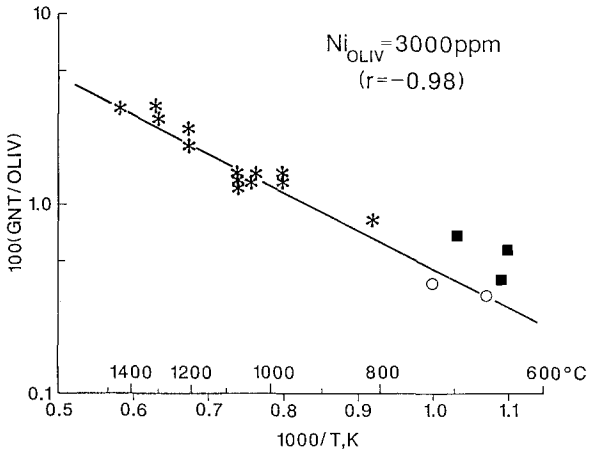

Fig. 2. $100K_D^{Ni}$ vs 1000/T, assuming $Ni_{oliv} = 3000$ ppm. Symbols as in Fig. 1. *Filled squares*, Garnet Ridge samples with Ni_{oliv} >4000 ppm, omitted from regression (see text)

other geothermometers used in the calibration (Finnerty and Boyd 1987).

Griffin et al. (1989b) present analyses of Ni in >50 chrome-pyrope inclusions in African diamonds. Only 5 of these give temperatures (using equation IIb) below 1000°, which represents the approximate intersection of the graphite-diamond reaction curve with a cratonic geotherm. None gave $T < 900°$ C. This result indicates that the calibration of the thermometer is reasonably accurate.

Discussion

The geothermometer appears to be insensitive to large variations in the Ca, Al and Cr contents of the garnets. There is some indication that variations in Fe/Mg may move the line in Fig. 1 slightly; the Fe-rich peridotites from the Matsoku kimberlite (LBM 36, 37) both fall below the line. However, even for these cases the garnet-Ni thermometer gives a T estimate within 10% of the values calculated by the two-pyroxene thermometer. Further study of a larger suite of xenoliths may resolve this point, as well as providing a more detailed calibration.

Although the garnet thermometer appears to be valid over a wide range of garnet compositions, its use on single garnet grains must assume the equilibration of garnet with olivine. In the case of most chrome pyrope garnets, this assumption is probably justified. However, some chrome pyropes might be derived from pyroxenites of the Cr-diopside peridotite suite, and equilibrated with clino- and/or orthopyroxene but not olivine. Further work on xenoliths of such rock types is necessary to see if their garnets can be distinguished consistently from peridotite garnets by major- or trace-element composition, and to establish how they deviate from the Ni-T relationship established here.

Because the samples used here are derived from different depths on similar (cratonic) geotherms (Finnerty and Boyd 1987), there is a built-in relationship between P and T which cannot be sorted out with this sample suite. The similar ionic radii and charge of Mg and Ni suggest that Ni partitioning between garnet and olivine should be mainly T-dependent. The linear relation shown in Fig. 1 also suggests that the pressure dependence of this thermometer is on the same order as that of the two geothermometers used for calibration (i.e. a few degress/km) (Finnerty and Boyd 1987; O'Neill and Wood 1979).

We have attempted to test this point by analysing a garnet+spinel lherzolite (sample 10429, Table 1) from Jugiong, New South Wales (Ferguson et al. 1979). This sam-

ple comes from a basaltic diatreme in an area with a very elevated geotherm (O'Reilly and Griffin 1985), where garnet + spinel lherzolite would be expected to occur at pressures of 16–20 kb and temperatures of 1050–1150° C (O'Neill and Wood 1979). This sample should therefore represent a ΔP of ca. 20 kb relative to the LT granular xenoliths from kimberlites (Table 1). The analyzed phases are homogeneous, and the Ni-partitioning T is 1085° C. Unfortunately, there is a wide discrepancy between the olivine-garnet T (1160°, 20 kb) and the pyroxene-solvus T (865°), so that the test is inconclusive. The discrepancy may reflect the differing response of the two thermometers to a relatively short-lived heating episode.

Further quantification of the pressure effect may be achieved by study of a larger suite of garnet-peridotite xenoliths from an area with an elevated geotherm, such as eastern Australia (O'Reilly and Griffin 1985) or Malaita (Nixon and Boyd 1979).

The ability to derive T estimates for single chrome-pyrope garnet grains has several important applications, especially to problems related to the genesis of diamond. It offers an independent test of the validity of other T estimates, for example those derived from inclusion pairs in single diamonds. It can be used to study the distribution of temperature within populations of diamonds containing chrome-pyrope inclusions. It also makes it possible to derive temperature distributions in garnet conentrates from individual diatremes; these can be converted to depth distributions if the local geotherm is known or can be inferred (Griffin et al. 1989b). This capability will be especially useful in cases where xenolith material is rare, such as in the West Australian lamproites.

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