Discrete Ti-Al±Ca metasomatism at ~53 kbar in chromite-garnet peridotites from Newlands kimberlite, South Africa

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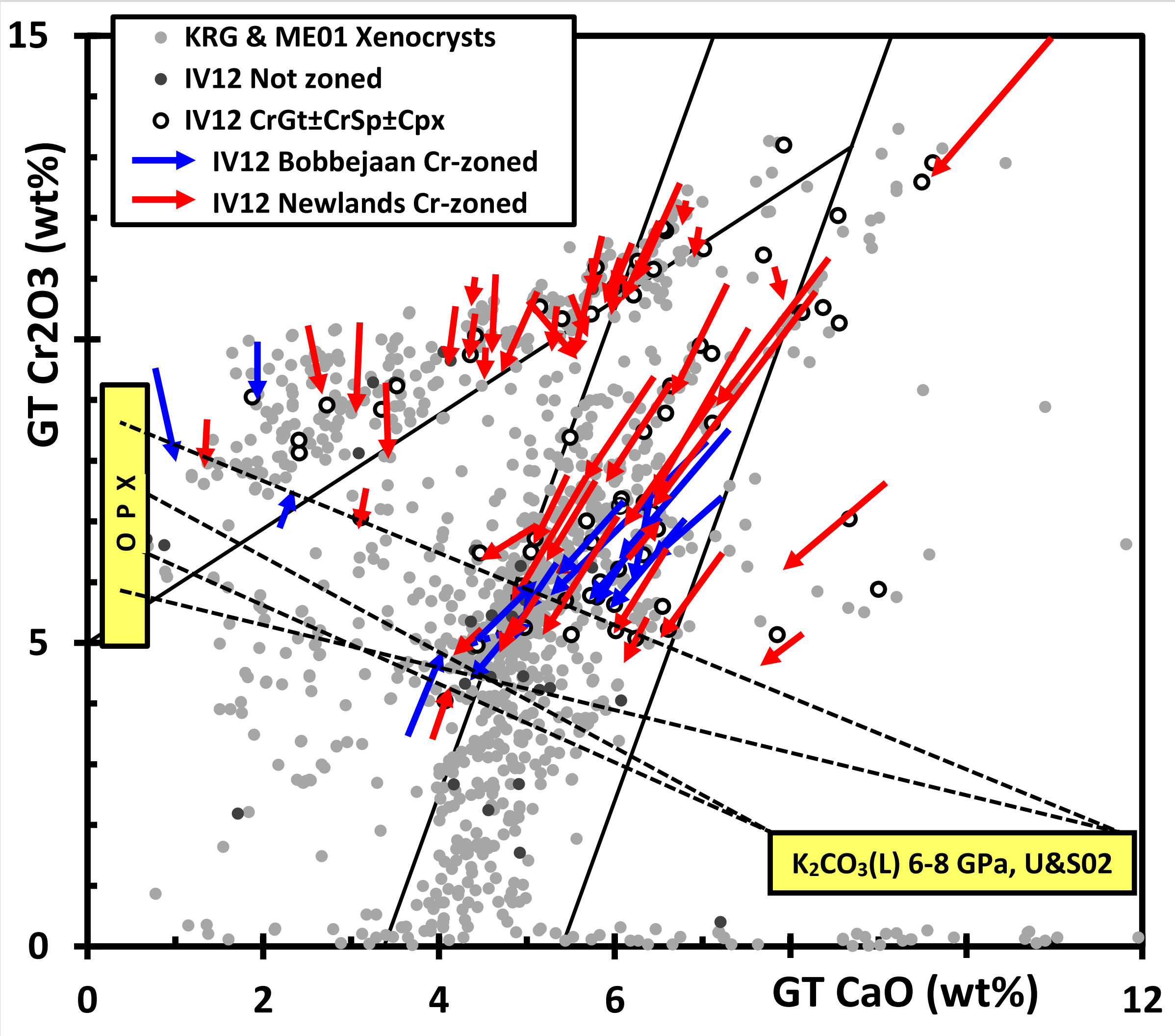

Figure 1: Cr_2O_3-CaO diagram showing Newlands garnet compositions (dots, circles) and core to rim Cr-zonation (arrows) of garnets from Newlands (red) and Bellsbank-Bobbejaan (blue). Down-Cr_2O_3 vs. up-Cr_2O_3 zonation vectors constrain an Opx-modulated interaction with carbonate melt (yellow boxes, dashed tielines).

Introduction

Peridotite xenoliths containing equilibrated, coexisting chromite+garnet assemblages are of special interest to mantle researchers because their low-variance assemblage(s) constrain critical P-T-X relationships among Olivine (Ol), orthopyroxene (Opx), clinopyroxene (Cpx), Cr-pyrope garnet (CrGt), chromite (CrSp) ± diamond ± graphite (Dia/Gph) (e.g. Grütter et al, 2006; Ziberna et al, 2013). A veritable treasure trove of such CrSp+CrGt±Dia assemblages from the ~114 Ma Newlands kimberlite and the ~118 Ma Bellsbank-Bobbejaan fissure were described in Ph.D. theses by Menzies (2001 [ME01]) and Ivanic (2007 [IV07]), and substantive portions of these valuable data sets are now published (Menzies et al., 1999 [ME99]; Ivanic et al., 2012 [IV12]). Cr-pyrope compositions in the IV12 data set cover a significant CaO range and show striking Cr-zoned trends (Fig. 1) that IV12 interpret as resulting from metamorphic re-equilibration during a postulated 10-20 kbar decompression event. A down-pressure evolution is one feasible explanation for down-Cr_2O_3 garnet zonation, *though not for up-Cr_2O_3 garnet zonation*, because high-Cr CrSp grains and serpentinized former peridotitic phases occur in intimate contact/intergrowths with the Cr-zoned garnets. We examined the unique IV12 data set to potentially derive a Ti-correction factor for our Cr/Ca-in-pyrope barometer (Grütter et al, 2006), though instead found tieline evidence of a discrete ~ 53 kbar, Ti-Al±Ca (carbonatitic) melt-metasomatic interaction modulated by peridotitic Opx that we hold accountable for the Cr-zoned garnet compositions (Fig. 1). Some of our findings are detailed below.

Metasomatic TiO_2 in garnet

Peridotitic CrGt±CrSp±Cpx micro-xenoliths and xenocrysts selected from coarse concentrate and respectively investigated by ME01 and IV12 show subtle, though distinct, differences in TiO2 content: Two-thirds of ME01 CrGt's have TiO2 ≤ 0.05 wt%, typical of unmetasomatised depleted peridotite, while two-thirds of IV12 CrGt's have TiO2 > 0.05 wt%, indicative of cryptic, metasomatic TiO2 enrichment (Figure 2). Ti-, Y-, Zr- and REE-enriched zones at CrGt exteriors are a well-known feature related to Fe-Ti melt-metasomatism in high-temperature "sheared" peridotite xenoliths (Griffin et al, 1996 and references there-in). However, none of the 79 Cr-zoned specimens investigated by IV12 contain a low-Ti CrGt core mantled by a higher-Ti exterior zone. IV12 Cr-zoned garnets instead contain mostly 0.1 to 0.7 wt% TiO2 *in their cores, and contain effectively uniform TiO2 content from cores to rims (Figure 2);* several samples show a subtle 0.02 to 0.04 wt% TiO2 *decrease* rimward. Consistent, equilibrated Ti partition for CrGt/CrSp is observed for 47 of 53 touching CrGt+CrSp±Cpx (sub)-assemblages analysed by IV12, with Ti-CrSp compositions overlapping those of metasomatised peridotite xenoliths from the Kimberley area: elevated CrGt TiO2 at Newlands is metasomatic !

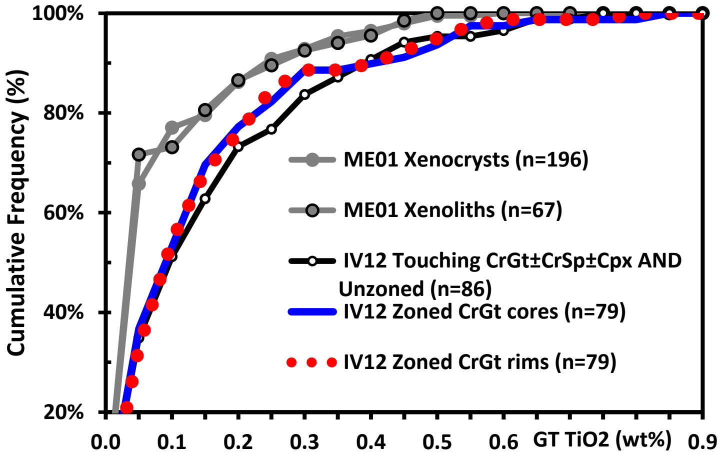

Figure 2: Comparative GT TiO2 contents for xenocrysts, micro-xenoliths and Cr-zoned garnets from Newlands (and Bobbejaan). Note essentially constant, *not-zoned* TiO2 from cores to rims of IV12's Cr-zoned garnets, even at 0.1 to 0.7 wt% GT TiO2.

An alkali-carbonatite metasome

We interpret the equilibrated, elevated, not-zoned and sample-specific Ti attributes in the Newlands & Bobbejaan Cr-zoned garnets as resulting from garnet growth in a metasomatically infiltrated peridotitic "closed" system characterised by internal buffering at low (< 1 ?) metasome/rock ratios. Based in part on the tieline evidence shown in Figure 1, we envisage the metasome to be similar to the Group-2 kimberlite-type alkali-carbonatitic liquids that Ulmer and Sweeney (2002 [U&S02]) experimentally equilibrated with garnet harzburgite mineralogy at 4.0 – 9.5 GPa and 1200 to 1500°C. The U&S02 alkali-carbonatitic liquids equilibrated with additional Cpx (i.e. garnet lherzolite) at lower temperatures, and contain somewhat more SiO2, Al2O3 and TiO2 than obtained by Sokol et al (2016 [SO16]) for alkali-carbonatitic liquids in H2O-absent sandwich experiments designed to simulate the interaction of "dry" carbonatite with peridotite (see Table 1).

Reference	Composition	SiO2	TiO2	Al2O3	Cr2O3	FeO	MnO	NiO	MgO	CaO	Na2O	K2O	Sum	CO2	H2O
U&S02	Liq / GPII	24.4	1.7	3.3	0.2	6.8	0.2	-	21.6	9.5	1.1	5.3	74.0	15.3	10.7
SO16	Liq / HC	2.3	0.6	0.6	0.0	4.7	0.2	0.2	12.3	13.2	1.9	16.4	55.2	47.7	-
SO16	Liq / LC	4.0	0.5	1.2	0.1	6.0	0.2	0.0	12.0	13.4	1.8	13.3	52.4	47.4	-
SO16	HC HZB	45.8	-	2.7	1.1	7.7	0.1	0.3	41.5	0.6	-	-	99.7		
SO16	LC LHZ	45.8	0.2	4.1	0.5	7.5	0.1	0.4	37.7	3.2	0.3	-	99.7		

Table 1: Average alkali-carbonatite liquid compositions equilibrated with typical harzburgite (HC) or lherzolite (LC) by Ulmer and Sweeney (2000 [U&S02]) or Sokol et al. (2016 [SO16]).

Al_2O_3, Cr_2O_3 and CaO in garnet

The core-to-rim zonation of garnet Cr2O3 content shown on Figure 1 reflects changing garnet Cr/(Cr+Al), in response to changing bulk Cr/(Cr+Al). A quick calculation shows some 5 modal% *completely new* garnet can be grown at progressively changing Cr/(Cr+Al) by progressively adding 0.9 wt% Al2O3 to a depleted peridotite. Since the U&S02 alkali-carbonatitic liquids in the peridotite-H2O-CO2 system contain significant Al2O3 (~3.3 wt%, Table 1) at very low Cr/(Cr+Al), the nett Al2O3 balance to grow the Newlands down-Cr zoned garnets *from scratch* would be completely satisfied by interacting 1 part U&S02 melt with ~3.6 parts peridotite. Up-Cr2O3 garnet growth occurs where initial garnets have Cr/(Cr+Al) lower than a tieline between Opx and percolating U&S02 melt (see Fig. 1).

Most harzburgitic garnets impacted by natural (or experimental) metasomatism show substantive increases in CaO from core-to-rim (e.g. Griffin et al, 1999). We ascribe the unique near-constant CaO observed by IV12 in harzburgitic garnets (Fig. 1) to low metasome/rock ratios and attendant effective internal buffering of CaO in garnet harzburgite-magnesite-U&S02 melt assemblages. IV12 uniquely also record garnet CaO content *decreasing* across the lherzolite field (Fig. 1), which we ascribe to metasomatically increased Na2O in Cpx coexisting with CrGt (see Sobolev et al., 1997).

Pressures and temperatures

Single-Cpx thermobarometry shows a ~ 38 mW/m^2 geotherm for Newlands, with no evidence of near-adabiatic high temperatures, nor thermal disturbances at high P&T. Cr/Ca-in-pyrope barometry (Grütter et al, 2006) gives real P_{38} of 26 to 53 kbar for IV12 CrGt+CrSp samples, and 44 to 53 kbar for the ten diamond-bearing CrGt+CrSp samples described by ME01. The P-T data are consistent with undetectable heat transfer during U&S02 melt interaction with opx-bearing peridotite across the pressure range 53 to 26 kbar. These P-T data support the internally buffered systems at low metasome/rock ratios that we implicate in the genesis of the Newlands Cr-zoned garnets.

References

Griffin WL, Shee SR, Ryan CG, Win TT, Wyatt BA (1999) Harzburgite to lherzolite and back again: metasomatic processes in ultramafic xenoliths from the Wesselton kimberlite, Kimberley, South Africa. Contrib Mineral Petrol 134: 232-250

Griffin WL, Smith D, Ryan CG, O'Reilly SY, Win TT (1996) Trace-element zoning in mantle minerals: metasomatism and thermal events in the upper mantle. Can Mineral 34:1179-1193.

Grütter H, Latti D, Menzies A (2006) Cr-saturation arrays in concentrate garnet compositions from kimberlite and their use in mantle barometry. J Petrol 47:801-820.

Ivanic T (2007) The chromite-garnet peridotite assemblages and their role in the evolution of the mantle lithosphere, PhD Thesis, University of Edinburgh, 249 pp. [IV07]

Ivanic TJ, Harte B, Gurney JJ (2012) Metamorphic re-equilibration and metasomatism of highly chromian, garnet-rich peridotitic xenoliths from South African kimberlites. Contrib Mineral Petrol 164:505–520. [IV12]

Menzies AH (2001) A detailed investigation into diamond-bearing xenoliths from Newlands kimberlite, South Africa. PhD Thesis, University of Cape Town [ME01]

Menzies AH, Shirey SB, Carlson RW, Gurney JJ (1999) Re–Os systematics of Newlands peridotite xenoliths: implications for diamond and lithosphere formation. Proceedings of the 7th International Kimberlite Conference. Red Roof Design, Cape Town, V2, pp. 566–583. [ME99]

Sobolev VN, Taylor LA, Snyder GA, Sobolev NV, Pokhilenko NP, Kharkiv AD (1997) A unique metasomatised peridotite from the Mir kimberlite, Siberia. Russian Geol. Geophys. 38: 218–228

Sokol AG, Kruk AN, Chebotarev DA, Palyanov YN (2016) Carbonatite melt–peridotite interaction at 5.5–7.0 GPa: Implications for metasomatism in lithospheric mantle. Lithos 248–251: 66–79.

Ulmer P and Sweeney RJ (2002) Generation and differentiation of group II kimberlites: Constraints from high-pressure experiments to 10 GPa. Geochim Cosmochim Acta 66: 2139–2153. [U&S02]

Ziberna L, Klemme S, Nimis P (2013) Garnet and spinel in fertile and depleted mantle: insights from thermodynamic modelling, Contrib Mineral Petrol 166: 411-421.