Lithos 112S (2009) 1167–1178

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos

Pyroxene xenocryst geotherms: Techniques and application

Herman S. Grütter *

BHP Billiton World Exploration Inc., #800 Four Bentall Centre, 1055 Dunsmuir Street, Vancouver, B.C., Canada V7X 1L2

ARTICLE INFO

Article history:
Received 25 September 2008
Accepted 15 March 2009
Available online 5 April 2009

Keywords:
Thermobarometry
Clinopyroxene
Orthopyroxene
Lithosphere evolution
Conductive geotherm
Advective heating

ABSTRACT

Pyroxene thermobarometry of mantle materials has matured with time, experimental investigation and experience to encompass solutions for both pressure and temperature based on the composition of garnet-facies peridotitic clinopyroxene alone. Application to data sets now available in the public domain show robust compositional, pressure (P) and temperature (T) trends for clinopyroxene as well as orthopyroxene xenocrysts, parallel to matching trends for coexisting pyroxenes in garnet lherzolite xenoliths. Investigation of the unified and well-populated xenolith plus xenocryst data set shows (i) natural pyroxenes in a closer approach to compositional equilibrium than typically obtained by reversed, high P–T experiments, (ii) inappropriate treatment by modern geobarometers of aluminous pyroxene compositions in spinel + garnet peridotite, (iii) model-conductive P–T conditions at mid-lithospheric pressures, and (iv) an effectively universal presence in kimberlite-hosted deep mantle materials of supra-conductive P–T conditions, typically also associated with compositional and/or textural modification. The available clinopyroxene and garnet xenocryst data from cold, high-pressure cratonic interiors (Slave, Yakutia, Sarfartoq, Botswana) and craton-margin settings (southern Superior, south-western Kaapvaal, Lesotho, Gibeon, Minas Gerais) combine with chronologic data to show that Cr/Al-rich, depleted peridotite forms a rheological and chemical layer of remarkably variable depth that must be underlain by a thermal boundary layer to ultimate depths of 200 to 250 km. High-pressure pyroxene xenocrysts faithfully record thermal spikes from conductive to adiabatic conditions, presumably caused by advective breaching of the thermal boundary layer during plume-impact or riftogenic processes that also act to generate kimberlite melts from within the decaying thermal boundary over a 10 to 40 Ma time-scale. The compositions of pyroxene xenocrysts and age of their host constitute a powerful means with which to investigate the thermo-tectonic evolution of garnet-facies depleted lithospheres and their contained diamond reservoir.

1. Introduction

Pyroxene-based thermobarometry of mantle xenoliths has benefited from nearly 40 years' worth of academic research in traditional hard-rock petrology disciplines like experimental petrology, thermodynamic modelling, diffusion kinetics and analytical routines, but ancillary work in the fields of mantle geochemistry and lithosphere-scale geophysics have also impacted interpretation of the origin and geological history of mantle-derived rock fragments brought to Earth's surface by alkaline magmas (see O'Reilly and Griffin, 2006). Advances in the thermobarometry disciplines over the past 10 to 15 years have enabled interested parties to focus on single-grain techniques, with the advantage that 10^2 to 10^3 full or partial pressure-temperature (P–T) data may be obtained by routine electron microprobe analysis of mantle-derived xenocryst populations in a matter of days, and at relatively low cost. The diamond exploration industry has naturally found substantial commercial application of the new-age single-grain thermobarometry techniques and various stakeholders posses a veritable "treasure trove" of xenocryst P–T–X data related to alkaline magmatic events that occurred through time and across Earth's landmass. Such data are now surfacing in the public domain via publications by geological surveys (e.g. Sage, 2000; Harvey et al., 2001; Jensen et al., 2004), land-use authorities in market-oriented jurisdictions (e.g. Armstrong, 2001, 2002) and academic contributions. While the accumulating public data set for garnet xenocryst populations has received much attention (e.g. Canil et al., 2003; Griffin et al., 2004), the integration of pyroxene xenocryst data has lagged behind. In choosing topics related to pyroxene xenocryst compositions for this invited address, I intend to build on earlier work (Grütter and Moore, 2003; Read et al., 2004) and show that (i) P–T data obtained from pyroxene xenocrysts are consistent with those of xenoliths from the same localities, (ii) the compositions of xenocryst orthopyroxenes challenge the "equilibrium" achieved in reversed high-P, moderate-T phase-petrology experiments, (iii) current Al-in-pyroxene barometry models for garnet peridotite assemblages are not appropriate for spinel + garnet peridotite assemblages, and (iv) single-grain thermobarometry techniques applied to pyroxene and garnet xenocryst populations provide

* BHP Billiton World Exploration Inc., P.O. Box 49223, Vancouver, B.C., Canada V7X 1L2. Fax: +1 604 683 4125.
E-mail address: herman.grutter@bhpbilliton.com.

0024-4937/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.lithos.2009.03.023

significant insight into the thickness and thermal evolution of depleted lithospheres, particularly when integrated with temporal constraints. Abbreviations used in this work are listed in Table 1.

2. Pyroxene compositions and thermobarometry

2.1. Single-cpx vs. conventional opx-based geotherms

Comprehensive reviews of various pyroxene-based thermobarometers applicable to mantle xenoliths are presented elsewhere (Finnerty and Boyd, 1984; Carswell and Gibb, 1987; Brey and Köhler, 1990; Taylor, 1998; Grütter, 2001) and are not repeated in detail here. Instead I wish to emphasize that the enstatite-in-Cpx thermometer of Nimis and Taylor (2000) was formulated to correct for non-trivial pressure and Al, Cr, Fe and Ti compositional effects on the Opx–Cpx solvus, that it reproduces experimental temperatures in a wide range of simple and complex natural bulk compositions to within ±40 °C (1σ) over the range 900 to 1600 °C and 0 to 7.5 GPa, and that it is readily applied to xenolith-borne as well as xenocrystic cpx because compositional terms related to coexisting opx have been eliminated. Taylor (1998) noted that a TNT00-like cpx-solvus thermometer combined with a modified PNG85 opx-grt barometer reproduced to within ±0.5 GPa and ±50 °C results for over 80% of 40 oxygen-buffered experiments at 1.0 to 3.5 GPa and 1050 to 1260 °C. This prompted Grütter and Moore (2003) to compare PNT00 with PNG85 and two other opx-grt barometers at TNT00 for a range of peridotite xenolith suites. Borrowing from that work, Fig. 1 shows PNT00 ≥ PNG85 at low P–T conditions and PNT00 ≤ PNG85 at high P–T conditions, resulting in PNT00-TNT00 geothermal arrays that cross over model conductive lithospheric geotherms. Attempts are being made to rectify this known artifact of the single-cpx barometer (Nimis, 2002; Nimis, pers. comm., August 2008) though the solution has to overcome significant T dependence and low Ca(Al,Cr)-Tschermacks activity at high P/T ratios, as well as a molar volume change for the PNT00 cpx-grt barometer less than one-half that of common opx-grt barometers (see Figs. 8 and 9 in Brey et al., 1990). These characteristics account for the observation that the PNT00-TNT00 combination yields geothermal arrays with approximately double the precision (i.e. twice the scatter) of the PNG85-TNT00 combination (cf. Fig. 1C and D).

The pyroxene compositions available for garnet lherzolite xenoliths from well-known Group-1 kimberlites across Southern Africa record no material variation in conductive geothermal conditions; the differences evident at high temperature for Gibeon and northern Lesotho are attributed to advected thermal transients (Fig. 1C and 1D; Bell et al., 2003). Geothermal arrays for each of three Canadian xenolith suites can be differentiated from one another over a complete mantle temperature range from 700 °C to ~1300 °C, irrespective of the barometer applied, and with no data at temperatures above a mantle adiabat with 1300 °C potential temperature (Fig. 1). The Canadian xenolith suites show significantly less evidence of thermal disturbance at high temperatures than xenolith suites from northern Lesotho or Gibeon. The relative geothermal gradients increase in the sequence Lac de Gras<Kirkland Lake<Somerset Island, forecasting a parallel decrease in diamond potential. The presence of diamond in several kimberlites at Kirkland Lake and in the Batty Bay kimberlite on Somerset Island (Kjarsgaard and Levinson, 2002) is qualitatively inconsistent with a predominance of graphite-facies PNT00-TNT00 results (Fig. 1), further demonstrating that PNT00 underestimates absolute P at high P–T conditions (Nimis, 2002). It is noted that PNG85 and other opx-grt barometers yield high-P, high-T points marginally inside the diamond stability field for Kirkland Lake and Batty Bay garnet lherzolite xenoliths (Fig. 1; see also Grütter and Moore, 2003). The single-cpx (PNT00-TNT00) thermobarometry results for Canadian localities nevertheless present a convenient *relative* P–T framework within which to consider clinopyroxene xenocryst populations derived from other kimberlite provinces, as discussed further below. Online supplementary Appendix A lists mineral compositions, references and P–T results for the Canadian xenolith suites.

2.2. Lherzolitic opx in nature vs. experiment

Orthopyroxene-based single-grain thermobarometry has long had proponents (Mercier, 1980). A simple portrayal of opx compositions from the afore-mentioned Canadian garnet lherzolite xenolith suites clearly outlines the relative disposition of three topical geothermal arrays (Fig. 2A). The systematic covariance of opx Al_2O_3 content with Ca/(Ca + Mg + Fe) constitutes undeniable evidence that pyroxenes in lherzolite xenoliths attain near-equilibrium compositions over a large range of mantle temperatures, and that isopleths for Al-in-opx (with grt) intersect cratonic geotherms at a significant angle. That the covariance extends to low Al_2O_3 and low Ca/(Ca + Mg + Fe) where spl + grt-facies lherzolite becomes stable (see Section 2.4 below) constitutes evidence in favour of two-pyroxene + garnet equilibration in slowly cooling mantle peridotite to temperatures as low as ~700 °C (Smith and Barron, 1991), and does not support earlier literature implicating mineral-scale differential closure in nature of P- and T-dependent exchange equilibria at temperatures less than ~1000 °C (see Sautter and Harte, 1990 and references therein). Given the compositional arrays cover a representative range of P, T and geotherms sampled by kimberlites, it is justified to translocate from Figs. 1B and 2A the approximate positions of the graphite-diamond phase boundary and a $T_p = 1300$ °C mantle adiabat. Both of these are known to have a fixed slope in P–T space (they are straight lines in Fig. 1), yet the available xenolith opx data requires them to be represented with pronounced curvature, specifically to accommodate the high P/T opx compositions characteristic of high-pressure xenoliths from the central Slave craton. It follows that the solubility of Al and particularly Ca in lherzolite-hosted opx is markedly depressed at $P > 5$ to 6 GPa, a feature now also confirmed by recent experiments (Fig. 2B; Brey et al., 2008).

Compositional equilibration of peridotitic minerals is notoriously difficult to achieve in high P–T experiments, as illustrated in Fig. 2B by

Table 1
Common mineral, rock type, thermobarometry and other abbreviations.

Am, am	Amphibole
Cpx, cpx	Clinopyroxene
Dia, dia	Diamond
Gph, gph	Graphite
Grt, grt	Garnet
Ol, ol	Olivine
Opx, opx	Orthopyroxene
Phl, phl	Phlogopite
Spl, spl	Spinel
G10, G9 etc.	Garnet classifications according to Grütter et al. (2004)
Lhz	Lherzolite (Ol + Opx + Cpx assemblage)
Hzb	Harzburgite (Ol + Opx assemblage, no Cpx)
Weh	Wehrlite (Ol + Cpx assemblage, no Opx)
Dun	Dunite (>90% Ol assemblage)
Ma, Ga	10^6, 10^8 years
P	Pressure in kilobar (kbar) or GigaPascal (GPa)
T	Temperature in degrees Celsius (°C)
TBKN	Cpx–opx solvus thermometer of Brey and Köhler (1990)
TNT00	Enstatite-in-cpx thermometer of Nimis and Taylor (2000)
TNi	Ni-in-pyrope xenocryst thermometer of Ryan et al. (1996)
TZn	Zn-in-chromite xenocryst thermometer of Ryan et al. (1996)
T-Mn	Mn-in-pyrope xenocryst thermometer of Grütter et al. (1999)
PMC74	Al–Opx + Grt barometer as formulated by Finnerty and Boyd (1984)
PNG85	(Al,Cr)Opx + Grt barometer of Nickel and Green (1985)
PBKN	(Al,Cr)Opx + Grt barometer of Brey and Köhler (1990)
PNT00	(Al,Cr)Cpx + Grt barometer of Nimis and Taylor (2000)
PCr	Cr-in-pyrope xenocryst barometer of Ryan et al. (1996)
P38	Cr/Ca-in-pyrope xenocryst barometer of Grütter et al. (2006), with numeral 38 (or 35 to 45) referring to model-conductive geotherms of Pollack and Chapman (1977)