Lithos 154 (2012) 193–209

Contents lists available at SciVerse ScienceDirect

Lithos

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

Evolution of the South African mantle — A case study of garnet peridotites from the Finsch diamond mine (Kaapvaal craton); part 1: Inter-mineral trace element and isotopic equilibrium

Marina Lazarov [a,*], Gerhard P. Brey [a], Stefan Weyer [b]

[a] Institut für Geowissenschaften, J.W. Goethe-Universität, Altenhöferallee 1, D-60438 Frankfurt am Main, Germany
[b] Institut für Mineralogie, Leibniz Universität Hannover, Callinstrasse 3, 30167 Hannover, Germany

ARTICLE INFO

Article history:
Received 30 September 2011
Accepted 5 July 2012
Available online 20 July 2012

Keywords:
Kaapvaal craton
Mantle xenoliths
Mineral equilibrium
Partitioning
Sm–Nd isotopes
Lu–Hf isotopes

ABSTRACT

A thorough assessment of inter-mineral equilibrium is essential for the understanding of trace element partitioning and also for the interpretation of isotopic data. Here we investigated high temperature (~1200 °C and 6 GPa) garnet peridotite xenoliths from the Kaapvaal craton (Finsch mine, South Africa), with exceptionally well equilibrated mineral major element compositions, for their trace element and isotopic inter-mineral equilibrium. Trace element compositions for all major mineral phases, i.e. olivine, orthopyroxene (opx), clinopyroxene (cpx) and garnet, were analysed by laser ablation inductively coupled plasma mass spectrometry (ICP-MS). Garnet, cpx and opx of selected samples were analysed for their Sm–Nd and Lu–Hf isotope compositions by multi collector ICP-MS.

Most important mineral characteristics include: a) olivines from most samples are enriched in high-field-strength elements relative to other incompatible trace elements. Their lithium content correlates negatively with Mg#, indicating a depletion signature; b) all other minerals are depleted in heavy and middle rare earth elements (H- and M-REE) and enriched in light REE and large ion lithophile elements. This implies a complex history of depletion and metasomatic overprint for the Finsch cratonic mantle; c) orthopyroxene has similarly shaped trace element patterns as cpx, with one to two orders of magnitude lower abundances; and d) both, garnet and cpx, display variable, mostly positive εHf coupled with moderate variations in εNd. Trace element partitioning between garnet/cpx, cpx/opx and garnet/opx, displays only a weak pressure and temperature dependency. However, equilibrium partitioning of most trace elements between garnet and cpx shows a strong compositional dependency, i.e. on the Cr- (and Ca-) content of the garnets. Garnet–cpx partition coefficients follow a second grade polynomial correlation with Cr_2O_3 of garnet, whereby high chromium garnets ($Cr_2O_3 > 6$ wt.%) have generally higher partition coefficients for all trace elements than low Cr garnets. Potentially, enhanced trace element compatibility in high-Cr garnets may be related to the formation of a knorringite component and its influence on the garnet crystal structure. However, some elements, especially the quadrivalent Zr and Hf and the small trivalent HREE, show increased scatter indicating deviation from complete inter-mineral equilibrium.

Garnet–cpx Sm–Nd isochrons of all analysed samples are consistent with the age of the Finsch kimberlite eruption (~118 Ma). This further demonstrates complete isotopic equilibration of Sm and Nd between garnet and cpx for these mantle samples. In contrast to Sm–Nd, the Lu–Hf garnet–cpx isochrons display an age range between 60 and 570 Ma, indicating Lu–Hf disequilibrium. Most probably slow diffusion of Hf and Lu, in the absence of a melt or fluid, resulted in incomplete Lu–Hf equilibration and the preservation of an "old" radiogenic Hf in garnet and cpx.

1. Introduction

Re-equilibration in magmatic and metamorphic rocks is caused by geodynamic processes through changes in pressure (P)–temperature (T)–oxygen fugacity (f_{O2}) conditions and mass flux, e.g. partial melting or metasomatism by melts or fluids. It is important for the interpretation of a rock's history to ensure, if complete equilibration of major-, trace-elements and isotopes between all minerals in a rock was achieved after such events, or if disequilibria are still partially preserved. Adjustment to equilibrium of a respective mineral assembly is driven by re-crystallisation (added by the presence of fluids or melts) or by diffusion, resulting in a redistribution of major and trace elements and their isotopes.

---

[*] Corresponding author at: Institut für Mineralogie, Leibniz Universität Hannover, Callinstrasse 3, 30167 Hannover, Germany. Tel.: +49 511 762 5974; fax: +49 511 762 2110.

E-mail address: m.lazarov@mineralogie.uni-hannover.de (M. Lazarov).

0024-4937/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.lithos.2012.07.007

Disequilibrium between the mineral phases in a sample is obvious when minerals are zoned. On the other hand chemical homogeneity of minerals does not necessarily imply that they are in equilibrium (Brey, 1991; Fraser and Lawless, 1978). Major element equilibrium between minerals can be ascertained by applying thermo-barometers to a mineral assemblage which are based on independent exchange equilibrium and are shown to be internally consistent. Brey and Kohler (1990) established such a series of geothermobarometers for peridotitic systems. They showed that the combinations of the two-pyroxene thermometer $T_{BKN}+$Al-in-orthopyroxene barometer (P_{BKN}; Brey and Kohler, 1990), the two-pyroxene thermometer $T_{BKN}+$Ca-in-olivine barometer (P_{KB}; Koehler and Brey, 1990), the garnet–clinopyroxene Fe–Mg exchange thermometer (Krogh, 1988)$+P_{BKN}$ and the garnet–olivine Fe–Mg exchange thermometer (O'Neill, 1980; O'Neill and Wood, 1979)$+P_{BKN}$ give mutually consistent P–T conditions within their respective errors. The recommended thermobarometer versions by Nimis and Grütter (2010) give very similar results. Accordingly, if the different geothermobarometers provide the same P–T conditions within analytical and experimental error, complete equilibration of major elements between coexisting minerals may be safely assumed. However, this may not always be coupled with complete minor and trace elements (and isotopic) equilibrium. Studying mineral–melt and mineral–mineral trace element partitioning and equilibration under different conditions was the focus of a number of experimental studies (Ganguly et al., 1998; Green et al., 2000; Johnson, 1998; Klemme et al., 2002; Salters et al., 2002; Tuff and Gibson, 2007; Van Orman et al., 2001, 2002; Van Westrenen, et al., 1999, 2000). These and many other studies demonstrate that the partitioning of trace elements mainly depends on pressure, temperature and major element contents and in some cases on oxygen fugacity. Furthermore, the achievement of equilibrium in nature is also crucially dependent on inter- and intra-mineral diffusion rates, which themselves, along P, T and buffering f_{O2}, also strongly depend on the presence of a liquid or fluid upon cooling.

Garnet peridotites originate from high temperatures and pressures, but it has been shown for a substantial number of samples from cratonic areas that they display disequilibria in their major and trace elements as well as isotopic compositions (Bedini et al., 2004; Brey, 1991; Fraser and Lawless, 1978; Shimizu, 1999; Simon et al., 2003). It seems that they are often metasomatically overprinted and are also highly sensitive to alteration by a percolating fluid or melt affecting the cratonic lithospheric mantle shortly prior or during the kimberlite eruption (Bedini et al., 2004; Simon et al., 2003). Clear evidence for full scale equilibrium has only been observed in rare cases (Glaser, et al., 1999; Ionov et al., 2005; Schmidberger, et al., 2002). Schmidberger et al. (2002) demonstrated it for low temperature peridotites (<1100 °C) from Somerset Island (Canada). Glaser et al. (1999) and Ionov et al. (2005) give convincing evidence for equilibrium of garnet peridotites from a rift setting, i.e. from relatively high temperatures at low pressure.

In this study, we focus on a high temperature peridotite xenolith suite from the Finsch diamond mine in South Africa (SA). The Finsch kimberlite (~118 Ma — Smith, 1983; Smith et al., 1985) belongs to the older group-II kimberlites with an age range between 150 and 120 Ma. In contrast to mantle samples from the younger group-I kimberlites (from 90 to 75 Ma — Smith et al., 1985) xenoliths from group-II kimberlites display little evidence of late metasomatic overprint prior to eruption (Bell et al., 2003; Griffin et al., 2003; Lazarov et al., 2009a). The set of samples investigated here has been shown to be in internal mineral equilibrium with respect to major elements (Lazarov et al., 2009a). Equilibrium was likely achieved over a long period (at least of around 400 Ma — Lazarov et al., 2009b, 2012—this issue of stable conditions. A study on major and trace elements on garnet (grt) and clinopyroxene (cpx) from an assorted set of Finsch xenoliths has recently been published by Gibson et al. (2008) and we include these data in the discussion of our results presented here.

Most of previous studies on mantle peridotites considered trace element exchange only between garnet and cpx, as they are the major hosts for these elements in mantle peridotites. However, though orthopyroxene (opx) has relatively low abundances for most trace elements its modal abundance in peridotites is relatively high and therefore its influence on trace element partitioning was also considered in this study.

The aim of part 1 of our study is the essential evaluation of trace element equilibrium and the parameters that affect trace element partitioning. Furthermore, we evaluate the effect of trace element equilibrium/disequilibrium on mineral (garnet–cpx) Lu–Hf and Sm–Nd isochron ages.

2. Sample overview

Twenty five garnet peridotites from the Finsch mine were collected during a field campaign in 2002. Detailed petrography with modal mineral abundances, major element composition and geothermobarometric calculations was published by Lazarov et al. (2009a). We selected 16 garnet peridotites from that study and were provided with 2 additional samples by H. Gruetter (samples 695 and 882; Skinner, 1986), and three diamond bearing peridotites by F. Viljoen (samples 554-XM46, 556-XM48 and 865; Shee et al., 1982; Viljoen et al., 1992). The whole suite comprises 3 garnet lherzolites (peridotites: F-13, F-15 and F-16), 14 garnet harzburgites (with only one cpx-free sample F-7), and 4 garnet dunites (peridotites: F-3 and F-8 with cpx and peridotites: F-2 and 882 without). One cpx-poor harzburgite (F-12) contains rutile and sulphide, and dunite 882 contains spinel.

Lazarov et al. (2009a) demonstrated major element homogeneity in all minerals from all samples of interest. The magnesium number (Mg# = [Mg/(Mg + Fe)] × 100) in olivine and opx is high ranging from 91.2 to 93.7 and from 92.3 to 94.6, respectively (Table 1). Clinopyroxenes have Mg# ranging between 91.8 and 95.1 and chromium numbers (Cr# = [Cr/(Cr + Al)] × 100) between 21.6 and 49.3. The majority of garnets fall into the “lherzolite” field of a CaO–Cr_2O_3 diagram, i.e. their composition is buffered by coexisting opx and cpx. Exceptions are two dunites (samples F-2 and 882) and one cpx-free harzburgite (sample F-7) that figure on the low Ca side of the “harzburgite” field. The Cr# in these garnets varies between 5.94 and 34.3 and the Mg# between 83.2 and 87.1 (Lazarov, et al., 2009a).

The application of independent geothermobarometers gave internally consistent results for pressure and temperature estimates. The combination of thermometer T_{BKN} (Brey and Kohler, 1990), or T_{OW} (O'Neill and Wood, 1979) for cpx-free samples, with the barometer P_{BKN} (Brey and Kohler, 1990) yields a temperature range from 1050 to 1240 °C and a pressure range from 4.4 to 6.5 GPa. Taking into account the effect of Fe^{3+} (measured by Mössbauer) on Fe–Mg exchange thermometry, temperatures calculated with T_{OW} increase by ~80 °C and all samples display a narrow temperature range of ~1150–1240 °C (Lazarov et al., 2009a). This indicates a restricted depth range for the Finsch peridotites of about 50 km between 170 and 220 km (5.2–6.5 GPa) along a 41 mW/m^2 (Chapman and Pollack, 1977) geothermal gradient with oxygen fugacity decreasing with depth (Lazarov et al., 2009a). As for other South African mantle peridotites (e.g. Bell et al., 2003; Griffin et al., 2003 and ref. therein), shallower Finsch xenoliths have a tendency to be more depleted than those from the cratonic root. This observation is also in accord with findings based on the investigation of subcalcic garnets from Finsch (from strongly depleted, cpx-free garnet harzburgites) which originated from depths between 150 and 180 km (Lazarov et al., 2009b).