Oxidation state beneath the Kaapvaal craton as revealed by xenoliths from the Finsch mine (South Africa)

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Introduction

Due to complex geochemical processes such as partial melting, recycling of oceanic lithosphere and metasomatic re-enrichment physical and chemical heterogeneities develop in the Earth's upper mantle. Those chemical processes always involve volatiles (C-O-H-S) whose speciation is a function of the prevailing oxygen fugacity.

The crystal chemistry of garnet suggests that the oxygen fugacity of an isochemical upper mantle should fall with increasing depth (Wood et al. 1990; Ballhaus, 1993). On the other hand, relative oxygen fugacity measured for lithospheric upper mantle is heterogeneous (e.g. Woodland et al. 1992). Changes in oxygen fugacity have been noted to occur with metasomatism in garnet peridotites (McCammon et al., 2001) as well as in shallower (spinel stability field) tectonic environments (Wood et al., 1990; Woodland et al. 1992; Ballhaus, 1995).

A suite of 21 mantle peridotites from the Finsch mine (South Africa) were analysed for mineral major and trace elements to determine metasomatic enrichment of the samples. We have also employed Mössbauer spectroscopy to measure $Fe^{3+}/\sum Fe$ in garnet (grt) and clinopyroxenes (cpx) from a subset of these samples. The garnet measurements were used to calculate oxygen fugacity ($\Delta \log fO_2$ [FMQ]) of the subcratonic mantle and to observe cpx-grt partitioning in peridotites. This study also gives constraints on changes in oxidation state of the lithospheric mantle caused by metasomatic re-enrichment processes.

Petrography, major and trace element composition of peridotites

All analysed samples are garnet-bearing peridotites. Two samples are cpx-free harzburgites, while all others have present cpx. Three samples (two lherzolites and one cpx-free harzburgite) are strongly depleted and have more than 90 mod.% of olivine. Only one sample is modally metasomatised peridotite, containing rutile and pentlandite, while all other samples have only minor secondary phases: spinel, phlogopite, amphibole and secondary clinopyroxne in the garnet kelyphite rims. According to the classification of Harte (1977) the majority of the samples have medium- to coarse-grained tabular to equant textures.

Based on electron microprobe (EPMA) and LA-ICP-MS data the mineral phases are homogeneous in all samples. The only exceptions are two cpx-bearing peridotites whose clinoproxenes show very narrow reaction rims. This zonation is detectable for EPMA, but is too fine for the LA-ICP-MS technique.

The Mg# values (Mg#=100xMg/(Mg+Fe)) of olivine and orthopyroxene (opx) average 92.4 and 93.3, respectively, and are in good agreement with values from other southern Africa kimberlite derived garnet peridotites (Woodland and Koch, 2003; Simon et al., 2007). They both indicate a depleted nature for the peridotites. Only a few opx have slightly elevated Na contents indicating a metasomatic overprint.

Garnets have highly variable Mg# and Cr# (Cr#=Cr/(Cr+Al)), which are on average higher than the "normal" garnets from other Kaapvaal craton garnet peridotites (Woodland and Koch, 2003; Simon et al. 2007). Most of the garnets are Ca-saturated and plot in the lherzolite field in a Ca-Cr diagram (Fig. 1). Only two garnets are Ca-undersaturated and belong to the harzburgitic group. The $Fe^{3+}/\Sigma Fe$ of garnet from 15 samples vary from 0.04 to 0.078 with the most common value of ~0.06. These ratios are similar to those reported for other Kaapvaal localities (Woodland and Koch, 2003).

Clinopyroxenes have relatively homogeneous Ca# (Ca#=Ca/(Ca+Mg)) with the average of 43.5, but show larger ranges in Mg# and Cr#. The $Fe^{3+}/\Sigma Fe$ of cpx in 6 samples range from 0.105 to 0.154. A couple of samples have cpx with slightly higher Na and Cr contents indicating a metasomatic overprint by a kimberlite-like melt, comparable to the MARID-suite Type II cpx of Gregoire et al. (2003). The rims of the two zoned clinopyroxenes have higher Mg#, Cr#, Ca# and TiO_2 and lower Na_2O and Al_2O_3 than the cores. These differences are explainable by reaction with the host kimberlite.

Except for the rutile-pentlandite-bearing peridotite with strongly elevated Ti contents in all phases, minerals from all other samples are undersaturated in a Ti-phase.

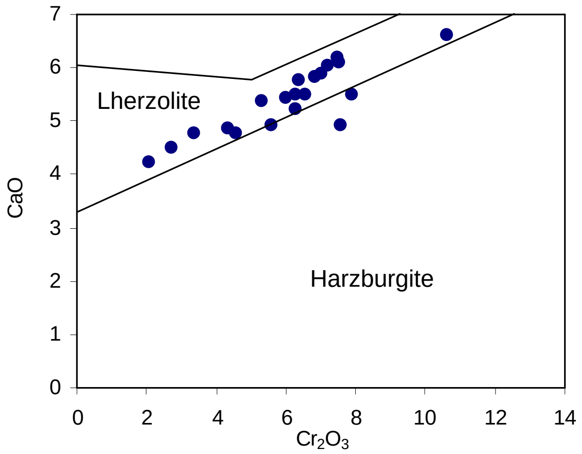

Fig. 1 CaO-Cr_2O_3 (in wt %) discrimination diagram for garnets from the Finsch mine peridotite xenoliths.

In contrast to the simple primitive major element characteristics, trace element and isotope compositions indicate a complex metasomatised history (see Lazarov et al. 2008, this volume).

Garnet thermobarometry and oxybarometry

Major element inter-mineral equilibrium was tested by comparing different mineral thermometers for a given barometer. For this purpose the garnet-opx barometer (P_{BKN}) of Brey and Köhler (1990) was used. All observed differences lie within the errors of the method, which suggests major element equilibrium in the Finsch peridotites.

We used the combination of the two-pyroxene-thermometer (T_{BKN}) together with garnet-opx barometer (P_{BKN}) of Brey and Köhler (1990) and solved iteratively for all lherzolites. For cpx-free peridotites, the combination of the olivine-garnet Fe-Mg exchange thermometer ($T_{O'Neill}$) (O'Neill and Wood, 1979) and P_{BKN} was used. The calculated temperatures range from 1050 to 1250 °C and the pressures from 4.4 to 6 GPa, indicating sample equilibration within the diamond stability field.

The Fe^{3+} content of garnet and cpx was obtained by Mössbauer spectroscopy. We calculated oxygen fugacity for fifteen peridotites from Finsch using the olivine-orthopyroxene-garnet equilibrium as calibrated by Gudmundsson and Wood (1995), including the typographical correction noted by Woodland and Peltonen (1999). Values of oxygen fugacity were calculated relative to the FMQ buffer ($\Delta \log fO_2$ [FMQ]) and range from -2.5 to -5.3. Uncertainties in fO_2 are estimated to be ±0.06 log units.

Discussion

The Fe^{3+} partitioning between garnet and cpx in all six observed pairs is consistent with the relation proposed by Canil and O'Neill (1996) (Fig. 2) and suggests equilibration of Fe^{3+} between these two phases (see also Woodland, 2008, this volume). Even for the rutile-pentlandite bearing lherzolite equilibrium of Fe^{3+} between garnet and cpx is reached.

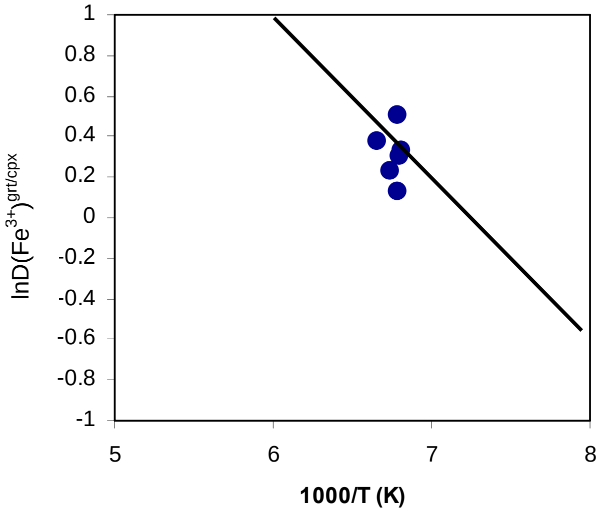

Fig. 2 Co-variation diagram of $\ln D(Fe^{3+})^{grt/cpx}$ partitioning and reciprocal temperature (in Kelvin) for Finsch mine peridotites. The line marks the correlation observed by Canil and O'Neil (1996) for Kaapvaal craton xenoliths.

Our sample suite is representative of high-temperature, primitive coarse-grained lithospheric mantle. The samples originated from a relatively limited depth range, from ~150 to ~200 km (corresponding to 4.4 - 6 GPa). Nevertheless, they exhibit a relatively large range in $\Delta \log fO_2$ [FMQ] that decreases more or less linearly with depth (Fig. 3). The fO_2 values of the lower pressure (<5GPa) samples compare well with literature data for Kaapvaal craton cold peridotites (Canil and O'Neill 1996; Woodland and Koch, 2003) (Fig. 3). The deepest Finsch samples record low fO_2s around the Fe-wüstite oxygen buffer and are some of the lowest yet reported. In contrast to that observed for xenoliths from Lesotho and other South African localities, (Woodland and Koch, 2003), no kink is observed in the trend of fO_2 with depth at ~150 km (4.5 GPa).

Five samples record slightly more oxidised conditions to that defined by the remaining ten samples (Fig. 3). These samples exhibit obvious signs of metasomatism (rutile-pentlandite bearing), or in one case have been affected by interaction with kimberlite melt (sample with zoned cpx). Their fO_2 values partly overlap with the sheared peridotites from other southern African localities (see Fig. 3).

Excluding the metasomatised samples from Finsch and the sheared peridotites from other southern African localities, an oxygen fugacity gradient of ~ -1 logfO_2 per GPa relative to the FMQ buffer is apparent (Fig. 3). This gradient is considerably higher than that modelled by Ballhaus (1995) (-0.6 log fO_2/GPa).

On the other hand, such a trend was predicted by Woodland and Koch (2003) for the situation that the depleted lithospheric mantle extended to greater depths. Thus the kink on their relation between fO_2 and depth can be attributed to either metasomatic effects or to a transition to more fertile bulk compositions.

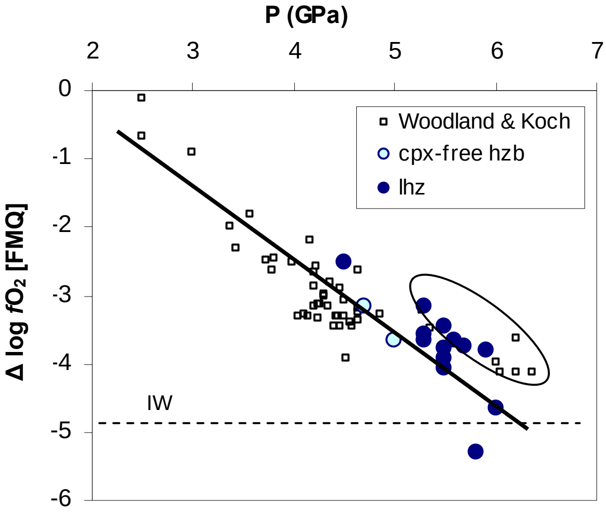

Fig. 3 Variation of ΔlogfO_2 [FMQ] with pressure for peridotites from Finsch mine. Samples from other southern African localities (Woodland and Koch, 2003) are plotted for comparison. Encircled samples are strongly metasomatised and sheared peridotites. The Fe-wüstite (IW) oxygen buffer equilibrium, calculated after O'Neill and Pownceby (1993), is also shown for reference. The line marks the linear correlation of fO_2 with the increasing pressure (depth) beneath the Kaapvaal craton (see text).

For the Finsch xenoliths, we conclude that the fO_2 in the subcratonic mantle decreases continuously with the depth, probably reaching metal saturation at depths >250 km. It appears that particular metasomatic events, such as Fe-Ti enrichment (rutile-pentlandite bearing sample), as well as the process leading to a sheared texture (Kimberley and Lesotho samples from Woodland and Koch, 2003) lead to localised oxidation. Short-lived metasomatic episodes have the capacity to create a somewhat more oxidising environment in the upper mantle, which over time can influence large regions.

References

Ballhaus, C., 1993. Redox states of lithospheric and asthenospheric upper-mantle. Contributions to Mineralogy and Petrology, 114(3): 331-348.

Ballhaus, C., 1995. Is the upper mantle metal-saturated? Earth and Planetary Science Letters, 132(1-4): 75-86.

Brey, G.P., and Köhler, T., 1990. Geothermobarometry in 4-phase lherzolites. 2. New thermobarometers, and practical assessment of existing thermometers. Journal of Petrology 31, 1353-1378.

Canil, D. and Oneill, H.S.C., 1996. Distribution of ferric iron in some upper-mantle assemblages. Journal of Petrology, 37(3): 609-635.

Harte, B., 1977. Rock nomenclature with particular relation to deformation and recrystallization textures in olivine-bearing xenoliths. Journal of Geology, 85(3): 279-288.

Gregoire, M., Bell, D.R. and Le Roex, A.P., 2003. Garnet lherzolites from the Kaapvaal craton (South Africa): Trace element evidence for a metasomatic history. Journal of Petrology, 44(4): 629-657.

Gudmundsson, G. and Wood, B.J., 1995. Experimental tests of garnet peridotite oxygen barometry. Contributions to Mineralogy and Petrology, 119(1): 56-67.

Lazarov M., Brey, G.P., Weyer, S., 2008. Timing of final depletion of the lithospheric mantle beneath the Kaapvaal craton: Constraints from Lu-Hf dating of garnet peridotites from the Finsch mine (South Africa). 9th Kimberlite Conference extended abstract A00393, this volume

McCammon, C.A., Griffin, W.L., Shee, S.R. and O'Neill, H.S.C., 2001. Oxidation during metasomatism in ultramafic xenoliths from the Wesselton kimberlite, South Africa: implications for the survival of diamond. Contributions to Mineralogy and Petrology, 141(3): 287-296.

Simon, N.S.C., Carlson, R.W., Pearson, D.G. and Davies, G.R., 2007. The Origin and Evolution of the Kaapvaal Cratonic Lithospheric Mantle. J. Petrology, 48(3): 589-625.

O'Neill, H.S.C., Wood, B.J., 1979. Experimental-study of Fe-Mg partitioning between garnet and olivine and its calibration as a geothermometer. Contributions to Mineralogy and Petrology, 70(1): 59-70.

Wood, B.J., Bryndzia, L.T. and Johnson, K.E., 1990. Mantle Oxidation State and Its Relationship to Tectonic Environment and Fluid Speciation. Science, 248(4953): 337-345.

Woodland, A.B., 2008. Ferric iron contents of clinopyroxene from cratonic mantle and partitioning behaviour with garnet. 9th Kimberlite Conference extended abstracts, this volume.

Woodland, A.B and Peltonen, P., 1999. Ferric iron contents of garnet and clinopyroxene and estimated oxygen fugacities of peridotite xenoliths from the eastern Finland kimberlite province. In: J.J. Gurney, J.L. Gurney, M.D. Pascoe and S.H. Richardson (eds), Proceedings of the 7th International Kimberlite Conference. Red Roof Design, Cape Town. p. 616-624.

Woodland, A.B. and Koch, M., 2003. Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa. Earth and Planetary Science Letters, 214(1-2): 295-310.

Woodland, A., Kornprobst, J., Wood, B.J., 1992. Oxygen thermobarometry of orogenic lherzolite massifs. J. Petrol. 33, 203-230.