CRYSTAL CHEMISTRY AND THERMOBAROMETRY OF THE CONSTITUENT PHASES OF A SUITE OF SPINEL PERIDOTITE XENOLITHS FROM HANNUOBA (NE CHINA)

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The North China Craton (NCC), located in the North-Easter China, is one of the oldest Archean cratons in the world and preserves crustal remnants as old as 3.8 Ga (Liu *et al.*, 1992). It is mainly composed by Late Archean to Paleoproterozoic terrains and by few preserved more ancient cores. Using lithological, structural, and geochronological data Zhao *et al.* (2000, 2001) divided the NCC into two blocks, the Western and Eastern ones, separated by a North-South trending orogenic belt named Central Zone (Fig. 1). Both the blocks have a basement dominated by Late Archean complexes often metamorphosed at about 2.5 Ga (Zhao *et al.*, 2001). The Eastern Block has been interpreted as an active-type continental margin and probably a coherent block since 3.6 Ga and consists of rare meta-sediments close to the Hadean-Archaean transitions (3.85 Ga), minor Early Archean granitic or gneissic cores as well as few granitoid complexes attributed to Middle Archean (3.3 Ga). The Western Block, instead, had a passive-type continental margin, on which Paleoproterozoic metasedimentary sequences, comprehending graphite-sillimanite bearing gneisses, calc-silicates and marbles (stable continental margin deposits according to Zhao *et al.*, 2000) are present. The Central Zone, interpreted as the evolution of the active type continental margin, is characterized by the presence of reworked Late Archean terrains (2.4-2.5 Ga) often present as dominantly high pressure granulite facies gneisses filled by 2.5 Ga mafic-ultramafic volcanic/plutonic and cumulitic rocks (ex Dongwanzi ophiolite; Kusky *et al.*, 2001) and interpreted as oceanic floor or meta-arc type magmatites. Such lithotypes were reworked by more juvenile crustal material that suffered metamorphic events at ~1.8 Ga, age supposed (Wu and Zhong, 1998) to represent the final amalgamation stage of the NCC. Notably, the Hannuoba basalts overlie these suture lithotypes and Os isotope on clinopyroxenes from mantle xenoliths of the same locality show ages of 1.9 Ga (Gao *et al.*, 2002). Unlike other Archean cratons, the NCC, after a period of magmatic and tectonic quiescence, experienced tectonothermal reactivation during the Late Mesozoic and Cenozoic as it is documented by the emplacement of voluminous Late Mesozoic granites and extensive Cenozoic

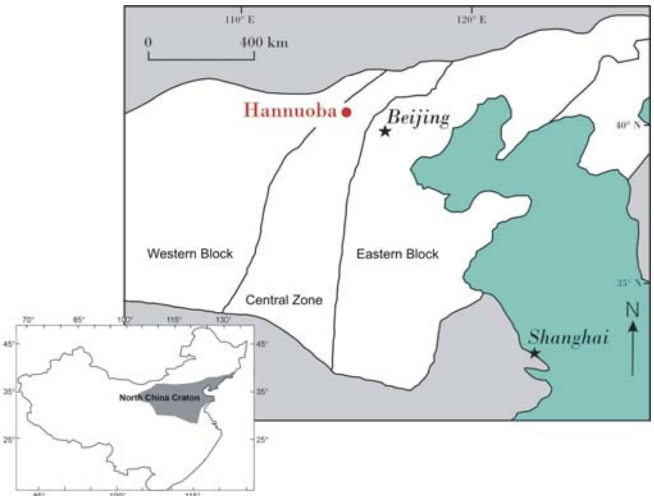

Fig. 1 – Map of North China Craton showing the Hannuoba basaltic plateau mentioned in the text. The subdivision is based on Zhao *et al.* (2000, 2001). Inset shows location of the North China Craton.

volcanism (*e.g.* Liu *et al.*, 2001). The latter is related to widespread Cenozoic rifting in the NCC and carries a variety of mantle and crustal xenoliths (Cao & Zhu, 1987). The Hannuoba basaltic plateau (200 km northwest of Beijing, within the NCC) covers an area of 1700 km^2 and it consists of intercalated alkalic and tholeiitic basalts, with the xenoliths hosted in the former.

In this PhD thesis a suite of 16 xenoliths from Hannuoba plateau has been studied by single crystal X-ray diffraction, EMPA and LA-ICP-MS. The xenoliths investigated are spinel lherzolites with protogranular texture whose chemical compositions (olivine $Fo_{89.2\text{-}90.6}$, orthopyroxene $En_{88.6\text{-}90.2}Fs_{8.4\text{-}9.9}Wo_{1.0\text{-}1.5}$, clinopyroxene $Wo_{43.8\text{-}48.5}En_{47.4\text{-}51.5}Fs_{3.4\text{-}5.2}$, Cr-spinel; Mg# of silicate minerals = 0.90-0.94; Cr# of Cr-spinel = 0.09-0.47) reflect those of the upper mantle rocks. No chemical differences are shown between cores and rims. Crystal chemical studies reveal that structural parameters and cation distribution resemble those of mineral phases crystallizing in high pressure conditions. Clinopyroxenes have T polyhedron near fully occupied by Si^{4+} (1.889-1.945 atoms per formula unit, apfu), as is typical for pyroxenes from ultramafic inclusions, and cell volumes between 433.34 Å^3 e 436.44 Å^3. Similarly, orthopyroxenes have T polyhedron near fully occupied by Si^{4+} (1.898-1.949 apfu) and cell volumes ranging from 833.15 Å^3 to 835.06 Å^3. Olivine cell volume shows very small variations (291.44-291.90 Å^3) related to Fo content. Spinels cell edge a_0 varies between 8.1332 Å and 8.2265 Å being related to Cr content and the oxygen coordinate u is about 0.2630 (0.2629-0.2631).

The closure temperatures of *intra*crystalline reactions (*i.e.* ion exchange reactions between non-equivalent sites of the same mineral) for the four constituent phases provide a mean value of 700-750°C suggesting a quite slow cooling rate and hence a thermal history consistent with the petrological enviroment (*flood basalts*). The *inter*crystalline temperature (*i.e.* temperature at which the ion exchange reactions between different coexisting phases ceased) shows values between 880-1050°C representing the last equilibration conditions of the constituent phases before the lherzolithic xenoliths were brought up to the surface by the alkaline magma. Calibrations based on the Fe-Mg exchange reaction between olivine and spinel (*i.e.* geothermometers of Ballhaus *et al.*, 1991, and O'Neill & Wall, 1987) gave temperatures coherent with values obtained from pyroxene geothermometers (Brey & Köhler, 1990; Sachtleben & Seck, 1991; Wells, 1977; Wood & Banno, 1973) suggesting a complete stage of equilibrium reached in the mantle.

Estimation of equilibration pressure is problematic for garnet-free rocks (such as Hannuoba lherzolites) because the only available geobarometer (Köhler & Brey, 1990) implies an accurate determination of Ca content (ppm) in olivine. This determinations has been made only for three samples, representative of the suite, giving a pressure range between 15.2 and 19.7 kbar. Other determinations have been made using Mercier (1980) barometers for both clinopyroxene and orthopyroxene compositions although the validity of the method for clinopyroxenes is not reliable, since it strongly depends on chemical parameter involved in the barometric formulation (Ca content in clinopyroxenes; see discussion in Princivalle *et al.*, 1994). Values obtained by Mercier barometers are 7-22 kbar for clinopyroxenes (out of spinel-peridotite field and hence in contrast with petrological evidence) and 16-20 kbar for orthopyroxenes, giving a mean value of 11-21 kbar. To obtained other barometric estimates, the structural parameters of cpx have been used too, since they are very sensitive to pressure and temperature of equilibration (Dal Negro *et al.*, 1984, 1989; Cundari *et al.*, 1986; Princivalle *et al.*, 1994, 2000a, 2000b). Although the structural barometer does not give a numerical indication it defines with precision the pertinent field: the studied cpx plot in the spinel peridotite field located between the spinel-garnet peridotite field (20-22 kbar; Nimis, 1995) and the spinel-plagioclase peridotite field (10-12 kbar; Nimis,

1995) (Fig. 2). The P-T conditions for the Hannuoba xenoliths are shown in Fig. 3 and correspond to a depth of about 50-60 km (Moho depth beneath the Hannuoba area at about 42 km; Chen *et al.*, 2001). The upper pressure boundary of 23 kbar (P max) has been determined using the method proposed by Webb & Wood (1986), based on Cr/Cr+Al (Cr#) spinel ratio.

Chondrite-normalised REE abundances in clinopyroxenes show a wide range of patterns, varying from LREE-depleted to LREE-enriched, confirming the origin of the studied xenoliths as peridotite restites (*i.e.* peridotites which suffered extraction of basaltic component in the mantle). Moreover some of them, after melt depletion, experienced metasomatic enrichment. Based on the different REE contents and ratios three groups have been defined (Fig. 4), namely depleted $(La/Yb)_n$ = 0.294-0.835, enriched $(La/Yb)_n$ = 2.564-10.492 and U-shaped $(La/Yb)_n$ = 1.426-4.673. Considering LILE and REE contents all the clinopyroxenes plot along mixing trends which, starting from a calculated DMM clinopyroxene (Depleted MORB Mantle; Workman & Hart, 2005), points towards crustal compositions (Upper and Lower Crust; Rudnick & Gao, 2003) (Fig. 5). No differences are shown between cores and rims. Moreover, the enriched clinopyroxenes show LREE pattern quite similar to those of the clinopyroxenes from pyroxenite xenoliths of the same area interpreted as derived by the involvement of crustal melts (Xu, 2002).

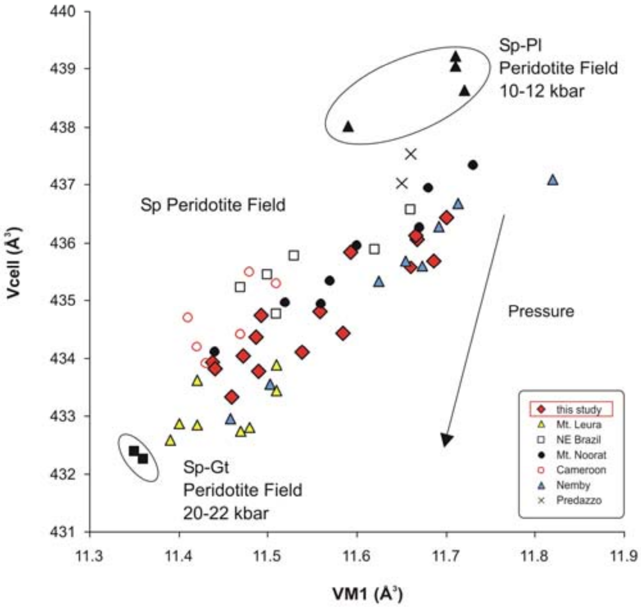

Fig. 2 – Variation of V_{M1} (volume of M1 polyhedron) *vs.* V_{cell} (volume of cell) for cpx. Areas with Sp-Pl and Sp-Gt, cpx from spinel-plagioclase and spinel-garnet peridotite respectively (Nimis, 1995). Other symbols i the figure are relative to cpx in peridotite xenoliths from: Mt. Leura and Mt. Noorat, Victoria, Australia (Dal Negro *et al.*, 1984; Cundari *et al.*, 1986); NE Brazil (Princivalle *et al.*, 1994); Cameroon (Princivalle *et al.*, 2000a); Predazzo (Carraro & Salviulo, 1998); Nemby, Paraguay (Princivalle *et al.*, 2000b).

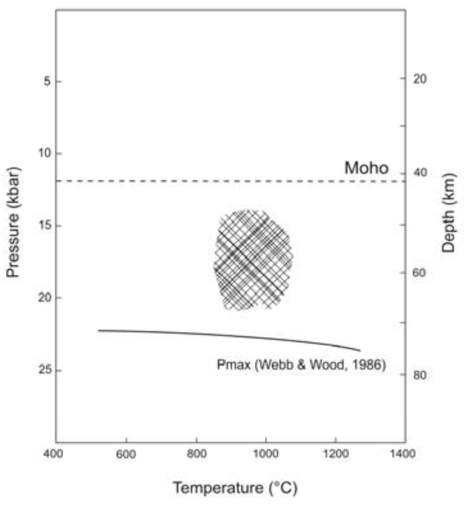

Fig. 3 – Equilibration pressures and temperatures of xenoliths determined by the combination of different geothermobarometers (see text for references). Maximum pressures estimate after Webb & Wood (1986).

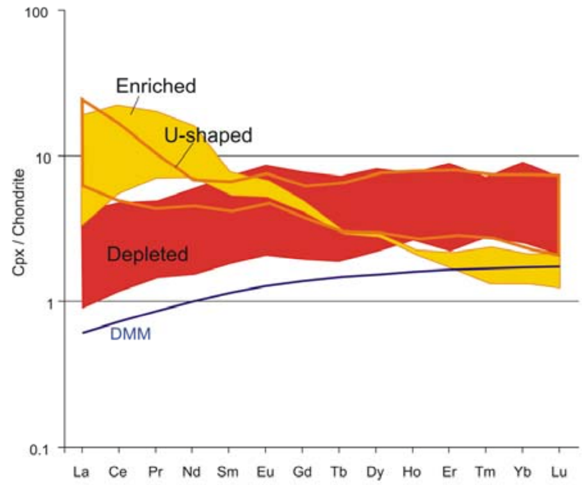

Fig. 4 – Chondrite-normalized REE pattern for Hannuoba clinopyroxenes. Chondrite values from Taylor & McLennan (1985); DMM (calculated composition for cpx Depleted MORB Mantle; Workman & Harte, 2005).

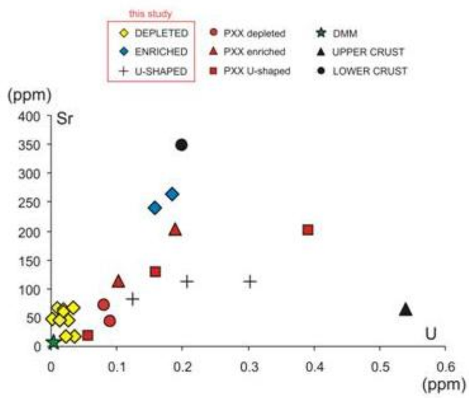

Fig. 5a – Incompatible trace element compositional variations for Hannuoba cpx. Data sources: PXX depleted, enriched and U-shaped (cpx from pyroxenite xenoliths from Hannuoba; Xu, 2002); Lower and Upper CRUST, recommended composition from Rudnick & Gao, 2003; DMM (calculated composition for cpx Depleted MORB Mantle; Workman & Harte, 2005).

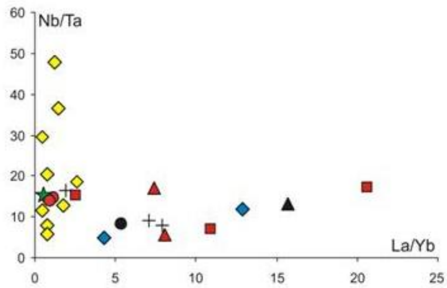

Fig. 5b – Incompatible trace element compositional variations for Hannuoba cpx. Symbols as in Fig. 5a.

Many authors (*e.g.* Xu, 2002; Rudnick *et al.* 2004) agree on the timing of melt depletion [in the Paleoproterozoic (1.9 Ga; as predict by Gao *et al.*, 2002, from Os isotopes), at the time of the final amalgamation of the NCC (Zhao *et al.*, 2000, 2001)], and on the metasomatism related to a subductional event of crustal material, but the timing and the "velocity" of the metasomatic overprinting is still controversial. The metasomatism could be an *ancient event* related to the subduction that leaded to the amalgamation of the NCC or a *recent event* related to the Late Mesozoic reactivation. Moreover the metasomatism could be a *fast event* (metasomatism due to diffusion along interfaces between grains; model by Hiraga *et al.*, 2007) or a *slow event* (metasomatism due to diffusion through grain interiors; La = 1 mm/Ga; Sr = 1 cm/Ga; data extrapoleted from Sneeringer *et al.*, 1984; Van Orman *et al.*, 2001).

The data collected in this work allow to formulate the present hypothesis on metasomatism based on these evidences: 1) the coexisting phases in the xenoliths do not show any chemical variation between core and rim, 2) the crystal-chemical parameters of all the phases suggest a P-T equilibrium stage in the mantle, 3) REE distribution in cpx is homogeneous both for high diffusivity element (*e.g.* Sr) and low diffusivity element (La), and considering that the NCC experienced a long period of magmatic and tectonic quiescence (that is a sufficient condition to justify the re-equilibration of all the elements in clinopyroxenes), the metasomatism has to be considered an ancient and slow event.

So, the studied xenoliths are representative of an heterogeneous mantle which experienced a metasomatic overprinting related to crustal subduction at the time of the final amalgamation of the NCC. And this is also coherent with the position of the Hannuoba basaltic plateau (in the Central Zone, which represents the suture of the NCC).

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