METASOMATISM *VS*. REFERTILISATION: NEW INSIGHTS FROM NORTHERN VICTORIA LAND MANTLE XENOLITHS (ANTARCTICA)

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INTRODUCTION AND AIM OF THE THESIS

As it is widely known, ultramafic xenoliths are an essential source of information on the nature and evolution of the lithospheric mantle. In this regard, the main objective of this thesis is to provide a complete petrological characterization of a wide area of the lithospheric mantle beneath Northern Victoria Land (NVL, Antarctica), focusing on the comprehension of the depletion and enrichment processes that affected the peridotite matrix (*i.e.,* melting, refertilisation, metasomatism), as well as on the constrains of the thermo-barometric conditions of the analysed area.

The occurrence of mantle xenoliths entrained in Cenozoic lavas from Northern and Southern Victoria Land were documented by several works (Coltorti *et al*., 2004; Perinelli *et al*., 2006, 2008, 2011; Melchiorre *et al*., 2011; Bonadiman *et al.*, 2014; Martin *et al*., 2015), providing petrological information on the large domain of the Sub Continental Lithospheric Mantle (SCLM) beneath the Antarctic region.

Recently, Martin *et al*. (2015) provided oxybarometer and geothermobarometer data from Southern Victoria Land in accord with those obtained in Northern Victoria Land (Perinelli *et al.*, 2012; Bonadiman *et al.*, 2014).

According to Zipfel & Wörner (1992), mantle xenoliths from Mt. Melbourne record three main evolutionary stages: 1) adiabatic rise and dynamic high temperature recrystallization of mantle phases at lower pressure; 2) cooling and re-crystallization under low pressure; 3) local heating of lithospheric mantle linked to the magmatism of the West Antarctic Rift System (WARS). Constraints on the nature and evolution of the mantle beneath this region were also suggested by Coltorti *et al.* (2004), who explained the presence of amphibole in mantle xenoliths from Baker Rocks as a reaction product between under-saturated alkaline-silicate metasomatic fluids and pre-existing clinopyroxene and spinel. At Greene Point (100 km a part from Baker Rocks), Perinelli *et al.* (2006) pointed out the presence of a lithospheric mantle portion originated in the garnet stability field and later re-equilibrated in the spinel stability field. Cryptic and modal metasomatism, characterized by Fe-Ti addition and variable Light Rare Earth Elements (LREE) enrichments were recognised as recent event following partial melting. Evidences for an eclogite component in the Greene Point mantle were highlighted by Melchiorre *et al.* (2011) to explain the extreme Os and Hf contents measured *in situ* in sulphides and clinopyroxenes, respectively.

Cenozoic basalts from NVL were described in detail in terms of major and trace element compositions, as well as isotopic ratios, by Nardini *et al.* (2009) with the aim to constrain the evolution of the WARS. On the basis of He isotopic ratio they excluded a mantle plume as the driving force responsible for the rifting processes, suggesting that the magmas originated in the lithospheric mantle were modified during a progressive replacement by asthenosphere-derived material. During the Cretaceous, small amounts of melt were generated, which were unable to reach the surface, but they strongly metasomatized the lithospheric domains. These enriched domains were successively melted as a consequence of the transtensional tectonics that formed the WARS. Finally, magmas erupted to the surface following a NW-SE fault system to form plutons, dykes, and lavas.

Most of the above mentioned studies concluded that the lithospheric mantle below the WARS was highly chemically and mineralogically heterogeneous. In order to contribute to this debate, in this work a detail petrological dataset (major, trace elements, and isotopic data) of three Antarctic mantle xenolith suites is presented: Greene Point (GP, 67°19’00’’ S, 165°57’00’’ E, Pelorosso *et al.*, 2016), Handler Ridge (HR, 72°31'00'' S, 167°18'00'' E) and Harrow Peaks (HP, 74°04'00'' S, 164° 45' 00'' E), these latter never studied before, extending the knowledge of the Antarctica SCLM over a large area. This allowed to investigate the depletion and enrichment processes such as metasomatism and refertilisation, and to implement the geothermobatometer dataset of NVL, also in comparison with recent mineralogical studies based on amphibole crystallochemistry (Bonadiman *et al.*, 2014; Gentili *et al*., 2015).

ANALYTICAL METHODS

Mineral and glass compositions (major elements) were determined by combined microscopic and Back-Scattered Electron (BSE) imaging, followed by microanalyses using a CAMECA SX100 electron microprobe equipped with four wavelength dispersive X-ray (WD) and one energy dispersive X-ray (ED) spectrometers at the Department of Lithospheric Research, University of Wien (Austria). The operating conditions were as follows: 15 kV accelerating voltage, 20 nA beam current, 20 s counting time on peak position. In order to minimise Na and K loss, a 5µm defocused beam and 10 s counting time on peak position were applied for glass analyses. Natural and synthetic standards were used for calibration and PAP corrections were applied to the intensity data (Pouchou & Pichoir, 1991). The concentration of trace elements in pyroxenes and glasses was obtained through a Laser Ablation Microprobe-Inductively Coupled Plasma Mass Spectrometry (LAM-ICP-MS) at Geosciences Montpellier Université de Montpellier. Each analysis included a background acquisition of 120 s, followed by 60 s data acquisition of the sample. The analysis was corrected with internal standards using CaO for clinopyroxenes (cpx) and glasses, and SiO_2 for orthopyroxenes (opx). Since the detection limit is a function of the ablation volume and counting time it was calculated for each analysis; in fact, the ablation volume, greatly depends on the instrument configuration. As a consequence, the detection limits decrease if spot size, beam power and cell gas flow are reduced. Since analyses for clinopyroxenes were performed using a smaller spot size and lower beam power, the detection limits for some elements was up to two times less than that of standard analyses. A beam diameter of 40-100 µm and a scanning rate of 20 µm/s were used. The theoretical limit of detection ranges between 10 and 20 ppb for Rare Earth Elements (REE), Ba, Th, U, and Zr and 2 ppm for Ti. Data were processed using the Glitter software (GEMOC, Macquire University, Australia). Element concentrations were calibrated against the NIST612 certified reference material, using the values of Pearce *et al.* (1997).

Isotopic analyses for Sr and Nd were performed at Geosciences Environment Toulouse (GET), Observatoire Midi-Pyrenées, Université Toulouse III. Clinopyroxene separates were first cleaned with ethanol, then dried and crushed using an agate mortar in a dust-free room. Following this, 100mg of clinopyroxene powder was weighed and leached in a Teflon_ beaker using 1N HCl for 10min. After centrifugation, the leaching solution was discarded and the samples were dissolved in a 2:1 mixture of HF^HNO_3. Nd and Sr were extracted from the matrix using a combination of Sr-spec, Thru-spec and Ln-spec resins. An equivalent of 500 ng Sr and 150 ng Nd was run on a Finnigan MAT261 mass spectrometer (GET, Université Toulouse III). NBS987 and La Jolla isotopic standards were regularly run during the measurements. Typical blanks are 50 pg for Nd and 150 pg for Sr. Taking into account the low concentration of Rb and Sm in the cpx, age corrections for Cenozoic age was not necessary because it was negligible.

NORTHERN VICTORIA LAND SUBCONTINENTAL LITHOSPHERIC MANTLE

Greene Point Mantle xenoliths

Greene Point xenoliths resulted mainly lherzolites, with some harzburgites, all showing protogranular texture. Based on mineral major and trace element models, this mantle domain was proposed to represent a residuum after 10% and 20% partial melting. Moreover, melting models and isotopic results for Sr and Nd systematics highlighted the substantial contribution of tholeiitic melts percolating through peridotites. Close correlation with trace element contents between cpx from Greene Point and those from Ferrar (Fig. 1; Kyle, 1980) and Karoo tholeiites, allowed us to ascribe this refertilisation event to the Jurassic age.

Moreover, a simple Sr-Nd linear mixing (Faure, 1998) between the Depleted Mantle Morb (DMM) component and Ferrar dolerites (Elliot *et al.*, 1999) isotopic compositions can reproduce Greene Point isotopic variability, inferring a contribution of ~5% for the Ferrar component (Fig. 2).

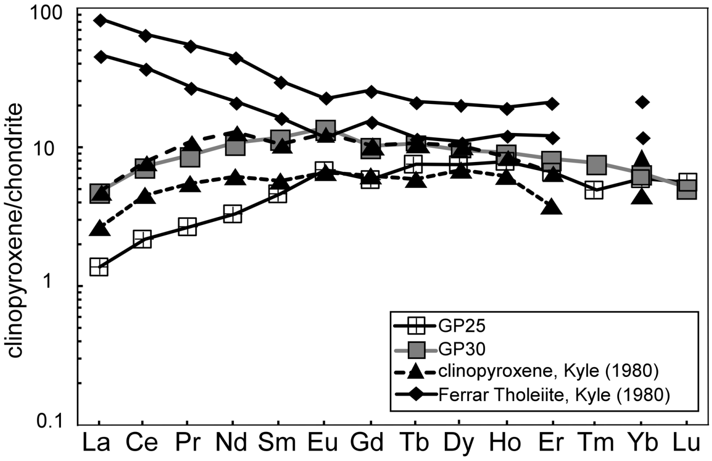

Fig. 1 - Comparison between REE patterns of Greene Point clinopyroxene and those calculated in equilibrium with the Ferrar Dolerites (Kyle, 1980), using the $K^{dcpx/th}$ from GERM database, after Pelorosso *et al*., 2016).

This asthenospheric melt was also able to transfer a garnet signature to the Northern Victoria Land mantle segment. The rare presence of glass and secondary phases indicate that Greene Point xenoliths were heterogeneously affected by alkaline metasomatism, probably related to the West Antarctic Rift System opening; this has also been widely observed in other Northern Victoria Land localities (*i.e.*, Baker Rocks, Coltorti *et al.*, 2004).

Taking into account the general equilibrium between olivine-orthopyroxene and spinel, the olivine-spinel thermometer of O'Neill & Wall (1987) modified by Ballhaus *et al.* (1991), was selected as the most reliable geothermometer for evaluating Greene Point thermal conditions. For the majority of the samples, temperatures were close to 950 °C, and redox conditions varied from $\Delta \log fO_2$ (QFM), -1.70 to -0.39 at a fixed pressure of 15 kbar.

These results confirmed the tendency of the anhydrous Greene Point xenolith population to have higher equilibration temperatures and comparable redox conditions, compared to the nearby amphibole-bearing peridotites from Baker Rocks (Bonadiman *et al.,* 2014).

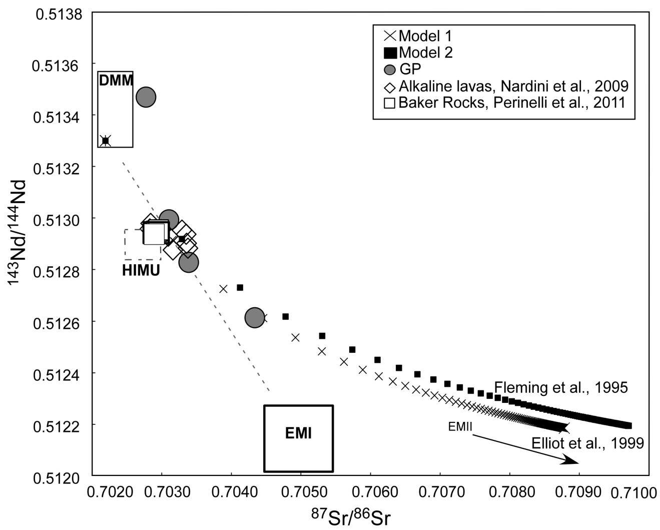

Fig. 2 - $^{143}Nd/^{144}Nd$ *vs*. $^{87}Sr/^{86}Sr$ plot of Greene Point clinopyroxene. Crossed line represents the mixing line (Model 1) between the DMM composition and the Ferrar Dolerites (Elliot *et al*., 1999); square line represents mixing line (Model 2) between DMM and Ferrar dolerites (Fleming *et al*., 1995). Amphibole-bearing Baker Rocks xenoliths and Cenozoic alkaline lavas also plot onto the mixing line. After Pelorosso *et al*., 2016.

Handler Ridge Mantle xenoliths

Mantle xenoliths from the newly found area of Handler Ridge (HR) are spinel lherzolites with protogranular texture. The study of this area, 400 km far from the previous studied area in the Mt. Melbourne district (*i.e.*, Baker Rocks and Greene Point), allowed to identify and characterize another portion of the Antarctic sub continental lithospheric mantle that presents interesting affinities and some differences with other well-known areas in Northern Victoria Land. Geothermobarometric constrains were provided, using Ballhaus *et al*. (1991), equation; the results showed that, HR subcontinental lithospheric mantle recorded the highest temperatures (> 1000 °C) and fugacity conditions (Δlog close to QFM or higher) of the entire region.

HR peridotite represent a residuum after ~ 7 to 18% of partial melting in the spinel stability field, which was variably modified by interaction with lithospheric alkaline melt that was able to strongly modify the chemical composition of the mantle, but not the modal proportion of the mineral phases (as instead observed in Greene Point).

Using the "inward diffusion" model of Griffin *et al.* (1996), derived by the application of the Crank's equation (1975), we calculated the diffusion time to completely hiding the primary (residual) peridotite by metasomatic feeding. The result reveals that this kind of process is extremely fast, in fact it occurs in a time-span of 10^2-10^3 years only (considering a size of crystal of 1500 μm), and it is probably related to the magma rising event.

In the case of Handler Ridge, metasomatism is strictly linked to the Cenozoic magmatism, as indicated by the similarity between the inferred metasomatizing melt and the lavas that brought up the xenoliths during the WARS opening.

Harrow Peaks Mantle xenoliths

Samples varied in composition from lherzolite to harzburgite with textural evidences of matrix/metasomatizing melt interaction (secondary minerals and spongy textures). Olivine and opx were mainly present as large primary grains, whereas cpx generally occurred as resorbed grains or newly formed small crystals, often associated to glassy patches. Spinel is present as small anhedral crystals or larger, dendritic grains. Amphiboles occurred both as disseminated and within veins; the latter were frequently associated with secondary cpx. Considering fusible element content in opx (*i.e.*, Al_2O_3 ~ 2.50 wt.%), Harrow Peaks lithosphere domain reflects a relatively residual character. On the other hand, Light Rare Earth Element content in cpx (La_N from 9 to 30) evidenced that they were strongly affected by enrichment processes, *i.e.*, metasomatism.

Amphiboles from Harrow Peaks can be classified as kaersutite, magnesio-hastingsite, and ferri-kaersutite with TiO_2 contents ranging from 2.74 wt.% to 5.30 wt.% (Gentili *et al*., 2015).

The comparison between Harrow Peaks and the nearby amphibole-bearing xenolith area of Baker Rocks (Coltorti *et al*., 2004; Bonadiman *et al*., 2014), allowed to reconstruct the amphibole genesis in relation to the metasomatic processes. Harrow Peaks amphibole presented a lower enrichment with respect to Baker Rocks (Fig. 3) that may be related to an incipient stage of peridotite/metasomatizing melt interaction.

Considering the inter-mineral equilibria among the main peridotitic phases, thermobarometric estimates were constrained. Temperature values ranged from 800 to 1100 °C at relatively reduced conditions (Δlog fO_2 (QFM) -2.78 to -0.24). The fugacity values, calculated by the anhydrous parageneses, strongly deviated from those obtained on the basis of amphibole dehydration equilibrium, applying the dissociation reaction that record extremely oxidizing conditions (ΔQFM = +5; +6.8; Gentili *et al*., 2015, Fig. 4). This decoupling was not observed for Baker Rocks amphibole-bearing peridotites, where both methods converge to the values of ΔQFM ~ -1.78 (Bonadiman *et al*., 2014). This may suggest that amphibole in Harrow Peaks was in strong disequilibrium with the anhydrous parageneses recording an early stage of peridotite-metasomatic melt interaction.

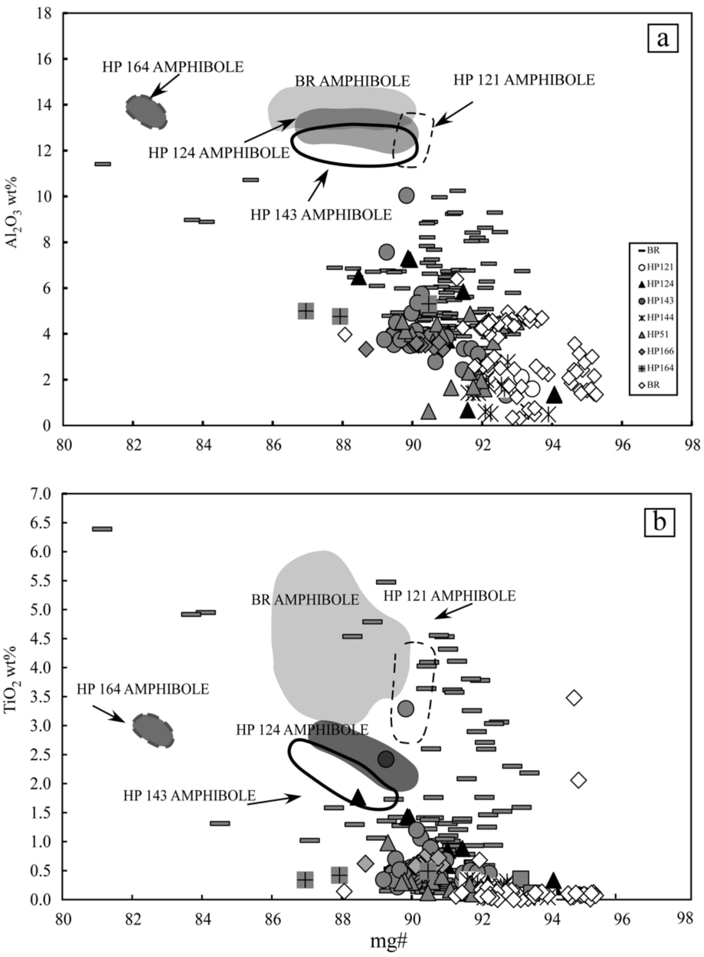

Fig. 3 - Harrow Peaks clinopyroxene compositional variation in terms of Al_2O_3 (a), and of TiO_2 (b); amphiboles are also reported (different areas). For comparison also cpx (grey tick marks and white diamonds) and amphiboles (grey area) from BR are included.

CONCLUSIONS

On the whole, applying the popular method based on the mantle Fe/Mg mineral exchange, the results reveal that amphibole-bearing xenolith populations (HP, BR) show the lowest temperatures (~ 850 °C) of the region (Fig. 4).

The highest temperatures (up to ~ 1050 °C) are recorded in HR mantle domain, and by the anhydrous group of HP. The presence of equilibrated hydrous phase seems do not influence the redox conditions that are comparable in GP, HP and BR (Fig. 4 see also, Bonadiman *et al.*, 2014).

After the main melting event (at least ~ 20% of partial melting), the sub continental lithospheric mantle of NVL suffered at least two enrichment processes related to two important geological events:

1) the tholeiitic magmatism that preceded the Gondwana break up in Jurassic: the locality that shows more the imprinting of this event is Greene Point, where the event is well testified by the Ferrar dolerites;

2) during Cenozoic, the alkaline metasomatism widely observed in NVL, related to the WARS opening, locally interacted with the previously re-fertilised peridotitic system, and in some cases (Baker Rocks and Harrow Peaks mantle segments) almost completely obscuring the previous refertilisation event. This last event is well identifiable where the interaction with the melt produced amphibole, even if it is possible to observe the different stage of these processes that are geochemically distinct.

Finally, HR, 400 km far from Mt. Melbourne district, reflects the presence of an alkaline metasomatism, strictly related to the Cenozoic magmatism, that in a time span of 10^2-10^3 years was able to completely blur the cpx primary chemical features, but not the modal proportion among the peridotite minerals.

Notwithstanding, refertilisation *vs*. metasomatism processes are still matter of debate the present study allowed to shed a light on the nature of these different enrichment styles, constraining their characteristics in term of geochemistry, melts involved, and time space/framework.

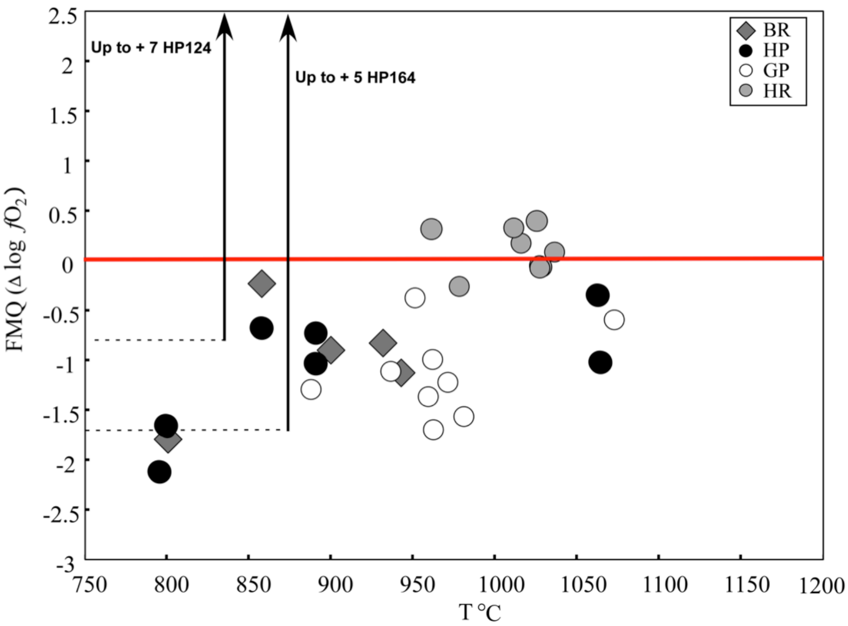

Fig. 4 - Temperature and ($\Delta logfO_2$) FQM = fO_2 relative to the buffer reaction FMQ evidenced by the red line, calculated with the formula of Ballhaus *et al*. (1991) for NVL. P is fixed at 15 Kbar. Data from South Victoria Land (Martin *et al*., 2015) and data of fO_2 for HP164 and HP124 calculated by oxygeothermobarometer with oxy-amphibole equilibrium Popp *et al*. (2006) are also reported Gentili *et al*. (2015).

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