

**BORSA SIMP 2008 PER UN SOGGIORNO DI STUDIO ALL'ESTERO:
RELAZIONE SULL'ATTIVITA' SVOLTA**

***IN SITU* TRACE ELEMENT ANALYSIS OF ORTHOPYROXENES WITH
FEMTOLASER ABLATION TECHNOLOGY AND Re-Os ISOTOPIC
DETERMINATIONS ON SULPHIDES IN MANTLE XENOLITHS**

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IN SITU MEASUREMENT OF OPX TRACE ELEMENTS

Previous works on amphibole generation in mantle xenoliths demonstrated that the trace element composition of this phase can be related to the geodynamic environment (Coltorti *et al.*, 2004; Coltorti *et al.*, 2007a). The possibility to discriminate the geodynamic setting where amphiboles form on the base of their geochemical characteristics, and the study of metasomatic phenomena in supra-subduction zones is a new frontier in petrology and could have bearings on some of the key petrological problems still unsolved, like the origin of Nb, Ta and Ti negative anomalies typical of arc magmas, as well as the recycling of crustal material within the Earth's mantle.

Similarly to amphibole, other mantle minerals forming during metasomatic stages may preserve an imprint of the geodynamic setting where they grew and resided. Cpx is the most suitable and normally more abundant than amphibole. However, subduction zones are usually characterized by strongly depleted lithologies, and cpx is very rare or even absent. In this case opx represents the only mineral whose geochemical features can record the petrological evolution of the mantle domain. The use of this phase was, so far, limited by its very low trace element contents (especially LILE and LREE), one or more order of magnitude lower than cpx; nevertheless, its almost ubiquitous presence in mantle rocks makes it a potentially powerful tool to investigate and reconstruct the petrological evolution of ultramafic rocks. Opx was not believed to form during metasomatism; however, recent works documented that secondary opx can be produced at the expense of olivine and/or grow in veins in mantle xenoliths from subduction zones, brought to the surface by calc-alkaline *s.l.* magmas or by Nb-enriched arc basalts (Arai *et al.*, 2003; Bryant *et al.*, 2007).

Opx trace element analyses were one of the topics of my stage at CNRS laboratoires in Toulouse (Observatoire Midi-Pyrénées, CNRS-Université Paul Sabatier). Ablation with "Femtolasers" LAM ICP-MS allowed precise and accurate determination of those elements normally difficult to detect in opx, even with large beam spots of traditional excimer lasers (like Ba and LREE), because of their scarce abundance in this mineral. Laser ablation converts a small quantity of mass from a solid sample into a vapour-phase and transports it efficiently into an analytical device (mass spectrometer coupled with plasma, ICP MS). The primary concern in using laser ablation for chemical analyses is the non-stoichiometric generation of vapour, a process called "fractionation". Fractionation is related to the laser properties, including pulse duration, energy, and beam diameter. Almost all previous analytical works made with laser ablation used nanosecond pulsed lasers. In this case during the laser pulse there is ample time for photon energy to dissipate in the lattice as heat. On the contrary, femtosecond lasers are capable to ablate well-defined craters with minimal thermal heating to the surrounding area; most of the laser energy is converted into the kinetic energy of the ablated vapour, drastically reducing fractionation. The very high intensity (on the order of 10^{14} W cm⁻²) and the short time duration of the pulse with respect to the phonon relaxation time in the solid material enable to convert photon energy into kinetic energy and thereby to minimize the heating of the lattice, considered one of the main causes of fractionation. Also, the very short - femtosecond - laser pulse will not interact with the plasma (vapour-phase) of

ablated mass leaving the sample surface, avoiding plasma shielding, a mechanism of energy loss and a possible contributor to fractionation (Russo *et al.*, 2002 and references therein). Thank to these characteristics of femtosecond laser ablation technology, currently in use at CNRS laboratories, it was possible to obtain very accurate measurements of the entire opx trace element dataset.

This technique was applied to a population of mantle xenoliths from Cerro del Fraile (Patagonia, Argentina), found in Quaternary alkali basalts erupted only 150 km off the trench where the Antarctic Plate is being currently subducted, thus representing fragments of the mantle wedge above an actual subduction zone (Kilian & Stern, 2002; Wang *et al.*, 2007). In this population opx can be found in two textural occurrences. The most common is constituted by large irregular crystals often clustered in groups, with triple junctions and well-developed exsolution lamellae. In the second case opx are smaller, disseminated between olivine, and devoid of exsolution lamellae; their shape is rounded and they can form clusters of two or more individuals with similar dimensions. In addition to peridotites, some websterites and orthopyroxenites have also been found, where large euhedral to subhedral opx and cpx form the backbone of a meso-cumulitic structure. Two samples are composite, consisting in dunites cut by clino- and orthopyroxenites.

The two types of opx in peridotites have similar major element compositions, but remarkably different trace element budgets, even within the same sample (Fig. 1):

- Type 1 opx, is characterized by very low $(La/Yb)_N$ ratios (0.02 - 0.21), Zr/Zr^* ratios generally higher than 20 (21.9 - 67.8), and $(Th)_N$ and $(U)_N$ varying between 0.20 and 1.64 per chondrite and between 0.66 and 3.16 per chondrite, respectively.

- Type 2 opx, has higher $(La/Yb)_N$ ratios (1.18 - 2.81), highly variable Zr/Zr^* ratios (18.5 - 67.8) and higher Th and U values [$(Th)_N$, 1.45 - 7.75 per chondrite; $(U)_N$, 2.92 - 9.56 per chondrite]. The overall REE pattern for Type 2 is upward concave with a minimum at Eu.

Opx in orthopyroxenites and websterites are characterized by lower MgO and Mg#, and higher TiO_2 with respect to opx in peridotites. In chondrite normalized spider diagrams they have similar patterns characterized by almost flat REE, and MREE values higher than, or comparable to, HREE; Zr/Zr^* ratios are lower than those of peridotitic samples and Th and U contents are higher (Fig. 1).

The occurrence of different kinds of opx within the same sample and the finding of orthopyroxenites and websterites with dominant opx as cumulus phase indicate that a silica-oversaturated melt should have interacted with the mantle column sampled by the alkali basalts carrying the samples. As can be seen from Fig. 1, Type 2 opx in peridotites have a composition approaching that of opx in websterites and orthopyroxenites, thus showing how mantle typical opx progressively enrich in LREE and MREE, whereas HREE do not show any variation. Enrichment involves also Th, U and Ti, this last having a good affinity for opx.

Enriched cpx and opx have been used to calculate the metasomatic melt. Partition coefficients (K_d) specific for both pyroxenes and andesitic melts have been used (<http://earthref.org/GERM/>). The particular trace element pattern shape of cpx, with Zr-Hf positive anomaly and high Th and U contents, indeed, indicate an interaction with a slab-melt (Coltorti *et al.*, 2007b), similar to adakites and andesitic to dacitic in composition. Melt in equilibrium with both cpx and opx of the peridotites resulted very similar to melts in equilibrium with opx and cpx of orthopyroxenites and websterites and to natural adakites erupted by the Austral Volcanic Zones volcanoes (Fig. 2). Calculation of metasomatic melts from opx trace element composition is a new tool to investigate the processes occurring in the mantle wedges, especially when cpx is absent and there is evidence of opx addition (*cf.* Kepezhinskis *et al.*, 1995; Arai *et al.*, 2003; Ishimaru *et al.*, 2006).

IN SITU MC-ICP-MS ANALYSIS OF Re-Os SYSTEMATICS ON SULPHIDES

The technique of Multiple Collector ICP-MS (MC-ICP-MS) is becoming more and more popular among petrologists, because it allows the precise measurement of isotopic compositions for a wide range of elements. The variety of applications, including analysis of radiogenic and stable isotopic ratios in solution and *in situ*,

using a laser ablation system, highlight the great relevance of MC-ICP-MS to present and future researches in various Earth science disciplines.

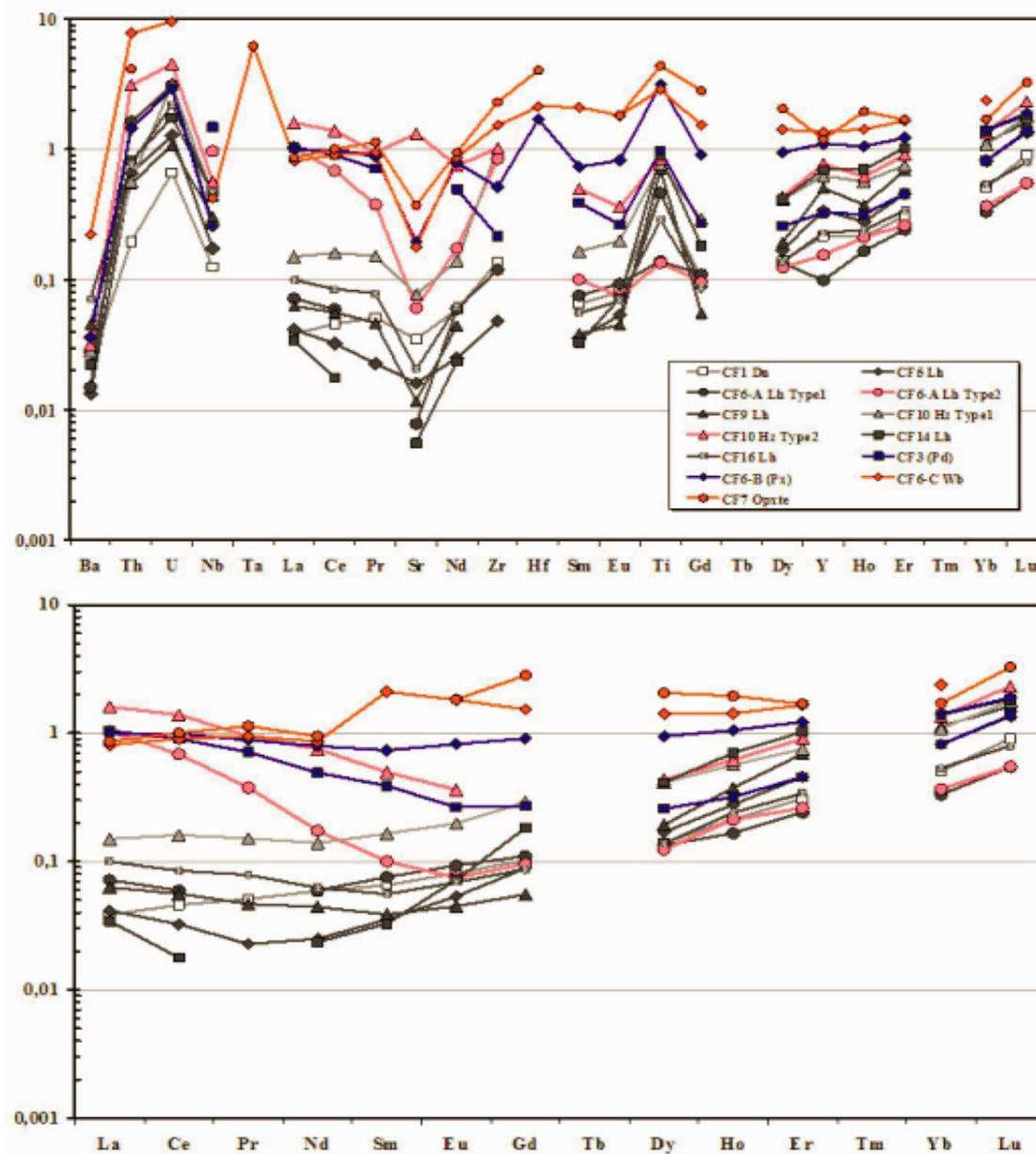


Fig. 1 - Chondrite normalised incompatible trace element and REE pattern diagrams of opx in the Cerro del Fraile peridotites (Type1, black and grey lines; Type2, pink lines), websterites and orthopyroxenites (red lines), and composite samples (blu lines).

MC-ICP-MS combines an inductively coupled plasma (ICP) source, an energy filter, a magnetic sector analyzer, and multiple collectors for the measurement of the ions. The positively charged ions obtained with the plasma torch are extracted by ion lenses, accelerated across an electrical potential gradient (up to 10 KV) and focused into a beam via a series of slits and electrostatically charged plates. In order to reach the high resolving power requested for isotopic analyses, in the so-called “double focussing” technology the ion beam passes through: 1) a focussing electrostatic analyser (ESA), 2) a magnet sector where the ions are separated on the basis of their mass to charge ratio and, finally, 3) another lens system that further focus each mass-resolved ion beam

into the correct slit of the detector, where it is converted into voltage (Fig. 3). The use of a detector array with multiple Faraday cups and ion counters allows the simultaneous collection of the separated isotopes, erasing the effect of a “noisy” signal on the isotope ratio measurement, avoiding problems of beam stability, and mass-dependent isotopic fractionation. The Faraday cups are independently movable, such that the collector “coincidences” can be adjusted to permit analyses of a wide range of elements having isotopes that display different mass dispersions (Rehkämper *et al.*, 2001); isotope ratios are then calculated by comparing voltages from the different collectors.

MC-ICP-MS instruments were designed specifically to overcome the limitations of other mass spectrometric techniques. Combining the Ar ICP-source of conventional ICP-MS instruments with the magnetic sector analyser and multiple-Faraday cup array of TIMS, MC-ICP-MS performs isotope ratio measurements for various elements with a precision below 50 ppm, which was previously only possible by using TIMS (Walczyk, 2004). The magnetic sector mass analysers of MC-ICP-MS instruments are similar to those used in TIMS, and they can achieve the flat-topped peaks necessary for high-precision isotope ratio measurements; precision reaches 0.001%, almost comparable to that achieved with TIMS.

At the same time, isotopic analysis is less time consuming, as by using a plasma ion source the sample can be presented directly in solution to be transformed into an aerosol and introduced into the instrument, making sample digestion superfluous. Moreover, adding a laser probe, the material can be extracted directly from the thin/thick section or slice of rock, allowing *in situ* measurement of the isotopic composition of the minerals.

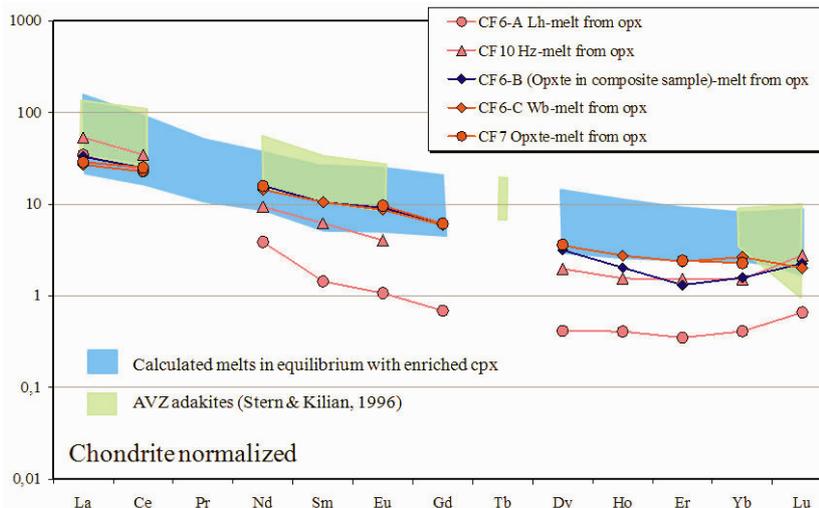


Fig. 2 - Calculated melts in equilibrium with opx in both mantle peridotites and websterites/orthopyroxenites. Kd's opx/andesite taken from GERM (<http://earthref.org/GERM/>). Melts in equilibrium with cpx in the same samples (blue field) and natural adakite REE patterns (yellow field) in the background are reported for comparison.

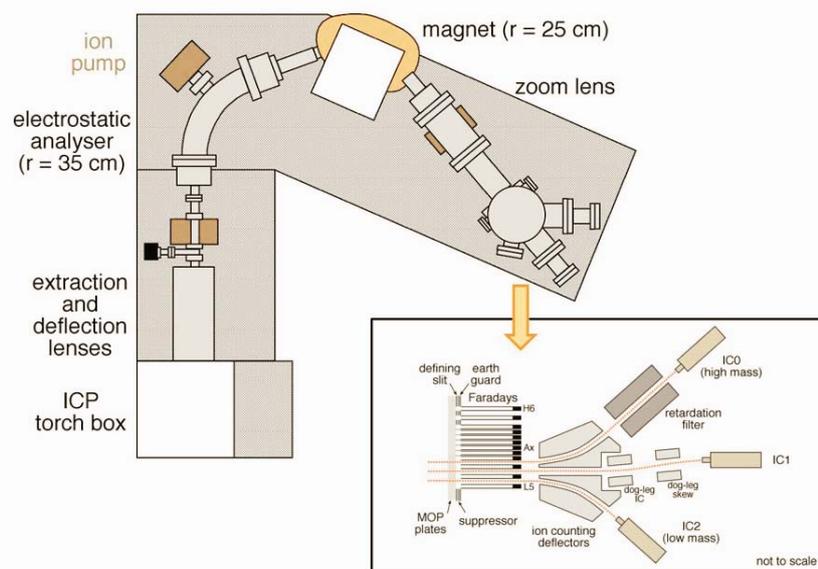


Fig. 3 - Schematic view of the Nu Plasma 1700 multicollector ICP MS and its detector.

Ionization efficiencies are usually higher when using ICP-MS, thus almost all elements of the periodic table are accessible to isotopic analysis. For terrestrial systems, common applications in geochronology and isotopic studies involve the following radiogenic isotopic systems: U-Th-Pb, Rb-Sr, Sm-Nd, Lu-Hf, Re-Os. The main stable isotope ratios measured are Li, B, Mg, Ca, Fe, Ni, Cu, Zn, Zr, Mo. As far as mantle studies are concerned, at present *in situ* isotopic ratios can be accurately performed on those minerals having a relatively high concentration of each element to be measured (for example U and Pb in zircons, Re and Os in sulphides and Sr in plagioclase and cpx). In the case of sulphides, the great advantage of MC-ICP-MS coupled with Laser Ablation Microprobe is the possibility to measure isotopic ratios and to recover age information on single grains, allowing to pinpoint a single geological event. Since platinoid metals have great affinity for sulphides and their abundance in silicate minerals is negligible, many workers are using bulk-rock Re-Os isotopic determinations in building their geodynamic models. Beside its greater precision, TIMS mixes together various sulphide populations with different isotopic signatures, leading to more precise age determinations that, however, simply represent an average. In this respect it is of particular interest to report the example of Re-Os isotope systematic applied to date partial melting events and melt extractions in the mantle, which can be related to global tectonics (Griffin *et al.*, 2004). After melting events, sulphide residuals have preferentially lost Re (more incompatible than Os) and they will develop an unradiogenic Os isotopic composition; on the other hand sulphides introduced by metasomatism are enriched in Re, gaining more radiogenic Os signatures with time. If several melting and metasomatic processes are recorded within a single mantle domain, the whole-rock Os isotopic determination can give meaningless data. Melt depletion ages estimated from individual sulphide inclusions are indeed systematically older than those obtained from whole rock analysis, suggesting that isotopic analyses on single sulphides could play a key role in unravelling the formation and evolution of the lithosphere (Alard *et al.*, 2002).

An analytical stage at Macquarie University (Sydney) gave me the possibility to know and use a MC-ICP-MS coupled with a laser ablation microprobe to determine the Re-Os isotopic composition of sulphides in spinel peridotite xenoliths from the Cape Verde Archipelago. The data acquired gave very old Re-depletion model ages, from Neoproterozoic to Archean, unexpected for oceanic mantle material, and lead to the conclusion that part of the Cape Verde Archipelago is underlain by a fragment of ancient subcontinental lithospheric mantle, left stranded in the oceanic lithosphere during the opening of the Atlantic Ocean (Bonadiman *et al.*, 2005; Coltorti *et al.*, 2010). Analogously, the $^{187}\text{Os}/^{188}\text{Os}$ isotopic ratios of sulphides in two mantle xenolith suites from Northern Victoria Land (NVL; Antarctica), Baker Rocks (BR) and Greene Point (GP), were analyzed at Macquarie University. GP samples are all unradiogenic whereas BR nodules bear sulphides that have both unradiogenic and highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ isotopic signatures. The unradiogenic group (all the GP samples plus a part of the BR samples), with $^{187}\text{Os}/^{188}\text{Os}$ ratios always below Primitive Upper Mantle (PUM; 0.1290), records melting event varying in age between Archean (two peaks at 3 and 3.3 Ga), Proterozoic (four peaks, 2.3 Ga, 1.3 - 1.4 Ga, 0.9 - 1.1 Ga and 588 Ma) and Mesozoic (one peak at 120 Ma, only registered in the BR samples). The last two ages are probably linked to the Ross Orogeny and the Ferrar basaltic plateau formation, respectively. The radiogenic group from the BR nodules, having $^{187}\text{Os}/^{188}\text{Os}$ ratios varying from 0.1318 to 0.379, has been, instead, interpreted as the consequence of the mixing of eclogitic material in the lithospheric mantle before the genesis of the basaltic rocks of the McMurdo Volcanic Province. Moreover, from model calculations the mixed material should be of Archean age, and would have been already present within the NVL lithospheric mantle as eclogites, probably related to a subduction event older than the Ross Orogeny (560 Ma), and subsequently mobilized during the West Antarctic Rift System opening phase (Fig. 4; Melchiorre *et al.*, 2011).

In these years, the technology of MC-ICP-MS is starting to diffuse in Europe. Unfortunately, all the reported applications, that are very promising from the petrological point of view, are hindered by the high costs of the instruments and by the operating expenses. As a consequence, only few laboratories in Europe own a MC-ICP-MS. Among others, they are the Department of Geochronology, Vienna University, Austria (Nu Plasma 1700 Multicollector ICP MS), the Observatoire Midi-Pyrénées, CNRS-Université Paul Sabatier, Toulouse,

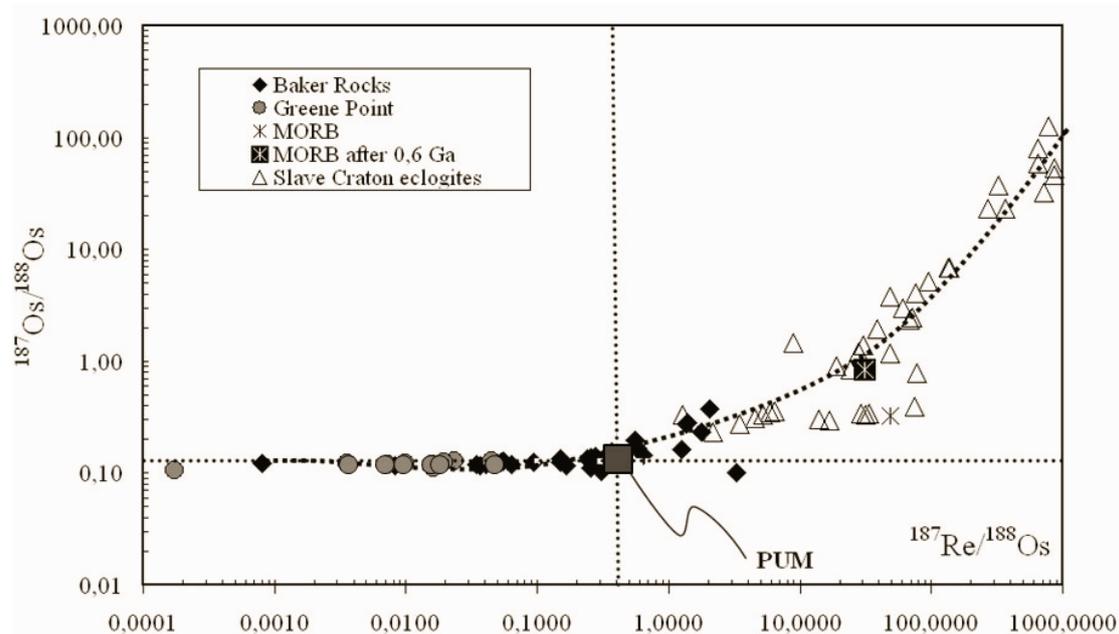


Fig. 4 - $^{187}\text{Os}/^{188}\text{Os}$ vs. $^{187}\text{Re}/^{188}\text{Os}$ plot of BR (black diamonds) and GP (grey circles) sulphides. Empty triangles are *in situ* analysis of sulphides from the Slave Craton eclogites (Aulbach *et al.*, 2009). Dotted line represents the mixing line between the BR sample with the minimum Re content and the most radiogenic Slave Craton eclogites (Aulbach *et al.*, 2009). MORB composition (asterisk) and its composition after 0.6 Ga (white asterisk over a black background) are also reported.

France (Thermo Finnigan “Neptune”) and the Department of Earth Sciences, Modena University, Italy (Thermo Finnigan “Neptune”). Various analytical stages were carried out in these localities (and contacts are continuously maintained) attempting to develop the Re-Os technique acquired at the Macquarie University. At the University of Vienna the MC-ICP-MS is dedicated to U-Pb analyses on zircons and it is not recommended to convert it for other isotope systematic measurements, like Re-Os. In Toulouse many attempts have been done in order to develop *in situ* determination of Rb-Sr isotopes on cpx, but to date the technique has to be improved to obtain reliable results. Moreover, as for Vienna University, the Rb-Sr setup of the machine prevents the full development of *in situ* Re-Os analysis. The purchase of a new MC-ICP-MS in Toulouse, specifically devoted to the isotopic determinations on sulphides, will open new opportunities of research, as those which are being developed in collaboration with the Modena University. Here, a new generation MC-ICP-MS is shared by various departments and the possibility to routinely switch it for analysis of different isotope systematics is currently under testing.

REFERENCES

- Alard, O., Griffin, W.L., Pearson, N.J., Lorand, J.-P., O’Reilly, S.Y. (2002): New insights into the Re-Os systematics of sub-continental lithospheric mantle from *in situ* analysis of sulphides. *Earth Planet. Sci. Letters*, **203**, 651-663.
- Arai, S., Ishimaru, S., Okrugin, V.M. (2003): Metasomatized harzburgite xenoliths from Avacha Volcano as fragments of mantle wedge of the Kamchatka arc: Implication for the metasomatic agent. *Island Arc*, **12**, 233-246, doi: 10.1046/j.1440-1738.2003.00392.x.
- Aulbach, S., Creaser, R.A., Pearson, N.J., Simonetti, S.S., Heaman, L.M., Griffin, W.L., Stachel, T. (2009): Sulphide and whole rock Re-Os systematics of eclogite and pyroxenite xenoliths from the Slave Craton, Canada. *Earth Planet. Sci. Letters*, **282**, 48-58.
- Bonadiman C., Beccaluva L., Coltorti M., Siena F. (2005): Kimberlite-like Metasomatism and ‘Garnet Signature’ in Spinel-peridotite Xenoliths from Sal, Cape Verde Archipelago: Relics of a Subcontinental Mantle Domain within the Atlantic Oceanic Lithosphere? *J. Petrol.*, **46**, n° 12, 2465-2493.

- Bryant, J.A., Yogodzinsky, G.M., Churikova, T.G. (2007): Melt-mantle interactions beneath the Kamchatka arc: Evidence from ultramafic xenoliths from Shiveluch volcano. *Geochem. Geophys. Geosyst.*, **8**, Q04007, doi: 10.1029/2006GC001443.
- Coltorti, M., Beccaluva, L., Bonadiman, C., Faccini, B., Ntaflos, T., Siena, F. (2004): Amphibole genesis via metasomatic reaction with clinopyroxene in mantle xenoliths from Victoria Land, Antarctica. *Lithos*, **75**, 115-139.
- Coltorti, M., Bonadiman, C., Faccini, B., Grégoire, M., O'Reilly, S., Powell, W. (2007a): Amphiboles from suprasubduction and intraplate lithospheric mantle. *Lithos*, **99**, 68-84.
- Coltorti, M., Bonadiman, C., Faccini, B., Ntaflos, T., Siena, F. (2007b): Slab melt and intraplate metasomatism in Kapfenstein mantle xenoliths (Styrian Basin, Austria). *Lithos*, **94**, 66-89.
- Coltorti M., Bonadiman C., O'Reilly S. Y., Griffin W. L., Pearson N. J. (2010): Buoyant ancient continental mantle embedded in oceanic lithosphere (Sal Island, Cape Verde Archipelago). *Lithos*, **120**, 223-233.
- Griffin, W.L., Graham, S., O'Reilly, S.Y., Pearson, N.J. (2004): Lithosphere evolution beneath the Kaapvaal Craton: Re-Os systematics of sulfides in mantle-derived peridotites. *Chem. Geol.*, **208**, 89-118.
- Ishimaru, S., Arai, S., Ishida, Y., Shirasaka, M., Okrugin, V.M. (2006): Melting and multi-stage metasomatism in the mantle wedge beneath a frontal arc inferred from highly depleted peridotite xenoliths from the Avacha volcano, southern Kamchatka. *J. Petrol.*, **48**, 395-433.
- Kepezhinskias, P.K., Defant, M.J., Drummond, M.S. (1995): Na metasomatism in the island-arc mantle by slab melt-peridotite interaction: evidence from mantle xenoliths in the North Kamchatka Arc. *J. Petrol.*, **36**, 1505-1527.
- Kilian, R. & Stern, C.R. (2002): Constraints on the interaction between slab melts and the mantle wedge from adakitic glass in peridotite xenoliths. *Eur. J. Mineral.*, **14**, 25-36.
- Melchiorre, M., Coltorti, M., Bonadiman, C., Faccini, B., O'Reilly, S., Pearson, N. (2011): The role of eclogite in the rift-related metasomatism and Cenozoic magmatism of Northern Victoria Land, Antarctica. *Lithos*, **124**, 319-330, doi: 10.1016/j.lithos.2010.11.012.
- Rehkämper, M., Schönbächler, M., Stirling, C.H. (2001): Multiple Collector ICP-MS: introduction to instrumentation, measurement techniques and analytical capabilities. *Geost. Newsletter*, **25**, 23-40, doi: 10.1111/j.1751-908X.2001.tb00785.x.
- Russo, R.E., Mao, X., Gonzales, J.J., Mao, S.S. (2002): Femtosecond laser ablation ICP-MS. *J. Anal. At. Spectrom.*, **17**, 1072-1075.
- Walczyk, T. (2004): TIMS versus multicollector-ICP-MS: coexistence or struggle for survival? *Anal. Bioanal. Chem.*, **378**, 229-231.
- Wang, J., Hattori, K.H., Kilian, R., Stern, C.R. (2007): Metasomatism of sub-arc mantle peridotites below southernmost South America: reduction of f_{O_2} by slab-melt. *Contrib. Mineral. Petrol.*, **153**, 607-624.