Sr-Nd-Pb-Hf- ISOTOPIC STUDY OF MANTLE ROCKS IN THE OPHIOLITIC SEQUENCES OF THE ALPINE-APENNINE OROGENIC BELT: IMPLICATIONS FOR HETEROGENEITY IN THE MORB SOURCES

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Studies of mid-ocean ridge basalts (MORBs) have documented that their mantle sources are chemically and isotopically heterogeneous and this variability can be linked both to ancient depletion events and recent melt-peridotite interaction events. This research was thus aimed at improving the knowledge of geochemical and isotopic composition of depleted mantle in a context of oceanic lithosphere formed at a slow/ultraslow spreading ridge setting. The investigation includes the collection of a comprehensive mineralogical, geochemical and isotopic dataset on selected samples from three bodies of residual peridotites belonging to ophiolitic sequences from the Northern Apennine (Internal Ligurian, IL), Tuscany (Monti Rognosi, MR) and Western Alps (Monte Civrari, MC). The main objectives of this research were to *i*) verify whether these mantle bodies represent the residue of MORB extraction, *ii*) put constraints on extent and timing of depletion, and *iii*) quantify the role of melt/rock interaction in modifying geochemical and isotopic signatures of residual mantle.

Modeling and interpretation of geochemical data showed that the investigated peridotites reflect variable degrees of melting at different depths and melt/rock interactions with MORB-type melts, most likely during the Jurassic rifting and oceanization. In particular, IL and MR clinopyroxene-poor lherzolites bear diffuse mineralogical and geochemical evidence of melt/rock interaction.

To provide constraints on the partial melting processes that affected these peridotites, trace element modelling, based both on whole rock and on clinopyroxene REE compositions, was carried out.

The results for Monti Rognosi peridotites indicate that bulk rock REE compositions apparently record small degrees (2-4%) of fractional melting of a Depleted Mantle Source (DMM; Salters & Stracke, 2004), whereas the clinopyroxenes do not match the computed REE compositions of any mantle residual clinopyroxene. Therefore, such peridotites, cannot represent simple partial melting residues. The clinopyroxene compositional variations may be the result of melt-rock interaction, as supported by textural evidences. In particular, the growth of secondary orthopyroxene + plagioclase at the expenses of clinopyroxene point to reaction with orthopyroxene-saturated, MORB-type melts that modified their composition during ascent by reactive porous flow through the lithospheric mantle (*e.g.*, Rampone *et al.*, 2008).

Whole-rock REE compositions of Internal Ligurian peridotites are compatible with 6-8 % degree of fractional melting of a DMM source in the spinel stability field, in contrast with the results obtained for clinopyroxenes, which have been significantly modified by melt-rock interactions, as testified by formation of secondary orthopyroxene and plagioclase.

The Assimilation and Fractional Crystallization (AFC) trace element modeling suggests that the impregnation process at plagioclase-facies conditions involved incremental melt fractions that survived unmixed before aggregation both for the Monti Rognosi and Internal Ligurian peridotite bodies. Higher amounts of residual liquids are needed for these latter in order to reproduce the observed clinopyroxene trace element modifications.

AFC models also show that the melt infiltration partially reset both Sm-Nd and Lu-Hf isotope systems (Fig. 1), but preservation of highly radiogenic ϵ_{Nd} (up to +15) at the time of the associated MORB-type magmatism (162 Ma) suggests ancient mantle reservoirs that experienced long-term depletion.

By contrast, the Monte Civrari mantle rocks attest the presence in the Jurassic Alpine ophiolites of refractory domains unaffected by refertilization processes.

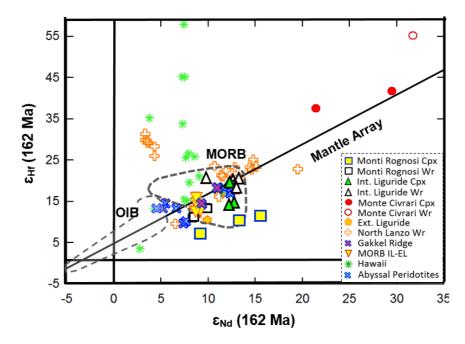


Fig. 1 - ε_{Hf} vs ε_{Nd} correlation diagram (modified after Guarnieri *et al.*, 2012) for the studied samples (Monti Rognosi, Internal Ligurian and Monte Civrari peridotite). ε_{Hf} vs ε_{Nd} are recalculated to 162 Ma. Data sources: Internal Ligurian, Monti Rognosi and Monte Civrari from this work; External Ligurian peridotites from Montanini *et al.* (2012); North Lanzo peridotites from Guarnieri *et al.*, (2012); Gakkel Ridge peridotites from Stracke *et al.* (2011); Hawaii (peridotite mantle xenoliths) from Bizimis *et al.* (2007); abyssal peridotites (Southwest Indian ridge) from Mallick *et al.* (2015). MORB (IL-EL) after Barry *et al.* (2017). The mantle array (ε_{Hf} = 1.36 ε_{Nd} = +3.0) is from Vervoort *et al.*, 1999; MORB data are taken from Nowell *et al.* (1998) and Salters & White (1998). OIB data after Salters & White (1998).

The MC peridotites are residual spinel harzburgites to cpx-poor lherzolites characterized by TiO₂ (0.05-0.15 wt.%) and Na₂O (< 0.1 wt.%)-poor Cpx, with prominent LREE depletion (Ce_N/Sm_N = 0.004-0.005), low HREE abundances (Yb_N ~ 5-6) and fractionated HREE (Gd_N/Yb_N = 0.4-0.5). Clinopyroxene REE compositions may be reproduced by small amounts (~5-6%) of fractional melting of a garnet lherzolite precursor followed by 10% melting in the spinel peridotite field (Fig. 2).

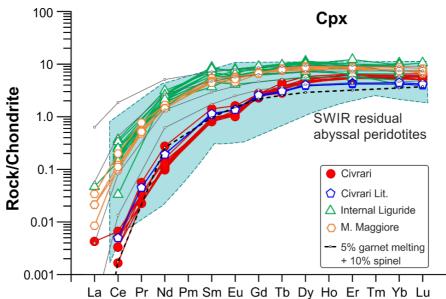


Fig. 2 - Chondrite-normalized REE patterns of Cpx porphyroclasts from Monte Civrari peridotites compared with results of fractional melting models of a DMM source. Data: "M. Maggiore" from Rampone *et al.*, (2008); "Civrari literature" from McCarthy & Muntener (2015).

As a whole, Pb isotope compositions (Fig. 3-a) for Monte Civrari bulk rocks fall within the MORB domain (²⁰⁸Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb). By contrast, in the ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb diagram (Fig. 3-b), the samples of this study have more radiogenic ²⁰⁷Pb/²⁰⁴Pb compared to the MORB field and most mantle peridotites, plotting close to the 4.53 Ga reference isochron.

The highly radiogenic Nd-Hf isotope compositions (initial ε_{Nd} and ε_{Hf} up to +29 and + 41, respectively) of clinopyroxenes from the Monte Civrari peridotites confirm the presence of refractory mantle domains with old ages of depletion in the Ligurian Tethys oceanic lithosphere (see Fig.1). The origin of these mantle domains has been previously attributed to incorporation of SCLM (SubContinental Lithospheric Mantle) derived from a late Variscan DMM melting event (*e.g.*, Mc Carthy & Muntener, 2015 and references therein).

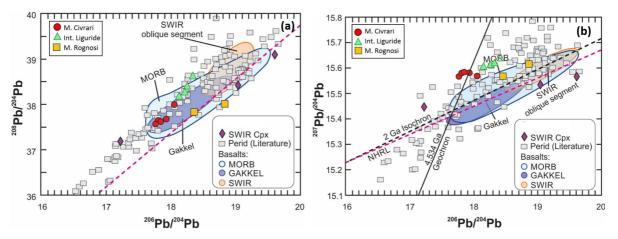


Fig. 3 - Variation of Pb isotopic composition for the studied samples (Monti Rognosi, Internal Ligurian and Monte Civrari peridotite. Data sources: Internal Ligurian, Monti Rognosi and Monte Civrari from this work; Clinopyroxene mineral separates from SWIR peridotites from Warren *et al.* (2009). The light blue shaded field outlines the general field for MORB (from PetDB; Lehnert *et al.*, 2000). The other fields outline basalts from the Gakkel Ridge (Goldstein *et al.*, 2008); SWIR Oblique Segment (Standish, 2006; Standish *et al.*, 2008). Grey squares for literature data of orogenic and xenolith peridotites from whole rock and mineral separate analyses (Hamelin & Allègre, 1988; Meijer *et al.*, 1990; Mukasa *et al.*, 1991; Hauri *et al.*, 1994; Carignan *et al.*, 1996; Rosenbaum *et al.*, 1997; Zangana *et al.*, 1997; Mukasa & Shervais, 1999; Witt-Eickschen *et al.*, 2003; Choi *et al.*, 2005, 2007, 2008; Malaviarachchi *et al.*, 2008). The geochron is the reference isochron for mantle evolution, which is calculated assuming that core formation ended at 4.534 Ga (Hart & Gaetani, 2006). The reference 2 Ga secondary isochron is calculated using $\mu = 8.25$ and the NHRL is the northern hemisphere reference line (Hart, 1984). Diagram modified after (Warren & Shirey, 2012).

However, geothermometry based on trivalent REE+Y exchange between clino- and ortho-pyroxene (Fig. 4), yields high T estimates (TREE) of 1170-1300 °C, associated with high T values obtained applying Ca-in Opx (1200-1280 °C) and pyroxene solvus methods (TBKN ~ 1100 °C). The thermal evolution of the most preserved and refractory mantle body (Monte Civrari) therefore suggests rapid cooling and exhumation from near-asthenospheric conditions similar to the modern abyssal peridotites. This finding is in contrast with a long residence time in the SCLM after the post-Variscan melting event and shed new light on the presence of asthenospheric mantle in the ophiolites from the Jurassic Ligurian Tethys.

REE and Nd-Hf isotope compositions of the Monte Civrari peridotites are consistent with Jurassic low degree melting of an asthenospheric source that underwent a first melting event, starting in the garnet stability field, in Palaeozoic times (> 300 Ma).

The Nd-Hf isotopic contrast between magmatic products (Barry *et al.*, 2017) and associated mantle rocks in the Jurassic Ligurian Tetyhs strengthens the notion that ancient depleted domains may be a significant constituent of the convecting upper mantle.

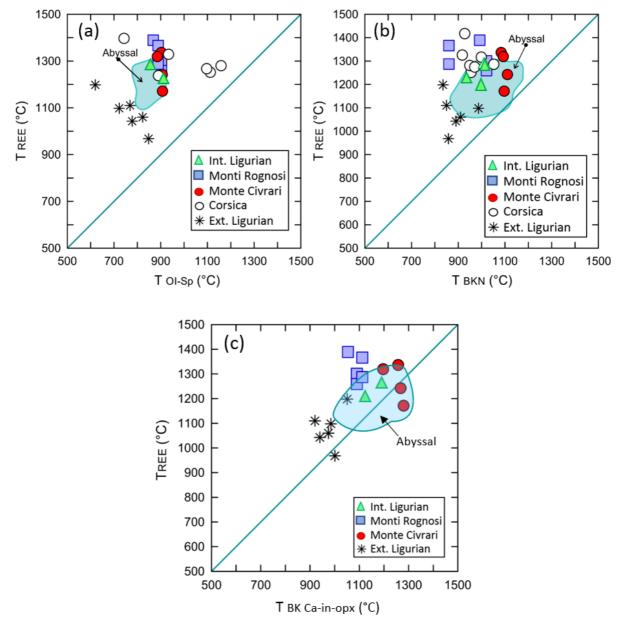


Fig. 4 - TREE vs. Ol-Sp, TBKN the TBK (Ca-in-opx) geothermometer diagrams for Internal Ligurian, Monti Rognosi and Monte Civrari peridotite compared to those of Corsica and External Liguride. TREE: REE-in-two-pyroxene geothermometer of Liang *et al.* (2013), based on trivalent REE+Y exchange between Cpx and Opx, yields high T values; (a) Ol-Sp: Equilibrium exchange of Mg and Fe between spinel and olivine (Li *et al.*, 1995); (b) TBKN: Pyroxene solvus (Brey & Koehler, 1990; Nimis & Taylor, 2000); (c) TBK: Ca-in-opx (Brey & Koehler, 1990).

REFERENCES

- Barry, T.L., Davies, J.H., Wolstencroft, M., Millar, I.L., Zhao, Z., Jian, P., Price, M. (2017): Whole-mantle convection with tectonic plates preserves long-term global patterns of upper mantle geochemistry. *Sci. Rep.-UK*, **7**(1), 1870.
- Bizimis, M., Griselin, M., Lassiter, J.C., Salters, V.J. M., Sen, G. (2007): Ancient recycled mantle lithosphere in the Hawaiian plume: Osmium–Hafnium isotopic evidence from peridotite mantle xenoliths. *Earth Planet. Sc. Lett.*, **257**, 259–273.
- Brey G.P. & Kohler T. (1990): Geothermobarometry in four phase lherzolites II. New thermobarometers, and practical assessment of existing thermobarometers. J. Petrol., **31**, 1353–1378.

- Carignan, J., Ludden, J.N., Francis, D. (1996): On the recent enrichment of sub- continental lithosphere: a detailed U–Pb study of spinel lherzolite xenoliths, Yukon, Canada. *Geochim. Cosmochim. Ac.*, **60 (21)**, 4241–4252.
- Choi, S.H., Kwon, T.-T., Mukasa, S.B., Sagong, H. (2005): Sr-Nd-Pb isotope and trace element systematics of mantle xenoliths from Late Cenozoic alkaline lavas, South Korea. *Chem. Geol.*, **221**, 40-64.
- Choi, S.H., Mukasa, S.B., Andronikov, A.V., Marcano, M.C. (2007): Extreme Sr-Nd- Pb-Hf isotopic compositions exhibited by the Tinaquillo peridotite massif, northern Venezuela: implications for geodynamic setting. *Contrib. Mineral. Petr.*, 153, 443–463.
- Choi, S.H., Mukasa, S.B., Zhou, X.-H., Xian, X.H., Andronikov, A.V. (2008): Mantle dynamics beneath East Asia constrained by Sr, Nd, Pb and Hf isotopic systematics of ultramafic xenoliths and their host basalts from Hannuoba, North China. *Chem. Geol.*, 248, 40–61.
- Goldstein, S., Soffer, G., Langmuir, C. H., Lehnert, K. A., Graham, D. W., Michael. P. J. (2008): Origin of a 'Southern Hemisphere' geochemical signature in the Arctic upper mantle. *Nature*, **453**, 89-93.
- Guarnieri, L., Nakamura, E., Piccardo, G.B., Sakaguchi, C., Shimizu, N., Vannucci, R., & Zanetti, A. (2012): Petrology, Trace Element and Sr, Nd, Hf Isotope Geochemistry of the North Lanzo Peridotite Massif (Western Alps, Italy). J. Petrol., 53(11), 2259–2306.
- Hamelin, B. & Allègre, C.J. (1988): Lead isotope study of orogenic lherzolite massifs. Earth Planet. Sc. Lett. 91,117-131.
- Hart, S.R. (1984): A large-scale isotope anomaly in the Southern Hemisphere mantle. Nature, 309, 753–757.
- Hart, S.R. & Gaetani, G.A. (2006): Mantle Pb paradoxes: the sulfide solution. Contrib. Mineral. Petr., 152, 295-308.
- Hauri, E.H., Wagner, T.P., Grove, T.L. (1994): Experimental and natural partitioning of Th, U, Pb and other trace elements between garnet, clinopyroxene and basaltic melts. *Chem. Geol.*, **117**, 149–166.
- Lehnert, K., Su, Y., Langmuir, C., Sarbas, B., Nohl, U., (2000): A global geochemical database structure for rocks. *Geochem. Geophy. Geosy.*, **1** (5), 1999GC000026
- Li, J., Kornprobst, J., Vielzeuf, D., Fabriès, J. (1995): An improved experimental calibration of the olivine-spinel geothermometer. *Chinese J. Geochem.*, 14, 68–77
- Liang, Y., Sun, C., Yao, L. (2013): A REE-in-two pyroxene thermometer for mafic and ultramafic rocks. *Geochim. Cosmochim. Ac.*, **102**, 246–260.
- Malaviarachchi, S.P.K., Makishima, A., Tanimoto, M., Kuritani, T., Nakamura, E. (2008): Highly unradiogenic lead isotope ratios from the Horoman peridotite in Japan. *Nat. Geosci.*, **1**, 859–863.
- Mallick, S., Standish, J.J., Bizimis, M. (2015): Constraints on the mantle mineralogy of an ultra-slow ridge: Hafnium isotopes in abyssal peridotites and basalts from the 9–25°E Southwest Indian Ridge. *Earth Planet. Sc. Lett.*, **410**, 42–53.
- McCarthy, A. & Müntener, O. (2015): Ancient depletion and mantle heterogeneity: Revisiting the Permian-Jurassic paradox of Alpine peridotites: *Geology*, **43**, 255–258.
- Meijer, A., Kwon, T.-T., Tilton, G.R. (1990): U-Th-Pb partitioning behavior during partial melting in the upper mantle: implications for the origin of high Mu components and the Pb Paradox. J. Geophys. Res., 95 (B1), 433–448.
- Montanini, A., Tribuzio, R., Thirlwall, M. (2012): Garnet clinopyroxenite layers from the mantle sequences of the Northern Apennine ophiolites (Italy): evidence for recycling of crustal material. *Earth Planet. Sc. Lett.*, **351–352**, 171–181.
- Mukasa, S.B. & Shervais, J.W. (1999): Growth of subcontinental lithosphere: evidence from repeated dike injections in the Balmuccia lherzolite massif, Italian Alps. *Lithos*, **48**, 287–316.
- Nimis, P. & Taylor, W. R. (2000): Single-clinopyroxene thermobarometry for garnet peridotites. Part I. Calibration and testing of a Cr-in-Cpx barometer and an enstatite-in-Cpx thermometer. *Contrib. Mineral. Petr.* **139**, 541–554.
- Nowell, G.M., Kempton, P.D., Noble, S.R., Fitton, J.G., Saunders, A.D., Mahoney, J.J., Taylor, R. N. (1998): High precision Hf isotope measurements of MORB and OIB by thermal ionization mass spectrometry: insights into the depleted mantle. *Chem. Geol.*, 149(3-4), 211–233.
- Rampone, E., Piccardo, G.B., Hofmann, A.W. (2008): Multi-stage melt-rock interaction in the Mt. Maggiore (Corsica, France) ophiolitic peridotites: microstructural and geochemical evidence. *Contrib. Mineral. Petr.*, **156**, 453–475.
- Rosenbaum, J.M., Wilson, M., Downes, H. (1997): Multiple enrichment of the Carpathian-Pannonian mantle: Pb–Sr–Nd isotope and trace element con-straints. J. Geophys. Res. 102 (B7), 14947–14961.
- Salters, V.J.M. & White, W.M. (1998): Hf isotope constraints on mantle evolution. Chem. Geol., 145, 447 460.
- Salters, V.J.M. & Stracke, A. (2004): Composition of the depleted mantle. Geochem. Geophy. Geosy., 5 (5), Q05B07.
- Standish, J.J. (2006): The influence of ridge geometry at the ultraslow-spreading Southwest Indian Ridge (91-251E): basalt composition sensitivity to variations in source and process. *Ph.D. Thesis*, MIT/WHOI Joint Program.
- Standish, J.J., Dick, H.J.B., Michael, P.J., Melson, W.G., O'Hearn, T. (2008): MORB generation beneath the ultraslow spreading Southwest Indian Ridge (9–251E): major element chemistry and the importance of process versus source. *Geochem. Geophy. Geosy.*, 9(5), Q05004.

- Stracke, A., Snow, J.E., Hellebrand, E., Von der Handt, A., Bourdon, B., Birbaum, K., Günther, D. (2011): Abyssal peridotite Hf isotopes identify extreme mantle depletion. *Earth Planet Sc. Lett.*, **308**, 359-368.
- Vervoort, J.D., Patchett, P.J., Blichert-Toft, J., Albare'de, F. (1999): Relationships between Lu-Hf and Sm-Nd isotopic systems in the global sedimentary system. *Earth Planet. Sc. Lett.*, **168**, 79–99.
- Warren, J.M., Shimizu, N., Sakaguchi, C., Dick, H.J.B., Nakamura, E. (2009): An assessment of upper mantle heterogeneity based on abyssal peridotite isotopic compositions. *J. Geophys. Res.*, **114**, B12203.
- Warren, J.M. & Shirey, S.B. (2012): Pb and Os isotopic constraints on the oceanic mantle from single abyssal peridotite sulfides, *Earth Planet Sc. Lett.*, 359-360, 279-296.
- Witt-Eickschen, G., Seck, H.A., Mezger, K., Eggins, S.M., Altherr, R. (2003): Litho- spheric mantle evolution beneath the Eifel (Germany): Constraints from Sr-Nd-Pb isotopes and trace element abundances in spinel peridotite and pyroxenite xenoliths. J. Petrol., 44 (6), 1077–1095.
- Zangana, N.A., Downes, H., Thirlwall, M.F., Hegner, E. (1997): Relationship between deformation, equilibration temperatures, REE and radiogenic isotopes in mantle xenoliths (Ray Pic, Massif Central, France): an example of plume- lithosphere interaction. *Contrib. Mineral. Petr.*, **127**, 187–203.