

# REACTIVE MELT MIGRATION CONTROLS THE TRACE ELEMENT BUDGET OF THE LOWER OCEANIC CRUST: INSIGHTS FROM THE TROCTOLITE-OLIVINE GABBRO ASSOCIATION OF THE PINETO OPHIOLITE (CORSICA, FRANCE)

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## ABSTRACT

The Pineto gabbroic sequence is a ~ 1.5 km-thick crustal section similar to those forming the oceanic core complexes at modern slow-spreading ridges. The sequence is subdivided into two sectors displaying different bulk compositions. The deeper sector consists of troctolites, with minor olivine gabbros and sparse olivine-rich troctolite intercalations. We carried out a thorough chemical characterization, including minerals and bulk rocks, of the troctolite/olivine gabbro association. Although the whole-rock compositions are mainly controlled by mineral proportions, the whole-rock variability of some minor (e.g., Cr, Ni) and trace (e.g., Y, REE) elements reveals formation by open-system crystallization processes. This interpretation is supported by the trace element mineral compositions. The incompatible trace element signature of clinopyroxene in the different rock types is nearly undistinguishable, whereas olivine and plagioclase show substantial variability of trace element compositions. In particular, olivine and plagioclase from the Ol-gabbros are typically depleted in incompatible elements compared to olivine and plagioclase from the troctolites. This chemical variability attests that fractional crystallization alone cannot have determined the compositions of these rocks, but requires an open system process where melts migrate and chemically interact with pre-existing crystal mushes leading to the redistribution of major and trace elements throughout the cumulate pile.

## INTRODUCTION

Mid-ocean ridge basalts (MORB), the most common volcanic rocks on Earth, originate by the decompression of the asthenospheric mantle and, due to buoyant forces and compact driven stresses, start to migrate upwards fractionating in multiple shallow magma chambers (Coogan, 2007). The products of these processes are a variety of gabbroic rocks that form the lower oceanic crust. Since most erupted MORB compositions plot along the olivine-plagioclase-clinopyroxene cotectic lines, a chemical evolution essentially controlled by physical separation of crystal and melt (c.f. fractional crystallization) in shallow magma chambers has been for decades considered the main process of formation of the lower oceanic crust (e.g., Grove et al., 1992). MORBs are thereby thought to reflect directly the compositions of the mantle sources, after being corrected for fractional crystallization process (e.g., Klein and Langmuir, 1987). However, numerous studies in the last years provided evidence that the lower crust evolves through open system crystallization processes that cannot be reduced to fractional crystallization alone (Coogan et al., 2000; Gao et al., 2007; Lissenberg and Dick, 2008; Drouin et al., 2009; Lissenberg et al., 2013; Sanfilippo et al., 2015a; Rampone et al., 2016; Basch et al., 2018). For instance, textural and chemical evidence in gabbros indicate that these rocks are the results of multiple stages of fractionation, dissolution and re-crystallization of new minerals by protracted events of melt migration throughout a crystal-rich mush (see Lissenberg and MacLeod, 2016 and reference therein). Melt-rock interaction is now regarded as the main process determining the evolution of crustal rocks, questioning on the use of fractional crystallization equations to correct the chemical composition of erupted MORB.

The present study provides new geochemical insights into the origin of a troctolite-gabbro association exposed in the ophiolitic section of Pineto (central Corsica, France). Based on microstructural observations and olivine chemical composition, it was previously proposed that the lithological transition from troctolite (olivine-rich to plagioclase-rich) to olivine gabbro ultimately, olivine-free gabbros, was the consequence of melt-rock reactions rather than low-pressure fractional crystallization (Sanfilippo and Tribuzio 2013a; 2013b; Sanfilippo et al., 2015b). Here, we expand our analyses on plagioclase and whole-rock compositions to shed further light on this process, discussing the effect of melt-rock reactions to redistribute the trace element budget throughout the entire lower crustal sequence exposed in the Pineto ophiolite.

## GEOLOGY OF THE PINETO OPHIOLITE

The Pineto ophiolite is located near the tectonic lineament separating the Alpine tectonic stack of Corsica (Alpine Corsica) from the Late Carboniferous-Early Permian continental basement (e.g., Rossi et al. 1994; Renna et al. 2007). This ophiolite is situated at the top of the Alpine Corsica and it is essentially unaffected by the Alpine orogenic metamorphism. Previous structural and geochemical studies of the Pineto ophiolite (Beccaluva et al., 1977; Saccani et al., 2000; Sanfilippo and Tribuzio, 2013a; 2013b) documented that it exposes a lower crustal section similar to those forming the gabbroic oceanic core complexes from Mid-Atlantic and the Southwest Indian Ridges (e.g., Dick et al., 2000; Ildefonse et al., 2007; Smith, 2014).

The Pineto lower crust covers an area of ~ 10 km<sup>2</sup> (Fig. 1) and may be subdivided into two main sectors displaying different bulk compositions (Sanfilippo and Tribuzio,

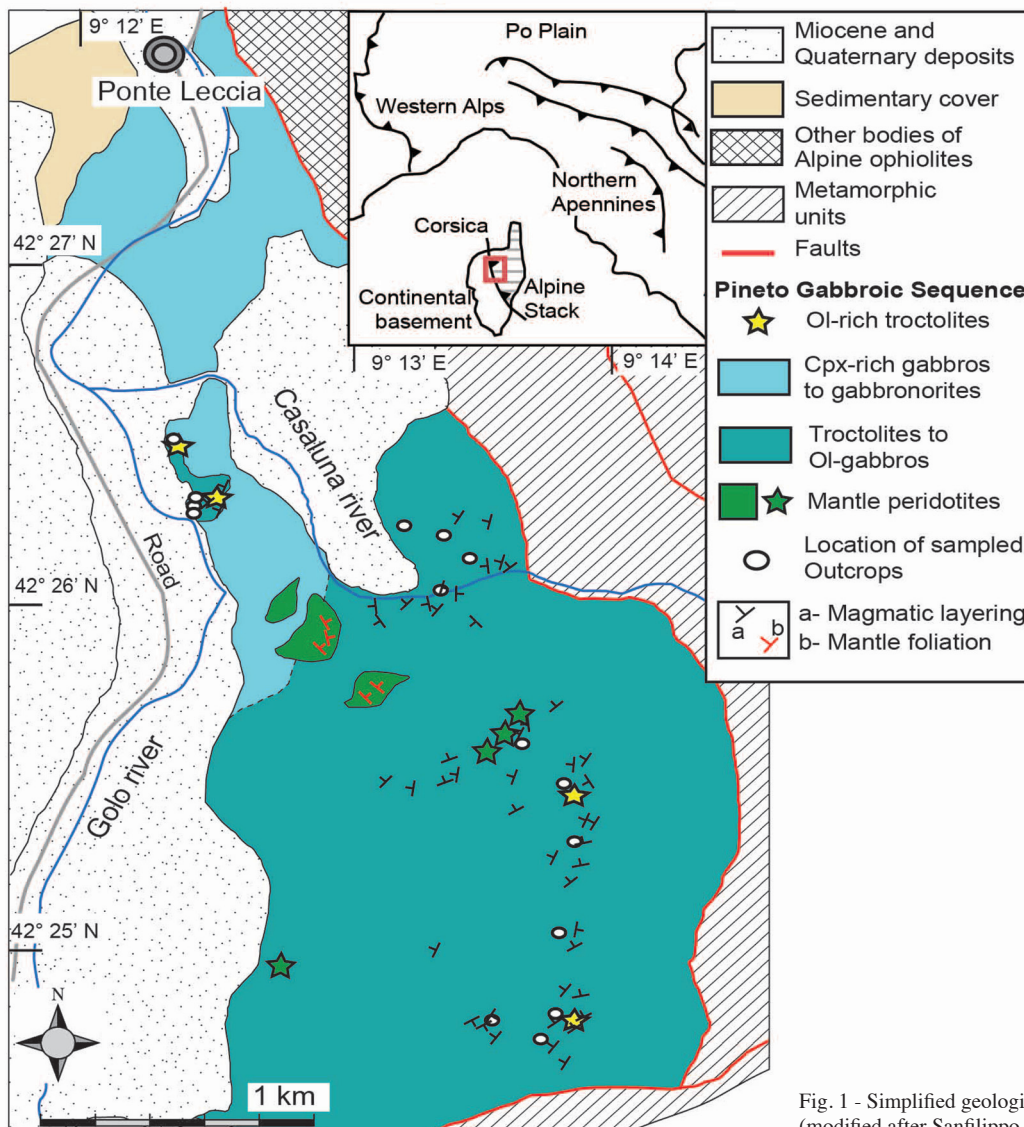


Fig. 1 - Simplified geological map of the Pineto gabbroic sequence (modified after Sanfilippo and Tribuzio, 2013a).

2013a). The northern sector (~ 500 m thick) mostly consists of clinopyroxene-rich gabbros to gabbronorites, displaying a weak grain-size layering, in places crosscut by basalt dykes and amphibole veins. These gabbroic rocks contain a ~ 0.1 km thick troctolite body, which in turn locally includes up to meter-scale thick olivine-rich (> 70 vol%) troctolite intercalations. The gabbroic sequence preserves primary contacts with a volcano-sedimentary cover that is typically few meters in thickness. From the bottom to the top, this volcano-sedimentary cover comprises polygenic tectono-sedimentary breccias containing angular gabbro and minor basalt clasts, locally covered by a discontinuous layer of pillowed basalts. Everything is then overlain by Middle-Late Jurassic radiolarian cherts and Cretaceous shaly pelagites (Durand-Delga et al., 2005; Saccani et al., 2008; Sanfilippo and Tribuzio, 2013a). The occurrence of the tectonic breccias indicates that the gabbroic sequence was exhumed to the seafloor during the Middle-Late Jurassic. Near the contact with the basalt-sedimentary cover, the gabbroic rocks are locally characterized by high temperature shear zones formed by porphyroclastic to mylonitic fabrics.

The southern sector of the Pineto ophiolite exposes a lower crustal sequence mainly made up of troctolites, with

minor olivine gabbro and sparse olivine-rich troctolite intercalations. The physical continuity with the gabbros from the northern sector and the geometry of the magmatic layering allowed Sanfilippo and Tribuzio (2013a; 2013b) to infer that this sector represents a stratigraphically lower portion of the crustal sequence. Mostly on the basis of the orientation of the troctolite grain size layering, which is locally associated with minor changes in modal compositions, Sanfilippo and Tribuzio (2013a) estimated a thickness of ~ 1 km for the troctolite/olivine gabbro association. The olivine gabbros form bodies that are up to tens of meters in thickness within the troctolites, constituting ~ 20 vol% of the association (see also Sanfilippo et al., 2015a; 2015b). Irregular clinopyroxene-rich veins locally occur within the troctolites near the olivine gabbros. It was argued that the troctolites including the clinopyroxene veins represent the lithological transition from troctolite to olivine gabbros, and are hereafter indicated as Cpx-rich troctolites (Cpx 5 to 15 vol%, Ol > 20 vol%) to be distinguished from the Ol-gabbros whose olivine never exceeds 15 vol%. The olivine-rich (Ol > 70 vol%) intercalations (up to m-scale thick) are mostly located toward the base of the troctolite/olivine gabbro sequence and interpreted as slivers of the crust-mantle boundary enclosed

within the lower crust (Sanfilippo and Tribuzio, 2013b).

The contact between the southern and the northern lower crust sequences is characterized by up to ~ 50 m thick serpentinitized peridotite slivers, interpreted as mantle portions entrapped during pluton growth (Sanfilippo and Tribuzio, 2013a). The serpentinite protoliths consist of porphyroclastic spinel-plagioclase-bearing clinopyroxene-poor lherzolites to harzburgites. The occurrence of variably evolved gabbros randomly distributed at different stratigraphic heights (Fig. 1) and the Ca-in olivine cooling rate estimates (-2.2 to -1.7 °C/year log units) led Sanfilippo and Tribuzio (2013a) to propose an accretion process ruled by multiple intrusions within a relatively cold mantle lithosphere.

## ANALYTICAL METHODS

This study includes major and trace element whole-rock and mineral analyses of three olivine-rich troctolites, seven troctolites, two clinopyroxene-rich troctolites and three olivine gabbros from the Pineto gabbroic sequence. Sample locations, main microstructure characteristics and major element whole-rock and mineral compositions are reported in Sanfilippo and Tribuzio (2013a). New major element mineral compositions were obtained for two samples using a JEOL JXA-8200 electron microprobe located at Dipartimento di Scienze della Terra, Università degli Studi di Milano (Italy). Conditions of analyses were 15 kV accelerating voltage and

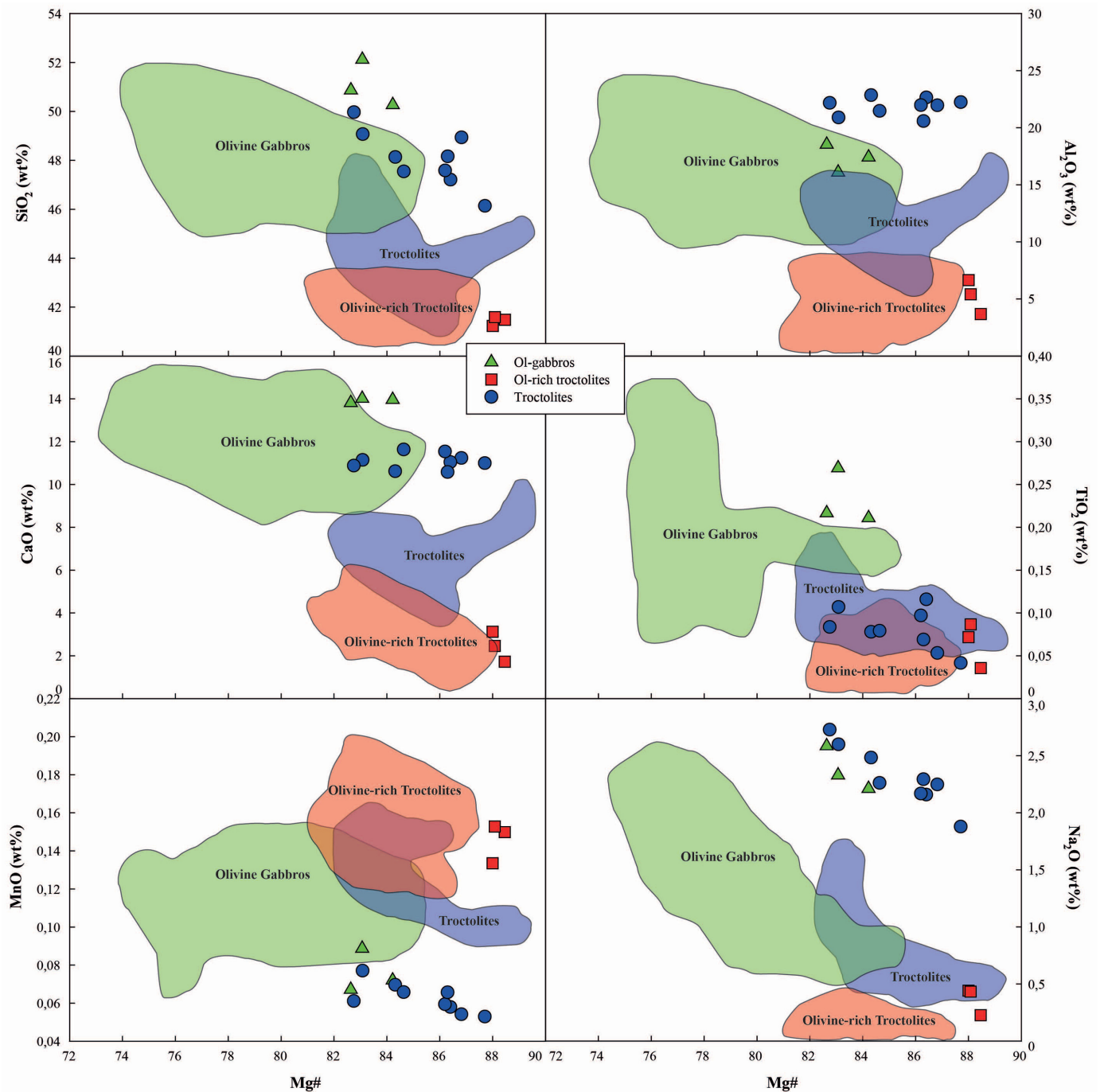


Fig. 2 - Whole-rock compositional variations: major elements (CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O and TiO<sub>2</sub>) versus Mg# [molar Mg/(Mg+Fe<sup>2+</sup>+tot) × 100]. The compositions of olivine gabbros, olivine-rich troctolites and troctolites from the Atlantis Massif (Godard et al., 2009) are also reported (colored fields).

15 nA beam current; counting time were 30 s on the peak and 10 s on the background.

Whole-rock trace element analyses (Suppl. Table 1) were carried out by inductively coupled plasma atomic emission spectroscopy at Activation laboratories (Ancaster, Ontario). The samples were melted through a lithium metaborate/tetraborate fusion and then analyzed with ICP-MS. This method was used to determine major and some trace element (Sc, Ti, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Cs, Ba, Rare Earth Elements, Hf, Ta, Pb, Th, U and W) concentrations. Detection limits are estimated to be 0.01% for most major and trace elements.

Trace element determinations of plagioclase and clinopyroxene cores (Suppl. Tables 2-3) were measured using a laser ablation inductively coupled plasma mass spectroscopy (ICPMS) at C.N.R., Istituto di Geoscienze e Georisorse (Unità di Pavia). This instrument couples a YAG laser operating at 266 nm with a quadrupole ICPMS (DRc-e, PerkinElmer). Analyses were carried out with a spot of 30  $\mu$ m. Data reduction was performed with the "Glitter" software package (Van Achterbergh et al., 2001). NIST SRM 612 was used as external standard while BRC2-g as reference glass for the accuracy testing. Olivine trace element compositions of ten samples (Sanfilippo et al. 2014; 2015a; 2015b) are also considered in this study.

## MAIN PETROLOGICAL CHARACTERISTICS AND WHOLE-ROCK COMPOSITIONS

Modal compositions of selected rock samples are reported in Table 1. The reported stratigraphic heights and the locations of the samples are taken from Sanfilippo and Tribuzio (2013a). The mineral modes are estimated on the basis of major element whole-rock and mineral compositions using MODAN software (Pactunk, 1997) with the following mineral densities: Ol = 3.32, Pl = 2.68-2.72, Cpx = 3.40-3.30, Opx = 3.20 and Ilm = 4.72.

### Olivine-rich troctolites

The olivine-rich troctolites show poikilitic texture, characterized by fine to medium grained (< 100-500 nm) polygonal olivine (Fo<sub>89-88</sub>), typically included in plagioclase (An<sub>72-68</sub>) and clinopyroxene oikocrysts. The latter have Mg# [molar Mg/(Mg + Fe)] ranging from 89 to 90. Spinel (Cr# = 52-55 and TiO<sub>2</sub> ~ 1.9 wt%) occurs as accessory phase, mostly included in clinopyroxene and plagioclase. Ti-rich amphibole and/or phlogopite are in places found within the spinel.

These rocks have high Mg# (~ 88), Ni (1200-1700 ppm) and Co (100-110 ppm). Cr concentrations are highly variable (640-3320 ppm), most likely in relation to different spinel modal amounts. The contents of Al<sub>2</sub>O<sub>3</sub>, CaO, Na<sub>2</sub>O and TiO<sub>2</sub> are low (3-6 wt%, ~ 2 wt%, 0.2-0.4 wt%, and 0.03-0.08 wt%, respectively, see Fig. 2). The olivine-rich troctolites also have low concentrations of incompatible trace elements (e.g., Zr ~ 3 ppm and Y = 0.7-1.3 ppm). The concentrations of incompatible trace elements normalized to chondrite (CI, Lyubetskaya and Korenaga, 2007) yield nearly flat patterns at ~ 0.5-1.0 times x CI. The patterns indeed display small positive Sr and Eu anomalies (Figs. 4 and 5), and a slight enrichment of LREE with respect to MREE and HREE.

### Troctolites

The troctolites are mainly made up of euhedral to subhedral plagioclase (An<sub>73-65</sub>) and olivine (Fo<sub>88-84</sub>). The clinopy-

roxene is present as films (Mg# = 86-90) around olivine and/or as small interstitial grains locally interconnected to form oikocrysts (Mg# = 88). Most troctolites contain orthopyroxene, which occurs as films or interstitial grains, typically associated with clinopyroxene, Ti-rich amphibole and/or ilmenite. Accessory spinel (Cr# = 50-66 and TiO<sub>2</sub> = 0.7-2.8 wt%) is also locally present.

The troctolites have Mg# ranging from 88 to 83, and higher Al<sub>2</sub>O<sub>3</sub> (20-22 wt%), CaO (10-11 wt%) and Na<sub>2</sub>O (1.81-2.68 wt%) than the olivine-rich troctolites (Fig. 2). The troctolite whole-rock compositions document a rough positive correlation between Mg# and compatible trace elements (e.g., Ni and Co), whereas moderately incompatible (Sc, V, Cu) and incompatible trace elements (e.g., Y and Zr) are negatively correlated with Mg# (Fig. 3). Cr concentrations range from 110 to 500 ppm and do not correlate with Mg#. The troctolites have CI normalized patterns overall similar to those of the olivine-rich troctolites, although the former typically have slightly higher concentrations (up to 0.5 times CI). The troctolites show positive Sr-Eu anomalies, which decrease with increasing REE and Y contents (Figs. 4 and 5); the LREE are variably enriched over MREE-HREE.

### Olivine gabbros

The olivine gabbros have a poikilitic texture with euhedral to subhedral olivine (Fo<sub>81-84</sub>) and plagioclase (An<sub>65-63</sub>) locally included within clinopyroxene oikocrysts (Mg# = 86-87). Orthopyroxene films and small orthopyroxene anhedral grains are also locally present, in places associated with Ti-rich amphibole and ilmenite.

The olivine gabbros have relatively low Mg# (82-84). They show lower Al<sub>2</sub>O<sub>3</sub> (16-18 wt%) and higher CaO (~ 14 wt%), Na<sub>2</sub>O (2.18-2.54 wt%) and TiO<sub>2</sub> (0.21-0.26 wt%) than the troctolites (Fig. 2). The olivine gabbros are also distinct for their high concentrations of Sc (27-37 ppm), V (96-118 ppm), Y (5.4-6.9 ppm) and REE. Although Ni in the olivine gabbros is lower than in the troctolites, the former are enriched in Cr, with concentrations variable from 840 to 1690 ppm. The CI (Lyubetskaya and Korenaga, 2007) normalized incompatible trace element patterns of the olivine gabbros are characterized by depletion of LREE with respect to MREE and HREE, and small positive Sr-Eu anomalies (Figs. 4 and 5). The olivine gabbros have higher REE concentrations than the troctolites.

## MINOR AND TRACE ELEMENT COMPOSITIONS OF MINERALS

Minor and trace element compositions of olivine are reported in previous studies (Sanfilippo et al., 2014; 2015a; 2015b) and will be hereafter summarized. Olivine shows gradual variations in forsterite component (81.7 to 88.5 mol%) and Ni (1900 to 1350 ppm) contents, which gradually decrease from the olivine-rich troctolites to the troctolites and the olivine gabbros. Mn (1900-1350 ppm) and Co (1900-1350 ppm) are negatively correlated with both forsterite molar proportions and Ni. The incompatible trace elements (Ti, Y, HREE and Zr) in olivine from the troctolites and olivine-rich troctolites display positive correlation with Mn. Olivine from the olivine gabbros is characterized by a relative depletion in incompatible elements which, at given Mn contents, are lower than those in the troctolites.

Plagioclase from the different rock types has chondrite-normalized patterns displaying enrichments in LREE with

Table 1 - Locations and petrography of the studied samples.

Sample Initial	Mineral modes (vol%)			Average Grain size (mm)					Accessory Spinel	Location	Estimated Stratigraphic height (m)
	Pl	Ol	Cpx	Opx	Pl	Ol	Cpx	Opx			
PI41a*	15	82	3	-	Oikocryst up to 10	Rounded to polygonal 0.3	Films up to 0.2	-	§	42°26' 21.51"N 9°12'28.09"E	1300
PI85*	23	76	1	-	Oikocryst up to 5	Rounded to polygonal 0.5	Interstitial up to 1	-	§	42°24' 47.57"N 9°13'58.27"E	150
PI80	20	79	1	-	-	-	-	-	§	-	-
PI44*	74	20	6	§	4.0	2.5	Discrete grain up to 1	Discrete grain up to 1	§	42°26' 21.51"N 9°12'28.09"E	1350
PI62*	72	20	8	§	2.0	1.5	Oikocryst up to 15	Films up to 0.2	-	42°26' 15.61"N 9°13'27.14"E	1000
PI56	70	25	5	§	3.0	2.0	Discrete grain up to 1	Films up to 0.2	§	42°26' 08.78"N 9°13'35.02"E	900
PI31*	76	17	7	§	1.5	1.0	Films up to 0.1	Films up to 0.1	§	42°26' 03.67"N 9°13'25.20"E	850
PI54*	74	22	4	§	7.0	4.0	Discrete grain up to 1	Films up to 0.3	§	42°25' 41.81"N 9°13'44.36"E	600
PI33*	73	22	5	§	3.0	2.0	Films up to 0.2	Films up to 0.2	§	42°25' 12.37"N 9°13'54.48"E	450
PI49*	74	20	6	-	0.7	0.2	Oikocryst up to 5	-	§	42°25' 02.08"N 9°13'53.47"E	250
PI19*	68	22	10	§	3.5	2.5	Oikocryst up to 25	-	§	42°24' 46.08"N 9°13'59.61"E	125
PI16*	75	24	1	-	1.5	0.7	Films up to 0.1	-	§	42°24' 44.14"N 9°13'57.58"E	120
PI32*	63	10	27	§	4.0	2.0	Oikocryst up to 30	Films up to 0.3	-	42°26' 03.67"N 9°13'25.20"E	850
PI34*	64	13	23	§	7.0	2.0	Oikocryst up to 30	Discrete grain up to 1	-	42°25' 00.57"N 9°13'27.98"E	400
PI18*	60	10	31	-	2.5	1.0	Oikocryst up to 15	Films up to 0.1	-	42°24' 46.08"N 9°13'59.61"E	130

The mineral modes are estimated on the basis of the whole rock and mineral compositions (Online Resources 2; 3; 4; 8) using MODAN software (Paetunk, 1997) and the following mineral densities: Ol 3.32; Pl 2.68-2.72; Cpx 3.40-3.30; Opx 3.20; Ilm 4.72. Coordinates are in WGS. Classification and nomenclature after Streckeisen (1967). Symbology and mineral abbreviations: § < 3%; -, mineral not present; Ol- Olivine; Opx- Orthopyroxene; Cpx- Clinopyroxene; Amp- Amphibole. The stratigraphic distances from the base of the sequence are given in metres and were evaluated on the basis of the average orientation of the grain-size/modal layering.

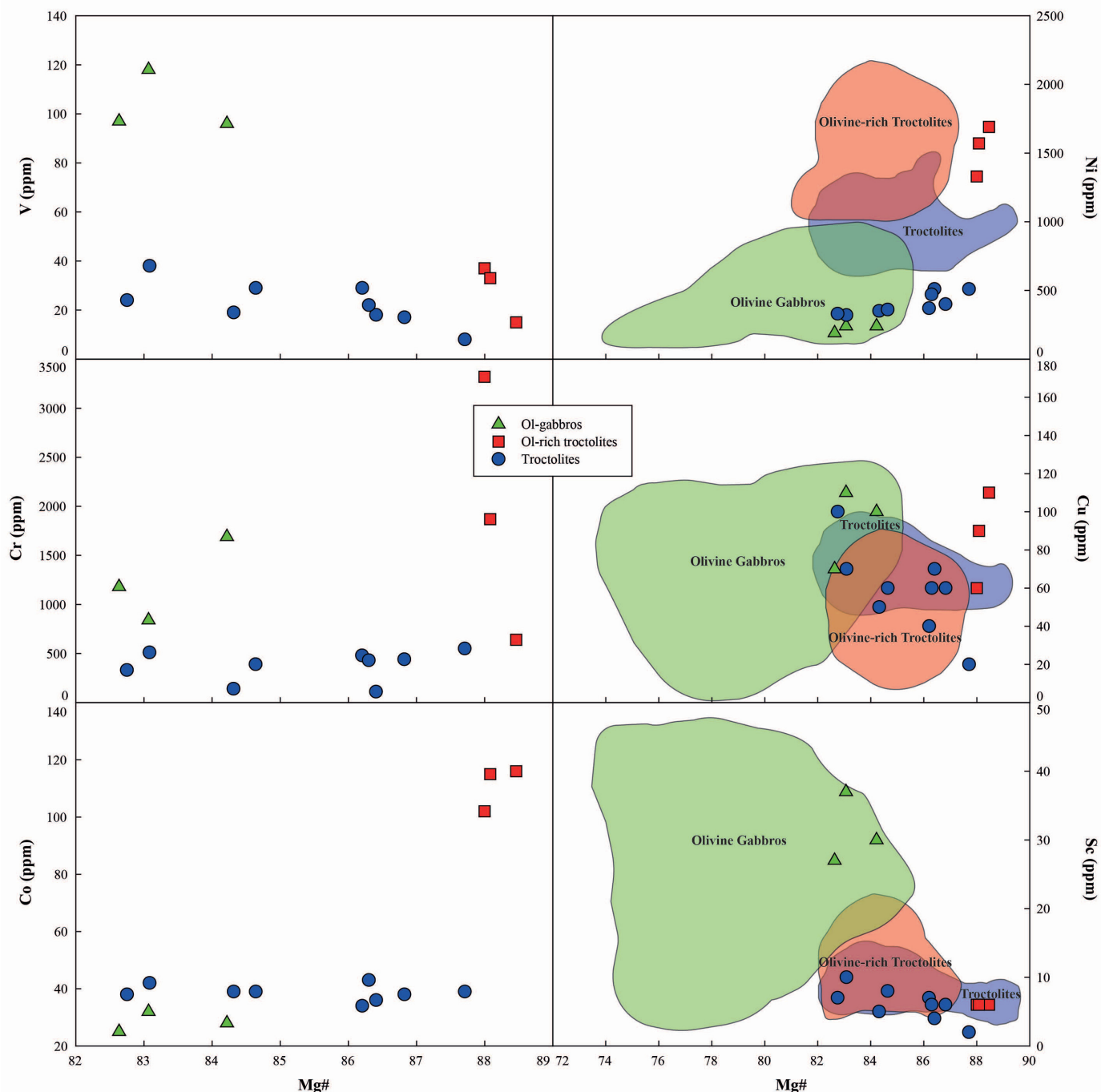


Fig. 3 - Whole-rock compositional variations: trace elements (V, Sc, Co, Ni, Cu and Cr) versus Mg# [molar  $Mg/(Mg+Fe^{2+}+tot) \times 100$ ]. The compositions of olivine gabbros, olivine-rich troctolites and troctolites from the Atlantis Massif (Godard et al., 2009) are also reported (colored fields).

respect to Y ( $La_N/Y_N = 1.8-6.0$ ), positive Sr-Eu anomalies, and slight Ba depletion with respect to La (Fig. 6). The highest and the lowest LREE enrichment is typically observed for plagioclase from the olivine-rich troctolites and the troctolites, respectively. Plagioclase from the olivine gabbros typically has slightly lower Y than plagioclase from the olivine-rich troctolites and the troctolites.

Oikocrystic clinopyroxene from each rock type has high Cr contents (2013-8630 ppm) and relatively low concentrations of incompatible trace elements. The chondrite-normalized patterns display LREE depletion with respect to MREE and HREE ( $La_N/Sm_N = 0.04-0.11$ ,  $Gd_N/Yb_N = 0.8-1.2$ ). The REE pattern of small interstitial clinopyroxene is generally

subparallel to that of oikocrystic clinopyroxenes but at higher absolute concentrations (Fig. 7). This clinopyroxene is also distinct in the Eu and Sr depletions relative to adjacent elements, and in the absence of negative Zr anomaly ( $Zr_N/Nd_N = 2.1-2.3$ , compared to 0.4-0.9 in oikocrystic clinopyroxenes). There is no correlation between Cr and incompatible element contents in clinopyroxene from the different rock-types. Taken as a whole, clinopyroxene from the Pineto gabbroic sequence (see also Sanfilippo et al., 2014; 2015a; 2015b) is chemically indistinguishable from clinopyroxene in modern abyssal gabbros (e.g., Drouin et al., 2009), thereby testifying chemical equilibrium with melts closely similar to variably evolved MORB.

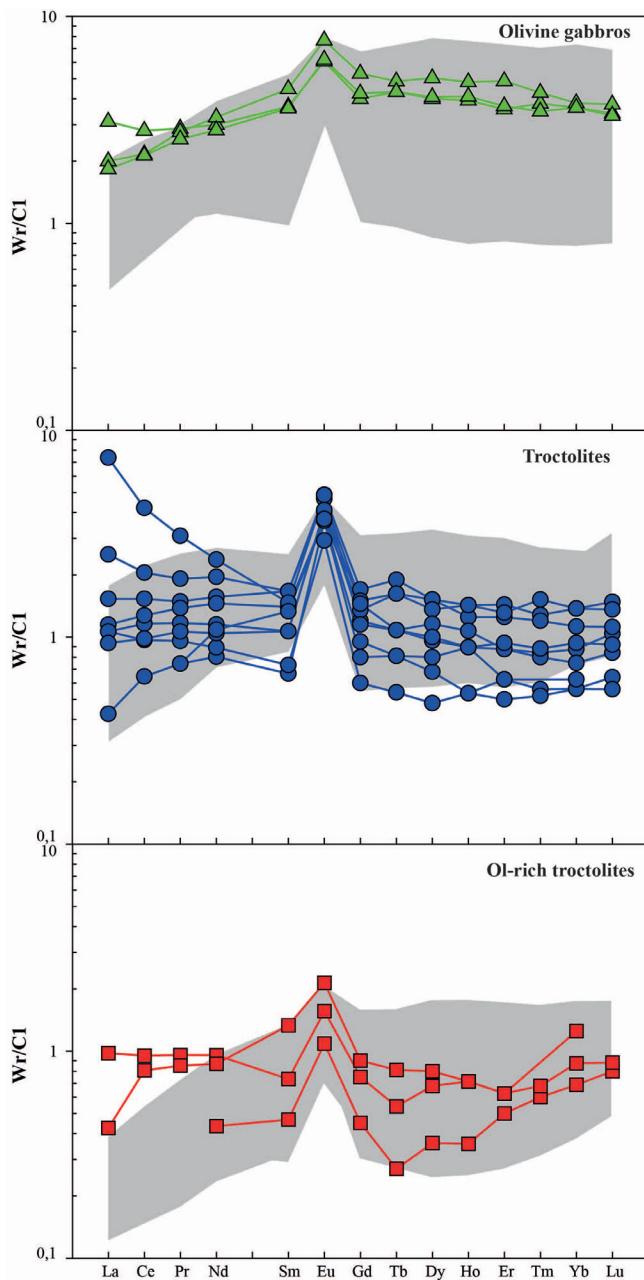


Fig. 4 - Whole-rock REE compositions, normalised to C1 chondrite (Lyubetskaya and Korenaga, 2007). The compositions of olivine gabbros, olivine-rich troctolites and troctolites from the Atlantis Massif (Godard et al., 2009) are also reported (colored fields).

## GEOOTHERMOMETRY

The REE in plagioclase-clinopyroxene geothermometer from Sun and Liang (2017) was applied to selected rock samples, assuming a confining pressure of 0.2 GPa and a  $H_2O$  melt content of 0.2 wt%. The results are reported in Table 2 together with the estimates from Sanfilippo and Tribuzio (2013b) obtained on the basis of the Ca-in-olivine method by Brey and Kohler (1990). We also calculated temperature estimates on the basis of the Ca-in-orthopyroxene method by Brey and Kohler (1990). The REE in plagioclase-clinopyroxene geothermometer (Sun and Liang, 2017) gave values ranging 1120 to 1170 °C, with no correlation with rock type. These temperature estimates are higher than those obtained on the

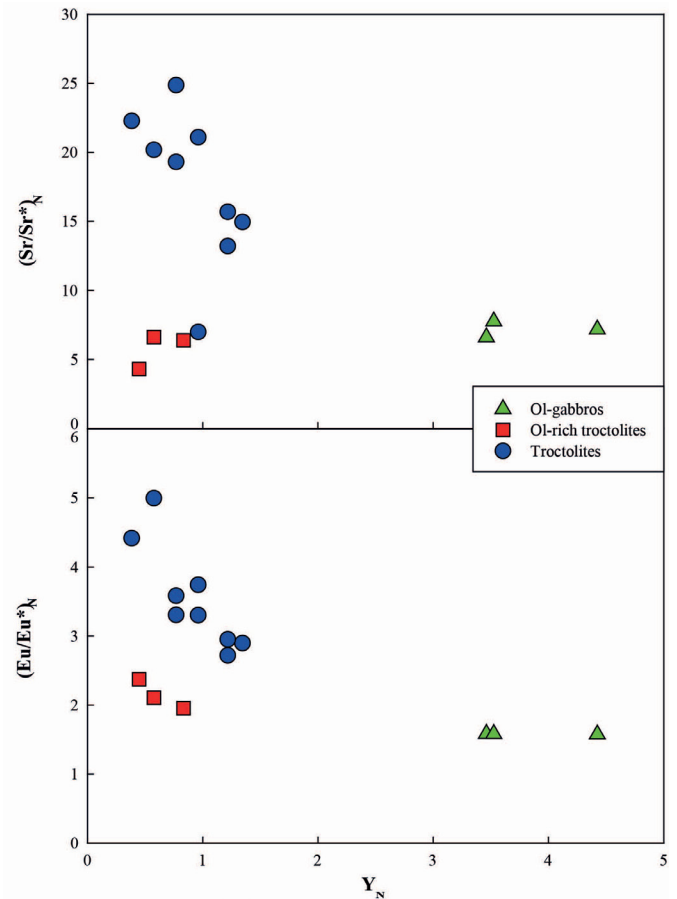


Fig. 5 - Plot of  $Sr/Sr^*$  ( $Sr^* = \sqrt{SrxCe}$ ) and  $Eu/Eu^*$  ( $Eu^* = \sqrt{SmxDy}$ ) vs.  $Y_N$  for whole-rocks, normalised to C1 chondrite (Lyubetskaya & Korenaga, 2007).

basis of Ca concentrations in orthopyroxene and olivine (Brey and Kohler, 1990), which yielded a temperature interval of 970-900 and 950-840 °C, respectively. Fig. 8 illustrates the distribution of computed temperature estimates in relation to the stratigraphic heights. The high values of the equilibrium temperature of REE between Cpx and Pl are close to the solidus temperatures for the two phases, thereby indicating that subsolidus re-equilibration did not affect the REE partitioning between these minerals. Conversely, olivine, clinopyroxene and orthopyroxene register a process of Ca diffusion under subsolidus conditions. These data confirm that the REE-in plagioclase-clinopyroxene thermometer can be used to constrain the crystallization temperature of plutonic rocks.

## DISCUSSION

### Evidence for an open system magmatic evolution

The whole-rock major element compositions discriminate the different rock-types. For instance, although the most evolved troctolites and the olivine gabbros have comparable Mg#, the latter are distinguished for lower  $Al_2O_3$  and NaO, and higher CaO and  $TiO_2$  contents, in response to the lower modal plagioclase/clinopyroxene ratios (Table 1). Similarly, the troctolites and the olivine gabbros display different incompatible trace element compositions, especially for those elements preferentially incorporated by clinopyroxene (Cr, Sc, V, Y, REE and Zr). Major and trace element whole-rock compositions are therefore controlled

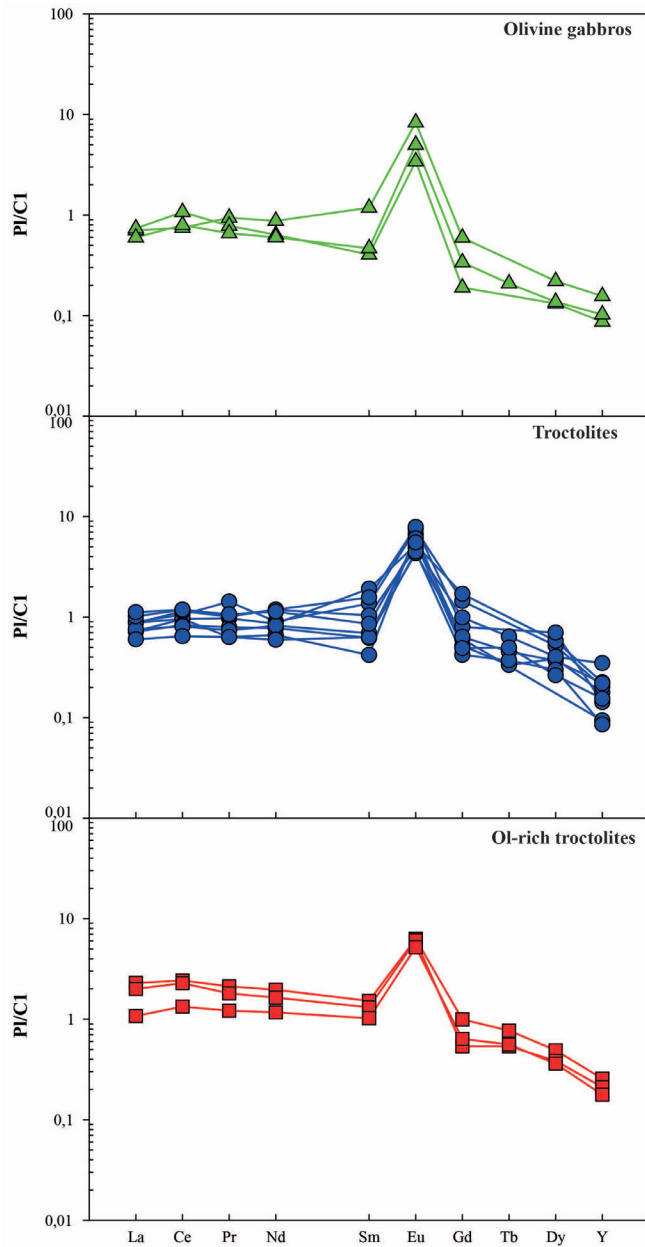


Fig. 6 - REE compositions of plagioclase cores normalised to C1 chondrite (Lyubetskaya and Korenaga, 2007).

by the modal compositions of the different rock types. Nevertheless, the troctolites show chemical variations that are not related to different modal compositions (Table 1), such as: (i) a positive correlation between Ni and Mg#, and (ii) negative correlations between incompatible elements (e.g., Na<sub>2</sub>O, TiO<sub>2</sub>, Y, Zr, Sc, V) and Mg#. For instance, the highest and lowest Ni contents pertain to troctolites PI44 and PI31 (510 ppm and 330 ppm, respectively), which are characterized by similar mineral proportions. Hence, the whole-rock compositions are also constrained by the chemistry of the melts forming these rocks.

The whole-rock incompatible trace element compositions cannot discriminate the olivine-rich troctolites from the troctolites. This is counterintuitive, as one would expect the olivine-rich troctolites having lower concentrations of incompatible trace elements than the troctolites, where plagioclase is up to 70 wt%. This is related to the fact that plagioclase from

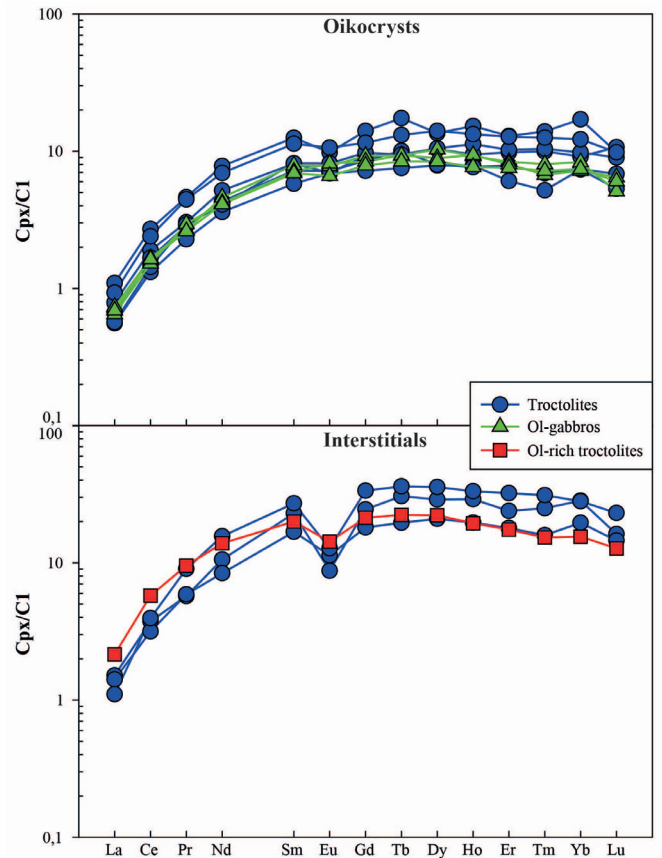


Fig. 7 - REE compositions of clinopyroxene oikocrysts and interstitials normalised to C1 chondrite (Lyubetskaya and Korenaga, 2007).

the olivine-rich troctolites is typically enriched in incompatible elements compared to plagioclase from the troctolites (and the olivine gabbros). In addition, the concentrations of incompatible trace elements in the olivine-rich troctolites and the troctolites radically change in conjunction with the clinopyroxene modal amounts.

The Cr contents of the olivine gabbros are higher than those of the troctolite at same Mg#. Among the different phases contained in these rocks, chromium is highly compatible in spinel, where it represents a major element, and clinopyroxene. Consistently, the olivine-rich troctolites have the highest spinel modal amounts and the highest Cr concentrations among the rocks considered in this study. However, spinel is not present in the olivine gabbros, thereby implying that clinopyroxene is the major Cr repository in these rocks. The Cr enrichment of the olivine gabbros agrees with the previous observation that clinopyroxene from these rocks has anomalously high Cr contents. Sanfilippo and Tribuzio (2013a) used this observation to propose that the clinopyroxene from the olivine gabbros formed by melts enriched in Cr by partial assimilation of a spinel-bearing troctolite matrix (see also Lissenberg and Dick, 2008).

The concentrations of incompatible trace elements in plagioclase (e.g. Y) are positively correlated with the anorthite molar proportion (Fig. 9). This is inconsistent with crystallization of plagioclase from a melt following the typical fractionation line of MORB melt under low pressure conditions (olivine → olivine + plagioclase → olivine + plagioclase + clinopyroxene; Grove et al., 1992), which would imply a plagioclase gradually more enriched in incompatible elements



Table 2 - Temperature estimates for selected samples.

Rock-type Sample Initial	Ol-rich troctolite PI85	Troctolite PI44	Troctolite PI62	Troctolite PI56	Troctolite PI31	Troctolite PI54	Troctolite PI33	Troctolite PI49	Troctolite PI19	Ol-gabbro PI32	Ol-gabbro PI18	Ol-gabbro PI34
REE-in-Cpx-Plg	1168 ± 14	1124 ± 4	1159 ± 3	1153 ± 11	1170 ± 11	1130 ± 16	1173 ± 13	1151 ± 9	1172 ± 16	1146 ± 17	1122 ± 20	1172 ± 11
Ca-in-Opx	-	972	904	913	924	945	953	-	966	919	935	934
Ca-in-Ol	-	857	-	878	-	954	904	747	-	842	895	950

(i) REE-in-Cpx-Pl: clinopyroxene-plagioclase by Sun and Liang, (2017), (ii) Ca-in-Opx: Ca-in-orthopyroxene by Brey and Kohler (1990) (iii) Ca-in-Ol: reported temperature estimates from Sanfilippo and Tribuzio (2013).

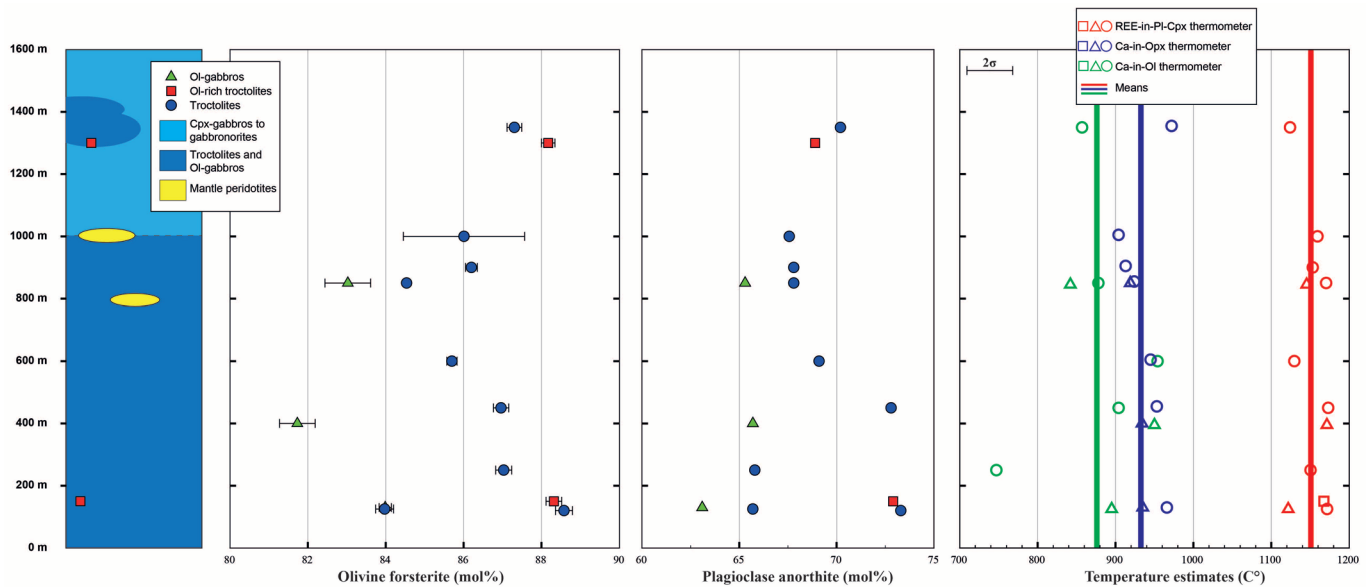


Fig. 8 - Forsterite proportion of olivines (mol%), anorthite content of plagioclases (mol%) (Sanfilippo and Tribuzio, 2013a; 2013b) and temperature estimates for the Pineto gabbroic sequence as a function of the stratigraphic height. The temperature estimates were obtained through the REE-in-Pl-Cpx geothermometer of Sun and Liang (2017) and the Ca-in-Opx geothermometer of Brey and Kohler (1990). The figure also reports the Ca-in-Ol temperature estimates from Sanfilippo and Tribuzio (2013a; 2013b). Data are averaged per sample; the error bars represent one SD of the mean value.

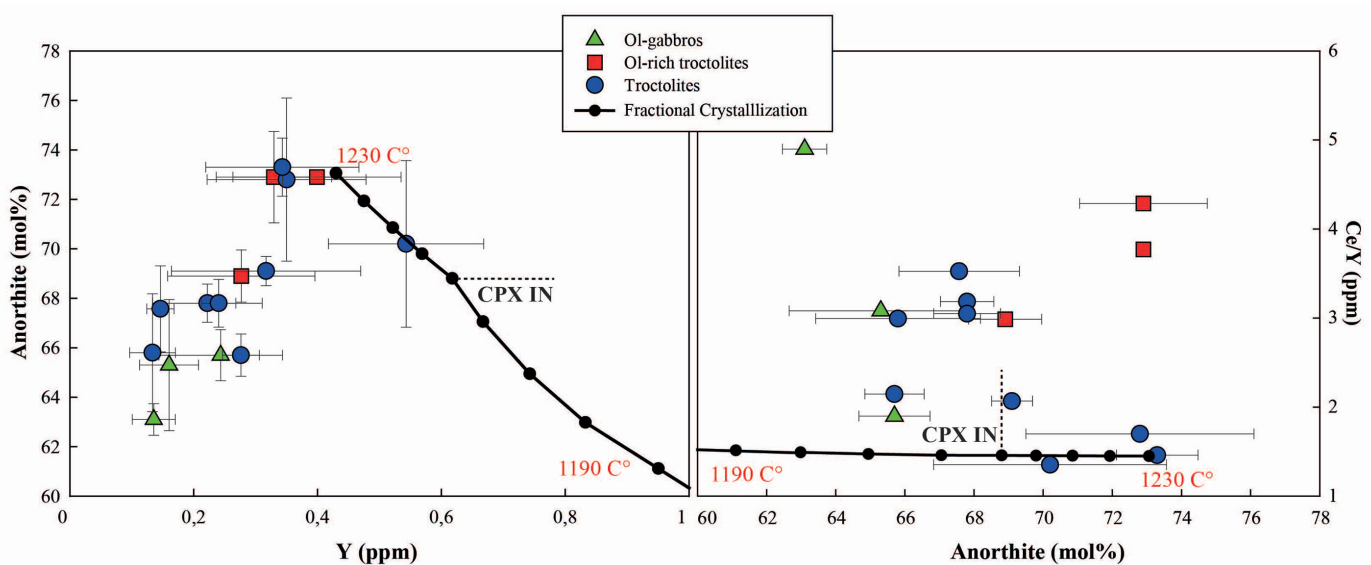


Fig. 9 - Anorthite contents of plagioclase vs. Y (ppm) and Ce/Y concentrations. The diagrams also report the composition of plagioclase in equilibrium with melt obtained by fractional crystallization using the program PELE (Boudreau, 1999). Parental melt has major element compositions of experimentally derived basalt from Kinzler and Grove (1993) ( $\text{SiO}_2 = 48.54$ ;  $\text{TiO}_2 = 0.9$ ;  $\text{Al}_2\text{O}_3 = 17.1$ ;  $\text{FeO} = 6.97$ ;  $\text{MgO} = 11.57$ ;  $\text{CaO} = 11.22$ ;  $\text{Na}_2\text{O} = 2.48$  wt%), and Y and Ce compositions (18.15 and 5.7 ppm respectively) of the melt in chemical equilibrium with the mean Y and Ce contents of the most primitive plagioclase (troctolite sample PI16). Each step consists in a decrease of 5 °C in temperature at constant pressure of 2.5 kbar. The dashed lines represent the appearance of clinopyroxene as crystallizing phase. The grey arrow indicates the theoretical path of the reactive crystallization identified by the sample suite.

as crystallization proceeds. Note that the restricted variations in anorthite component of the plagioclase indicate no substantial changes in plagioclase/melt Y partitioning during the magmatic evolution. We modeled a fractional crystallization process documenting that the most primitive troctolite (PI16) may be produced by fractionation of a primitive melt saturated in olivine + plagioclase (Fig. 9). As suggested before, this fractional crystallization model also predicts Y increase in the melt, thereby implying Y increase in the crystallizing plagioclase. Hence, the chemical evolution of the plagioclase from the different rock-types cannot be related to fractional crystallization of parental melts with similar compositions.

Olivine from the olivine gabbros and troctolite PI56 (including clinopyroxene oikocrysts) has lower concentration of incompatible trace elements than olivine from troctolites free of clinopyroxene oikocrysts, although the latter has slightly higher forsterite amounts (see also Sanfilippo et al., 2015). Similar to what observed in plagioclase, this characteristic is inconsistent with formation of the olivine gabbros from the melt residual from the troctolite formation. The low abundances of incompatible trace elements in olivine from the olivine gabbros were instead interpreted to be produced by incomplete dissolution of pre-existing olivine and concomitant crystallization of clinopyroxene during a process of reactive melt migration. Anomalous concentrations of highly incompatible elements (Zr, Hf, Ti and HREE) in olivine were also observed in troctolites and olivine gabbros from other lower crustal sections of Alpine ophiolites (Rampone et al., 2016). In particular, the Erro-Tobbio (Ligurian Alps) troctolites have olivine with higher contents of Zr, Hf, Ti and HREE compared to those in the olivine gabbros, thereby leading Rampone et al. (2016) to hypothesize a magmatic evolution controlled by olivine dissolution-recrystallization.

In summary, the major element bulk rock and mineral compositions of the troctolite/olivine gabbro association from the Pineto ophiolite are inconsistent with formation by MORB melts following a fractional crystallization path. The trace elements compositions of olivine, plagioclase and clinopyroxene document that the trace element budget of these rocks was instead controlled by crystallization in an open system, where a crystal mush mostly formed by olivine and plagioclase was continuously percolated by melt interacting with the mineral matrix and crystallizing high Mg#-clinopyroxene. Hereafter, we will discuss how interactions with migrating melts led to redistribution of the trace elements among the pre-existing mineral phases.

### Origin of the trace element variability in olivine, plagioclase and clinopyroxene

Sanfilippo et al. (2014; 2015a; 2015b) proposed that the troctolite/olivine gabbro association of the Pineto ophiolite formed by a two-stage model in which a crystal mush including olivine + plagioclase + spinel ( $\pm$  clinopyroxene) experienced a protracted event of reactive melt migration. During the early phases, olivine experienced dissolution-recrystallization, thereby producing new olivine with subhedral habits and a large variability in incompatible trace element compositions (e.g., Ti, Zr and Y). As the reactive migration process proceeded, the percolating melts evolved through a process of assimilation-fractional crystallization (DePaolo, 1981), follow a liquid line of descent distinct from that expected by fractional crystallization alone. This process led to the early saturation of high-Mg# clinopyroxene at decreasing melt mass and temperature. The formation of clinopyroxene at the

expenses of the dissolved olivine enabled olivine depleted in incompatible trace elements to be physically separated from the melt, as observed in the olivine gabbros and the troctolites with large clinopyroxene oikocrysts.

The olivine reactive dissolution evolution could be associated with dissolution-recrystallization of plagioclase. Evidence for plagioclase dissolution-recrystallization was provided by chemical maps of abyssal olivine gabbros and troctolites, where resorbed cores enriched in anorthite component are locally present within plagioclase grains embedded in clinopyroxene oikocrysts (Lissenberg et al., 2013; Lissenberg and MacLeod, 2016). A process of dissolution of anorthite-rich plagioclase followed by reprecipitation of anorthite-poor plagioclase may explain the anomalously high concentrations of incompatible elements observed for plagioclase from the troctolites and the olivine gabbros.

Among the troctolite suite, sample PI16 has plagioclase and olivine with the highest amount of anorthite and forsterite component, and the highest whole-rock Mg# and Ni values. In addition, troctolite PI16 lacks clinopyroxene, orthopyroxene, amphibole and Fe-Ti-oxide phases, and has the lowest concentrations of incompatible trace elements (e.g., LREE). We assume this sample as the one that crystallized from the most primitive melt or, under a melt-rock reaction perspective, the least reacted with the migrating melts. However, plagioclase from this sample has relatively high concentrations of incompatible trace elements and no pronounced positive Eu anomaly. Similarly, olivine from troctolite PI16 is relatively rich in incompatible trace elements compared to olivine from the olivine gabbros.

A crystal-mush with a composition similar to troctolite PI16 could be percolated by a melt dissolving olivine and plagioclase and crystallizing the same phases ( $\pm$  clinopyroxene) with slightly lower amounts of forsterite and anorthite component. This process produces a variation in the incompatible element ratios of the crystallizing phases (Coogan et al., 2000; Gao et al., 2007; Lissenberg et al., 2013; Sanfilippo et al., 2014). This process leads to a sharp increase of the highly incompatible elements (Zr, Ti, LREE) compared to moderately incompatible elements (Y, HREE), thereby explaining the Zr/REE fractionation typically observed in clinopyroxene core-rim traverses (see also Coogan, 2007; Lissenberg and MacLeod, 2016). At high mass assimilated/mass crystallized ratio, this process may lead to a gradual decrease in moderately incompatible trace elements, such as Y, thereby forming melts gradually depleted in these elements as the melt mass decreases (see also Sanfilippo et al., 2014). This process may explain why Y contents in plagioclase from the troctolites and the olivine gabbros decreases with decreasing anorthite component, whereas highly incompatible elements such as La and Ce remain nearly constant.

In summary, we propose a reactive scenario where a crystal mush formed by olivine and plagioclase is locally resorbed by percolating melts, which re-crystallize olivine and plagioclase at lower Fo and An contents. This process formed minerals retaining no textural evidence of dissolution processes, but with the composition gradually shifted toward that of the migrating magma (e.g., Kvassnes and Grove, 2008; Lissenberg and MacLeod, 2016). The interacting melt followed a liquid line of descent different to that typically inferred for fractional crystallization processes, favouring the formation of high-Mg# clinopyroxene. Our data therefore sustain the idea that the lithological transition from troctolites to Ol-gabbros in the Pineto gabbroic sequence was controlled by magmatic evolution in an open system.

### Role of reactive migration process on the bulk-rock incompatible trace element compositions

Fig. 10 depicts a mass balance calculation aimed at quantifying the role of each mineral phase into the incompatible trace element budget of the different rock types. To avoid any uncertainty related to analytical precision (e.g., some of the measures carried out for olivine and plagioclase show concentrations close to detection limits), we considered Y to represent the incompatible trace elements. Note that the high temperature estimates resulting from REE partitioning between plagioclase and clinopyroxene (Fig. 8) allow us to exclude that subsolidus diffusion considerably changed the original Y distribution of magmatic origin. The calculation considers the modal compositions, computed on the basis of major element compositions of whole-rocks and minerals (Sanfilippo and Tribuzio, 2013a), and the trace element mineral compositions reported in this and previous studies (Sanfilippo et al., 2014; 2015a; 2015b).

The calculation documents that clinopyroxene has the main control on the Y budget of these rocks. However, the different rock types display considerable differences in the Y partitioning. In the troctolites and the olivine-rich troctolites, clinopyroxene incorporates 75-85% of the whole-rock Y budget, whereas in the olivine gabbros Y is almost entirely incorporated into clinopyroxene (more than 95%). Olivine and plagioclase respectively include 0.6-12% and 10-20% of the whole-rock Y budget in the troctolites and the olivine-rich troctolites, whereas they contribute only to a minor extent in the olivine gabbros (< 0.3% for olivine and 2-4% for plagioclase). Note that the weighted sum of the Y contents of the different phases is often lower than the whole-rock Y compositions. This can be related to: (i) the role of interstitial accessory phases (such as amphibole), and/or (ii) to the trace element zoning of clinopyroxene (e.g., rims typically Y-enriched with respect to the cores), as documented in MOR-type olivine gabbros worldwide (e.g., Tribuzio et al., 1999). The difference between calculated and observed whole-rock values reaches 50% in the olivine gabbros.

The mass balance calculations therefore document that the distribution of incompatible trace elements among olivine, plagioclase and clinopyroxene varies in conjunction with the rock-type. In particular, the role of clinopyroxene as Y repository is more important in the olivine gabbros than in the troctolites and the olivine-rich troctolites. This observation is consistent with the fact that plagioclase and olivine from the olivine gabbros have lower concentrations of incompatible trace elements than expected if the magmatic evolution was ruled by fractional crystallization (see previous section). We conclude that reactive melt migration redistributed the incompatible trace elements in this section of lower oceanic crust.

## CONCLUSIONS

This study underlines the importance of a complete characterization of gabbroic samples to understand their geochemical evolution. Based on major element bulk rock and mineral compositions, we conclude that the troctolite/olivine gabbro association from the Pineto ophiolite formed as cumulates by crystallization of MORB-type melts. These melts evolved in shallow magma chambers following the typical low-pressure crystal line of descent of abyssal gabbros exposed at modern slow-spreading ridge. However, the trace element compositions of olivine, plagioclase and clinopyroxene document that the trace element budget of these rocks was controlled by crystallization in an open system. Interaction between the pre-existing crystal matrix and migrating melts led to substantial modifications in the incompatible element signature, causing deviation from trends expected during fractional crystallization. Reactive melt migration controlled the whole-rock budget of the different rock types and produced variations unexpected based on fractional crystallization alone. In particular, independently on the overall bulk composition of the rock, the relative amount of incompatible trace elements incorporated in olivine, plagioclase and clinopyroxene varies significantly with the rock type, showing a preferential uptake of trace elements in clinopyroxene in the olivine gabbros compared to the troctolites. This indicates that reactive melt migration redistributes the incompatible trace elements throughout the lower oceanic crust.

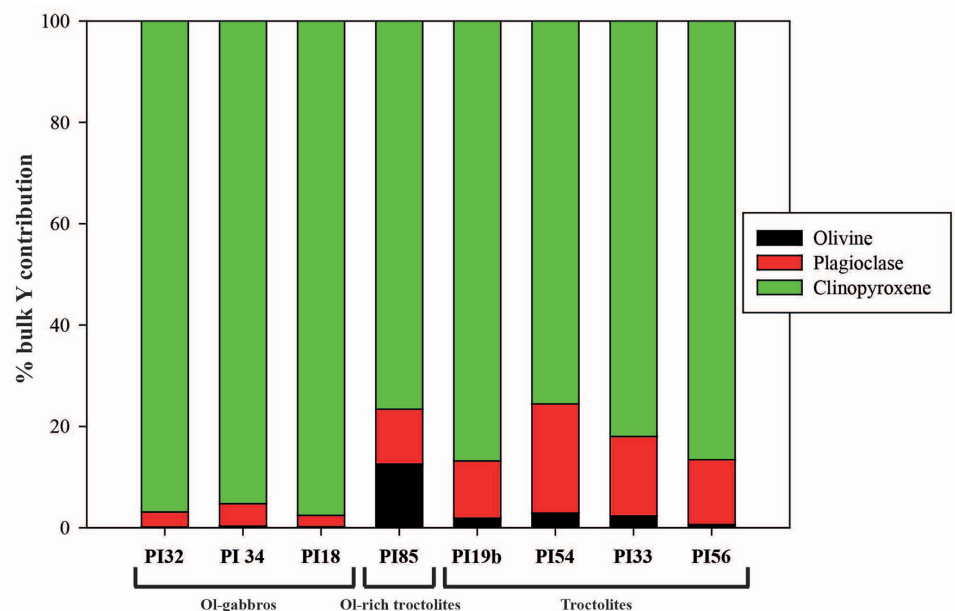


Fig. 10 - Mass balance calculation showing the Y distribution among olivine, plagioclase and clinopyroxene for selected samples.

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