ROLE OF MELTING PROCESS AND MELT-ROCK REACTION IN THE FORMATION OF JURASSIC MORB-TYPE BASALTS (ALPINE OPHIOLITES)

4

Maria Rosaria Renna^a, Riccardo Tribuzio^{b,c}, Alessio Sanfilippo^{b,c}, Matthew Thirlwall^d

- 7
- ^a Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra,
- 9 Università di Messina, Viale F. Stagno D'Alcontres 31, 98166 Messina, Italy
- ^b Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, Via Ferrata 1, 27100
 Pavia, Italy
- ^c C.N.R. Istituto di Geoscienze e Georisorse, U. O. di Pavia, Via Ferrata 1, 27100 Pavia, Italy
- ^d Department of Earth Sciences, Royal Holloway University of London, Egham TW20 0EX, UK
- 14
- 15 Corresponding author:
- 16 Maria Rosaria Renna
- 17 e-mail: <u>mrenna@unime.it</u>
- 18
- 19

20 Abstract

21 This study reports a geochemical investigation of two thick basalt sequences, exposed in the Bracco-Levanto ophiolite (northern Apennine, Italy) and in the Balagne ophiolite (central-northern 22 23 Corsica, France). These ophiolites are considered to represent an oceanward and a continent-near 24 paleogeographic domain of the Jurassic Liguria-Piedmont basin. Trace elements and Nd isotopic 25 compositions were examined to obtain information about: (i) mantle source and melting process, 26 and (ii) melt-rock reactions during basalt ascent. Whole-rock analyses revealed that the Balagne 27 basalts are slightly enriched in LREE. Nb and Ta with respect to the Bracco-Levanto counterparts. 28 These variations are paralleled by clinopyroxene chemistry. In particular, clinopyroxene from the 29 Balagne basalts has higher Ce_N/Sm_N (0.4-0.3 vs. 0.2) and Zr_N/Y_N (0.9-0.6 vs. 0.4-0.3) than that 30 from the Bracco-Levanto basalts. The basalts from the two ophiolites have homogeneous initial Nd isotopic compositions (initial ε_{Nd} from +8.8 to + 8.6), within typical depleted mantle values, thereby 31 32 excluding an origin from a lithospheric mantle source. These data also reject the involvement of 33 contaminant crustal material, as associated continent-derived clastic sediments and radiolarian cherts have a highly radiogenic Nd isotopic fingerprint (ε_{Nd} at the time of basalt formation = -5.5 34 35 and -5.2, respectively). We propose that the Bracco-Levanto and the Balagne basalts formed by partial melts of a depleted mantle source, likely containing a garnet-bearing enriched component. 36 37 The decoupling between incompatible elements and Nd isotopic signature can be explained either by different degrees of partial melting of a similar asthenospheric source or reaction of the 38 39 ascending melts with a lower crustal crystal mush. Both hypotheses are reconcilable with the 40 formation of these two basalt sequences in different domains of a nascent oceanic basin.

42 Introduction

43 The chemistry of mid-ocean ridge basalts (MORBs) is conventionally used for obtaining information about composition, temperature and pressure of mantle sources as well as the processes 44 of melting and differentiation that occur between melt generation at depth and eruption on the sea 45 46 floor. Analysis of basalts within individual ridge segments and/or ocean basin has revealed 47 significant heterogeneity, in terms of major, trace element and radiogenic isotope geochemistry (e.g., Hémond et al. 2006; Stracke et al. 2005; Standish et al. 2008; Waters et al. 2011; O'Neill and 48 49 Jenner 2012; Wilson et al. 2013). This chemical heterogeneity was mainly attributed to: (1) 50 compositional variations in the mantle source (le Roux et al. 2002; Meyzen et al. 2003), (2) 51 different degree and depth of melting reflecting variations in temperature and pressure of mantle 52 (Klein and Langmuir 1987), (3) different mechanisms of melt aggregation, mixing and fractional 53 crystallization during ascent (Grove et al. 1993), (4) processes of interaction of ascending melts with surrounding rocks within the mantle (e.g., Kelemen et al. 1995; Collier and Kelemen 2010; 54 55 Paquet et al. 2016) and/or the crust (e.g., Lissenberg et al. 2013), (5) variation of spreading rate (Regelous et al. 2016). 56

57 The Jurassic Alpine ophiolites (Fig. 1a) are considered the lithospheric remnants of the Liguria-58 Piedmont basin (e.g., Vissers et al. 2013). They comprise remnants of oceanic crust associated with 59 continental lithospheric material (e.g., Manatschal and Muntener 2009), and "slow spreading ridge type" lithosphere (e.g., Lagabrielle and Cannat 1990; Sanfilippo and Tribuzio 2011), which were 60 61 inferred to represent marginal and oceanward domains of the basin, respectively. The ophiolitic bodies exposed along Western Alps, Alpine Corsica and Northern Apennine are characterized by a 62 63 substrate of serpentinized mantle rocks and gabbroic intrusions discontinuously overlain by basalts, 64 which locally form thick lava sequences typically associated with Middle-Upper Jurassic sediments, 65 mainly polymict breccias and radiolarian cherts (e.g., Principi et al. 2004).

Previous geochemical investigations showed that the incompatible trace element signatures of 66 67 Jurassic basalts overall range from normal to transitional MORB-like affinity (Venturelli et al. 1981; Vannucci et al. 1993; Rampone et al. 1998; Desmurs et al. 2002). This chemical 68 69 heterogeneity was interpreted to reflect (i) different degrees of fractional melting of an 70 asthenospheric MORB-type source (Vannucci et al. 1993; Rampone et al. 1998) or (ii) two distinct 71 sources, namely a depleted asthenospheric mantle source for the normal-MORB and an 'enriched' 72 mantle for the transitional-MORB (Desmurs et al. 2002). More recently, the HREE-depleted 73 patterns showed by basalts from External Ligurian (Northern Apennine, Italy) and Alpine Corsica 74 ophiolites, and exemplified by relatively elevated Sm/Yb ratios, were interpreted to reflect an origin 75 by a heterogeneous mantle source containing a garnet-bearing enriched component (Montanini et al. 76 2008; Saccani et al. 2008).

77 The present work reports data on two thick basalt sequences exposed in the Balagne ophiolite 78 (central-northern Corsica, France) and Bracco-Levanto ophiolite (Northern Apennine, eastern 79 Liguria, Italy). The Balagne basalt sequence locally includes layers of quartzo-feldspathic clastic 80 sediments, thereby documenting that the Balagne ophiolite was originally adjacent to a continental 81 margin (Durand-Delga et al. 1997, Marroni and Pandolfi 2007; Renna et al. 2017). On the basis of 82 incompatible trace element compositions, the Balagne basalts were proposed to have transitional-83 MORB affinity (e.g., Venturelli et al. 1981), which was attributed to either crustal contamination 84 (Durand-Delga et al. 1997) or a contribution from a lithospheric mantle source (Saccani et al. 2008). 85 The Bracco-Levanto ophiolite does not include continental material and is considered to be formed 86 in an oceanward domain of the Jurassic basin (e.g., Tribuzio et al. 2016). Previous geochemical 87 studies of basalts collected at the top of the Bracco-Levanto ophiolite showed that they have a 88 MORB-type elemental and isotopic signature (Rampone et al. 1998; Barry et al. 2016).

In the present study, whole-rock and clinopyroxene major and trace element analyses, coupled with Nd isotope whole-rock determinations were examined to obtain information about the mantle source materials and to shed light about the processes responsible for the formation of basalts with 92 heterogeneous incompatible elements signatures. We will present evidence for an origin of the 93 basalts from a depleted mantle source. We discuss two different petrogenetic scenarios where 94 different degrees of partial melting and/or reaction within the lower oceanic crust produced basalts 95 characterized by similar Nd isotope compositions but slightly different incompatible element 96 signatures.

97 Geological framework

98 **Balagne ophiolite**

99 The Balagne ophiolite is located at the top of Alpine Corsica stack and is unaffected by the 100 high pressure/low temperature metamorphism typical of tectonic units from the Schistes Lustrés 101 units (e.g., Molli and Malavieille 2011). The ophiolite (Fig. 1) is mainly made up of pillow basalts 102 locally interlayered with levels of massive basalts previously interpreted as dolerite layers (Baud 103 1975; Gruppo di Lavoro sulle Ofioliti Mediterranee 1977; Durand-Delga 1984). The massive 104 basalts layers are up to 10 metres thick and typically occur in the upper sector of the basalt 105 sequence. Each layer shows grain size decrease from the center to the margins of the layer. In 106 addition, the contact between the different layers is characterized by the occurrence of vesicles 107 typically filled with calcite. Fine-grained pelagic sediments are also locally intercalated between 108 each basalt layer. The pillow basalts are primarily associated with: (i) polymict breccias containing 109 gabbro and basalt clasts, which mostly occur at the stratigraphic base of the ophiolite, and (ii) 110 guartzo-feldspathic clastic sediments mostly derived from Permian continental material (Durand-111 Delga et al. 2001; Rossi et al. 2002; Marroni and Pandolfi 2003; Renna et al. 2017). The pelagic 112 sediments capping the basalts are Middle-Upper Jurassic radiolarian cherts grading upward into 113 Cretaceous Calpionella limestones and Palombini shales (Chiari et al. 2000; Bill et al. 2001; 114 Peybernés et al. 2001; Danelian et al. 2008). The Calpionella limestones are locally overlain by a 115 sequence of massive calcarenite-breccia, which contains fragments of volcano-clastic material, 116 granites and metamorphic rocks interpreted to derive from the Corsica batholith (Durand-Delga et al. 1997). The thickness of the entire succession was estimated to be ~500 m (Marroni and Pandolfi
2003).

119 The Balagne ophiolite also includes a ~100 m thick tectonic slice composed of an intrusive 120 sequence (gabbronorites, oxide-rich gabbros and albitites) topped by basalts (Fig. 1). U-Pb zircon 121 geochronology dated the formation of this intrusive sequence at 159 ± 3 Ma (Renna et al. 2017), 122 which is contemporaneous with the formation of the ophiolitic gabbros from the adjacent Schistes Lustrés units (Li et al. 2015). A slightly older U-Pb zircon age of 169 ± 3 Ma was obtained for a 123 124 leucocratic felsic dyke crosscutting an oxide-rich gabbro clast in the polymict breccias (Rossi et al. 125 2002). It is worth noting that the U-Pb zircon ages of 159 ± 3 Ma and of 169 ± 3 Ma are associated 126 with a relatively high MSWD (6.3, n = 18 and 8.4, n = 11, respectively), thereby suggesting that 127 further geochronological investigations are needed to assess a precise and accurate age of the lower 128 crust formation for the Balagne ophiolite (see further discussion in Renna et al. 2017). For the scope 129 of this study, we will consider an average age of 164 Ma for the basalts sampled in the Balagne ophiolite. 130

131 Bracco-Levanto ophiolite

132 The Bracco Levanto ophiolite consists of a basement made up of gabbros intruding depleted 133 mantle peridotites, and a heterogeneous basalt-sedimentary sequence (Cortesogno et al. 1987; 134 Principi et al. 2004). The mantle sequences are formed by spinel to plagioclase harzburgites to 135 clinopyroxene-rich lherzolite, locally including replacive, dunite bodies (Sanfilippo et al. 2014). 136 The stratigraphic top of the mantle sequences is characterized by faulted serpentinites rich in 137 calcite-veins and hematite, which developed in conjunction with seafloor exposure (Treves and 138 Harper 1994; Schwarzenbach et al. 2012). The gabbroic sequences formed at 162-161 Ma (Tribuzio 139 et al. 2016) and mainly consist of olivine gabbro to clinopyroxene-rich gabbro with a MOR-type 140 geochemical signature (Rampone et al. 1998; Sanfilippo and Tribuzio 2011). They include olivine-141 rich troctolite bodies and mantle peridotite slivers at different stratigraphic levels (Renna and Tribuzio 2011; Renna et al. 2016). The gabbroic bodies include granulite facies ductile shear zones
that are locally crosscut at a high angle by hornblende veins documenting migration of seawaterderived fluids (Tribuzio et al. 1995; 2014).

The basalt-sedimentary sequence typically shows interlayering among basalts, polymict 145 146 breccias and Middle to Upper Jurassic radiolarian cherts (Abbate et al. 1980). The thickness of the 147 basalt-sedimentary sequence is however in places reduced to a few meters or even absent, with the 148 gabbro-peridotite basement directly overlain by Cretaceous shaly pelagites (Cortesogno et al. 1987). 149 The rocks considered in the present study were collected in the Bonassola area, where a thick 150 basalt-sedimentary sequence is exposed (Fig. 1, see also Principi et al. 2004). The basalt-151 sedimentary succession here shows at the base a thin level of serpentinitic breccia, which 152 unconformably overlies the faulted serpentinite basement and is locally associated with Middle 153 Jurassic radiolarian cherts (Chiari et al. 2000). The serpentinitic breccia is covered by a layer (up to 154 400 m thick) mainly consisting of massive basalts layers, which show grain size decrease from the 155 center to the margins of the layer and are interlayered with up to m-scale thick levels made up of 156 basalt breccias and radiolarian cherts. The basalt-sedimentary layer is covered by a polymict breccia 157 containing clasts of gabbros, basalts and serpentinites. In the more western sector, this polymict 158 breccia is overlain by conspicuous pillow lava (up to 200 m thick), in turn capped by pelagic 159 deposits represented by radiolarian cherts grading upward to Cretaceous Palombini shales.

160 Selected samples

We selected eight samples from the massive basalt layers, in particular four samples from Balagne (N1, N10, N21, RF2) and four from Bracco-Levanto (ROS12, ROS10, ROS6, ROS9) ophiolites. They were collected in the medium-grained centers of the layers and at different stratigraphic positions, from the top to the bottom of the main basalt-sedimentary succession (Fig. 1, Table 1). The selected samples display sub-ophitic texture (Fig. 2a). They mostly consist of euhedral to subhedral plagioclase (60-50 vol%) and subhedral to anhedral clinopyroxene (45-30

vol%). The latter has concentric or patchy optical zoning, with pale brown cores and brown rims. 167 All samples contain accessory to minor amount of skeletal Fe-Ti oxides (up to 5 vol%) and 168 169 accessory acicular apatite, which is commonly hosted by plagioclase and clinopyroxene. Two 170 samples (ROS6 and ROS10) from the Bracco-Levanto succession contain minor amounts of 171 anhedral quartz (5 vol%) generally associated with/or rimmed by chlorite (Fig. 2b). The quartz-172 chlorite association commonly hosts prismatic to acicular apatite and locally includes epidote ± Fe-Ti oxides \pm actinolite. In all samples, plagioclase is replaced by fine-grained aggregates of albite \pm 173 174 epidote \pm chlorite and clinopyroxene by chlorite \pm actinolite, Fe-Ti oxides is locally rimmed by 175 leucoxene.

176 Within the Balagne basalt-sedimentary succession, we also considered a sample of quartzo-177 feldspathic breccia (PC11) and a sample of carbonate-rich quartzitic sandstone (PP1) from two 178 levels of quartzo-feldspathic clastic sediments (Fig. 1). These samples were described by Renna et 179 al. (2017). Sample PC11 consists of a microcrystalline siliceous matrix including (i) medium to 180 coarse-grained clasts of locally prismatic feldspars, (ii) quartz mainly with engulfed shape or as 181 irregular grains locally partially recrystallized to fine-grained aggregates, (iii) rare fine-grained dark 182 mica replaced by fine-grained aggregates of chlorite + white mica + titanite. Quartzitic sandstone 183 PP1 is made up of a calcite-rich microcrystalline matrix including fine-grained clasts of (i) quartz as 184 engulfed single crystal or polygonal aggregates, (ii) feldspars and (iii) calcite as irregular grains or 185 shell fragments of crinoids and foraminifera (see also Rossi et al. 2001).

186 Two samples (ROS22 and ROS25) of radiolarian cherts from a meter-scale thick layer included 187 within the massive basalt succession of Bracco-Levanto were also selected (Fig. 1). The samples are 188 fine-grained and dark red in color and mainly consist of quartz, minor chlorite and accessory 189 hematite. Radiolarians constitute 10 vol% and 40 vol% of sample ROS22 and ROS25, respectively. 190 Sample ROS25 also contains accessory amounts of calcic amphibole.

191 Analytical technique

192 Whole rock major and trace element analyses of the selected samples (Table 2) were carried out at Activation Laboratories LTD (Ancaster, Ontario) by inductively coupled plasma (ICP) optical 193 194 emission spectroscopy and ICP mass spectrometry (method 4Lithores - Lithium 195 Metaborate/Tetraborate Fusion - ICP and ICP/MS). Three blanks and five controls (three before 196 sample group and two after) were analyzed per group of samples. Detection limits and values for 197 standard material during the analyses are compiled in a table uploaded as supplementary material. 198 Precision and accuracy of trace element analyses are assessed to be within 10%.

199 Whole rock Nd isotopic ratios and Sm-Nd concentrations of selected samples (Table 3) were 200 determined at the Department of Geology, Royal Holloway, University of London on a multi-201 collector VG354 mass spectrometer using multidynamic techniques procedures and normalization 202 described in Thirlwall (1991a,b). All errors are 2SE and relate to the last significant digits. The whole rock powders were leached for 1 h in hot 6 M HCl. Nd were separated for isotope analyses 203 using conventional ion exchange technique after dissolution in Savillex beakers. The ¹⁴³Nd/¹⁴⁴Nd 204 205 value of Aldrich laboratory standard on the day of analyses was 0.511404 (2SD = 0.000004, n = 5), within error of the long-term Aldrich laboratory mean of 0.511405 (2SD = 0.000006, n = 117). 206 Daily variations in 143 Nd/ 144 Nd ratios were normalized to 143 Nd/ 144 Nd = 0.511409. Mass bias 207 corrections were made using ${}^{146}Nd/{}^{144}Nd = 0.7219$. 208

The pale brown cores of clinopyroxene were analysed for major and trace element concentrations. Major element analyses (Table 4) were carried out at the Dipartimento di Scienze della Terra, Università di Milano with a JEOL 8200 Super Probe, in wavelength-dispersive mode. Operating conditions were 15 kV accelerating voltage, 15 nA beam current and a counting time of 30 s on the peaks and 10 s on the backgrounds. Natural silicates were used as standards.

Trace element analyses of clinopyroxene cores were carried out using laser ablation inductively coupled plasma spectrometry at C.N.R. – Istituto di Geoscienze e Georisorse of Pavia (Table 5). 216 The laser probe consisted of a Q-switched Nd:YAG laser, model Quantel (Brilliant), whose fundamental emission in the near-IR region (1064 nm) was converted into 213 nm wavelength 217 218 using three harmonic generators (Jeffries et al. 1998). Spot diameter was typically 40 µm. The 219 ablated material was analyzed by using an Elan DRC-e quadrupole mass spectrometer. Helium was 220 utilized as carrier gas and mixed with Ar downstream of the ablation cell. NIST SRM 610 was 221 utilized as external standard. The CaO content determined by electron microprobe was used as internal standard, scaled on the 44Ca+ signal. Precision and accuracy were assessed from repeated 222 223 analyses of the BCR2-g standard and resulted usually better than 10% at ppm concentration level. 224 Detection limits were typically in the range of 1.0-0.5 ppm for Cr and Ti, 0.5-0.1 ppm for Sc, 100-225 10 ppb for Sr, Zr, Ba, Rb, V and Gd, 10–1 ppb for Y, Nb, REE, Hf and Ta.

226 Whole-rock geochemistry

227 Basalts

The selected samples from the massive layers of the Balagne and Bracco-Levanto ophiolites fall in the trachybasalt and in the basalt field, respectively, of the total alkali versus silica diagram (TAS, Le Maitre 1989). They will be hereafter referred to as basalts.

231 Balagne basalts have Mg# [molar MgO/(MgO+FeO_t) \times 100] and Al₂O₃ contents varying from 232 63.3 to 36.6 and from 16.4 to 13.4 wt%, and relatively high TiO₂ contents (3.2-1.5 wt%). The Mg#, 233 Al₂O₃ and TiO₂ values of selected Bracco-Levanto basalts largely overlap those of Balagne basalts 234 (64.5 - 44.5, 17.3 - 12.8 wt% and 2.9 - 1.1 wt%). Both Balagne and Bracco-Levanto basalts show 235 TiO₂ increase with decreasing Mg# (Fig. 3). Balagne basalts have slightly lower CaO than Bracco-236 Levanto basalts (7.1 - 6.4 wt% vs. 9.5 - 8.9 wt%). The concentrations of Cr and Ni are relatively 237 low (up to 130 ppm and up to 100 ppm, for Balagne basalts, up to 220 ppm and up to 150 ppm for 238 Bracco-Levanto basalts). Balagne and Bracco-Levanto basalts show similar ranges of V contents 239 (351 – 184 ppm and 375 – 138 ppm), which are inversely correlated with Mg# (Table 2). The basalts LOI values range from 5.8 to 2.4, and most likely reflect the moderately altered nature ofthese rocks.

242 The chondrite (Anders and Ebihara 1982) normalized REE patterns (Fig. 4a) of the Balagne 243 basalts are characterized by HREE depletion relative to MREE ($Gd_N/Yb_N = 1.3-1.2$) and moderate LREE enrichment ($Ce_N/Sm_N = 1.2-1.0$). Bracco-Levanto basalts have HREE patterns nearly parallel 244 245 to those of Balagne basalts, but show slight LREE depletion relative to MREE ($Ce_N/Sm_N = 0.8-0.7$). The negative Eu anomaly of both Balagne and Bracco-Levanto basalts is slight to absent and 246 247 increases with total REE contents (Table 2). The incompatible trace element patterns normalized to 248 chondrite of Balagne basalts display slight enrichment of Zr and Hf relative to REE, Y and Ti, and 249 Nb and Ta depletion with respect to LREE (Fig. 5). Sr overall varies from enriched to depleted relative to adjacent REE, thereby suggesting that Sr concentrations were affected by low 250 251 temperature alteration. Bracco-Levanto basalts mainly differ in showing a slightly more marked 252 depletion of Nb and Ta relative to LREE. For both Balagne and Bracco-Levanto basalts, the highest 253 concentrations of incompatible trace elements pertain to sample showing the lowest Mg# (i.e. 254 sample N10 and ROS6).

We calculated initial ε_{Nd} values of Balagne basalts at 164 Ma, which is the average age proposed for the lower crust of Balagne ophiolite (see section 2). The ε_{Nd} values fall within a restricted range (from +8.8 to +8.6, Table 3, Fig. 6). Bracco-Levanto basalts have homogeneous Nd isotopic compositions with initial ε_{Nd} values calculated at 161 Ma (from +8.8 to +8.6) falling within the same range of Balagne basalts. The ε_{Nd} values yielded by Bracco-Levanto basalts are similar to those obtained by Rampone et al. (1998) and Barry et al. (2017) for basalts from the top of the same basalt-sedimentary succession (+9.1 to +8.6).

262 Sedimentary rocks

263 The quartzo-feldspathic sediments from the Balagne ophiolite are arkoses. SiO_2 and Al_2O_3 264 contents range from 71 to 55 wt% and from 14 to 5.0 wt%. The contents of Fe₂O₃, MgO and MnO are generally low (2.9-1.0 wt%, 1.0-0.7 wt% and ~0.2 wt%). The samples have nearly parallel REE patterns resembling that of NASC (North American Shale 357 Composite, Gromet et al. 1984) and are characterized by a marked LREE enrichment and a slight HREE depletion relative to MREE, and a significant negative Eu anomaly (Fig. 4b). The selected sample of quartzo-feldspathic sediment has enriched Nd isotopic compositions with ε_{Nd} at 164 Ma of -5.5 (Table 3).

270 The radiolarian cherts have relatively high contents of SiO₂ (~75 wt%), Al₂O₃ (~4.6 wt%), Fe₂O₃ 271 (~9.8 wt%), MgO (~4.7 wt%), CaO (~1.0 wt%) and low of TiO₂ (~0.2 wt%). The concentrations of MnO, V, Cr, Ni, Co and Sc (~0.3 wt%, ~98 ppm, ~345 ppm, ~303 ppm, ~56 ppm and ~8.0 ppm) 272 273 are relatively high, which could reflect a significant input from hydrothermal deep-sea sediments 274 constituents. In the chondrite-normalized REE diagram the samples show a steady decrease from 275 LREE to HREE, slight Ce depletion relative to La and Pr and moderate negative Eu anomaly (Fig. 276 4b). The ε_{Nd} of the selected radiolarian chert at the time of the Bracco-Levanto lower crust formation (161 Ma) is -5.2 (Table 3). This value nearly falls within the range of initial ε_{Nd} (-5.3 to -277 278 9.1, Stille et al. 1989) found for the cherts from the Platta ophiolitic unit (eastern central Alps).

279 Clinopyroxene major and trace element chemistry

The Mg# (Table 4) of clinopyroxene from the Balagne and Bracco-Levanto basalts mainly ranges from 78 to 63 and from 82 to 66 (Fig. 7). The concentrations of TiO₂ (2.3–1.2 wt% and 1.3– 0.7 wt%) are directly correlated with Al₂O₃ (4.3-2.0 wt% and 3.9-1.6 wt%) and Na₂O (0.7-0.4 wt% and 0.6-0.3). Clinopyroxene from Balagne basalts has overall higher TiO₂ and Na₂O than that from Bracco-Levanto basalts. MnO contents of clinopyroxene from Balagne and Bracco-Levanto basalts are overlapping and overall range from 0.4 to 0.1 wt%, in particular, clinopyroxene with the lowest Mg# has the highest MnO contents (Table 4).

Clinopyroxene from the Balagne basalts has a chondrite-normalized (Anders and Ebihara 1982) REE pattern (Fig. 8) characterized by LREE depletion relative to MREE ($Ce_N/Sm_N = 0.4-0.3$ for Sm_N = 63-27), negative Eu anomaly (Eu/Eu* 0.8-0.7), and slight depletion of HREE relative to MREE ($Gd_N/Yb_N = 1.5$ to 1.4 for $Yb_N = 44-21$). Normalization to chondrite abundances shows that clinopyroxene has Nb, Ta, Sr, Zr, Hf and Ti depletion relative to adjacent REE (Fig. 9). With respect to clinopyroxene from Balagne, that from Bracco-Levanto is slightly depleted in LREE, MREE, Nb-Ta, Sr, Zr-Hf. Within both ophiolitic successions, clinopyroxene with the lowest Mg# is also characterized by the highest incompatible trace element contents and the most pronounced negative Eu and Sr anomalies.

296 **Discussion**

297 Asthenospheric source and basalt evolution

The Balagne (central-northern Corsica) and Bracco-Levanto (Northern Apennine, eastern Liguria) ophiolites represent a continent-near and an oceanward paleogeographic domain of the Jurassic Liguria-Piedmont ophiolitic basin. They preserve a primary Jurassic association of pillow lavas and massive basalt layers with Middle-Upper Jurassic sediments, mainly constituted by polymict breccias and radiolarian cherts (e.g., Marroni and Pandolfi 2007). In the Balagne ophiolite, in addition, the basalts include levels made up of quartzo-feldspathic clastic sediments derived from Permian continental material (see also Renna et al. 2017).

305 The Bracco-Levanto basalts locally contain quartz in association with chlorite (Table 1; Fig. 2b). 306 The development of chlorite-quartz assemblage was documented in hydrothermally altered oceanic 307 basalts (e.g., Alt et al. 1986, 1996; Gillis and Thompson 1993) and experimentally reproduced by 308 basalt-seawater interaction (Mottl 1983). The guartz-chlorite associations from the Bracco-Levanto 309 basalts are most likely pseudomorphic after primary clinopyroxene + plagioclase assemblage and 310 produced by interaction with seawater-derived fluids under greenschist facies conditions. Note that 311 clinopyroxene analyses from both Bracco-Levanto and Balagne basalts are consistent. Whole-rock 312 and clinopyroxene trace element compositions, for instance, consistently reveal that the Balagne 313 basalts are slightly enriched in LREE relative to the Ligurian counterparts (Figs. 4 and 8). This

314 indicates that the immobile trace elements and isotope whole rock signatures of basalts were not 315 modified by low temperature hydrothermal alteration processes.

The Balagne basalts are slightly enriched in LREE, Nb, Ta, Zr and Hf with respect to typical 316 317 normal-MORB compositions (Figs. 4 and 5; see also Venturelli et al. 1979), and show affinity to 318 transitional-MORB. The REE patterns of the Bracco-Levanto basalts mostly parallel those typical 319 of normal-MORB (Fig. 4). The basalts from the two ophiolitic successions have homogeneous Nd 320 isotopic compositions with initial ε_{Nd} falling within typical depleted mantle (DM) values and 321 averaging $\sim +8.7$ for both successions. A typical DM-like isotopic signature is also confirmed by the 322 initial ε_{Hf} of +13.6 found for a basalt sample from the top of the Bracco-Levanto succession (Barry 323 et al. 2017). Furthermore, Balagne and Bracco-Levanto basalts overall have relatively high (Sm/Yb)_{DM} values (1.5–1.8, Table 2), which suggest that the depleted mantle source was 324 325 characterized by a garnet-bearing component (see also Montanini et al. 2008; Saccani et al. 2015).

326 The homogeneous depleted Nd isotopic signature shown by basalts from both Bracco-Levanto 327 and Balagne ophiolitic successions argues against an origin by primitive melts derived from an 328 isotopically enriched lithospheric mantle source. We may also exclude that the parental melts of the 329 basalts experienced assimilation of sediments, as the associated quartzo-feldspathic clastic 330 sediments and radiolarian cherts are characterized by highly radiogenic Nd isotope fingerprints (ε_{Nd} 331 at the time of the basalt formation of -5.5 and -5.2, Table 3). In particular, for the Bracco-Levanto 332 sequence, by assuming +8.7 as the initial ε_{Nd} of the parental mantle-derived melt and a 5 wt% fraction of contaminant material with ε_{Nd} of -5.2, which is equivalent to the modal abundance of 333 quartz in the basalts (Table 1), a ε_{Nd} of +8.0 for the contaminated basalt melt was estimated. This 334 335 estimate contrasts with the fact that Bracco-Levanto basalts containing minor amounts of quartz 336 have initial ε_{Nd} values of +8.8 to +8.7, which are equivalent to those yielded by the quartz-free basalts (Table 3). Nd isotope data thus confirm that the local occurrence of minor quartz in the 337 Bracco-Levanto basalts was not produced by assimilation of crustal material. 338

339 Basalts from Bracco-Levanto and Balagne ophiolitic successions have relatively low Mg# (63-37 340 and 65-45), which are lower than those experimentally determined for primary normal-MORB-type melts (Mg# ~76-73, Kinzler and Grove 1992) and overlap the mean composition of mid-ocean 341 342 ridge basalts (Mg# = 59 ± 7 , White and Klein 2014). This indicates that the studied basalts were not 343 in equilibrium with presumed mantle olivine compositions (Mg# = 90; Roeder and Emslie 1970). 344 Within both successions, basalts overall show a decrease of Al₂O₃ and a slight deepening of 345 negative Eu anomaly with decreasing Mg#, thereby suggesting a process controlled by fractional 346 crystallization of clinopyroxene and plagioclase. The decrease of Mg# is also correlated with an 347 increase of TiO₂, MnO and V (Fig. 3, Table 2). In particular, the Balagne and Bracco-Levanto 348 basalts showing the lowest Mg# have TiO₂, FeO^t and FeO^t/MgO values similar to those typical of 349 ferro-basalts (le Roex et al. 1982; Harper 2003). Chemical compositions of clinopyroxene from 350 these ferro-basalts differ in having the lowest Mg# values, the highest incompatible elements 351 concentrations and the most pronounced negative Eu and Sr anomalies (Tables 4 and 5; Figs. 7 to 352 9), thereby confirming the evolved geochemical signature of these rocks.

353 On the basis of clinopyroxene/basalt partition coefficient determined under low-pressure conditions (Shi and Libourel 1991; $K_dCpx/basalt^{Fe/Mg} = 0.26$), we calculated the Mg# of the melt in 354 equilibrium with the clinopyroxene from the Balagne and Bracco-Levanto ferro-basalts 355 356 (clinopyroxene Mg# = 65 and 70). Computed Mg# of clinopyroxene equilibrium melts are 32 and 38, respectively. Assuming that the fractionation was controlled by separation of clinopyroxene + 357 358 plagioclase, and starting from a melt with the FeO and MgO composition of the least evolved basalt 359 (Table 2), calculated Mg# yield, for both successions, a degree of fractional crystallization of ~60%. This estimate is confirmed by whole-rock trace elements (La, Ce, Nd, Zr, Sm, Ti, Dy, Y, Yb) 360 361 modeling. We assumed for the Balagne and Bracco-Levanto basalts a fractional crystallization process with a fractionating assemblage of 0.6 plagioclase + 0.4 clinopyroxene and of 0.5362 363 plagioclase + 0.5 clinopyroxene, respectively, in agreement with the estimated modal compositions 364 (Table 1). We also assumed the set of clinopyroxene/melt and plagioclase/melt partition coefficients determined experimentally for a basaltic system (Tiepolo et al. 2002). The compositional range from the most primitive (Mg# = 63) to the most evolved basalt (Mg# = 37) from Balagne was reproduced with F (fraction of remaining liquid) = 0.4 (Fig. 10a). By assuming the whole-rock composition of the least evolved Bracco-Levanto basalt (Mg# = 65), incompatible element compositions of the most evolved ferro-basalt (Mg# = 45) was reproduced assuming F = 0.3 (Fig. 10b). For both ophiolitic successions, thus, the development of ferro-basalt compositions involved a process of extensive fractional crystallization.

372 Chemical variations between basalts as revealed by bulk vs. clinopyroxene chemistry

373 Clinopyroxene is, together with plagioclase, the main constituent of the basalts and is the main 374 repository for REE and other incompatible trace elements in these rocks. Clinopyroxene from 375 basalts is typically chemically zoned, showing significant core-to-rim variations characterized by an 376 increase of Ti and incompatible trace elements such as Zr, Hf, Nb, Ta, REE, Y, Th and U (Vannucci 377 et al. 1993; Renna et al. 2011). These chemical variations reflect conditions of rapid crystallization, 378 and are thought to be independent of the liquid composition (Claeson et al. 2007) and related to the 379 interplay between crystal-growth phenomena and kinetic effects (Lofgren et al. 2006; Schwandt and 380 McKay 2006). The chemistry of clinopyroxene cores is interpreted to approach the equilibrium 381 conditions and to represent primary compositions of melt giving rise to basalt.

382 In the present study, the compositions of clinopyroxene cores allowed recognition of slight but 383 significant chemical differences between basalts from the Balagne and Bracco-Levanto ophiolites. 384 Clinopyroxenes from the Balagne basalts are enriched in TiO₂ and Na₂O relative to that from the 385 Bracco-Levanto basalts (Fig. 7). Whole rock data (Table 2, Fig. 3) do not exhibit well-defined TiO₂ 386 differences between the two successions, which could reflect the influence of Ti-rich clinopyroxene 387 rims and/or Fe-Ti oxides on whole rock compositions. In addition, the bulk Na₂O contents are 388 relatively high for all basalts, which may be likely attributed to the moderate degree of alteration of 389 the samples as reflected in their fairly high L.O.I. values.

390 The most significant differences between Balagne and Bracco-Levanto basalts are the ratios 391 between highly to moderately incompatible trace elements, which remain nearly constant during a 392 differentiation controlled by fractional crystallization of clinopyroxene and plagioclase (± olivine). 393 In particular, clinopyroxene from the Balagne basalts shows higher Ce_N/Sm_N ratios than the clinopyroxene from Bracco-Levanto (0.4-0.3 vs. 0.2). Similarly, bulk data of Balagne basalts show 394 395 higher Ce_N/Sm_N than Bracco-Levanto (1.2-1.0 vs. 0.8-0.7). Whole-rock analyses of Balagne basalts 396 display higher Nb_N/Y_N and Ta_N/Y_N than Bracco-Levanto counterparts (Nb_N/Y_N = 1.4-0.8 vs. 0.7-0.4 and $Ta_N/Y_N = 1.7-0.9$ vs. 0.5-0.4). Clinopyroxene from the Balagne and Bracco-Levanto basalts 397 398 does not reveal appreciable differences of Nb_N/Y_N and Ta_N/Y_N ratios, which most likely reflects the 399 low compatibility of these elements for clinopyroxene due to crystal-chemical effects (e.g., Blundy 400 and Wood 1994, Hart and Dunn 1993).

401 Clinopyroxene from the Balagne basalts has higher Zr_N/Y_N and Hf_N/Y_N with respect to that from 402 Bracco-Levanto ($Zr_N/Y_N = 0.9-0.6$ vs. 0.4-0.3 and $Hf_N/Y_N = 1.3-0.9$ vs. 0.9-0.5). No substantial Zr-Hf differences are conversely revealed by whole-rock analyses (e.g., $Zr_N/Y_N = 2.1-1.6$ vs. 1.9-1.3). 403 404 Late crystallizing portions of clinopyroxene from oceanic basalts and lower oceanic crust generally 405 display variable enrichment of more to less incompatible elements (e.g., Zr/Y) with respect to the 406 inner, early crystallizing mineral portions (e.g., Vannucci et al. 1993; Coogan and O'Hara 2015; 407 Lissenberg et al. 2013; Sanfilippo et al. 2015a). We presume that the significant chemical zoning of 408 clinopyroxene could variably affect the whole rock Zr-Hf budget of the analyzed basalts, thereby 409 decoupling the Zr-Hf signature of clinopyroxene cores and bulk data.

In summary, significant chemical differences between Balagne and Bracco-Levanto basalts are shown by both clinopyroxene and bulk data (i.e., LREE and Nb-Ta). Clinopyroxene also enabled to identify chemical differences that are not well-defined by whole rock analyses (i.e., TiO₂, Na₂O and Zr-Hf). Chemical differences are observed for whole-rock and clinopyroxene data with similar Mg# ranges, which imply that these differences are not the result of magmatic evolution. The geochemical signature of Balagne melts was slightly enriched in most incompatible elements
(including Na₂O and TiO₂) with respect to that of the Bracco-Levanto parental melts.

417 Homogeneous vs. heterogeneous mantle sources

418 The Balagne and Bracco-Levanto basalts show different incompatible element signatures and 419 homogeneous Nd isotopic compositions (Figs. 4 to 6). Numerous geochemical studies generally 420 document highly heterogeneous isotopic and elemental compositions of oceanic basalts, thereby 421 indicating that mantle sources are chemically heterogeneous and consist of complex assemblages of 422 two or more enriched and depleted peridotite components (e.g., Hofmann 2003; Salters and Dick 423 2002; Stracke et al. 2005). The different trace element signature of the basalts from the Bracco-424 Levanto and Balagne ophiolites may be thus ascribed to melts formed by different amounts of 425 enriched and depleted lithologies in their asthenospheric mantle sources. However, this hypothesis 426 would also require a different Nd isotopic signature for the two basalt series, as the occurrence of 427 enriched sources in the asthenosphere is expected to produce melts with unradiogenic Nd isotopic 428 compositions (Stracke 2012; Wilson et al. 2013).

To explain the observed decoupling between the Balagne and Bracco-Levanto basalts, we may 429 hypothesize a process of mixing of partial melts containing different fractions of the various 430 431 components present within the source, which are both elementally and isotopically distinct. This 432 mixing process should efficiently homogenize the Nd isotopic compositions of the mantle source, 433 whereas heterogeneities in incompatible element ratios were at least partly preserved. Stracke and 434 Bourdon (2009) presented a melting model for heterogeneous mantle (pyroxenites-bearing 435 peridotite) and carried numerical experiments with the aim to investigate how and to what extent 436 isotope and trace element signatures are conveyed from source to melt. They showed that in mixed 437 partial melts differences in highly incompatible trace element ratios are more efficiently averaged 438 than their Nd isotopic compositions. The results by Stracke and Bourdon (2009) thus showed that 439 mixed partial melts, derived from different enriched and depleted mantle components, and characterized by similar Nd isotopic compositions, should also have similar incompatible trace element compositions. We thereby suggest that the different incompatible element signatures, with similar Nd isotopic compositions, shown by the two basalt sequences could not be ascribed to different proportions of enriched and depleted components in their asthenospheric mantle sources. Chemically homogeneous mantle sources therefore provide the most plausible origin for the Balagne and Bracco-Levanto basalts.

446 **Basalt petrogenesis**

447 Two major hypotheses may be formulated to explain the decoupling between incompatible 448 elements and Nd isotopic signatures. In the first, we may postulate that the Balagne and Bracco-449 Levanto primitive melts formed by different extents of melting of compositionally homogeneous, 450 asthenospheric sources. Accordingly, assuming a homogeneous mantle peridotite source, a different 451 degree of partial melting is suggested by the lower CaO/Al₂O₃ whole-rock ratios shown by Balagne 452 basalts relative to those from Bracco-Levanto (Fig. 11), which is interpreted to indicate origin by lower extent of melting (Klein and Langmuir 1987). This idea is also sustained by the higher 453 Ce_N/Sm_N , Nb_N/Y_N and Ta_N/Y_N ratios shown by the Balagne basalts over Bracco-Levanto. An origin 454 455 by lower degree of partial melting may also explain the higher TiO₂, Na₂O, Ce_N/Sm_N, Zr_N/Y_N and 456 Hf_N/Y_N exhibited by the clinopyroxene from the Balagne basalts with respect to that from Bracco-457 Levanto. Furthermore, this petrogenetic hypothesis is reconcilable with the different 458 paleogeographic domains of Balagne and Bracco-Levanto ophiolitic sequences. The Balagne 459 ophiolite is interpreted to represent a continent-near domain, and should therefore be characterized 460 by a colder thermal regime with respect to the oceanward position of the Bracco-Levanto ophiolite. The latter was most likely typified by a hotter mantle, which intersected the solidus deeper and 461 462 experienced greater extent of melting (Klein 2003) than the colder mantle of the Balagne domain, 463 thereby accounting for the different incompatible elements signatures reflecting different melting 464 degrees.

465 The second petrogenetic hypothesis implies that primitive melts originally had similar incompatible elements and Nd isotopic signatures, and that a process of interaction between 466 467 ascending mantle-derived melts and surrounding rocks was subsequently responsible for enriching 468 in highly incompatible elements the parental melts of the Balagne basalts. This process is consistent 469 with compositionally homogeneous partial melts derived by similar melting degrees of the mantle 470 source. Following the melting model by Stracke and Bourdon (2009), however, the proposed process could also be consistent with partial melts derived by enriched and depleted mantle 471 472 components, which were isotopically and elementally homogenized by mixing process. The 473 petrogenetic hypothesis of interaction between ascending mantle-derived melts and surrounding 474 rocks is suggested by the overall parallel REE and incompatible elements patterns shown by 475 clinopyroxene cores from the Bracco-Levanto basalts and the clinopyroxene cores from lower 476 crustal rocks (i.e. gabbros and olivine-rich troctolites) of the Internal Ligurian ophiolites (Figs. 8-9). 477 This interaction process is generally referred as reactive melt migration and will be discussed in the 478 next section.

479 Reactive melt migration and the formation of incompatible elements enriched basalts

In modern spreading ridges and ophiolites the process of reaction between ascending MORB-480 481 like melts and surrounding rocks has been indicated within (i) the mantle, leading to the formation 482 of impregnated plagioclase peridotite (e.g. Dick et al., 1984; Bonatti et al., 1992; Dygert et al. 2016) 483 and of replacive dunite (e.g., Dick 1977; Kelemen et al. 1995), (ii) at the mantle-crust transitions zone, leading to formation of olivine-rich troctolites (e.g., Suhr et al. 2008; Drouin et al. 2009, 484 485 2010; Renna and Tribuzio 2011; Sanfilippo et al 2013, 2015a), and within the lower oceanic crust (e.g., Bédard et al. 2000; Coogan et al. 2000; Gao et al. 2007; Lissenberg and Dick 2008; Renna et 486 487 al. 2016; Lissenberg and MacLeod 2016). The process of reactive melt migration produces reactive 488 dissolution of pre-existing mineral, modification of the composition of the migrating melt and 489 crystallization of new phases (see also Collier and Kelemen 2010; Lissenberg et al. 2013).

490 Paquet et al. (2016) have recently proposed that the composition of the erupted basalts from the 491 Southwest Indian Ridge (61°-67°E) is controlled by reaction between their parental melts and the 492 surrounding lithospheric mantle rocks (plagioclase-bearing peridotites). This interpretation was 493 explained by the similar trace element signatures found for the erupted basalts and the melts at 494 equilibrium with clinopyroxene from the associated plagioclase-bearing peridotites. The process of 495 melt impregnation of mantle peridotite under plagioclase facies conditions is documented in the 496 mantle section of the Jurassic Alpine ophiolites (e.g., Piccardo et al. 2007; Rampone et al. 2008; 497 Müntener et al. 2010; Sanfilippo and Tribuzio 2011), and it is typically attributed to infiltration of 498 orthopyroxene-saturated melts that caused partial dissolution of mantle clinopyroxene and 499 replacement by plagioclase and orthopyroxene. Note, however, that the chondrite-normalized REE 500 and incompatible trace element patterns of clinopyroxene from the plagioclase-bearing peridotites 501 of the Internal Ligurian ophiolites show marked depletion of LREE, Sr, Zr and Hf with respect to 502 clinopyroxene from the basalts (Figs. 8 and 9). In addition, plagioclase-bearing peridotites have 503 heterogeneous Nd isotopic compositions with ε_{Nd} calculated at the age of the basalt formation that 504 range from +15 to +12 (Rampone et al. 1996, 1998) and thus significantly differ from the homogeneous initial ε_{Nd} value of ~+8.7 found for the basalts. We therefore exclude that the 505 506 chemical compositions of the basalts were controlled by interaction with mantle rocks.

507 Within the lower oceanic crust, reactive processes typically occur between migrating melts and 508 gabbroic crystal mush (Coogan et al. 2000; Gao et al. 2007; Lissenberg and Dick 2008; Lissenberg 509 et al. 2013). These processes are responsible for the redistribution of incompatible elements from 510 the pre-existing cumulate phases into the interstitial melt and late crystallizing minerals (see also 511 Lissenberg and MacLeod 2016). Olivine-rich troctolites are the most primitive rocks of the lower 512 oceanic crust and their petrogenesis is generally attributed to reaction between an olivine-rich 513 matrix and a migrating MORB-like melt crystallizing mainly plagioclase and clinopyroxene. The 514 origin of the olivine-rich matrix is explained as the production of either magmatic crystallization of primitive melts injected into the growing lower crust or melt-mantle reaction at the mantle-crust 515

516 transition (cf. Sanfilippo et al. 2015a; Renna et al. 2016). Melt-rock reaction processes have been 517 suggested to explain the major and trace element compositions of olivine from troctolites and 518 olivine-gabbros in different gabbroic sections of the Liguria and Corsica ophiolites (Sanfilippo et al. 519 2014; 2015b). There is general agreement that both gabbros and olivine-rich troctolites from the 520 Liguria and Corsica ophiolites are rocks preserving melt-rock reaction signatures, acquired within 521 the lower crust or at the mantle-crust transition. Gabbro and olivine-rich troctolites of Internal Ligurian ophiolite have $\varepsilon_{Nd (161 \text{ Ma})}$ of +8.6 and +8.4 ± 0.3 (Rampone et al. 1998), which are similar 522 to the initial ε_{Nd} value of ~+8.7 found for the Bracco-Levanto basalts. The similar Nd isotopic 523 524 compositions in tandem with the similar clinopyroxene incompatible elements signatures (Figs. 8 525 and 9) shown by basalts, gabbros and olivine-rich troctolites from Internal Ligurian ophiolites 526 therefore suggest that the interaction with the lower crustal crystal mush could affect the chemical 527 composition of basalt parental melts.

528 The cores of clinopyroxenes from gabbros and olivine-rich troctolites of Jurassic Alpine 529 ophiolites display a range of Ce_N/Sm_N ratios that encompass the values of Ce_N/Sm_N shown by the 530 clinopyroxene cores from the Balagne and Bracco-Levanto basalts (Fig. 12). With respect to 531 clinopyroxene cores from gabbros and olivine-rich troctolites of Jurassic Alpine ophiolites and to 532 those from Bracco-Levanto basalts, however, the Balagne clinopyroxene cores differ in having higher Zr_N/Y_N ratios. The latter values are, in particular, comparable to those shown by the rims of 533 534 clinopyroxenes from gabbros and olivine-rich troctolites of Jurassic Alpine ophiolites. The enrichment of incompatible elements (e.g., Ti, Zr, and REE) from core to rim of clinopyroxene has 535 536 been observed in oceanic gabbros and olivine-rich troctolites and ascribed to crystallization from 537 reactive melts dissolving a pre-existing crystal assemblage (Lissenberg and Dick 2008; Coogan et 538 al. 2000; Gao et al. 2007; Coogan 2007; Lissenberg et al. 2013; Sanfilippo et al. 2015a). 539 Enrichments of incompatible elements, associated with increasing degree of fractionation between 540 incompatible elements (e.g., Zr to Y), are explained by an AFC (assimilation and concomitant 541 fractional crystallisation) process involving assimilation by the reactively migrating MORB-like

542 melt of (i) various proportion of early crystallized olivine, plagioclase and clinopyroxene for 543 oceanic gabbros, and (ii) mantle peridotites for olivine-rich troctolites. Within the context of gabbro 544 evolution, in particular, it is proposed that migrating melts become increasingly more evolved and 545 trace elements-enriched by the reactive process, thereby promoting the crystallization of trace 546 elements-enriched clinopyroxene marginal portions and leaving depleted olivine, plagioclase and 547 clinopyroxene cores.

548 Lissenberg et al. (2013) proposed a model for melt evolution in the lower oceanic crust with the 549 following sequence of events: (i) mantle-derived melts form a crystal mush of olivine, plagioclase 550 and clinopyroxene; (ii) some residual MORB-like melts may be rapidly extracted, escape melt-rock 551 reaction and may locally erupt; (iii) the remainder MORB-like melts reactively migrate within the 552 crystal mush; incompatible elements are redistributed from the cumulate minerals into the migrating 553 melts, which become increasingly enriched in most incompatible elements and result in 554 crystallization of enriched clinopyroxene rims (and other late crystallizing accessory minerals); (iv) 555 the residual, evolved and incompatible elements-enriched melt is delivered to shallow level melt 556 lens where it may mix with the unreacted MORB-like melt prior to eruption. The proposed scenario 557 result in the eruption of basalts ranging from depleted to variably enriched in most incompatible 558 elements. We speculate that a similar petrogenetic sequence of events may be envisaged to explain 559 the decoupling between incompatible elements and Nd isotopic signature of Bracco-Levanto and 560 Balagne basalts. The reactive process less efficiently modifies the ratios of Sm/Nd relative to those 561 between highly to moderately incompatible elements (e.g. Zr/Y), because Sm and Nd have a similar 562 geochemical behavior. The chemical compositions of Bracco-Levanto and Balagne basalts could be 563 thus controlled by the interaction with the lower crustal crystal mush, which had similar Nd isotopic 564 signature and therefore did not modify the Nd isotopic composition of primitive basalt melts. The 565 slight enrichment in highly incompatible elements shown by the Balagne relative to Bracco-Levanto basalts may be explained by a higher contribute, in Balagne parental basalt melts, of more evolved 566 567 and slightly more trace elements-enriched reactively migrating melts.

During the process of reactive melt migration, the reactively migrating melts become 568 569 progressively more evolved and enriched in incompatible trace elements due to the local 570 assimilation of crystal phases and synchronous crystallization at decreasing melt mass (Lissenberg 571 et al. 2013). It implies that a melt reactively migrating within a crystal mush with a relatively high 572 melt/crystal ratio has a lower enrichment in incompatible elements than a melt reactively migrating 573 within a crystal mush characterized by a lower melt/crystal ratio. We may speculate that the two different trace element signatures of the Balagne and Bracco-Levanto basalts reflected different 574 575 melt/crystal ratios of the crystal mush, namely the primitive melts giving rise to the Bracco-Levanto 576 basalts interacted with a crystal mush characterized by a higher melt/crystal ratio with respect to the 577 crystal mush that interacted with the Balagne primitive melts. These different melt/crystal ratios of 578 the crystal mush could reflect the different thermal conditions between the continent-near Balagne 579 domain and the oceanward position of Bracco-Levanto ophiolite.

580 8 Summary and concluding remarks

The Balagne (central-northern Corsica, France) and Bracco-Levanto (northern Apennine, Italy) ophiolites are respectively marginal and oceanward fragments of a Jurassic slow or ultraslow spreading basin, commonly referred as Liguria-Piedmont basin. These ophiolitic bodies expose thick basalt sequences typically associated with Middle-Upper Jurassic sediments, mainly polymict breccias and radiolarian cherts (e.g., Marroni and Pandolfi 2007). In addition, continent-derived clastic sediments are included within the Balagne basalt sequence (see also Renna et al. 2017).

The basalts from the two ophiolites have slightly different incompatible elements signatures, as consistently shown by both whole-rock and clinopyroxene compositions. Normal-MORB affinity characterizes the Bracco-Levanto basalts, whereas transitional-MORB typifies the Balagne basalts. The two basalt successions, however, have similar initial Nd isotopic compositions, plotting within typical depleted mantle values. The primitive melts giving rise to the two basalt successions formed by an asthenospheric mantle source likely containing a garnet-bearing enriched component. The 593 magmatic evolution of both basalt successions included a stage of protracted crystallization ruled by 594 separation of clinopyroxene and plagioclase, which finally led to melts with ferro-basaltic 595 compositions.

The decoupling between incompatible elements and Nd isotopic signatures could reflect different degrees of partial melting from similar mantle sources. Alternatively, the decoupled incompatible trace elements and Nd isotope compositions were acquired by a process of reactive melt migration within a lower crustal crystal mush. Both hypotheses are reconcilable with the interpretation that the Balagne and Bracco-Levanto basaltic sequences formed in continent-near and oceanward domains of a nascent oceanic basin.

602

603 Acknowledgments

We are grateful to V. Salters and an anonymous reviewer for the constructive comments that considerably improved the quality of this study. This work was financially supported by Programma di Ricerca di Interesse Nazionale of the Italian Ministero dell'Università e della Ricerca, and Fondi Ricerca Giovani of Università degli Studi di Pavia.

609 **References**

610	Abbate E, Bortolotti V, Principi G (1980)	Apennine	ophiolites:	a peculiar	oceanic	crust.	Ofioliti	1:
611	59-96.							

- 612 Alt JC, Honnorez J, Laverne C, Emmermann R (1986) Hydrothermal alteration of a 1 km section 613 through the upper oceanic crust, Deep Sea Drilling Project Hole 504B: Mineralogy, chemistry 614 and evolution of seawater-basalt interactions. J Geophys Res-Sol Ea, 91: 10309-10335 615 Alt JC, Laverne C, Vanko DA, Tartarotti P, Teagle DA, Bach W, Zuleger E, Erzinger J, Honnorez 616 J, Pezard PA, Becker K, Salisbury MH, Becker K (1996). 34. Hydrothermal alteration of a 617 section of upper oceanic crust in the Eastern Equatorial Pacific: a synthesis of results from site 618 504 (DSDP LEGS 69, 70, and 83, and ODP LEGS 111, 137,140, and 148). Proceedings of the 619 Ocean Drilling Program, Scientific Results, Vol. 148 620 Anders E, Ebihara M. (1982). Solar-system abundances of the elements. Geochim Cosmochim 621 Ac 46: 2363-2380 Barry TL, Davies JH, Wolstencroft M, Millar IL, Zhao Z, Jian P, Safanova I, Price M (2017). 622
 - Whole-mantle convection with tectonic plates preserves long-term global patterns of uppermantle geochemistry. Sci Rep 7: 1870
 - Baud J.P. (1975) Étude géologique du massif de roches vertes de Haute-Balagne (Corse). PhD
 thesis
 - 627 Bédard JH (2000) Betts Cove ophiolite and its cover rocks, Newfoundland. Natural Resources628 Canada, No. 550.
 - 629 Bill M, O'Dogherty L, Guex J, Baumgartner PO, Masson H (2001) Radiolarite ages in Alpine-
 - Mediterranean ophiolites: constraints on the oceanic spreading and the Tethys-Atlantic
 connection. Geol Soc Am Bull 113: 129–143
 - 632 Blichert-Toft J, Rosing MT, Lesher CE, Chauvel C (1995) Geochemical constraints on the origin of
 - the late Archean Skjoldungen Alkaline Igneous Province, SE Greenland. J Petrol 36: 515-561

- Blundy J, Wood B (1994) Prediction of crystal-melt partition coefficients from elastic moduli.
 Nature 372: 452-454
- 636 Bonatti E, Peyve A, Kepezhinskas P, Kurentsova N, Seyler M, Skolotnev S, Udintsev G (1992)
- 637 Upper mantle heterogeneity below the Mid-Atlantic Ridge, 0–15 N. J Geophys Res-Sol Ea 97:
- 638 4461-4476
- Borghini G, Rampone E (2007) Postcumulus processes in oceanic-type olivine-rich cumulates: the
 role of trapped melt crystallization versus melt/rock interaction. Contrib Mineral Petr 154: 619633
- 642 Chiari M, Marcucci M, Principi G (2000) The age of the radiolarian cherts associated with the
 643 ophiolites in the Apennines (Italy). Ofioliti 25: 141–146
- 644 Claeson DT, Meurer WP, Hogmalm KJ, Larson SÅ (2007) Using LA-ICPMS mapping and sector
- conation to understand growth and trace-element partitioning in sector-zoned clinopyroxene
 oikocrysts from the Norra Ulvö Gabbro, Sweden. J Petrol 48: 711-728
- 647 Collier ML, Kelemen PB (2010) The case for reactive crystallization at mid-ocean ridges. J Petrol
 648 51: 1913-1940
- 649 Coogan LA, Saunders AD, Kempton PD, Norry MJ (2000) Evidence from oceanic gabbros for
- 650 porous melt migration within a crystal mush beneath the Mid-Atlantic Ridge. Geochem Geophy
- 651 Geosy 1: Paper number 2000GC000072
- Coogan LA, O'Hara MJ (2015) MORB differentiation: In situ crystallization in replenished-tapped
 magma chambers. Geochim Cosmochim Ac 158: 147-161
- 654 Cortesogno L, Galbiati B, Principi G (1987) Note alla "carta geologica delle ofioliti del Bracco" e
 655 ricostruzione della paleogeografia giurassico-cretacea. Ofioliti 12: 261-342
- 656 Danelian T, De Wever P, Durand-Delga M (2008) Revised radiolarian ages for the sedimentary
- 657 cover of the Balagne ophiolite (Corsica, France). Implications for the palaeoenvironmental
- evolution of the Balano-Ligurian margin. B Soc Geol Fr 179: 289-296
 - 27

- 659 Desmurs L, Müntener O, Manatschal G (2002) Onset of magmatic accretion within a magma-poor
- rifted margin: a case study from the Platta ocean-continent transition, eastern
 Switzerland. Contrib Mineral Petr, 144(3): 365-382
- Dick HJ (1977) Partial melting in the Josephine Peridotite; I, The effect on mineral composition and
 its consequence for geobarometry and geothermometry. Am J Sci 277: 801-832
- Dick HJ, Fisher RL, Bryan WB (1984) Mineralogic variability of the uppermost mantle along mid ocean ridges. Earth Planet Sc Lett 69: 88-106.
- 666 Drouin M, Godard M, Ildefonse B, Bruguier O, Garrido CJ (2009) Geochemical and petrographic
- 667 evidence for magmatic impregnation in the oceanic lithosphere at Atlantis Massif, Mid-Atlantic
- 668 Ridge (IODP Hole U1309D, 30 N). Chem Geol 264: 71-88
- 669 Drouin M, Ildefonse B, Godard M (2010) A microstructural imprint of melt impregnation in slow
- 670 spreading lithosphere: Olivine-rich troctolites from the Atlantis Massif, Mid-Atlantic Ridge, 30
- 671 N, IODP Hole U1309D. Geochem Geophy Geosy 11: Q06003, doi:10.1029/2009GC002995
- 672 Durand-Delga M. (1984) Principaux traits de la Corse Alpine et corrélations avec les Alpes Ligures.
- 673 Memorie della Società Geologica Italiana 28: 285–329
- 674 Durand-Delga M, Peybernès B, Rossi P (1997) Arguments en faveur de la position, au Jurassique,
- 675 des ophiolites de Balagne (Haute-Corse, France) au voisinage de la marge continentale
- 676 européenne. Cr Acad Sci II A, 325: 973-981
- Durand-Delga M, Lahondère D, Puccinelli A, Rossi P, Vellutini P (2001) Pre-Meeting transect
 Corsica-Elba Isalndsouthern Tuscany Guidebook-Corsica. Ofioliti 26: 303-320
- 679 Dygert N, Liang Y, Kelemen PB (2016) Formation of plagioclase lherzolite and associated dunite-
- 680 harzburgite-lherzolite sequences by multiple episodes of melt percolation and melt-rock
- reaction: an example from the Trinity Ophiolite, California, USA. J Petrol 57: 815-838
- 682 Gale A, Dalton CA, Langmuir CH, Su Y, Schilling JG (2013) The mean composition of ocean ridge
- basalts. Geochem Geophy Geosy 14: 489-518

- Gao Y, Hoefs J, Hellebrand E, von der Handt A, Snow JE (2007) Trace element zoning in
 pyroxenes from ODP Hole 735B gabbros: diffusive exchange or synkinematic crystal
 fractionation?. Contrib Mineral Petr 153: 429-442
- 687 Gillis KM, Thompson G, Kelley DS (1993) A view of the lower crustal component of hydrothermal
 688 systems at the Mid-Atlantic Ridge. J Geophys Res-Sol Ea, 98: 19597-19619
- 689 Gromet LP, Haskin LA, Korotev RL, Dymek RF (1984). The "North American shale composite":
- 690 its compilation, major and trace element characteristics. Geochim Cosmochim Ac 48: 2469-2482
- 691 Grove TL, Kinzler RJ, Bryan WB (1993) Fractionation of mid-ocean ridge basalt (MORB). Mantle
- flow and melt generation at mid-ocean ridges, 281-310
- 693 Gruppo di Lavoro sulle Ofioliti Mediterranee (1977) I complessi ofiolitici e le unità cristalline della
 694 Corsica alpina. Ofioliti 2: 265–324
- Harper GD (2003) Fe-Ti basalts and propagating-rift tectonics in the Josephine Ophiolite. Geol Soc
 Am Bull 115: 771-787
- Hart SR, Dunn T (1993) Experimental cpx/melt partitioning of 24 trace elements. Contrib Mineral
 Petr 113: 1-8
- 699 Hemond C, Hofmann AW, Vlastelic I, Nauret F (2006) Origin of MORB enrichment and relative
- trace element compatibilities along the mid-Atlantic Ridge between 10 and 24 N. Geochem
- 701 Geophy Geosy 7(12): Q12010, doi:10.1029/2006GC001317
- Hirschmann MM, Stolper, EM (1996) A possible role for garnet pyroxenite in the origin of the
 "garnet signature" in MORB. Contrib Mineral Petr 124: 185-208
- Hofmann AW (2003) Sampling mantle heterogeneity through oceanic basalts: isotopes and trace
 elements. Treatise on geochemistry 2: 61-101
- 706 Jeffries, T. E., Jackson, S. E., & Longerich, H. P. (1998). Application of a frequency quintupled Nd:
- 707 YAG source (λ = 213 nm) for laser ablation inductively coupled plasma mass spectrometric
- analysis of minerals. J Anal Atom Spectrom 13: 935-940

Kelemen PB, Shimizu N, Salters VJ (1995) Extraction of mid-ocean-ridge basalt from the
upwelling mantle by focused flow of melt in dunite channels. Nature 375: 747-753

Kinzler RJ, Grove TL (1992) Primary magmas of mid-ocean ridge basalts 1. Experiments and
methods. J Geophys Res-Sol Ea 97: 6885-6906

- Klein EM, Langmuir CH (1987) Global correlations of ocean ridge basalt chemistry with axial
 depth and crustal thickness. J Geophys Res-Sol Ea 92: 8089-8115
- 715 Klein EM (2003) Geochemistry of the igneous oceanic crust. Treatise on geochemistry 3, 433-463.
- 716 Kretz R (1983) Symbols for rock-forming minerals. Am mineral 68: 277-279
- Lagabrielle Y, Cannat M (1990) Alpine Jurassic ophiolites resemble the modern central Atlantic
 basement. Geology 18: 319-322
- 719 Le Maitre RW (1989) A classification of igneous rocks and glossary of terms. Blackwell, Oxford
- Le Roex AP, Dick HJB, Reid AM, Erlank AJ (1982) Ferrobasalts from the Spiess ridge segment of
 the Southwest Indian ridge. Earth Planet Sc Lett 60: 437-451
- 722 Le Roux PJ, le Roex A, Schilling J-G, Shimizu N, Perkins WW, Pearce NJG (2002) Mantle
- heterogeneity beneath the southern Mid-Atlantic Ridge: Trace element evidence for
 contamination of ambient asthenospheric mantle. Earth Planet Sc Lett 203: 479-498
- 725 Li XH, Faure M, Rossi P, Lin W, Lahondere D (2015) Age of Alpine Corsica ophiolites revisited:
- 726 Insights from in situ zircon U–Pb age and O–Hf isotopes. Lithos 220: 179-190
- Lissenberg CJ, Dick HJ (2008) Melt–rock reaction in the lower oceanic crust and its implications
 for the genesis of mid-ocean ridge basalt. Earth Planet Sc Lett 271: 311-325
- 729 Lissenberg CJ, MacLeod CJ, Howard KA, Godard M (2013) Pervasive reactive melt migration
- through fast-spreading lower oceanic crust (Hess Deep, equatorial Pacific Ocean). Earth Planet
 Sc Lett 361: 436-447
- 732 Lissenberg CJ, MacLeod CJ (2016) A reactive porous flow control on mid-ocean ridge magmatic
- 733 evolution. J Petrol 57: 2195-2220

- Lofgren GE, Huss GR, Wasserburg GJ (2006) An experimental study of trace-element partitioning
 between Ti-Al-clinopyroxene and melt: Equilibrium and kinetic effects including sector zoning.
 Am Mineral 91: 1596-1606
- Manatschal G, Müntener O. (2009) A type sequence across an ancient magma-poor ocean–
 continent transition: the example of the western Alpine Tethys ophiolites. Tectonophysics 473:
 4-19
- Marroni M, Pandolfi L (2003) Deformation history of the ophiolite sequence from the Balagne
 Nappe, northern Corsica: insights in the tectonic evolution of Alpine Corsica. Geol J 38: 67-83
- Marroni M, Pandolfi L (2007) The architecture of an incipient oceanic basin: a tentative
 reconstruction of the Jurassic Liguria-Piemonte basin along the Northern Apennines–Alpine
- 744 Corsica transect. Int J Earth Sci 96: 1059-1078
- Meyzen CM, Toplis MJ, Humler E, Ludden JN, Mével C (2003) A discontinuity in mantle
 composition beneath the southwest Indian ridge. Nature 421: 731-733
- Molli G, Malavieille J (2011) Orogenic processes and the Corsica/Apennines geodynamic
 evolution: insights from Taiwan. Int J Earth Sci 100: 1207-1224
- Montanini A, Tribuzio R, Vernia L (2008) Petrogenesis of basalts and gabbros from an ancient
 continent-ocean transition (External Liguride ophiolites, Northern Italy). Lithos 101: 453-479
- Mottl MJ (1983) Metabasalts, axial hot springs, and the structure of hydrothermal systems at mid ocean ridges. Geol Soc Am Bull 94: 161-180
- 753 Müntener O, Manatschal G, Desmurs L, Pettke T (2010) Plagioclase peridotites in ocean-continent
- transitions: refertilized mantle domains generated by melt stagnation in the shallow mantle
 lithosphere. J Petrol 51: 255-294
- 756 O'neill HSC, Jenner FE (2012) The global pattern of trace-element distributions in ocean floor
- 757 basalts. Nature 491: 698-705

- Paquet M, Cannat M, Brunelli D, Hamelin C, Humler E (2016) Effect of melt/mantle interactions
 on MORB chemistry at the easternmost Southwest Indian Ridge (61°–67° E). Geochem Geophy
 Geosy 17: 4605-4640
- 761 Peybernès B, Durand-Delga M, Cugny P (2001) Reconstitution, en Corse, au Jurassique moyen-
- supérieur, de la marge européenne de l'océan Liguro-Piémontais, grâce à des niveaux repères à
- 763 Praekurnubia crusei (foraminifère). Cr Acad Sci II A 332: 499–506
- Piccardo GB, Zanetti A, Müntener O (2007) Melt/peridotite interaction in the Southern Lanzo
 peridotite: field, textural and geochemical evidence. Lithos 94: 181-209
- 766 Principi G, Bortolotti V, Chiari M, Cortesogno L, Gaggero L, Marcucci M, Saccani E, Treves B
- 767 (2004) The pre-orogenic volcano-sedimentary covers of the Western Tethys oceanic basin: a
 768 review. Ofioliti 29: 177-212
- Rampone E, Hofmann AW, Piccardo GB, Vannucci R, Bottazzi P, Ottolini L (1996) Trace element
 and isotope geochemistry of depleted peridotites from an N-MORB type ophiolite (Internal
 Liguride, N. Italy). Contrib Mineral Petr 123: 61-76
- Rampone E, Piccardo GB, Vannucci R, Bottazzi P (1997) Chemistry and origin of trapped melts in
 ophioiitic peridotites. Geochim Cosmochim Ac 61: 4557-4569
- Rampone E, Hofmann AW, Raczek I (1998) Isotopic contrasts within the Internal Liguride
 ophiolite (N. Italy): the lack of a genetic mantle–crust link. Earth Planet Sc Lett 163: 175-189
- 776 Rampone E, Piccardo GB, Hofmann AW (2008) Multi-stage melt-rock interaction in the Mt.
- Maggiore (Corsica, France) ophiolitic peridotites: microstructural and geochemical evidence.
 Contrib Mineral Petr 156: 453-475
- 779 Regelous M, Weinzierl CG, Haase KM (2016) Controls on melting at spreading ridges from
- correlated abyssal peridotite-mid-ocean ridge basalt compositions. Earth Planet Sc Lett 449: 111
- 782 Renna MR, Tribuzio R (2011) Olivine-rich troctolites from Ligurian ophiolites (Italy): evidence for
- impregnation of replacive mantle conduits by MORB-type melts. J Petrol 52: 1763–1790

- Renna MR, Tiepolo M, Tribuzio R (2011) In situ U-Pb geochronology of baddeleyite-zircon pairs
 using laser-ablation ICPMS: the case-study of quartz gabbro from Varney Nunatak (central
 Victoria Land, Antarctica). Eur J Mineral 23: 223-240
- Renna MR, Tribuzio R, Ottolini L (2016) New perspectives on the origin of olivine-rich troctolites
 and associated harrisites from the Ligurian ophiolites (Italy). J Geol Soc London 173: 916-932
- 789 Renna MR, Tribuzio R, Sanfilippo A, Tiepolo M (2017) Zircon U–Pb geochronology of lower crust
- and quartzo-feldspathic clastic sediments from the Balagne ophiolite (Corsica). Swiss J
 Geosci 110: 479-501
- 792 Roeder PL, Emslie R (1970) Olivine-liquid equilibrium. Contrib Mineral Petr 29: 275-289
- 793 Rossi P, Durand-Delga M, Lahondere JC (2001) Carte Géologique de France (1/50000), feuille
- Santo-Pietro-di-Tenda (1106). In: Orleans BRGM. Notice explicative par (eds Rossi, P., Durand-

795 Delga, M., Lahondere, J. C. & Lahondere, D.), 224. BRGM Orléans, France

- Rossi P, Cocherie A, Lahondère D, Fanning C.M. (2002) La marge européenne de la Téthys
 jurassique en Corse: datation de trondhjémites de Balagne et indices de croûte continentale sous
- 798le domaine Balano-Ligure. C R Geosci 334: 313-322
- Saccani E, Principi G, Garfagnoli F, Menna F (2008) Corsica ophiolites: geochemistry and
 petrogenesis of basaltic and metabasaltic rocks. Ofioliti 33: 187-207
- 801 Saccani E (2015) A new method of discriminating different types of post-Archean ophiolitic basalts
- and their tectonic significance using Th-Nb and Ce-Dy-Yb systematics. Geosci Front 6: 481-501
- Salters VJ, Dick HJ (2002) Mineralogy of the mid-ocean-ridge basalt source from neodymium
 isotopic composition of abyssal peridotites. Nature 418: 68-72
- 805 Sanfilippo A, Tribuzio R (2011) Melt transport and deformation history in an "non-volcanic"
- 806 ophiolitic section (Northern Apennine, Italy): implications for crustal accretion at slow spreading
- settings. Geochem Geophy Geosy 12: Q0AG04, http://doi: 101029/2010GC003429
- 808 Sanfilippo A, Dick HJ, Ohara Y (2013) Melt-rock reaction in the mantle: mantle troctolites from
- the Parece Vela ancient back-arc spreading center. J Petrol 54: 861-885

- 810 Sanfilippo A, Tribuzio R, Tiepolo M (2014) Mantle–crust interactions in the oceanic lithosphere:
 811 Constraints from minor and trace elements in olivine. Geochim Cosmochim Ac 141: 423-439
- 812 Sanfilippo A, Morishita T, Kumagai H, Nakamura K, Okino K, Hara K, Tamura A, Arai S (2015a)
- 813 Hybrid troctolites from mid-ocean ridges: inherited mantle in the lower crust. Lithos 232: 124-
- 814 130
- 815 Sanfilippo A, Tribuzio R, Tiepolo M, Berno D (2015b) Reactive flow as dominant evolution
 816 process in the lowermost oceanic crust: evidence from olivine of the Pineto ophiolite (Corsica).
 817 Contrib Mineral Petrol 170: 1-12
- Schwandt CS, McKay GA (2006) Minor-and trace-element sector zoning in synthetic enstatite. Am
 Mineral 91: 1607-1615
- 820 Schwarzenbach EM, Früh-Green GL, Bernasconi SM, Alt JC, Shanks III WC, Gaggero L, Crispini
- L (2012) Sulfur geochemistry of peridotite-hosted hydrothermal systems: comparing the
 Ligurian ophiolites with oceanic serpentinites. Geochim Cosmochim Ac 91: 283-305
- Shi P, Libourel G. (1991) The effects of FeO on the system CMAS at low pressure and implications
 for basalt crystallization processes. Contrib Mineral Petr 108: 129-145
- Standish JJ, Dick HJB, Michael PJ, Melson WG, O'Hearn T (2008) MORB generation beneath the
 ultraslow spreading Southwest Indian Ridge (9–25 E): Major element chemistry and the
 importance of process versus source. Geochem Geophy Geosy 9: Q05004
- 828 Stille P, Clauer N, Abrecht J (1989) Nd isotopic composition of Jurassic Tethys seawater and the
- genesis of Alpine Mn-deposits: Evidence from Sr-Nd isotope data. Geochim Cosmochim Ac 53:
 1095-1099
- 831 Stracke A, Hofmann AW, Hart SR (2005) FOZO, HIMU, and the rest of the mantle zoo. Geochem
 832 Geophy Geosy 6: Q05007
- 833 Stracke A, Bourdon B (2009) The importance of melt extraction for tracing mantle heterogeneity.
- 834 Geochim Cosmochim Ac 73: 218-238

- 835 Stracke A. (2012) Earth's heterogeneous mantle: A product of convection-driven interaction
 836 between crust and mantle. Chem Geol 330: 274-299
- 837 Suhr G, Hellebrand E, Johnson K, Brunelli D (2008) Stacked gabbro units and intervening mantle:
- A detailed look at a section of IODP Leg 305, Hole U1309D. Geochem Geophy Geosy 9:
- 839 Q10007, doi:10.1029/2008GC002012
- 840 Thirlwall MF (1991a) Long-term reproducibility of multicollector Sr and Nd isotope ratio
 841 analysis. Chemical Geology: Isotope Geoscience section 94: 85-104
- 842 Thirlwall MF (1991b) High-precision multicollector isotopic analysis of low levels of Nd as
 843 oxide. Chem Geol 94: 13-22
- 844 Tiepolo M, Tribuzio R, Vannucci R (2002) The compositions of mantle-derived melts developed
 845 during the Alpine continental collision. Contrib Mineral Petr 144: 1-15
- 846 Treves BE, Harper GD (1994) Exposure of serpentinites on the ocean floor: sequence of faulting
 847 and hydrofracturing in the Northern Apennine ophicalcites. Ofioliti 19: 435-466
- 848 Tribuzio R, Riccardi MP, Ottolini L (1995) Trace element redistribution in high-temperature
- 849 deformed gabbros from East Ligurian ophiolites (Northern Apennines, Italy): constraints on the
- origin of syndeformation fluids. J Metamorph Geol 13: 367-377
- 851 Tribuzio R, Tiepolo M, Vannucci R, Bottazzi P (1999) Trace element distribution within olivine-
- bearing gabbros from the Northern Apennine ophiolites (Italy): evidence for post-cumulus
 crystallization in MOR-type gabbroic rocks. Contrib Mineral Petr 134: 123-133
- Tribuzio R, Renna MR, Dallai L, Zanetti A (2014) The magmatic–hydrothermal transition in the
 lower oceanic crust: Clues from the Ligurian ophiolites, Italy. Geochim Cosmochim Ac 130:
 188-211
- 857 Tribuzio R, Garzetti F, Corfu F, Tiepolo M, Renna MR (2016) U-Pb zircon geochronology of the
- Ligurian ophiolites (Northern Apennine, Italy): Implications for continental breakup to slow
- seafloor spreading. Tectonophysics 666: 220-243
 - 35

860	Vannucci R, Rampone E, Piccardo GB, Ottolini L, Bottazzi P (1993) Ophiolitic magmatism in the
861	Ligurian Tethys: an ion microprobe study of basaltic clinopyroxenes. Contrib Mineral Petr 115:
862	123-137

- Venturelli G, Thorpe RS, Potts PJ (1981) Rare earth and trace element characteristics of ophiolitic
 metabasalts from the Alpine-Apennine belt. Earth Planet Sc Lett 53: 109-123
- 865 Vissers RL, van Hinsbergen DJ, Meijer PT, Piccardo GB (2013) Kinematics of Jurassic ultra-slow
 866 spreading in the Piemonte Ligurian ocean. Earth Planet Sc Lett 380: 138-150
- 867 Waters CL, Sims KW, Perfit MR, Blichert-Toft J, Blusztajn J (2011) Perspective on the genesis of
- 868 E-MORB from chemical and isotopic heterogeneity at 9–10 N East Pacific Rise. J Petrol 52:
 869 565-602
- White WM, Klein EM (2014) 4.13 Composition of the Oceanic Crust. Treatise on Geochemistry
 (Second Edition). 457-496
- Wilson SC, Murton BJ, Taylor RN (2013) Mantle composition controls the development of an
 Oceanic Core Complex. Geochem Geophy Geosy 14(4): 979-995

875 Figure captions

Fig. 1 (a) Geological sketch map of the main ophiolitic bodies of the Northern Apennine, Western Alps and Corsica (slightly modified after Sanfilippo et al. 2014) and geographical location of the Balagne and Bracco-Levanto ophiolites (red squares). (b) and (c) Stratigraphic reconstruction of the Balagne and Bracco-Levanto basalt-sedimentary sequences, and location of selected samples (light blue star). In (b), a simplified reconstruction of the Moltifao slice (not to scale) is also shown and correlated to the main basalt-sedimentary section assuming that the gabbros in the lowermost part of the Moltifao slice represent the substrate of the Balagne ophiolite (see also Renna et al. 2017).

883

Fig. 2 Thin section photomicrographs: (a) poikilitic clinopyroxene (Cpx) partially replaced by chlorite (Chl) and enclosing altered plagioclase (Pl), (sample RF2); anhedral quartz (Qtz) rimmed by chlorite and enclosing acicular apatite (Ap), (sample ROS6).

887

Fig. 3 Major element whole-rock variation (calculated water free): TiO₂ versus Mg#.

889

Fig. 4 Whole-rock REE compositions of the basalts (a) and (b) the associated sedimentary rocks
normalized to chondrite (Anders and Ebihara 1982). The compositions of normal- and enrichedMORB (N- and E-MORB, Gale et al. 2013), and of NASC (North American Shale Composite,
Gromet et al. 1984) are reported for comparative purposes.

894

Fig. 5 Whole-rock incompatible trace element compositions of the basalts, normalized to chondrite
(Anders and Ebihara 1982). The compositions of normal- and enriched-MORB (N- and E-MORB,
Gale et al. 2013) are reported for comparative purposes.

- **Fig. 6** Plot of initial ε_{Nd} versus ¹⁴⁷Sm/¹⁴⁴Nd. Initial ε_{Nd} and ¹⁴⁷Sm/¹⁴⁴Nd values of basalts from the top of the Bracco-Levanto succession after Rampone et al. (1998) are also shown.
- 901

902 **Fig.** 7 Variation of Mg#, Al₂O₃ and Na₂O versus TiO₂ in the clinopyroxene cores.

903

Fig. 8 REE compositions of the clinopyroxene cores, normalized to chondrite (Anders and Ebihara
1982). The REE compositions of clinopyroxene cores from plagioclase-rich peridotites (Rampone
et al. 1997; Sanfilippo and Tribuzio 2011), olivine-rich troctolites (shaded grey area, Renna and
Tribuzio 2011) and gabbros (Sanfilippo and Tribuzio 2011; Tribuzio et al. 2014) from Internal
Ligurian ophiolites are also reported for comparative purposes.

909

Fig. 9 Chondrite normalized (Anders and Ebihara 1982) incompatible trace element compositions
of the clinopyroxene cores. The incompatible trace element compositions of clinopyroxene cores
from plagioclase-rich peridotites (Rampone et al., 1997; Sanfilippo and Tribuzio 2011), olivine-rich
troctolites (shaded grey area, Renna and Tribuzio 2011) and gabbros (Sanfilippo and Tribuzio 2011;
Tribuzio et al. 2014) from Internal Ligurian ophiolites are also reported for comparative purposes.

915

916 Fig. 10 Incompatible trace elements (La, Ce, Nd, Zr, Sm, Ti, Dy, Y, Yb) compositions of melts 917 calculated through a process of fractional crystallization, normalized to average N-MORB (Gale et al. 2013). The set of mineral/liquid partition coefficients experimentally determined and reported in 918 Tiepolo et al. (2002) were used. $^{Cpx/liq}D$ values are: La = 0.05, Ce = 0.09, Nd = 0.2, Zr = 0.1, Sm = 919 0.33, Ti = 0.28, Dy = 0.45, Y = 0.43, Yb = 0.39. $^{Pl/liq}D$ values are: La = 0.217, Ce = 0.166, Nd = 920 0.138, Zr = 0.001, Sm = 0.124, Ti = 0.06, Dy = 0.06, Y = 0.043, Yb = 0.02. Calculation were 921 922 carried out assuming: (a) a fractionating assemblage 0.60 plagioclase and 0.40 clinopyroxene and 923 that the composition of samples RF2 (Mg# = 63) and N10 (Mg# = 37) represent those of the most primitive and most evolved basalt, respectively; (b) a fractionating assemblage 0.50 plagioclase and 0.50 clinopyroxene and that the compositions of samples ROS10 (Mg# = 65) and ROS6 (Mg# = 45) represent those of the most primitive and most evolved basalt, respectively. F is the fraction of remaining liquid (see text for further details).

- 928
- 929 Fig. 11 Whole-rock basalt variation of CaO/Al_2O_3 vs. Ce_N/Sm_N
- 930

Fig. 12 Variation of Zr_N/Y_N versus Ce_N/Sm_N in the clinopyroxenes. Literature data for (i) clinopyroxene from plagioclase-rich peridotites (Rampone et al. 1997; Sanfilippo and Tribuzio 2011; Sanfilippo et al. 2014), olivine-rich troctolites (Borghini and Rampone 2007; Renna and Tribuzio 2011) and gabbros (Rampone et al. 1997; Tribuzio et al. 1999; Sanfilippo and Tribuzio 2011; Tribuzio et al. 2014; Sanfilippo et al. 2015a) from the Jurassic Alpine-Apennine ophiolites are also plotted.



Figure 1











Figure 3











Figure 6

Click here to download Figure fig07_R1.ppt 🛓













Figure 11





 Modal composition (vol. %) and petrographic features of the selected basalts, obtained by visual estimates.

ophiolite	Localization	Sample	locality	Pl		Срх		Fe-Ti oxides		Qtz		Ap	Pl secondary transformation	Cpx secondary transformation
				vol%	grain size (mm)	vol%	grain size (mm)	vol%	grain size (mm)	vol%	grain size (mm)			
Balagne	Corsica	N1	Rio Casapola	60	0.8-4.0	35	0.3-2.0	5	0.2-0.6	_	_	tr	+++	++
Balagne	Corsica	N21	Rio Casapola	55	1.0-3.0	40	0.8-3.5	5	0.2-0.9	_	—	tr	+++	++
Balagne	Corsica	N10	Piantella	60	0.1-0.5	40	0.8-3.0	tr	0.2-0.6	_	—	tr	+++	++
Balagne	Corsica	RF2	Rio Forci	60	0.6-4.0	40	0.6-3.0	tr	0.3-1.5	_	_	tr	+++	+
Bracco-Levanto (Internal Ligurian units)	Northern Apennine	ROS6	Rossola	55	1.5-4.0	30	1.0-4.0	5	<0.8	5	0.2-0.8	tr	+++	++
Bracco-Levanto (Internal Ligurian units)	Northern Apennine	ROS9	Framura	55	1.0-5.0	45	0.5-2.0	tr	<0.2	_	_	tr	+++	++
Bracco-Levanto (Internal Ligurian units)	Northern Apennine	ROS10	Rossola	50	1.0-3.0	45	0.7-2.5	tr	<0.6	5	0.6-1.5	tr	+++	++
Bracco-Levanto (Internal Ligurian units)	Northern Apennine	ROS12	Rossola	60	0.5-3.5	40	1.0-3.0	tr	0.2-0.7	_	_	tr	+++	++

tr, < 4%; —, mineral not present in the rock

 $\mbox{ Extent of secondary transformation of plagioclase and clinopyroxene: +, \le 30\%; ++, 30-90\%; +++, \ge 90\%. \label{eq:extent}$

Mineral abbreviations after Kretz (1983).

Table 2 Whole-rock r	naior and	trace eler	nent com	positions	of selected s	amples						
Sample	RF2	N21	N1	N10	ROS10	ROS12	ROS9	ROS6	PC11	PP1	ROS22	ROS25
rock-type	basalt	basalt	basalt	basalt	basalt	basalt	basalt	basalt	quartz-rich breccia	quartzitic sandstone	rad	rad
ophiolite Major elemer	Balagne nts (wt%)	Balagne	Balagne	Balagne	Br-Lev (IL)	Br-Lev (IL)	Br-Lev (IL)	Br-Lev (IL)	Balagne	Balagne	Br-Lev (IL)	Br-Lev (IL)
SiO ₂	51.3	49.5	50.1	49.9	46.9	48.1	48.9	47.7	71.1	54.9	76.3	73.2
TiO ₂	1.51	1.85	2.16	3.23	1.07	1.37	1.53	2.91	0.24	0.17	0.17	0.17
Al_2O_3	16.4	15.0	15.7	13.4	16.5	17.3	15.3	12.8	13.6	4.97	4.62	4.60
Fe ₂ O ₃ ^{tot}	7.40	10.1	9.67	13.6	8.57	8.34	9.54	14.6	2.89	0.95	9.86	9.77
MnO	0.17	0.16	0.19	0.23	0.11	0.15	0.17	0.21	0.06	0.05	0.15	0.36
MgO	6.43	7.55	4.84	3.97	7.86	7.42	7.36	5.92	0.69	1.06	4.35	4.96
VaO Nao	0.30 5.55	0.52 4.20	0.42 4 95	7.14 5.30	9.47	9.01	8.92 3.88	3.62	3.08	20.1	0.50	0.13
K ₂ O	0.12	1.11	1 32	0.07	0.03	0.15	0.60	0.12	4 56	1.02	0.12	0.15
P2Oc	0.12	0.27	0.30	0.57	0.05	0.15	0.00	0.12	0.07	0.04	0.13	0.20
L.O.I	3.08	3.30	2.75	2.44	5.78	3.96	3.58	2.87	1.99	16.2	2.99	2.69
CO ₂	_	_	_	_	_	_	_	_	_	15.2	_	_
Total	98.6	99.6	98.4	100.0	98.5	99.9	100.0	100.0	99.5	100.5	99.4	97.9
Mg#	63.3	59.7	49.8	36.6	64.5	63.8	60.4	44.5	32.1	68.9	46.6	50.1
CaO/Al ₂ O ₃	0.39	0.43	0.41	0.53	0.57	0.52	0.58	0.70	_	_	_	_
FeO ^{tot} /MgO	1.04	1.20	1.80	3.08	0.98	1.01	1.17	2.22	_	_	_	—
Trace elemen	ts (ppm)											
V Cr	184	240	255	351	138	220	264	375	17	16	92 220	103
Sc	22	32	29	~20 29	20	27	33	37	<20 5	3	8	8
Co	27	39	25	34	32	32	36	38	3	<1	56	55
Ni	60	100	<20	<20	150	100	110	< 20	<20	<20	285	320
Cu	720	50	<10	20	50	50	50	40	<10	<10	40	70
Zn	<30 14	80 15	<30	120	40 14	< 30 14	50 15	110	40	<30	55 7	70
Sn	14	<1	10	4	14	< 1	2	3	3	2	1.0	< 1
Rb	<1	9.0	11.0	<1	< 1	4	12	1	196	34	7	7
Sr	374	304	275	72	43	260	180	165	92	111	50.5	52
Ba 7-	17	32	33	13	6	8	35	10	528	101	31.0	39
Zr Nh	147 6 50	6.80	164 5 30	304 103	85 1.50	92 3.00	2.10	235 4 00	140	97.0 3.7	35.5 2.6	35 1.8
Y	30.3	34.7	40.4	70.0	22	27.2	33.3	58.3	27.8	16.4	26.7	19.7
Hf	3.20	3.90	3.70	7.60	2.30	2.40	3.90	5.60	4.30	2.40	0.80	0.4
Ta	0.48	0.30	0.38	0.60	0.08	0.13	0.14	0.27	1.25	0.46	0.16	0.02
Pb Th	<5 0.40	<5 0.30	<5 0.30	<5 0.78	< 5	< 5 0.24	< 5 0.16	< 5	11	12	8 2.60	19
U	0.17	0.11	0.20	0.28	0.08	0.24	0.09	0.32	3.29	2.10	0.50	0.54
La	7.69	7.40	7.72	16.20	2.46	3.62	3.35	6.72	36.0	15.2	17.2	16.2
Ce Pr	21.4	20.1	23.0	44.6 6.66	8.12	11.6	12.6	22.8	68.9 7.47	26.2	30.0 4.27	27.2
Nd	15.0	15.5	18.1	31.9	7.52	1.98	12.1	21.0	26.0	12.2	17.6	17.4
Sm	4.38	4.81	5.59	9.13	2.70	3.38	4.13	7.16	5.08	2.48	4.10	3.91
Eu	1.48	1.63	1.81	2.71	0.97	1.26	1.40	2.36	0.77	0.46	1.14	0.85
Gd	5.19	5.85	6.85	10.40	3.41	4.35	5.39	9.63	4.49	2.23	4.34	3.55
10 Dv	0.93 5.61	6.53	7 40	12.00	3.98	4.89	6.26	1.75	0.78 4.80	2.33	0.77 4 41	0.38
Но	1.20	1.31	1.59	2.43	0.85	1.07	1.35	2.29	0.99	0.48	0.87	0.67
Er	3.41	3.78	4.43	7.06	2.35	3.00	3.78	6.43	2.96	1.41	2.37	1.91
Tm	0.52	0.57	0.70	1.06	0.38	0.46	0.59	1.00	0.45	0.21	0.34	0.28
Yb	3.34	3.72	4.47	7.14	2.31	3.03	3.74	6.32	3.01	1.38	2.07	1.71
Cev/Smy	1 19	1.02	1.00	1.10	0.33	0.42	0.33	0.90	0.30 4 44	3.84	2.63	2.60
Gd_N/Yb_N	1 28	1 30	1.00	1 20	1.22	1 19	1 19	1.26	1 23	1 34	1 74	1 72
Eu/Eu*	0.94	0.93	0.89	0.84	0.97	1.00	0.90	0.86	0.49	0.59	0.82	0.69
Nb _N /Y _N	1.36	1.24	0.83	0.93	0.43	0.70	0.40	0.44	_	_		
Ta _N /Y _N	1.74	0.95	1.03	0.94	0.40	0.53	0.46	0.51	_	_	_	_
Zr _N /Y _N	1.92	1.97	1.61	2.06	1.53	1.34	1.90	1.58	_	_	_	_
Hf_N/Y_N	1.58	1.69	1.37	1.63	1.57	1.32	1.76	1.44	_	_	_	_
$(Sm/Yb)_{DM}$	1.79	1.76	1.70	1.74	1.59	1.52	1.50	1.54	—	_	_	_

rad, radiolarian chert; Br-Lev (IL), Bracco-Levanto (Internal Ligurian units)

L.O.I. loss on ignition. Mg# = $100 \times \text{molar Mg/(Mg+Fe}^{2+}_{tot})$

--, not determined; (Sm/Yb)_{DM}, Sm/Yb normalized to depleted mantle ratios (see Hirschmann and Stolper, 1996)

Sample	rock-type	ophiolite	143 Nd/ 144 Nd ± 2 s.e.	Sm	Nd	¹⁴⁷ Sm/ ¹⁴⁴ Nd	$^{143}\mathrm{Nd/}^{144}\mathrm{Nd}~_{(164~\mathrm{Ma})}$	$\epsilon_{ m Nd}$	E _{Nd (164Ma)}
RF2	basalt	Balagne	0.513048 ± 4	3.9601	14.157	0.1705	0.51287 ± 4	+8.0	$+8.6 \pm 0.1$
N10	basalt	Balagne	0.513064 ± 4	8.6910	30.435	0.1740	0.51288 ± 4	+8.3	$+8.8 \pm 0.1$
N1	basalt	Balagne	0.513067 ± 4	5.1997	17.771	0.1783	0.51288 ± 4	+8.4	$+8.8 \pm 0.1$
N21	basalt	Balagne	0.513069 ± 4	4.5068	15.277	0.1798	0.51288 ± 4	+8.4	$+8.8 \pm 0.1$
PC11	quartzo- feldspathic breccia	Balagne	0.512269 ± 4	4.5772	23.652	0.1179	0.51214 ± 4	-7.2	-5.5 ± 0.1
		=	143 Nd/ 144 Nd ± 2 s.e.	Sm	Nd	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd (161Ma)	ε _{Nd}	E _{Nd (161Ma)}
ROS6	basalt	Bracco-Levanto	0.513086 ± 4	3.1666	9.8610	0.1957	0.51288 ± 4	+8.7	$+8.8 \pm 0.1$
ROS9	basalt	Bracco-Levanto	0.513095 ± 4	2.5091	7.1434	0.2141	0.51287 ± 4	+8.9	$+8.6 \pm 0.1$
ROS10	basalt	Bracco-Levanto	0.513090 ± 4	7.2307	21.7887	0.2022	0.51288 ± 4	+8.8	$+8.7 \pm 0.1$
ROS12	basalt	Bracco-Levanto	0.513094 ± 4	3.9663	11.9496	0.2023	0.51288 ± 4	+8.9	$+8.8 \pm 0.1$
ROS23	radiolarian chert	Bracco-Levanto	0.512315 ± 4	3.6082	15.239	0.1443	0.51216 ± 4	-6.3	-5.2 ± 0.1

Table 3 Nd isotope compositions of selected samples

2 s.e. is the uncertainty on measured 143 Nd/ 144 Nd (internal precision). The assessment of errors on calculated 143 Nd/ 144 Nd ratios and corresponding ε values was done using the error propagation equation reported in Blichert-Toft et al. (1995)

Representative major element clinopyroxene compositions (wt%)											
Sample	RF2	N21	N1	N10	ROS10	ROS12	ROS9	ROS6			
ophiolite	Balagne	Balagne	Balagne	Balagne	Br-Lev (IL)	Br-Lev (IL)	Br-Lev (IL)	Br-Lev (IL)			
SiO ₂	50.3	50.3	50.3	49.5	51.2	52.1	51.2	51.5			
TiO ₂	1.84	1.84	1.68	1.74	1.00	0.97	1.14	0.95			
Al_2O_3	3.67	3.67	3.75	3.33	2.50	2.18	3.61	2.14			
Cr ₂ O ₃	0.12	0.12	0.09	0.04	0.25	0.10	0.35	0.05			
FeO	7.91	7.9	7.82	11.41	7.67	7.97	8.30	10.3			
MnO	0.21	0.21	0.23	0.29	0.21	0.19	0.20	0.36			
NiO	< 0.02	< 0.02	0.02	< 0.02	< 0.02	0.06	0.05	< 0.02			
MgO	14.2	14.2	15.0	11.7	15.5	15.9	15.1	13.3			
CaO	21.7	21.7	20.9	20.7	19.2	20.1	19.9	20.7			
Na ₂ O	0.61	0.61	0.51	0.65	0.42	0.40	0.42	0.49			
K ₂ O	0.01	0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01			
Sum	100.5	100.5	100.3	99.3	98.0	100.0	100.2	99.8			
Mg#	76.2	76.2	77.3	64.7	78.3	78.0	76.4	69.8			

Table 4 Representative major element clinopyroxene compositions (wt%

Br-Lev (IL), Bracco-Levanto (Internal Ligurian units)

Mg#, $[100 \times Mg/(Mg+Fe^{2+}_{tot}))$, in atoms per formula unit]

Table 5	
Trace element compositions of the clinopyroxenes (ppm)	

Sample	RF2	N21	N1	N10	ROS10	ROS12	ROS9	ROS6
ophiolite	Balagne	Balagne	Balagne	Balagne	Br-Lev (IL)	Br-Lev (IL)	Br-Lev (IL)	Br-Lev (IL)
V	576	512	572	629	369	347	512	484
Cr	1,410	578	662	11	1,200	1,260	1,600	155
Sc	152	132	163	136	128	109	147	140
Ti	11,200	8,840	10,100	9,630	6,930	5,780	8,260	7,480
Rb	0.07	0.06	< 0.04	< 0.04	< 0.04	0.05	0.05	0.08
Sr	21.9	18.5	17.9	23.1	8.49	9.09	9.34	8.71
Ba	0.21	0.28	0.13	0.20	0.06	0.10	0.24	0.17
Zr	81.8	50.5	58.5	128	20.2	18.3	40.7	30.7
Nb	0.08	0.04	0.05	0.11	0.03	0.02	0.05	0.04
Y	36.1	35.0	35.5	66.4	30.3	22.9	40.0	43.6
Hf	3.25	2.05	2.47	5.25	1.09	0.83	2.28	1.53
Та	0.02	0.02	0.01	0.03	< 0.01	< 0.01	0.02	0.01
La	1.62	1.15	1.12	2.79	0.36	0.34	0.69	0.70
Ce	8.29	6.25	5.58	14.7	1.81	1.95	3.63	3.25
Pr	1.83	1.44	1.35	3.40	0.53	0.52	0.96	0.82
Nd	12.0	9.99	9.32	22.2	4.51	4.13	7.81	6.58
Sm	4.73	4.32	3.98	9.31	2.59	1.99	3.69	3.22
Eu	1.49	1.37	1.27	2.34	0.92	0.64	1.15	1.09
Gd	6.40	6.06	5.92	12.1	4.73	3.38	5.98	5.82
Tb	1.05	1.03	1.03	2.01	0.82	0.59	1.10	1.06
Dy	7.48	7.38	6.98	14.5	5.50	4.22	7.99	8.02
Но	1.43	1.42	1.42	2.73	1.14	0.91	1.64	1.70
Er	4.05	3.84	3.72	7.65	3.35	2.53	4.39	5.01
Tm	0.52	0.52	0.51	1.05	0.49	0.36	0.60	0.69
Yb	3.47	3.47	3.46	7.22	3.05	2.09	3.97	4.50
Lu	0.47	0.53	0.50	0.96	0.43	0.32	0.59	0.67
La_N/Sm_N	0.43	0.35	0.34	0.39	0.17	0.24	0.24	0.25
Eu/Eu*	0.82	0.81	0.79	0.67	0.80	0.75	0.75	0.77
Sr/Sr*	0.15	0.16	0.17	0.09	0.20	0.21	0.12	0.13
Gd_N/Yb_N	1.53	1.44	1.42	1.39	1.28	1.34	1.24	1.07
Nb_N/Y_N	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ta_N/Y_N	0.06	0.05	0.04	0.05	-	—	0.05	0.03
Hf_N/Y_N	1.35	0.88	1.04	1.19	0.54	0.55	0.85	0.53
Zr_N/Y_N	0.90	0.57	0.65	0.76	0.26	0.32	0.40	0.28

Br-Lev (IL), Bracco-Levanto (Internal Ligurian units) Eu/Eu* = Eu_N/(Sm_N x Gd_N)^{1/2}; Sr/Sr* = Sr_N/(Ce_N x Nd_N)^{1/2}

Electronic supplementary material

Click here to access/download Electronic supplementary material QC_WR analyses (SM).xlsx