

1 **Nitrogen recycling in subducted mantle rocks and**
2 **implications for the global nitrogen cycle**

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23 **Abstract**

24 The nitrogen concentrations [N] and isotopic compositions of ultramafic mantle rocks that
25 represent various dehydration stages and metamorphic conditions during the subduction cycle
26 were investigated to assess the role of such rocks in deep-Earth N cycling. The samples
27 analyzed record low-grade serpentinization on the seafloor and/or in the fore-arc wedge (low-
28 grade serpentinites from Monte Nero/Italy and Erro Tobbio/Italy) and two successive stages
29 of metamorphic dehydration at increasing pressures and temperatures (high-pressure (HP)
30 serpentinites from Erro Tobbio/Italy and chlorite harzburgites from Cerro del Almirez/Spain)
31 to allow for the determination of dehydration effects in ultramafic rocks on the N budget.

32 In low-grade serpentinites, $\delta^{15}\text{N}_{\text{air}}$ values (-3.8 to +3.5‰) and [N] (1.3-4.5 $\mu\text{g/g}$) are elevated
33 compared to the pristine depleted MORB mantle ($\delta^{15}\text{N}_{\text{air}} \sim -5\text{‰}$, [N] = $0.27 \pm 0.16 \mu\text{g/g}$),
34 indicating input from organic-sedimentary sources, at the outer rise during slab bending
35 and/or in the forearc mantle wedge during hydration by slab-derived fluids. Both HP
36 serpentinites and chlorite harzburgites have $\delta^{15}\text{N}_{\text{air}}$ values and [N] overlapping with low-grade
37 serpentinites, indicating no significant loss of N during metamorphic dehydration and
38 retention of N to depths of 60-70 km. The best estimate for the $\delta^{15}\text{N}_{\text{air}}$ of ultramafic rocks
39 recycled into the mantle is $+3 \pm 2\text{‰}$. The global N subduction input flux in serpentinized
40 oceanic mantle rocks was calculated as $2.3 \times 10^8 \text{ mol N}_2/\text{year}$, assuming a thickness of
41 serpentinized slab mantle of 500 m. This is at least one order of magnitude smaller than the N
42 fluxes calculated for sediments and altered oceanic crust. Calculated global input fluxes for a
43 range of representative subducting sections of unmetamorphosed and HP-metamorphosed
44 slabs, all incorporating serpentinized slab mantle, range from 1.1×10^{10} to $3.9 \times 10^{10} \text{ mol}$
45 N_2/year . The best estimate for the $\delta^{15}\text{N}_{\text{air}}$ of the subducting slab is $+4 \pm 1\text{‰}$, supporting models
46 that invoke recycling of subducted N in mantle plumes and consistent with general models for
47 the volatile evolution on Earth. Estimates of the efficiency of arc return of subducted N are

48 complicated further by the possibility that mantle wedge hydrated in forearcs, then dragged to
49 beneath volcanic fronts, is capable of conveying significant amounts of N to subarc depths.

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52 **1. INTRODUCTION**

53 Knowledge of the amount of N being subducted and the extent to which N is released
54 from subducting rocks during devolatilization is of fundamental importance in understanding
55 Earth's nitrogen (N) cycle and the evolution of volatile elements throughout Earth's history.
56 Significant differences in the N isotopic composition of Earth's major reservoirs make N
57 isotopes a useful tracer of crustal and volatile recycling. Estimates of the amounts and
58 isotopic compositions of subducted N are critical in evaluating whether or not the N isotope
59 compositions of certain mantle-derived magmas reflect retention of N in deeply subducted
60 oceanic lithosphere and sediments (Marty and Dauphas, 2003; Jia et al., 2003). It is also
61 critical in attempts to balance subduction zone N inputs from the subducting plate with N
62 outputs in arc volcanic gases (Elkins et al., 2006; Li et al., 2007; Mitchell et al., 2010). For N,
63 the presence of a significant imbalance between a large, isotopically heavy subducted flux
64 compared to an isotopically light, relatively small outgassed flux suggests that significant
65 amounts of N were trapped in the mantle during Earth's history (Javoy, 1997; 1998).

66 Nitrogen in the Earth's mantle as sampled by diamonds and MORB is depleted
67 relative to the atmosphere in the heavy isotope ^{15}N ($\delta^{15}\text{N} \sim -5\%$, where $\delta^{15}\text{N} =$
68 $[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{air}} - 1] \cdot 1000$) (Cartigny et al., 1998; Marty and Dauphas, 2003). In
69 contrast, N in sedimentary rocks is generally enriched in ^{15}N , with $\delta^{15}\text{N}$ values for modern
70 sediment mostly in the range of 0 to +10‰ (Kerrich et al., 2006). Because the abundance of
71 N in the lithosphere is largely tied to its fixation by organic processes in sedimentary
72 environments, N is a sensitive tracer of sediment-derived fluids (Bebout, 1997). Despite lower

73 N concentrations than in sediments, altered oceanic crust (AOC) is also an important
74 contributor to the subduction zone nitrogen budget due to its comparatively large volume (Li
75 et al., 2007; Mitchell et al., 2010). On the other hand, little is known about the role of the slab
76 mantle section (Philippot et al., 2007; Halama et al., 2010). Whereas the N content in the
77 unmodified mantle is much lower than in sediment or AOC, the effects of seafloor alteration
78 and serpentinization could potentially lead to an increase in N concentration and the
79 incorporation of isotopically heavier N, as observed for seafloor-altered oceanic crust, caused
80 by the addition of sedimentary-organic N from pore fluids (Busigny et al., 2005; Li et al.,
81 2007). Moreover, the volume of hydrated slab mantle being subducted is potentially greater
82 than that of crust and sediment. It has previously been demonstrated that the slab mantle can
83 convey significant amounts of H₂O (Rüpke et al., 2004) and a variety of trace elements
84 (Scambelluri et al., 1997; 2004), including halogens (John et al., 2011), to great depths in
85 subduction zones. The magnitude of N subduction in hydrated slab mantle must be evaluated
86 to better constrain the degree to which N is retained in subducting slabs or returned to the
87 atmosphere or various forearc reservoirs.

88 There has been considerable debate regarding whether initially subducted N largely
89 enters the deep mantle beyond subarc depths or whether it is returned via forearc
90 devolatilization or arc volcanism (Sano et al., 2001; Hilton et al., 2002; Fischer et al., 2002;
91 Snyder et al., 2003; Busigny et al., 2003; Li and Bebout, 2005). Recent studies of the volcanic
92 arc return of subducting N in the Central America and Izu-Bonin-Mariana margins, taking
93 into account N subduction in sediment and AOC, demonstrate that a large proportion of the N
94 entering these trenches is either lost in forearcs or delivered to the deep mantle beyond sub-
95 arc depths (Elkins et al., 2006; Mitchell et al., 2010; Sadofsky and Bebout, 2003). For the Izu-
96 Bonin-Mariana margin, Mitchell et al. (2010) estimated that only 4-17% of the N being
97 subducted in sediments and AOC (total subduction input of 6.65×10^8 mol N₂/year) is being
98 returned via arc volcanism (0.25 to 1.11×10^8 mol N₂/year, calculated by three different

99 methods). Taking into account the additional N input flux in subducted oceanic lithospheric
100 mantle, which depends on the degree of N enrichment by serpentinization, would create an
101 even greater imbalance between the subduction inputs and the arc volcanic outputs. Yet
102 another possibility is that parts of the forearc mantle wedge are hydrated and enriched in slab-
103 derived N, then dragged to beneath volcanic fronts, potentially conveying significant amounts
104 of N to subarc depths. This mechanism of down-dragging and deeper dehydration of forearc
105 serpentinite has been invoked in a number of geochemical studies of arc lavas (e.g., Tatsumi
106 and Kogiso, 1997; Straub and Layne, 2003; Tonarini et al., 2007; Johnson et al., 2009) and of
107 serpentinized peridotites from forearc serpentine seamounts (Savov et al., 2005; 2007).

108 Several studies of metasedimentary rocks have evaluated whether there is significant
109 loss of isotopically fractionated N during prograde metamorphic dehydration in forearcs.
110 Based on study of low-grade units of the Catalina Schist and a traverse of HP/UHP
111 metasedimentary rocks in the Italian Alps, it appears that along relatively cool prograde
112 metamorphic P-T paths such as those experienced in most modern-Earth subduction zones,
113 sedimentary N is largely retained during forearc metamorphism to depths beneath arcs
114 (Bebout and Fogel, 1992; Busigny et al., 2003). In contrast, increased $\delta^{15}\text{N}$ values and
115 decreased N concentrations with increasing metamorphic grade, interpreted as the result of
116 preferential loss of ^{14}N to the fluid phase, occur in subducting sediments that experienced
117 higher-T prograde metamorphic paths (Bebout and Fogel, 1992; Haendel et al., 1986;
118 Mingram and Bräuer, 2001). In metamorphosed basaltic rocks, N concentrations and $\delta^{15}\text{N}$
119 overlapping with those of AOC indicate negligible effects of metamorphic devolatilization,
120 but some eclogite suites show evidence for fluid-mediated addition of a sedimentary N
121 component (Halama et al., 2010).

122 The primary goals of this study are (1) to document the concentrations and isotopic
123 compositions of N in hydrated mantle rocks through analyses of samples reflecting different
124 stages of the subduction zone cycle, from oceanic alteration to high-pressure metamorphism,

125 (2) to assess redistribution and isotope fractionation of N by ultramafic dehydration, and (3)
126 to gain information regarding the source of the fluids responsible for the serpentinization of
127 these mantle rocks. The results place constraints on the extent to which N can be retained in
128 mantle rocks to depths approaching those beneath arcs, information that can be used to
129 calculate a global N subduction flux in ultramafic rocks that can be compared with N fluxes
130 in subducting sediments and basaltic crust.

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132

133 **2. SAMPLING STRATEGY AND SAMPLE LOCATIONS**

134 Serpentinized and metamorphosed mantle peridotites and associated high-pressure veins
135 were investigated from three sites of ultramafic rocks in ophiolite units (Monte Nero/Northern
136 Apennine, Erro Tobbio/Western Alps, Cerro del Almirez/Betic Cordillera), chosen because
137 they record increasing P-T conditions representing the evolution of the hydrated slab mantle
138 from alteration on the ocean floor to subduction metamorphism beyond the breakdown of
139 antigorite serpentine (Fig. 1). Because antigorite contains 12.3 wt.% of H₂O (Schmidt and
140 Poli, 1998), this latter process has been proposed to be responsible for major fluid release in
141 subduction zones (Ulmer and Trommsdorff, 1995; Scambelluri et al., 2001). Although the
142 samples are derived from distinct orogenic terranes, they share petrologic and compositional
143 characteristic as serpentinized mantle rocks and are therefore suitable for investigating
144 progressive dehydration of mantle rocks during subduction. The majority of the samples was
145 petrographically described and analyzed for halogen concentrations by John et al. (2011), and
146 fluid inclusion and oxygen isotope analyses of the samples from Cerro del Almirez were
147 presented in Scambelluri et al. (2004).

148

149 **2.1. Monte Nero, Northern Apennine, Italy**

150 Serpentinized peridotites from Monte Nero (External Liguride Units) form a several
151 kilometer-sized body and represent pre-subduction oceanic alteration in mantle peridotite
152 (Fig. 1). The Liguride units belong to the Alpine orogenic system and are interpreted as
153 remnants of oceanic and transitional lithosphere of the Western Tethys basin located between
154 the continental margins of Europe and Adria (Marroni et al. 1998; Marroni and Pandolfi,
155 2007). In the External Ligurides, ultramafic and volcanic rocks occur as large olistoliths
156 within Late Cretaceous sedimentary mélanges (Abbate et al., 1980; Beccaluva et al., 1984).
157 The ultramafic rocks are slices of subcontinental lithospheric mantle emplaced at the surface
158 by early rifting of the ocean basin during the Jurassic (Rampone et al., 1995). They consist
159 of fertile spinel lherzolites with pyroxenite bands (Rampone et al., 1995) and were affected by
160 variable degrees of serpentinization (Rampone et al., 1995). At Monte Nero, olistoliths
161 comprise MORB dikes and gabbroic bodies (Marroni et al., 1998) and Sr and Nd isotope
162 compositions of clinopyroxenes are typical of MORB-type mantle (Rampone et al., 1995).
163 Partial metamorphic re-equilibration in the plagioclase stability field occurred at 164 ± 20 Ma
164 (Rampone et al., 1995). The ultramafic mantle rocks from Monte Nero show several lines of
165 evidence for emplacement into the shallow oceanic lithosphere and fluid influx by
166 serpentinizing fluids: First, they are cut by basaltic dikes, which post-date plagioclase
167 crystallization; second, they are serpentinized and third, they are locally disrupted by breccias
168 consisting of serpentine matrix with serpentinized peridotite clasts (Marroni et al., 1998;
169 Montanini et al., 2006). The degree of serpentinization in the peridotites is variable and
170 reaches up to ~80%. The texturally earliest mineral assemblage consists of porphyroclasts of
171 olivine + orthopyroxene + clinopyroxene with tiny trails of brown spinel. This spinel-facies
172 paragenesis is replaced by a plagioclase-bearing assemblage, resulting in the formation of
173 plagioclase and olivine as reaction products around spinel and replacement of primary
174 porphyroclasts by aggregates of olivine, plagioclase and pyroxenes. Serpentine minerals
175 replace olivine forming mesh-type structures and orthopyroxene forming bastite structures.

176 XRD analyses reveal that the serpentine minerals are chrysotile and lizardite. The low-grade
177 serpentinites from Monte Nero may represent oceanic serpentinization associated with
178 halogen input from sedimentary sources (John et al., 2011).

179

180 **2.2. Erro Tobbio, Western Alps, Italy**

181 The Erro Tobbio peridotites are the mantle section of the Voltri massif, which is the
182 largest ophiolite exposure in the European Alps. The pre-subduction history is similar to the
183 Monte Nero peridotites and involves a primary origin as subcontinental mantle, which was
184 exhumed and hydrated during opening of the Jurassic Tethyan ocean basin. Prior to the
185 Jurassic, the pristine peridotites equilibrated at spinel-facies conditions in the subcontinental
186 lithosphere of the Europe-Adria system (Piccardo and Vissers, 2007). Decompressional
187 recrystallization caused the formation of plagioclase- and hornblende-bearing assemblages
188 (Hoogerduijn Strating et al., 1993). During exhumation and emplacement at the seafloor, the
189 peridotites interacted with MORB-type melts (Piccardo and Vissers, 2007). Serpentinization
190 of peridotites and concurrent rodingitization of mafic dikes point to interaction with seawater-
191 derived fluids (Scambelluri et al., 1997). The low-grade serpentinite assemblage consists of
192 chrysotile and/or lizardite, chlorite, magnetite and brucite and indicates serpentinization at
193 temperatures below 300°C (Scambelluri et al., 1997). These low-grade serpentinites are
194 preserved in peridotite volumes that were unaffected by the subduction-related deformation
195 and it is currently debated whether they have been serpentinized on the ocean floor or in the
196 fore-arc mantle wedge (e.g., John et al., 2011, Scambelluri and Tonarini, 2011). During alpine
197 subduction and high-pressure recrystallization, partial dehydration occurred via the reaction:

198 $\text{antigorite} + \text{brucite} = \text{olivine} + \text{fluid}$ (Fig. 1),

199 which consumes brucite and leaves antigorite in equilibrium with olivine, diopside, chlorite,
200 titanian clinohumite and magnetite as the peak metamorphic assemblage (Scambelluri et al.,

201 2001). Metamorphic veins within the serpentized peridotites also contain metamorphic
202 olivine and titanian clinohumite. The veins are interpreted to have channelized fluids released
203 at peak metamorphic conditions (Scambelluri et al., 1997) and their composition appears to be
204 controlled by the host rocks (Scambelluri et al., 2001). Based on an eclogitic paragenesis in
205 metagabbros, maximum P-T conditions were estimated at 2-2.5 GPa and 550-600 °C
206 (Messiga et al., 1995). Final exhumation of the Erro Tobbio peridotites occurred during the
207 late stages of Alpine collision.

208

209 **2.3. Cerro del Almirez, Betic Cordillera, Spain**

210 The chlorite harzburgites from Cerro del Almirez are ultramafic rocks that have been
211 subjected to antigorite dehydration during subduction metamorphism (Fig. 1), representing
212 one of the few field examples of high-pressure breakdown of antigorite (Trommsdorff et al.,
213 1998; Garrido et al., 2005; Padrón-Navarta et al., 2011). The three ultramafic bodies of Cerro
214 del Almirez are part of a ~400m thick and ~2km wide thrust sheet, which comprises antigorite
215 serpentinites and chlorite harzburgites. These ultramafic rocks are interlayered with
216 metapelites and marbles and together they are part of the Nevado-Filábride Complex of the
217 Betic Cordillera (Trommsdorff et al., 1998). The serpentinites are very similar to occurrences
218 of serpentized peridotites in the Penninic Zone of the Alps. Prograde Alpine subduction
219 zone metamorphism has overprinted previous stages of oceanic hydration and alteration
220 (Trommsdorff et al., 1998; Puga et al., 1999). Within the serpentinites, veins of titanian
221 clinohumite and olivine and minor boudins of rodingite occur. The veins formed at 475°C and
222 1.3 GPa due to simultaneous breakdown of clinopyroxene and brucite (López Sánchez-
223 Vizcaíno et al., 2009).

224 The predominant type of chlorite harzburgite has a spinifex-like texture consisting of
225 olivine blades and needles and elongated enstatite in a matrix of chlorite, tremolite and

226 magnetite (Trommsdorff et al., 1998; Puga et al., 1999). Olivine from the spinifex-like
227 textured rocks contain abundant multiphase inclusions containing aqueous fluid and mineral
228 phases that derive from trapping of a homogeneous fluid and precipitated minerals at P-T
229 conditions beyond the stability of antigorite (Scambelluri et al., 2001). Subordinately, a
230 medium- to coarse-grained chlorite harzburgite with granofelsic texture occurs, alternating in
231 meter- to decimeter-scale bodies with the spinifex-like textured rocks throughout the chlorite
232 harzburgite sequence (Padrón-Navarta et al., 2011). Synmetamorphic orthopyroxenite veins
233 with very coarse-grained enstatite, containing the same mineral assemblage as the chlorite
234 harzburgite with very coarse-grained enstatite, occur close to the boundary between
235 serpentinites and harzburgites (López Sánchez-Vizcaíno et al., 2005). The origin of these
236 veins, which have diffuse contacts with the host chlorite harzburgite, is not entirely clear (J.A.
237 Padrón-Navarta, personal communication). The samples analyzed in this study comprise 4
238 spinifex-textured chlorite harzburgites and 3 orthopyroxene-rich veins.

239 Thermodynamic calculations show that the serpentinites dehydrated directly to chlorite
240 harzburgite due to a temperature increase from 635 to 695°C at pressures of 1.7-2.0 GPa
241 (López Sánchez-Vizcaíno et al., 2005). Hence, the contact between serpentinites and chlorite
242 harzburgites represents the antigorite-out isograd, which represents the major dehydration
243 reaction:

244 antigorite = enstatite + olivine + chlorite + fluid (Fig. 1).

245 This deserpentinization reaction can release significant amounts of water during subduction.
246 At Cerro del Almirez, the H₂O release is limited to about 6-7 wt.% because of the stability of
247 chlorite beyond the antigorite breakdown (Trommsdorff et al., 1998). Peak metamorphic
248 conditions reached by the chlorite harzburgites are ~700 °C and 1.6-1.9 GPa (Puga et al.,
249 1999; Padrón-Navarta et al., 2010). They record the highest metamorphic grade of the sample
250 suite of this study.

251

252

253 **3. Analytical methods**

254 **3.1. Whole-rock geochemistry**

255 Fused glass discs, prepared from fine-grained whole-rock powders of the ultramafic
256 rocks, were analyzed for major elements and five trace elements (V, Cr, Ni, Zn, Sr) by X-ray
257 fluorescence analysis using a PHILIPS PW 1480 spectrometer at the Institut für
258 Geowissenschaften, Universität Kiel, Germany. The relative standard deviation is typically
259 <0.3% for SiO₂, TiO₂, Al₂O₃, Fe₂O₃^T, MnO and CaO, between 0.8 and 1.3% for MgO, Na₂O,
260 K₂O and P₂O₅ and <10% for the trace elements. Averages and uncertainties of reference
261 material analyzed during the course of this study are given in the supplementary material, and
262 long-term reproducibility based on repeat analyses of the BHVO-1 standard were presented
263 by van der Straaten et al. (2008).

264

265 **3. 2. Nitrogen concentrations and isotopic compositions**

266 Nitrogen contents and isotopic compositions were analyzed at Lehigh University
267 employing the methods described by Bebout et al. (2007) and Li et al. (2007) involving
268 transfer of extracted N (as N₂) into a Finnigan MAT 252 mass spectrometer using a Finnigan
269 Gas Bench II and a U-trap interface in which small samples of N₂ are entrained in a He
270 stream. About 250 mg of sample powder (grain size as fine as ~ 1 µm) were used and tests
271 with analyses of fine-grained powders, involving varying evacuation times and heating
272 regimens for the quartz tubes before sealing, indicate that atmospheric contamination is
273 minimal. Baseline N yields for analyses of 250 mg of fine-grained powder of extremely low-
274 N samples are at blank levels, demonstrating that there is no atmospheric N incorporated
275 beyond blank levels. Based on this testing, all quartz tubes containing samples and Cu/CuO_x
276 reagent are evacuated for ~24 hours before sealing, with intermittent heating to ~100 °C.

277 Nitrogen extraction is accomplished at 1000 °C, temperatures at which complete N extraction
278 has been demonstrated for metasedimentary rocks, basalts and ultramafic rocks (Bebout et al.,
279 2007; Busigny et al. 2005; Halama et al., 2010; Li et al., 2007; Philippot et al., 2007). All N
280 isotope compositions presented and/or discussed in this paper are reported relative to the
281 composition of atmospheric N₂ (air).

282 Yields for the gas extractions from unknowns, and thus N concentrations, are obtained
283 by measurement of the *m/z* 28 peak area and using calibrations from analyses of laboratory
284 standards. Uncertainties for N concentrations are usually <5% (Bebout et al., 2007).
285 Measured yields and isotope compositions are corrected for the total system blank, which is
286 largely due to the addition of Cu/CuO_x reagents and reproducible in both size and isotopic
287 composition. During the course of this study, measurements of the reagent blank gave δ¹⁵N =
288 -7.3±1.3‰ (n=10, 1σ) at 153±30 mV on the peak. For peridotite samples, the voltage was
289 typically between 1000 and 3000 mV. Uncertainties in δ¹⁵N are ± 0.15‰ for samples with >
290 5 μg/g N and ~0.6‰ for samples with 1-2 μg/g N. One sample with <1 μg/g N required such
291 a substantial blank correction that the resulting δ¹⁵N value is considered less reliable and thus
292 is not reported. The accuracy of the δ¹⁵N measurements was evaluated by repeat
293 measurements of two reference materials, a fuchsite (Cr-rich phengitic white mica; # 2-1-36)
294 and a blueschist (# 9150) (Bebout et al., 2007). The results (δ¹⁵N = +2.4±0.2‰ (n=10, 1σ)
295 for # 2-1-36 and 2.5±0.3‰ (n=13, 1σ) for # 9150 agree well with previous measurements
296 (Bebout, 1997; Bebout et al, 2007).

297 Previous experiments on ultramafic rocks used a slightly different technique, where
298 samples were pre-heated and degassed at 450 °C, in the presence of oxygen, in order to
299 remove organic contamination and atmospheric N (Philippot et al., 2007; Busigny et al.,
300 2005). It is conceivable that, in the case of hydrated ultramafic rocks, this procedure also
301 removes some N from the rock matrix and thereby fractionates N isotopes. The different

302 analytical protocols could explain some of the difference between our results and the work by
303 Philippot et al. (2007; see Fig. 2); however, experimental testing for partial N loss at low
304 temperatures would clearly be necessary to further evaluate this possibility. Alternatively, and
305 also quite conceivably, sample heterogeneity could be responsible for the variations in $\delta^{15}\text{N}$.

306

307

308 **4. Results**

309 Nitrogen concentrations and $\delta^{15}\text{N}$ are presented in Table 1 and Fig.2, and the major and
310 trace element contents of the bulk samples are listed in the supplementary material. Figure 3
311 shows the relationship between the N elemental and isotopic signatures with loss on ignition
312 (LOI) and frequency distribution diagrams (Figs. 4 and 5) summarize the $\delta^{15}\text{N}$ of the samples
313 and other subduction-related rocks. Overall, all ultramafic rocks investigated have N
314 concentrations that are elevated compared to the depleted MORB source mantle (0.27 ± 0.16
315 $\mu\text{g/g}$; Marty and Dauphas, 2003) and they are quite variable in $\delta^{15}\text{N}$, with an overall range of -
316 4 to +5‰ (Table 1, Fig. 2). For the massive serpentinites reflecting different degrees of
317 hydration and rehydration, there is no systematic variation of N content or $\delta^{15}\text{N}$ with rock
318 type, major element chemistry or LOI (Figs. 2 and 3).

319

320 **4. 1. Low-grade serpentinites**

321 Low-grade serpentinites from Monte Nero (samples MNS 1-4) have moderately high
322 contents of Al_2O_3 (1.9-3.4 wt.%) and CaO (0.95-2.95 wt.%; see supplementary material). The
323 variable values for LOI (5.7-9.9 wt.%) reflect different degrees of serpentinitization. The four
324 samples cover a wide range in $\delta^{15}\text{N}$ (-3.8 to +2.8‰; Fig. 2), with the lowest values
325 overlapping the depleted mantle composition (-5 ± 2 ; Marty and Dauphas, 2003) and the
326 heavier values within the range of modern marine sediments ($\delta^{15}\text{N} = -2$ to +10; Fig. 5).

327 Nitrogen concentrations of the low-grade serpentinites from Monte Nero are low (1.3-2.1
328 $\mu\text{g/g}$).

329 The low-grade serpentinites from Erro Tobbio (samples ET Cl-2 and ET Cl-3) are
330 similar in major element composition to those from Monte Nero, but are characterized by
331 slightly more positive $\delta^{15}\text{N}$ values (+3.1 to +3.5‰) and higher N concentrations (2.7-4.5
332 $\mu\text{g/g}$). Their N isotopic compositions fall into the range for modern marine sediments and
333 subduction-related metasediments ($\delta^{15}\text{N} = 0$ to +12‰; Fig. 5).

334

335 **4. 2. High-pressure serpentinites**

336 The high-pressure serpentinites from Erro Tobbio have moderate Al_2O_3 (1.5-2.9 wt.%)
337 and CaO (0.84-1.78 wt.%) contents and high LOI values (7.6-11.9 wt.%; see supplementary
338 material). The positive $\delta^{15}\text{N}$ values (+1.6 to +4.7‰) with a weighted average of +3.4‰
339 overlap with the low-grade serpentinites (Table 1, Fig. 4) and there appears to be a positive
340 correlation between [N] and $\delta^{15}\text{N}$ (Fig. 2). The high-pressure veins within the Erro Tobbio
341 serpentinites have MgO contents broadly similar to their host rocks, but $\text{Fe}_2\text{O}_3^{\text{T}}$ contents are
342 higher and Al_2O_3 ($\leq 1\text{wt.}\%$) and LOI are significantly lower. Three pairs of host HP
343 serpentinites and associated veins show a systematic difference in $\delta^{15}\text{N}$, with the veins
344 isotopically lighter by $2.2\pm 0.6\%$ (Table 1; Fig. 3). Nitrogen concentrations, however, do not
345 show a systematic difference between serpentinites and veins.

346

347 **4. 3. Chlorite harzburgites**

348 The chlorite harzburgites from Cerro del Almirez have Al_2O_3 contents (2.0-3.2 wt.%)
349 that are similar to the low-grade and high-pressure serpentinites, but their CaO contents (0.05-
350 0.07 wt.%) and LOI values (4.0-4.9 wt.%) are significantly lower, whereas SiO_2 is slightly
351 enriched (up to 45 wt.%). Nitrogen concentrations scatter between 1.7 and 4.3 $\mu\text{g/g}$ for three

352 samples, but one chlorite harzburgite is exceptionally enriched in N with 21 $\mu\text{g/g}$ (Table 1,
353 Fig. 2). The weighted average in $\delta^{15}\text{N}$ is +1.1‰, but the range is considerable (-2.4 to +2.7‰)
354 and completely overlaps with low-grade serpentinites. The Cerro del Almirez veins have
355 relatively high Al_2O_3 (3.1-4.3 wt.%) and low CaO (0.06-0.13 wt.%) contents. Nitrogen
356 concentrations (1.3-4.0 $\mu\text{g/g}$) and $\delta^{15}\text{N}$ of the veins largely overlap with the chlorite
357 harzburgites, but the veins are, on average, isotopically heavier (weighted average for $\delta^{15}\text{N}$ =
358 +3.1‰).

359

360

361 **5. Discussion**

362 **5. 1. Nitrogen in ultramafic rocks**

363 Based on studies of various igneous mantle-derived rocks and diamonds, the Earth's
364 mantle appears to be heterogeneous in its N isotopic composition and its N concentration.
365 Negative $\delta^{15}\text{N}$ values in diamonds and MORBs demonstrate that the mantle contains non-
366 atmospheric N (Cartigny et al., 1998; Marty and Zimmermann, 1999). However, it is disputed
367 whether subduction processes are the key factor for producing some of the variability
368 (Dauphas and Marty, 1999; Jia et al., 2003) or whether degassing and fractionation within the
369 mantle are the main cause for these variations (Cartigny et al., 2001b). Estimates for the N
370 concentration in the mantle range from 0.27 to 40 $\mu\text{g/g}$ (Cartigny et al., 2001a; Marty and
371 Dauphas, 2003), with peridotite xenolith data scattering at the lower end of this range (0.1-0.8
372 $\mu\text{g/g}$ N; Yokochi et al., 2009). The $\delta^{15}\text{N}$ of the depleted mantle is around -5‰ (Marty and
373 Dauphas, 2003; Cartigny et al., 2001), whereas enriched plume mantle is thought to be
374 characterized by a positive $\delta^{15}\text{N}$ value of about +3‰ reflecting incorporation of heavy N from
375 recycled subducted slabs (Marty and Dauphas, 2003).

376 Orogenic peridotites represent an important source of information regarding the
377 chemistry of the Earth's mantle. Previously analyzed serpentinitized peridotites contain 1-15
378 $\mu\text{g/g N}$ (Philippot et al., 2007; Halama et al., 2010), consistent with the data obtained in this
379 study. However, it is not clear whether the large variability in N contents observed is inherited
380 from the primary mantle rocks, or whether is due to the effects of seafloor alteration or
381 subduction-zone metamorphism. The lack of any significant correlation of N contents with
382 metamorphic grade and the large overlap in $\delta^{15}\text{N}$ values between low-grade serpentinites, HP
383 serpentinites and chlorite harzburgites suggest that the variability in N concentrations is a
384 feature from a pre-subduction or early subduction stage. Here, we consider whether this
385 variability is inherited from a heterogeneous mantle or is due to addition of sedimentary-
386 organic N during serpentinitization. Addition of N to hydrating slab ultramafic rocks could
387 conceivably occur in the outer rise region or in shallow parts of the forearc, along normal
388 faults produced during slab bending. Alternatively, N could be added to mantle wedge
389 ultramafic rocks by H_2O -rich fluids liberated during forearc devolatilization reactions.

390 Some of the low-grade serpentinites (samples MNS-2 and MNS-3 from Monte Nero)
391 overlap in $\delta^{15}\text{N}$ with what are considered typical depleted mantle N isotopic compositions.
392 Hence, they are interpreted to preserve a primary mantle signature with no significant effects
393 of serpentinitization and metamorphism. The positive $\delta^{15}\text{N}$ values of the other low-grade
394 serpentinites (samples MNS-1 and MNS-4 from Monte Nero and samples ET Cl-2 and ET Cl-
395 3 from Erro Tobbio) likely reflect N input and related N isotopic changes due to interaction
396 with serpentinitizing fluids. For those samples, a plume mantle origin can be discarded because
397 of LREE-depleted REE patterns typical for depleted mantle (Scambelluri et al., 2001) and, in
398 case of Monte Nero, depleted Sr-Nd isotopic compositions (Rampone et al., 1995) and the
399 close spatial association to peridotite samples with negative $\delta^{15}\text{N}$ values representing depleted
400 mantle.

401 The weighted average of the HP peridotites ($\delta^{15}\text{N} = +3.3\text{‰}$) and the positive $\delta^{15}\text{N}$
402 values of the chlorite harzburgites (weighted average of $\delta^{15}\text{N} = +1.1\text{‰}$) overlap with
403 subduction-related metasediments and are also very similar to mafic eclogites and blueschists
404 (Fig. 4). The positive $\delta^{15}\text{N}$ values of HP peridotites from Erro Tobbio are unlikely to reflect
405 primary mantle, since the REE patterns indicate a depleted mantle source (Scambelluri et al.,
406 2001) for which negative $\delta^{15}\text{N}$ values are expected. In agreement with observations based on
407 noble gas data (Kendrick et al., 2011) and halogen concentrations (John et al., 2011), they are
408 interpreted to reflect addition of N from organic-sedimentary sources via serpentinizing fluids
409 before or during the early stages of subduction. Moreover, the weak positive correlation
410 between [N] and $\delta^{15}\text{N}$ in the Erro Tobbio samples indicates that addition of N is coupled to an
411 increase in $\delta^{15}\text{N}$. The interpretation of N input by serpentinizing fluids also applies to the
412 positive $\delta^{15}\text{N}$ values of HP peridotites from Ecuador, which represent oceanic lithospheric
413 mantle with a relative LREE depletion, although some metasomatized eclogites from this
414 locality have also been affected by a high-pressure fluid-mediated overprint (John et al., 2010;
415 Halama et al., 2010; 2011).

416 In contrast to the LREE-depleted serpentinites, chondrite-normalized REE patterns of
417 the Cerro del Almiraz chlorite harzburgites are moderately U-shaped with only a slight
418 depletion of LREE relative to HREE (Garrido et al., 2005). These harzburgites and associated
419 serpentinites with relatively flat REE patterns (Garrido et al., 2005) represent mantle of sub-
420 continental lithospheric origin (Trommsdorff et al. 1998, Gómez-Pugnaire et al. 2000), but it
421 is difficult to distinguish between a primary positive $\delta^{15}\text{N}$ signal, potentially from a plume
422 mantle source, or derivation of the positive $\delta^{15}\text{N}$ value due to pre-subduction hydration. The
423 grossly different N concentrations in the Cerro del Almiraz samples, however, are more
424 consistent with different degrees of N addition. Assuming that the peridotite xenoliths
425 analyzed for N (Yokochi et al., 2009) represent the pristine mantle with some heterogeneity in

426 N concentrations (0.1-0.8 $\mu\text{g/g N}$), the large variability in N contents in the chlorite
427 harzburgites (1.7–20.6 $\mu\text{g/g N}$) is more consistent with variable interaction with
428 serpentinizing fluids than inheritance from a heterogeneous mantle source. A comparable
429 conclusion was reached for high-pressure metamorphosed basaltic rocks, which largely reflect
430 the N contents and $\delta^{15}\text{N}$ values of AOC (Halama et al., 2010). Importantly, the majority of the
431 ultramafic mantle rocks that have experienced HP subduction have positive $\delta^{15}\text{N}$ values, so
432 that the preferred interpretation for this observation is adding N during serpentinization and
433 hydration on the seafloor or during the early stages of subduction. The available data are
434 consistent with addition of N with organic-sedimentary origin during exposure of the
435 ultramafic rocks on the seafloor, during slab bending and related circulation of fluids through
436 the oceanic mantle (Ranero et al., 2003; Halama et al., 2010; John et al., 2011) or in the fore-
437 arc mantle wedge. Based on the available evidence, it appears unlikely that the positive $\delta^{15}\text{N}$
438 values represent a primary mantle feature.

439

440 **5. 2. Behavior of nitrogen during dehydration**

441 Comparisons between low-grade and high-grade rocks and between host rocks and
442 veins can provide information regarding the behavior of N and potential isotopic fractionation
443 during dehydration. Increasing $\delta^{15}\text{N}$ with increasing metamorphic grade in some
444 metasedimentary suites was interpreted to reflect dehydration of N-bearing silicates at the
445 higher grades (e.g., Bebout and Fogel, 1992; Mingram and Bräuer, 2001). However, other
446 metasedimentary suites with large ranges in metamorphic grade show relatively little shift in
447 N concentration and $\delta^{15}\text{N}$ with increasing grade. Busigny et al. (2003) suggested that the
448 apparent lack of N loss, and related isotopic shift, in a Western Alps metasedimentary
449 traverse reflects subduction of the rocks along very low temperature prograde P-T paths,
450 resulting in little devolatilization. Pitcairn et al. (2005) noted little systematic change in N

451 concentration and $\delta^{15}\text{N}$ with increasing grade in the Otago and Alpine Schists, New Zealand,
452 and suggested that some subtle N isotope variation in these rocks could reflect maturation of
453 kerogen (i.e. the transformation of kerogen-bound C-H-N compounds to NH_4^+ structurally
454 sited in K-bearing minerals) or multiple metamorphic episodes rather than dehydration of
455 silicates. Systematic trends in [N] and $\delta^{15}\text{N}$ are absent not only in metabasalts and
456 metagabbros investigated by Halama et al. (2010) and Busigny et al. (2011), but also in the
457 ultramafic rocks of this study. The lack of evidence for loss of N in these ultramafic rocks
458 warrants further discussion.

459 For metasedimentary rocks, it is well established that N is largely fixed as NH_4^+ in
460 micas and hence the stability of mica strongly influences the release of N during subduction.
461 Determining the mineral residency of N in ultramafic rocks is more difficult because of the
462 lack of potassic phases, which commonly serve as hosts for N (because of the similarity of K^+
463 and NH_4^+ in charge and ionic radius), and because N occurs in these rocks at only trace
464 concentrations. It appears unlikely that N is hosted in the mineral lattice of serpentine
465 minerals or chlorite, based on the crystal chemistry of these phases. However, tremolite could
466 in some cases contain some N, and the tremolite in some Almirez samples contains up to 0.53
467 wt. % K_2O (J. A. Padrón-Navarta, personal communication). Another possibility is that N
468 could reside in sealed voids and cracks produced during serpentinization (Philippot et al.,
469 2007), as has been proposed for NaCl derived from seawater (Sharp and Barnes, 2004). A
470 possibility that was advocated for noble gas retention in HP ultramafic rocks is the leakage of
471 H^+ out of fluid inclusions by diffusion and the retention of heavier solutes in the desiccated
472 inclusions (Kendrick et al., 2011). If that is the case for N in chlorite harzburgites, the N
473 budget would represent a mixture of rock residue and incorporated fluid. A variable N
474 contribution by fluid inclusions is consistent with the common occurrence of inclusions in the
475 chlorite harzburgites (Scambelluri et al., 2001) and the highly variable N contents (Table 1).

476 Three pairs of host HP serpentinites and associated veins from Erro Tobbio show a
477 systematic difference in $\delta^{15}\text{N}$, with the veins isotopically lighter by $2.2\pm 0.6\text{‰}$ (Fig. 3), in
478 agreement with residual N in the host rock becoming heavier due to preferential release of ^{14}N
479 by dehydration reactions (Haendel et al., 1986; Bebout and Fogel, 1992). Based on the
480 fractionation factors for $\text{N}_2\text{-NH}_4^+$ exchange given by Hanschmann (1981) the calculated
481 $\Delta^{15}\text{N}_{\text{fluid-rock}}$ ($\Delta^{15}\text{N} = \delta^{15}\text{N}_{\text{fluid}} - \delta^{15}\text{N}_{\text{rock}}$) would be $\sim -2.2\text{‰}$ for peak temperature conditions at
482 Erro Tobbio. This concordance between calculated and measured N isotope fractionation
483 supports an origin of these veins by dehydration, assuming that the veins reflect the fluid N
484 isotope composition. In contrast, the orthopyroxene-rich veins from Cerro del Almirez are
485 slightly heavier than the associated chlorite harzburgites. This lack of a systematic change in
486 $\delta^{15}\text{N}$ between host peridotites and veins (Fig. 4) with degree of water uptake and release does
487 not indicate significant ($>5\text{‰}$) N isotope fractionation during dehydration. However, nitrogen
488 isotopic changes due to dehydration may have been overprinted by the influx of N from
489 metasediments during exhumation, as the ultramafic suites are associated with or enclosed
490 within metasedimentary rocks. Such an influx of an exhumation-related, metasediment-
491 derived fluid appears highly unlikely because field, petrographic and independent
492 geochemical evidence for interaction with the respective metasedimentary units is lacking.
493 Alternatively, the non-systematic relationship of the orthopyroxenite veins and their host
494 rocks at Cerro del Almirez could be unrelated to dehydration processes, in which case no
495 dehydration-related N isotope fractionation would be expected. To conclude, if the observed
496 N isotope fractionation between veins and host rocks at Erro Tobbio is due to dehydration
497 reactions, its effect is still small ($< 3\text{‰}$) relative to the variability in $\delta^{15}\text{N}$ observed on outcrop
498 scale.

499

500 **5. 3. The isotopic composition of nitrogen in the subducted slab**

501 The determination of $\delta^{15}\text{N}$ values in ultramafic rocks with both a pre-subduction
502 signature and a HP subduction signature (Fig. 4) allows an assessment of the role of N stored
503 in ultramafic rocks and how the ultramafic rocks affect the total N budget in the subducting
504 slab. Although there is a significant variability in N concentrations, $\delta^{15}\text{N}$ and thickness of the
505 lithologies depending on the subduction zone investigated, a global approach is justified
506 because there is currently no present-day subduction zone where all lithologies have been
507 investigated for [N] and $\delta^{15}\text{N}$, and subduction-related metamorphosed rocks where N data are
508 available for all lithologies (Halama et al., 2010) only provide information regarding paleo-
509 subduction. A compilation of [N] and $\delta^{15}\text{N}$ data for marine sediments, metasediments,
510 oceanic lithosphere and metamorphosed oceanic lithosphere (Table 2) reveals that nearly all
511 lithologies have positive $\delta^{15}\text{N}$ values. Regarding the average values listed, key features of a
512 comparison between unmetamorphosed and metamorphosed rocks are discussed in the
513 following paragraphs.

514 For the sediments/metasediments, metamorphosed rocks tend to have lower [N] and
515 lower $\delta^{15}\text{N}$ values (Table 2, Fig. 5). Two explanations for this observation have been put
516 forward (Sadofsky and Bebout, 2003; 2004). First, most of the metasedimentary rocks
517 investigated are derived from trench sediments and accretionary prisms that are characterized
518 by enhanced contributions of terrestrial organic matter with a relatively low $\delta^{15}\text{N}$ (+1.8;
519 Minoura et al., 1997) compared to the marine component with $\delta^{15}\text{N} \sim +8$. Hence, the
520 difference in $\delta^{15}\text{N}$ between unmetamorphosed and metamorphosed sediments is likely
521 attributable to greater proportions of terrestrial organic matter in the sedimentary protoliths
522 (Sadofsky and Bebout, 2004). A second explanation is the loss of a high- $\delta^{15}\text{N}$ component,
523 perhaps as nitrate (NO_3^-), during diagenesis. This possibility is supported by experimental
524 studies, which suggest that a negative shift in $\delta^{15}\text{N}$ by about 1-3‰ may be common in
525 oceanic sediments (Lehmann et al., 2002).

526 Nitrogen concentrations of the oceanic lithosphere upper mantle section are one to two
527 orders of magnitude lower than those of (meta)sediments, and they are broadly similar for the
528 unmetamorphosed rocks and their metamorphosed equivalents. Nitrogen isotopic
529 compositions are quite variable, but negative $\delta^{15}\text{N}$ values are conspicuously lacking for
530 samples of metamorphosed oceanic lithosphere (Table 2, Fig. 5). Because the depleted mantle
531 and igneous rocks derived from the depleted mantle are associated with a negative $\delta^{15}\text{N}$
532 signature of $\sim 5\text{‰}$ (Cartigny et al., 1998; Marty and Dauphas, 2003), this feature, observed for
533 a variety of samples from different localities, suggests uptake of N from a sedimentary-
534 organic source. Incorporation of sedimentary-organic N in serpentinized ultramafic rocks is
535 expected to occur in oceanic slab mantle, at transform or bending-related faults, and in the
536 forearc mantle wedge, for the latter setting resulting from infiltration by H_2O -rich fluids
537 emanating from subducting slabs. There are very few N data available for subduction-related
538 ultramafic rocks (Philippot et al., 2007; this study), and the exact setting (slab mantle or
539 mantle wedge) is somewhat uncertain for at least the Erro Tobbio rocks. Given the
540 uncertainties, we suggest that it is valid, as a first pass, to consider our data as representing
541 plausible compositions of subducting slab mantle that could, at greater depths, dehydrate and
542 release its N into the subarc mantle wedge or retain this N to greater depths in the mantle.
543 Additions of sedimentary-organic N to ultramafic rocks in either setting would in general tend
544 to produce $\delta^{15}\text{N}$ values higher than those of the upper, depleted mantle (near -5‰) and likely
545 $>0\text{‰}$.

546 Estimates of the global contributions of the three major lithologies in a subducting slab
547 – marine sediment, igneous oceanic crust and serpentinized mantle – show that the amount of
548 N stored in serpentinized ultramafic rocks is relatively small (Fig. 6). An average thickness of
549 500 m serpentinized mantle would carry into the subduction zone about two orders of
550 magnitude less N than a sediment section of similar thickness. For the igneous oceanic crust,
551 the degree of alteration is important as AOC tends to be enriched in N compared to fresh

552 MORB (Busigny et al., 2005; Li et al., 2007). Thus, a completely altered section of crust may
553 transport an amount of N comparable to that of the sedimentary rocks into the subduction
554 zone (Table 3).

555 For a typical section of the incoming plate with 500 m of sediment, 6 km of igneous
556 crust and 500 m of serpentinized mantle, contributions of 86%, 13% and 1% were calculated
557 (Fig. 6), resulting in an average $\delta^{15}\text{N}$ value of +4.9‰. The 86% fraction delivered by
558 sediments is similar to the sedimentary N contribution to the Central American Arc (~80% of
559 subducted N; Li and Bebout, 2005), whereas a considerably smaller sedimentary contribution
560 of ~33% of the total subducted N was estimated for the Izu-Bonin-Mariana arc system
561 (Mitchell et al., 2010). The great variability from margin to margin in terms of diverse
562 thicknesses of the lithological units and significant variability in N contents for different
563 sediment types allows for large differences in these estimates, and a more complete data base
564 is clearly desirable. One critical factor in comparing the values for different trenches with
565 global values is the amount of sediment scraped off during the early stages of subduction and
566 incorporated into an accretionary prism. If, in the model slab section, the thickness of
567 subducted sediment is reduced by a factor of 5 (case B in Table 3), its contribution would be
568 reduced to 55% and the total slab $\delta^{15}\text{N}$ would be +2.8‰. If, on the other hand, a greater depth
569 of serpentinization (10 km; case C in Table 3) is taken into account (Ranero et al., 2003), the
570 contribution of ultramafic mantle rocks to the overall N budget increases to 12% and results
571 in a bulk slab $\delta^{15}\text{N}$ values of +4.5‰ (Fig. 6). For the ultramafic mantle rocks, the key point is
572 that the amount of serpentinization is an important parameter regarding the overall
573 contribution of these rocks to the subduction volatiles budgets. As argued earlier in the text,
574 the N elemental and isotopic signature of serpentinized ultramafic rocks in slab mantle and
575 forearc mantle is likely to be similar, but the amount of serpentinization is largely unknown,
576 in particular for the hydrated wedge mantle. By assuming differing amounts of serpentinized
577 slab mantle rock in the calculations and evaluating the effect on the N flux, scenarios with or

578 without down-dragged forearc wedge mantle are accounted for. Despite significant
579 uncertainties associated with the calculations, the overall picture emerging, based on presently
580 available data, is that the globally subducted N has a positive $\delta^{15}\text{N}$ value of approximately
581 $+4\pm 1\%$.

582 By combining the thicknesses of the different lithological units of the incoming slab
583 with N data from metamorphosed rocks, a metamorphosed equivalent of a typical subducting
584 plate section is obtained. The calculated bulk $\delta^{15}\text{N}$ of the metamorphosed slab is $+3.2\%$, a
585 decrease of 1.7% compared to the unmetamorphosed slab entering the subduction zone,
586 largely reflecting the effect of decreasing $\delta^{15}\text{N}$ values in metasediments compared with their
587 unmetamorphosed protoliths. The metamorphosed crust and mantle parts have a more
588 significant influence on this value than in the unmetamorphosed case, but it is still the $\delta^{15}\text{N}$ of
589 the metasediments that exerts the most prominent influence. However, a reduced sediment
590 thickness of 100 m in the metamorphosed slab would result in a bulk slab $\delta^{15}\text{N}$ value of
591 $+3.9\%$, dominated by the contribution of metamorphosed oceanic crust (55%). Assuming that
592 the metamorphosed slab is representative for the residual N after dehydration, the calculations
593 for the N budget ($\delta^{15}\text{N} = 3.2\text{-}3.9\%$) can be compared to results for the Izu-Bonin-Mariana
594 arc, where the residual N subducted into the mantle was estimated at $\delta^{15}\text{N} = -1.9\%$, based on
595 estimates of the relative contribution of sediment and AOC to the arc volcanic output
596 (Mitchell et al., 2010). This difference is the result of a relatively small sedimentary N
597 contribution to the total subducted N budget at the Izu-Bonin-Mariana arc and relatively light
598 N isotopic compositions of the AOC in front of the Izu-Bonin-Mariana trench compared to
599 other sites (see Table 2).

600

601 5. 4. Implications for global nitrogen recycling

602 The N isotope composition of the residual slab is important for two aspects of global N
603 cycling. First, it is crucial to the interpretation that positive $\delta^{15}\text{N}$ values in plume-related
604 igneous rocks were derived from mantle sources that contain recycled material (Tolstikhin
605 and Marty, 1998; Marty and Dauphas, 2003; Fischer et al., 2005). Second, models that
606 attempt to explain the N isotopic imbalance between the Earth's external and internal
607 reservoirs require that N delivered into the mantle is enriched in ^{15}N (Cartigny et al., 1998;
608 Javoy, 1997, 1998; Tolstikhin and Marty, 1998).

609 Igneous rocks that are sourced from the deep mantle are characterized by positive $\delta^{15}\text{N}$
610 values. For instance, ultrapotassic rocks from India show a range in $\delta^{15}\text{N}$ from +1.6 to +8.7
611 (Jia et al., 2003), and ultramafic rocks and carbonatites from the Kola Peninsula have $\delta^{15}\text{N}$ of
612 -0.2 to +6.5 (Dauphas and Marty, 2003). Both suites show no evidence of crustal
613 contamination, so that their N isotopic composition was interpreted to reflect the recycling of
614 crustal material into the deep mantle and incorporation of this isotopic signature in the mantle
615 melts. The positive $\delta^{15}\text{N}$ values determined for individual lithological components of the
616 metamorphosed slab and for the bulk slab (Table 3) shows that at least up to depths of about
617 70 km, subducted components preserve a positive $\delta^{15}\text{N}$ signature. If this signature is
618 representative of subducted material that enters the deep mantle beyond sub-arc depths, it
619 may well provide a source of heavy N in plume-related rocks.

620 Since formation of the Earth, N had to be recycled into the mantle in significant
621 amounts to drive the mantle's N isotopic composition from an initial $\delta^{15}\text{N}$ value of -30‰ to
622 the present-day $\delta^{15}\text{N}$ value of -5‰ (Javoy, 1997; Tolstikhin and Marty, 1998). Models of
623 volatile recycling show that significant trapping on N by the mantle during the Earth's history
624 must have occurred (Javoy, 1997). Accumulation of N in the mantle could have been aided by
625 the presence of osbornite (TiN) as stable mantle nitride (Dobrzhinetskaya et al., 2009) or by
626 the formation of high-pressure K-phases, which are expected to be able to incorporate large

627 amounts of NH_4^+ into their structures, thus providing a means for N transport into the deep
628 mantle (Watenpuhl et al., 2010). The N isotopic evolution of the mantle requires subduction
629 of an isotopically heavy component, in agreement with the calculated $\delta^{15}\text{N}$ of the bulk
630 metamorphosed slab. Thus despite significant local variations in the $\delta^{15}\text{N}$ values of subducted
631 material (e.g. Mitchell et al., 2010), a globalization of the available data points to a
632 positive $\delta^{15}\text{N}$ of material that is subducted into the deep mantle.

633 The estimates of the total flux of subducted N (Table 3) for a typical slab section are in
634 good agreement for the pre-subduction (3.3×10^{10} mol/year) and the metamorphosed ($3.9 \times$
635 10^{10} mol/year) slab. These values are also close to the 4.5×10^{10} mol/year estimate from
636 Hilton et al. (2002). The individual flux estimates for the sediment and the igneous crustal
637 sections of the slab are also similar to those of Busigny et al. (2011). These fluxes of
638 subducted N are larger than the amount of excess (non-atmospheric) N_2 emitted from arc
639 volcanoes, implying that a significant amount of N may not reach the zones of arc magma
640 generation and/or is retained in the deeper mantle (Hilton et al., 2002). The retention of N in
641 subducted oceanic crust (Busigny et al., 2011; Halama et al., 2010) and in serpentinized
642 peridotites (this study) up to depths of about 70 km suggests that at least some N reaches the
643 deep mantle, where it may later be mobilized in mantle plumes.

644

645

646 **6. Conclusions**

647 The investigation of serpentinized peridotites, reflecting different stages of subduction
648 zone metamorphism, and the integration of these data with those from sedimentary and mafic
649 igneous rocks, are summarized in the following conclusions:

650 1. Low-grade serpentinized peridotites that formed during early stages of subduction have
651 variable $\delta^{15}\text{N}$ values. At the lower end, $\delta^{15}\text{N}$ values are close to the composition of the

652 depleted mantle (-5‰), whereas the isotopically heavier values overlap with those typical of
653 modern marine sediments as well as metamorphosed sedimentary rocks. This suggests an
654 addition of organic-sedimentary N to the peridotites, incorporated via serpentinization during
655 bending-related faulting of the slab and/or via metasomatic additions during hydration in the
656 forearc mantle wedge.

657 2. Nitrogen is retained in HP peridotites down to depths of at least 60-70 km, and there is
658 apparently no significant loss of N due to dehydration. The $\delta^{15}\text{N}$ of N subducted in
659 serpentinized ultramafic rocks to sub-arc depths, and possibly beyond, is about +1 to +4‰.
660 This N isotopic signature is interpreted to derive from interaction of ultramafic rocks with
661 serpentinizing fluids, which carry a sedimentary N isotope signature, before and/or in the
662 early stages of subduction. This sedimentary signature is largely preserved during prograde
663 dehydration of the slab. Hence, the N system provides a great example of how serpentinite
664 and sediment-derived components can mix during the subduction cycle.

665 3. A systematic decrease of $\delta^{15}\text{N}$ values is observed in veins from the Erro Tobbio peridotite
666 body compared to their host rocks, suggesting equilibrium N isotope fractionation during
667 fluid release. However, this fractionation is small relative to inherited inhomogeneities in the
668 N isotopic composition due to variable degrees of serpentinization by fluids.

669 4. The contribution of N stored in serpentinized ultramafic rocks to the budget of subducting
670 N is small (1-12%) compared to the amount of N in sediments and altered oceanic crust.

671 5. Based on the combined data for an unmetamorphosed and a high-pressure metamorphosed
672 typical slab section, the isotopic composition of subducted N can be estimated at $+4\pm 1\%$.
673 This positive $\delta^{15}\text{N}$ value is in agreement with models for the evolution of volatiles on Earth
674 and with the concept of recycling of subducted N in mantle plumes.

675

676

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684

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919 **Figure captions:**

920 Fig. 1: Pressure-temperature diagram showing the metamorphic evolution of oceanic mantle
921 during subduction and some important dehydration reactions (modified from Scambelluri
922 et al., 2004 and Padrón-Navarta et al., 2010). The arrow delineates the transition from
923 oceanic serpentinites at low grades via high-pressure serpentinites to metamorphic chlorite
924 peridotites at elevated P-T conditions.

925 Fig. 2: Plot of $\delta^{15}\text{N}_{\text{air}}$ values and N concentrations in ultramafic rocks. The field for the
926 depleted mantle is from Marty and Dauphas (2003). Arrows indicate data points that plot
927 outside the diagram limits. Abbreviations: LG serp. = low-grade serpentinite, HP serp. =
928 high-pressure serpentinite, chl. hzbg. = chlorite harzburgite. Data for Raspas (Ecuador) and
929 Cabo Ortegal (Spain) serpentinites from Halama et al. (2010). Data from Philippot et al.
930 (2007) for peridotites from the South-West Indian Ridge (SWIR) and for peridotites and
931 serpentinites from Erro Tobbio (ET-P07) are shown for comparison.

932 Fig. 3: Nitrogen concentrations and isotopic compositions of ultramafic rocks plotted against
933 loss on ignition (LOI) as a measure of dehydration (symbols as in Fig. 2). The arrow
934 indicates a data point that plots outside the diagram limits. Note that the chlorite
935 harzburgites have consistently lower LOI values, but [N] and $\delta^{15}\text{N}_{\text{air}}$ are indistinguishable
936 from high-pressure serpentinites. Dashed lines connect host serpentinite – vein pairs from
937 Erro Tobbio.

938 Fig. 4: Frequency distribution diagrams of $\delta^{15}\text{N}_{\text{air}}$ values for low-grade serpentinites, high-
939 pressure peridotites and high-pressure ultramafic veins. Data for HP serpentinites include
940 analyses from the Raspas Complex (n=3) and from Cabo Ortegal (n=2) by Halama et al.
941 (2010). DM = Depleted MORB source mantle from Marty and Dauphas (2003). Note the
942 predominance of positive $\delta^{15}\text{N}_{\text{air}}$ values and the overlap between HP serpentinites, chlorite
943 harzburgites and HP veins.

944 Fig. 5: Frequency distribution diagrams of $\delta^{15}\text{N}_{\text{air}}$ values for oceanic rocks (marine sediments
945 and basaltic oceanic crust) and their respective subduction zone metamorphosed
946 equivalents (metasediments and eclogites/blueschists representing metamorphosed oceanic
947 crust). For data sources, see Table 2.

948 Fig. 6: Summary of the N budget calculations (Table 3) for the incoming plate consisting of
949 marine sediments, igneous crust and serpentinized ultramafic rocks. Numbers in the pie
950 diagrams give the contributions (in %) of the lithological units to the total N budget in the
951 slab. Model slab sections used are depicted below.

952

953

Fig. 1

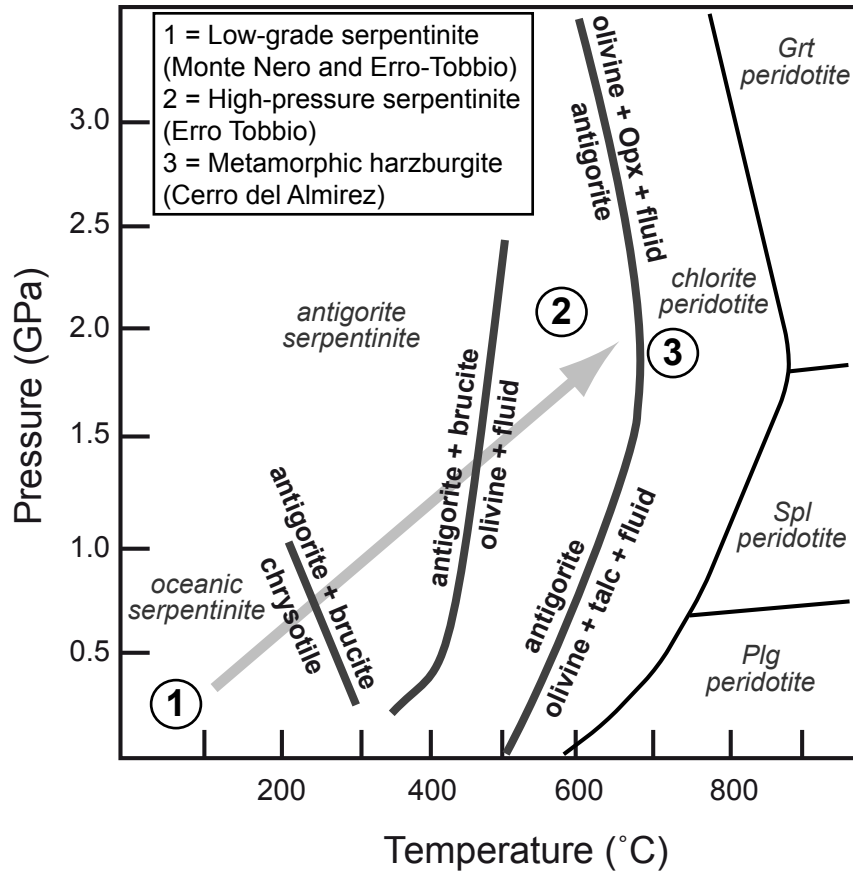


Fig. 2

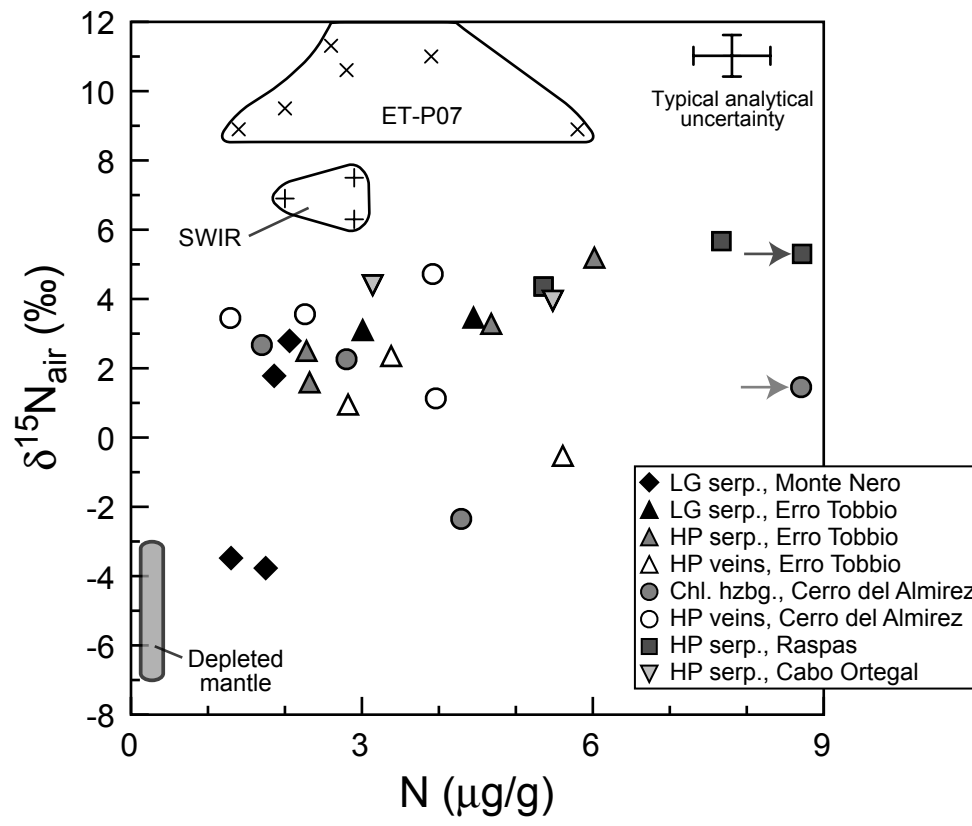


Fig. 3

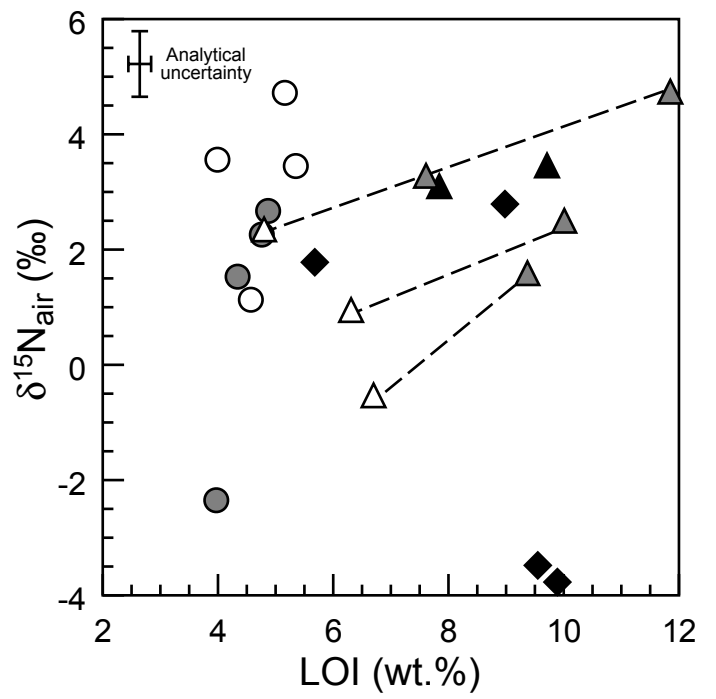
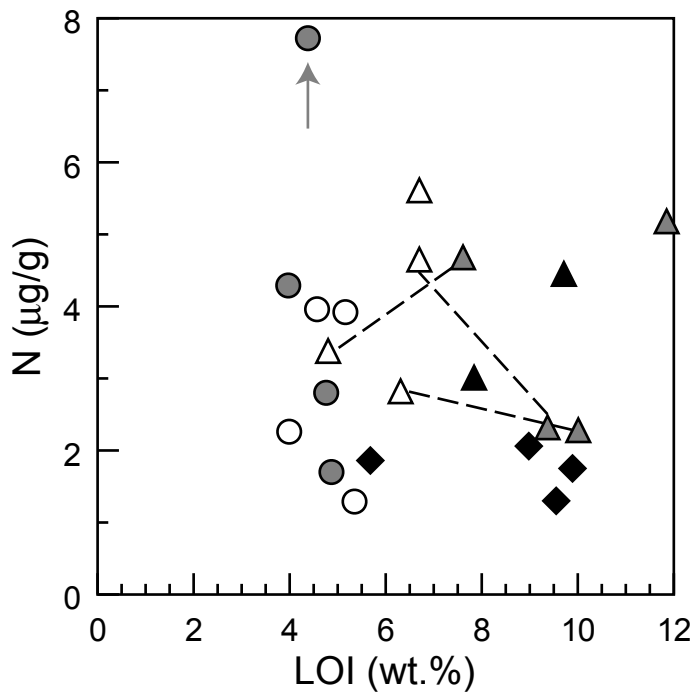


Fig. 4

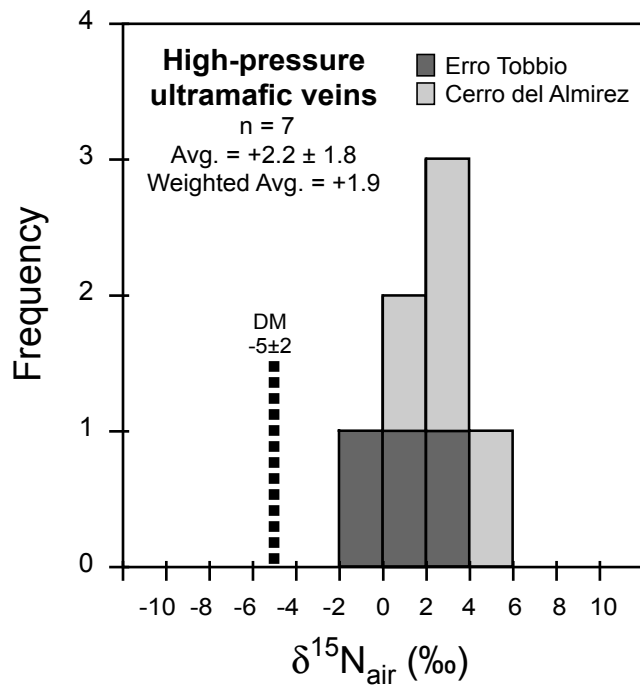
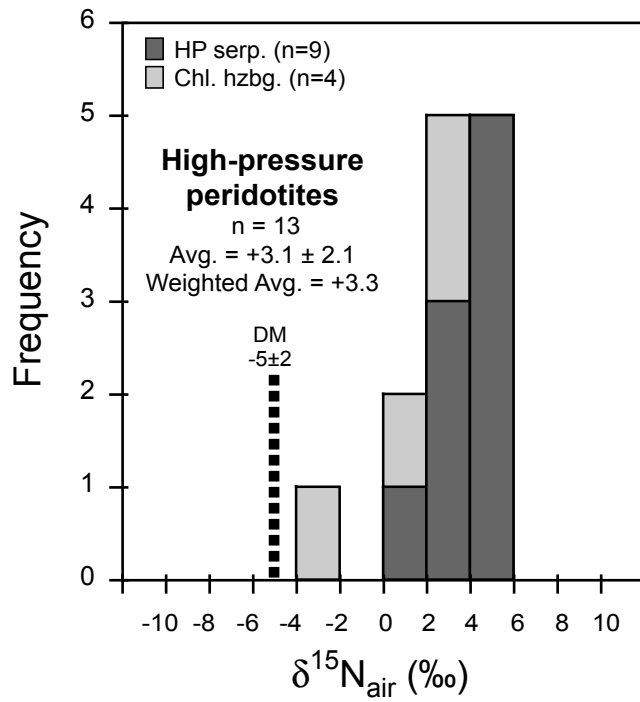
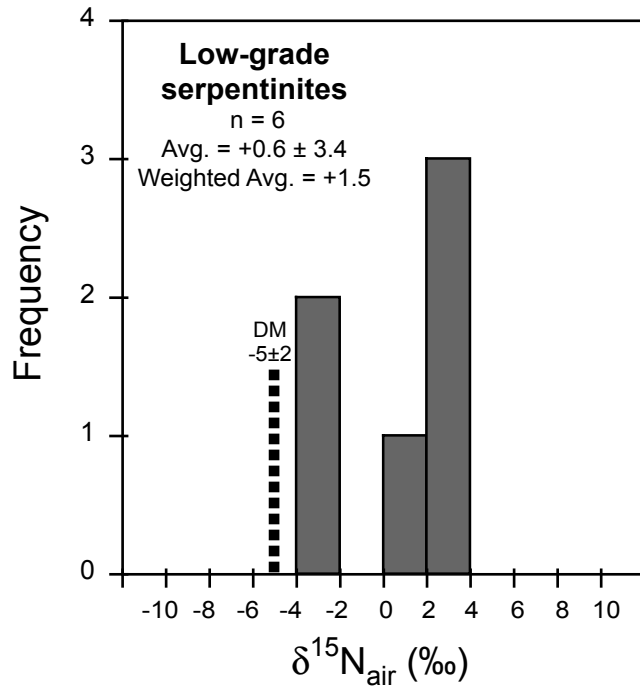


Fig. 5

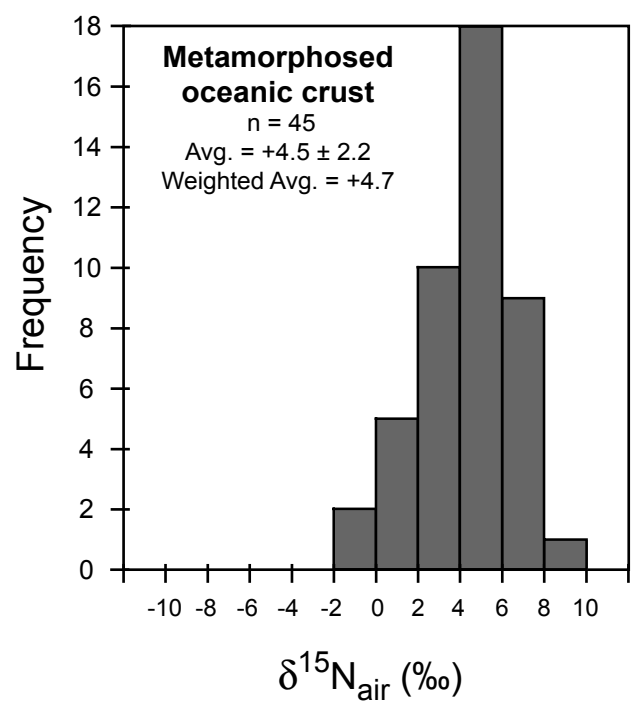
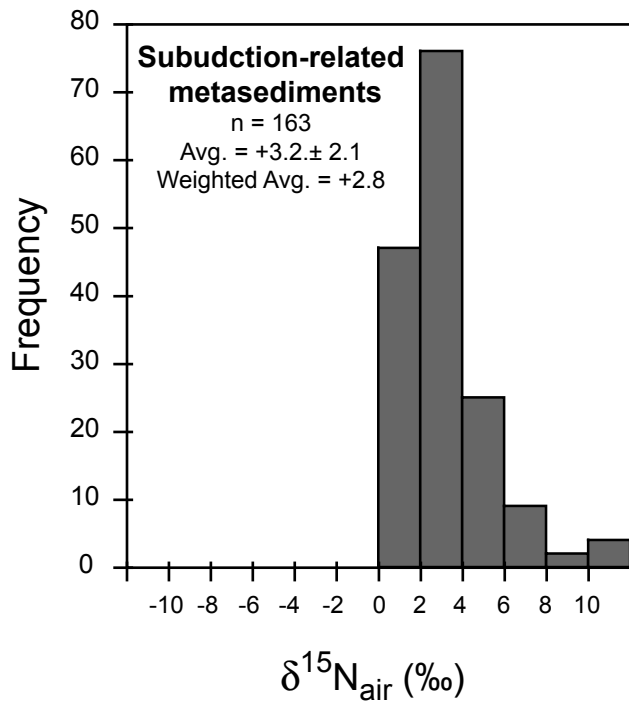
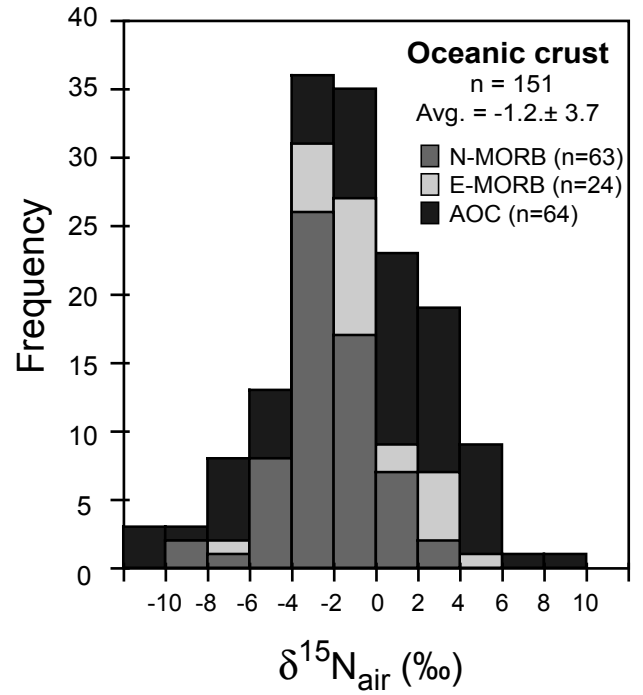
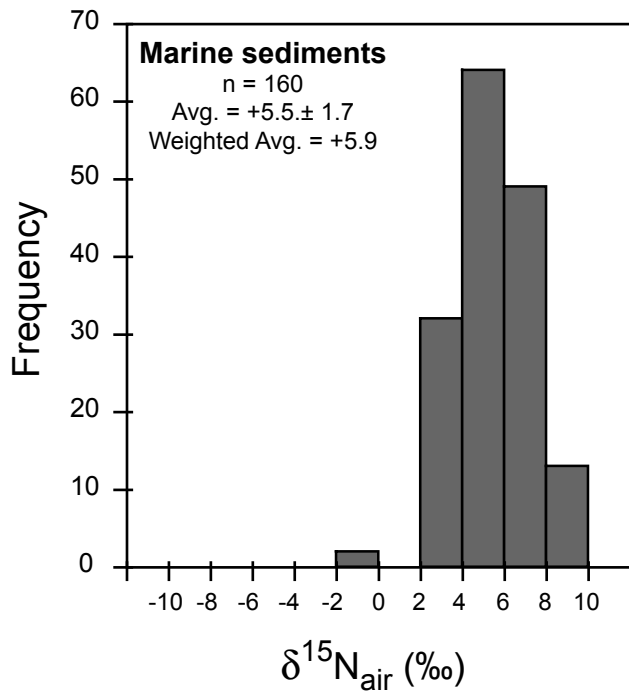


Table 1: Nitrogen concentrations and isotope compositions of ultramafic rocks

Sample #	Location	Rock type	Analysis #	[N] ($\mu\text{g/g}$)	$\delta^{15}\text{N}_{\text{air}}$ (‰)
MNS-1	Monte Nero	Low-grade serpentinite	1	2.06	2.79
MNS-2	Monte Nero	Low-grade serpentinite	1	1.75	-3.77
MNS-3	Monte Nero	Low-grade serpentinite	1	1.30	-3.48
MNS-4	Monte Nero	Low-grade serpentinite	1	1.86	1.78
ET CI-2	Erro Tobbio	Low-grade serpentinite	1	3.01	3.33
			2	2.45	2.87
			AVG	2.73	3.10
ET CI-3	Erro Tobbio	Low-grade serpentinite	1	4.45	3.46
Weighted average (n=6) low-grade serpentinites					1.5
ET CI-4-1b-I	Erro Tobbio	HP serpentinite	1	6.02	5.19
			2	4.33	4.28
			AVG	5.18	4.74
ET CI-7-1b-I	Erro Tobbio	HP serpentinite	1	2.28	2.50
ET CI-7-4-I	Erro Tobbio	HP serpentinite	1	4.68	3.28
ET CI-7-6-I	Erro Tobbio	HP serpentinite	1	0.54	
ET CI-7-6-II	Erro Tobbio	HP serpentinite	1	2.32	1.59
Weighted average (n=4) HP serpentinites (Erro Tobbio)					3.4
ET CI-4-1b-v	Erro Tobbio	HP vein	1	3.38	2.35
ET CI-7-1b-v	Erro Tobbio	HP vein	1	2.82	0.95
ET CI-7-6-v	Erro Tobbio	HP vein	1	5.61	-0.53
Weighted average (n=3) HP veins (Erro Tobbio)					0.6
ALM-1	Almirez	Chlorite harzburgite	1	4.29	-2.35
ALM-6	Almirez	Chlorite harzburgite	1	1.70	2.67
ALM-8	Almirez	Chlorite harzburgite	1	2.80	2.26
ALM-95-64	Almirez	Chlorite harzburgite	1	20.3	1.58
			2	20.9	1.48
			AVG	20.6	1.53
Weighted average (n=4) chlorite harzburgites (Almirez)					1.1
ALM-11	Almirez	HP vein	1	3.92	4.72
ALM-11v	Almirez	HP vein	1	1.29	3.45
ALM-13v	Almirez	HP vein	1	3.96	1.13
ALM-13/3v	Almirez	HP vein	1	2.26	3.56
Weighted average (n=4) HP veins (Almirez)					3.1

Table 2: Compilation of nitrogen concentrations and $\delta^{15}\text{N}$ data of slab lithologies and their metamorphosed equivalents

	n	AVG [N] µg/g	STDEV [N] µg/g	Median [N] µg/g	AVG $\delta^{15}\text{N}_{\text{air}}$ ‰	STDEV $\delta^{15}\text{N}_{\text{air}}$ ‰	Weighted AVG $\delta^{15}\text{N}_{\text{air}}$ ‰	Reference
Marine sediments								
Northwest Pacific, Izu-Bonin arc	36	286	142	312	4.7	1.7	5.0	Sadofsky & Bebout 2004
East Pacific, west off Costa Rica	65	771	682	699	5.5	1.5	6.2	Li & Bebout 2005
Northeast Pacific	55				6.1	1.8		Peters et al. 1978
Unmetamorphosed sediments, Western Alps	4	416	251	338	3.9	0.7	4.0	Busigny et al. 2003
Subduction-related metasediments								
Western Alps, Schistes Lustrés	12	643	545	485	3.5	0.7	3.4	Busigny et al. 2003
Western Baja Terrane	5	390	183	305	1.8	1.0	2.0	Sadofsky & Bebout 2003
Franciscan Complex	27	420	283	385	1.7	0.8	1.9	Sadofsky & Bebout 2003
Franciscan Complex	44	405	298	325	2.5	1.2	2.3	Bebout & Fogel 1992
Raspas Complex, Ecuador	3	123	98	143	3.8	0.8	4.2	Halama et al. 2010
Erzgebirge, European Variscan Belt	58	243	204	195	4.5	2.6	3.6	Mingram & Bräuer 2001
Otago and Alpine Schist, New Zealand	15	296	136	369	3.5	1.3	3.7	Pitcairn et al. 2005
Oceanic lithosphere								
N-MORB	63				-2.3	2.3		MZ1999, MH1997, C2001
E-MORB (includes T- and P-MORB)	24				-0.4	2.6		MZ1999, MH1997, C2001
AOC, Site 1256, Pacific	15	2.8	0.8	3.0	3.9	1.2	3.9	Busigny et al., 2005
AOC, Site 801	26	6.9	5.4	4.3	-2.5	4.0	-0.7	Li et al., 2007
AOC, Site 1149	9	2.0	0.5	2.1	-5.2	3.1	-5.0	Li et al., 2007
AOC, North Atlantic	5	11.4	2.5	11.9	2.5	5.2	2.9	Li et al., 2007
AOC, Philippine Sea	2	9.1	3.7	9.1	3.6	0.4	3.6	Li et al., 2007
AOC, Antarctic	2	4.0	1.0	4.0	2.4	2.6	2.7	Li et al., 2007
Low-grade serpentinites	6	2.4	1.1	2.0	0.6	3.4	1.5	This study
Metamorphosed oceanic lithosphere								
Undeformed and low-strain metagabbros	8	9.4	8.3	6.4	5.0	2.3	3.8	Busigny et al., 2011
Mylonites and veins, Western Alps	7	18.3	17.2	15.9	2.9	1.8	3.2	Busigny et al., 2011
Blueschists	3	24.5	19.0	14.0	5.7	1.7	6.4	Halama et al., 2010
MORB-type eclogites	25	6.0	3.8	4.9	4.1	1.9	4.0	Halama et al., 2010
Metasomatic eclogites	9	5.4	2.8	4.9	4.5	3.1	5.4	Halama et al., 2010
High-pressure peridotites, Ecuador and Spain	5	7.3	4.5	5.5	4.8	0.8	5.1	Halama et al., 2010
High-pressure peridotites, Western Alps/Italy	5	3.0	1.9	2.3	3.0	1.3	3.4	This study
High-pressure ultramafic veins, Western Alps/Italy	3	3.9	1.5	3.4	0.9	1.4	0.6	This study
Chlorite harzburgites, Betic Cordillera/Spain	4	7.4	8.9	3.6	1.0	2.3	1.1	This study
High-pressure ultramafic veins, Betic Cordillera/Spain	4	2.9	1.3	3.1	3.2	1.5	3.1	This study

MZ1999 = Marty and Zimmermann, 1999; MH1997 = Marty and Humbert, 1997; C2001 = Cartigny et al., 2001

Table 3: Calculations for the flux of subducted nitrogen and its isotopic composition

	Thickness m	Density g/m ³ × 10 ⁶	[N] g/g × 10 ⁶	Flux g/year × 10 ⁹	Flux mol/year × 10 ⁹	δ ¹⁵ N _{air} ‰	Flux contribution %	Data source
Sediment	500	2.00	286	629	22.5	5.0		Sadofsky and Bebout, 2004
Sediment	500	2.00	771	1696	60.6	6.2		Li and Bebout, 2005
AOC	6000	2.89	2.80	107	3.81	3.9		Busigny et al., 2005
AOC	6000	2.89	6.90	263	9.40	-0.7		Li et al., 2007
AOC	6000	2.89	11.4	435	15.5	2.9		Li et al., 2007
Serpentinized mantle	500	2.90	1.80	5.74	0.205	-0.3		This study, MNS samples only
Serpentinized mantle	500	2.90	2.40	7.66	0.273	1.5		This study, all oceanic peridotites
Unmetamorphosed slab section:								
Case A								
Sediment	500	2.00	365	803	28.7	5.9	86	
AOC	6000	2.89	3.30	126	4.50	-1.2	13	
Serpentinized mantle	500	2.90	2.00	6.38	0.228	1.5	1	
Total				935	33.4	4.9	100	
Case B: Reduced sediment thickness								
Sediment	100	2.00	365	161	5.74	5.9	55	
AOC	6000	2.89	3.30	126	4.50	-1.2	43	
Serpentinized mantle	500	2.90	2.00	6.38	0.228	1.5	2	
Total				293	10.5	2.8	100	
Case C: Increased serpentinization depth								
Sediment	500	2.00	365	803	28.7	5.9	76.0	
AOC	6000	2.89	3.30	126	4.50	-1.2	11.9	
Serpentinized mantle	10000	2.90	2.00	128	4.56	1.5	12.1	
Total				1057		4.5	100	
Metamorphosed slab section:								
Case A								
Metasediment	500	2.70	287	852	30.4	2.8	77.3	
Met. Oceanic crust	6000	3.50	5.10	236	8.42	4.7	21.4	
Met. Serpentinized mantle	500	3.00	4.50	14.9	0.530	3.3	1.3	
Total				1103	39.4	3.2	100	
Case B: Reduced sediment thickness								
Metasediment	100	2.70	287	170	6.09	2.8	40.5	
Met. Oceanic crust	6000	3.50	5.10	236	8.42	4.7	56.0	
Met. Serpentinized mantle	500	3.00	4.50	14.9	0.530	3.3	3.5	
Total				421	15.0	3.9	100	
Case C: Increased serpentinization depth								
Sediment	500	2.70	287	852	30.4	2.8	61.5	
AOC	6000	3.50	5.10	236	8.42	4.7	17.0	
Serpentinized mantle	10000	3.00	4.50	297	10.6	3.3	21.4	
Total				1385		3.2	100	

The calculations assume a convergence rate of 0.05 m/year and a total arc length of 44000 km (Straub and Layne, 2003)

Densities for the metamorphosed lithological components are based on data for metamorphosed MORB and harzburgite at 600°C and 25 kbar (Hacker et al., 2003)

The N concentrations given for the bulk slab calculations reflect median values.