

1 **Fluid-induced breakdown of white mica controls**
2 **nitrogen transfer during fluid-rock interaction in**
3 **subduction zones**

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6 **Ralf Halama^{1,*}, Gray E. Bebout², Horst R. Marschall^{3,4}, Timm John⁵**

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8 ¹ School of Geography, Geology and the Environment, Keele University, Keele, ST5 5BG, United
9 Kingdom

10 ² Department of Earth and Environmental Sciences, Lehigh University, 1 West Packer Avenue,
11 Bethlehem, Pennsylvania 18015, USA

12 ³ Department of Geology and Geophysics, Woods Hole Oceanographic Institution, 266 Woods Hole
13 Rd., Woods Hole, Massachusetts 02543, USA

14 ⁴ Goethe-Universität Frankfurt, Institut für Geowissenschaften, Altenhöferallee 1, 60348 Frankfurt
15 am Main, Germany

16 ⁵ Institut für Geologische Wissenschaften, Freie Universität Berlin, Malteserstr. 74-100, 12249
17 Berlin, Germany

18

19 * Corresponding author contact information:

20 Ralf Halama

21 School of Geography, Geology and the Environment

22 Keele University, Keele, ST5 5BG, United Kingdom

23 E-mail: r.halama@keele.ac.uk

24 Tel: +44-1782-734960

25

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28 **Abstract**

29

30 In order to determine the effects of fluid-rock interaction on nitrogen elemental and isotopic
31 systematics in high-pressure metamorphic rocks, we investigated three different profiles
32 representing three distinct scenarios of metasomatic overprinting. A profile from the Chinese
33 Tianshan (ultra)high pressure – low temperature metamorphic belt represents a prograde, fluid-
34 induced blueschist-eclogite transformation. This profile shows a systematic decrease in N
35 concentrations from the host blueschist (~26 µg/g) via a blueschist-eclogite transition zone (19-23
36 µg/g) and an eclogitic selvage (12-16 µg/g) towards the former fluid pathway. Eclogites and
37 blueschists show only a small variation in $\delta^{15}\text{N}_{\text{air}}$ ($+2.1\pm 0.3\text{‰}$), but the systematic trend with
38 distance is consistent with a batch devolatilization process. A second profile from the Tianshan
39 represents a retrograde eclogite-blueschist transition. It shows increasing, but more scattered N
40 concentrations from the eclogite towards the blueschist and an unsystematic variation in $\delta^{15}\text{N}$
41 values ($\delta^{15}\text{N} = +1.0$ to $+5.4\text{‰}$). A third profile from the high-*P/T* metamorphic basement complex
42 of the Southern Armorican Massif (Vendée, France) comprises a sequence from an eclogite lens via
43 retrogressed eclogite and amphibolite into metasedimentary country rock gneisses.
44 Metasedimentary gneisses have high N contents (14-52 µg/g) and positive $\delta^{15}\text{N}$ values ($+2.9$ to
45 $+5.8\text{‰}$), and N concentrations become lower away from the contact with 11-24 µg/g for the
46 amphibolites, 10-14 µg/g for the retrogressed eclogite, and 2.1-3.6 µg/g for the pristine eclogite,
47 which also has the lightest N isotopic compositions ($\delta^{15}\text{N} = +2.1$ to $+3.6\text{‰}$).

48 Overall, geochemical correlations demonstrate that phengitic white mica is the major host of N
49 in metamorphosed mafic rocks. During fluid-induced metamorphic overprint, both abundances and
50 isotopic composition of N are controlled by the stability and presence of white mica. Phengite
51 breakdown in high-*P/T* metamorphic rocks can liberate significant amounts of N into the fluid. Due
52 to the sensitivity of the N isotope system to a sedimentary signature, it can be used to trace the
53 extent of N transport during metasomatic processes. The Vendée profile demonstrates that this
54 process occurs over several tens of meters and affects both N concentrations and N isotopic
55 compositions.

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58 **Keywords:**

59 Nitrogen, N isotopes, white mica, fluid-rock interaction, subduction, high-pressure metamorphic
60 rocks

61

61 **1. Introduction**

62

63 Understanding the processes that affect both elemental concentrations as well as isotopic
64 signatures in subducting rocks are of fundamental importance for the assessment of subduction zone
65 cycling of elements (e.g., Bebout 2007, 2014; Marschall *et al.* 2007a; Halama *et al.* 2011; John *et*
66 *al.* 2004, 2011; Spandler and Pirard 2013; Konrad-Schmolke and Halama 2014; Bebout and
67 Penniston-Dorland 2016). Elemental and isotopic fractionation during subduction-zone
68 metamorphism and metasomatism influences the balance of input and output in subduction zones
69 and the geochemical signatures transported into the deep mantle beyond the arc, potentially
70 resurfacing via plume-related magmatism. Metamorphic rock sequences that record the successive
71 advance of a metamorphic/metasomatic process provide a valuable means to evaluate the
72 magnitude and extent of geochemical effects via fluid-rock interaction during subduction cycling.

73 The nitrogen (N) isotope system has a great potential as geochemical tracer for crustal and
74 volatile recycling due to the large isotopic differences in the various terrestrial reservoirs (Busigny
75 and Bebout 2013; Halama *et al.* 2014; Johnson and Goldblatt 2015; Bebout *et al.* 2016; Mikhail and
76 Howell 2016). Nitrogen is a sensitive tracer for fluid-rock interaction and metasomatic processes
77 (Bebout 1997; Halama *et al.* 2010; Li *et al.* 2014), in particular for sediment-derived fluids because
78 N is largely fixed by organic processes in sedimentary environments (Bebout 1997; Bebout *et al.*
79 2016). However, direct evidence of spatially constrained transport of N is rare, and the processes
80 that cause N mobilization and fractionation of N isotopes need to be better understood. It has been
81 established for some metasedimentary suites that N contents decrease and $\delta^{15}\text{N}$ values increase with
82 increasing metamorphic grade during subduction (Bebout and Fogel 1992; Mingram and Bräuer
83 2001). However, other suites show relatively little change and N appears to be retained to depths
84 approaching those beneath arcs (Busigny *et al.* 2003; Pitcairn *et al.* 2005). Similarly,
85 metamorphosed mafic and ultramafic rocks appear to largely retain N to depths of at least 60-70 km
86 (Halama *et al.* 2010, 2012; Busigny *et al.* 2011).

87 In this study, we use spatially constrained profiles of metamorphosed mafic igneous rocks that
88 represent the frozen-in advance of fluid-induced metamorphic/metasomatic processes to investigate
89 the behaviour of N and N isotopes during prograde and retrograde metamorphic changes. Three
90 profiles were selected that represent i) a prograde transformation of blueschist into eclogite due to
91 fluid ingress from a major fluid conduit (Beinlich *et al.* 2010; John *et al.* 2012), ii) a retrograde
92 transformation of eclogite into blueschist during exhumation within a subduction channel (van der
93 Straaten *et al.* 2012), and iii) an exhumation-related interaction of an eclogite body with
94 surrounding felsic gneisses in a collisional context. The first two sample sequences come from the

95 south-eastern Tianshan (China) high-pressure low-temperature (HP-LT) belt, whereas the third
96 profile is from the Variscan Belt in the Vendée (France). We find that prograde dehydration can
97 release large amounts of N due to the breakdown of white mica, in which N is incorporated as
98 ammonium (NH_4^+), whereas the associated isotopic changes are relatively small ($< 1\%$). Hence,
99 non-altered eclogites should largely reflect the N isotopic composition of their protoliths. In
100 contrast, interaction with retrograde fluids can impart the N elemental and isotopic characteristics of
101 the rocks with which the fluid equilibrated and hence cause significant perturbations of the N
102 systematics.

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105 **2. Geologic setting and sample description**

106

107 ***2.1. Tianshan orogen, (ultra)high-pressure low-temperature ((U)HP-LT) metamorphic belt,*** 108 ***China***

109

110 Two profiles were sampled in a (U)HP-LT belt of metamorphic rocks in the Chinese part of the
111 Tianshan orogen (Figure 1a). The Tianshan orogen extends morphologically over 2500 km from
112 north-western China in the east over Kyrgyzstan and Kazakhstan to Tajikistan and Uzbekistan in
113 the west along the southwestern margin of the Central Asian Orogenic Belt, also known as the
114 Altaid Tectonic Collage (e.g., Şengör *et al.* 1993). In China, the western Tianshan, which includes
115 the (U)HP metamorphic terrane, is situated between the Junggar plate in the north and the Tarim
116 plate in the south (Gao *et al.* 2009 and references therein). The HP-LT rocks are interpreted as relics
117 of the Palaeozoic South Tianshan Ocean basin and whole rock geochemical data of the mafic rocks
118 show oceanic basalt affinities including former seamounts and young arcs, subducted during
119 Silurian and Carboniferous time (Windley *et al.* 1990; Şengör and Natal'in 1996; Gao *et al.* 1998;
120 Gao and Klemd 2003; John *et al.* 2008). The (U)HP-LT metamorphic terrane comprises
121 predominantly metasediments, which form the host rocks of mafic metavolcanic rocks,
122 metavolcaniclastics, marbles, and ultramafic rocks, and is considered to represent a tectonic
123 mélange formed within an accretionary wedge-like setting on the southern margin of the Central
124 Tianshan Arc terrane during the subduction of the South Tianshan Ocean (e.g., Gao *et al.* 1999; van
125 der Straaten *et al.* 2008; Klemd *et al.* 2011). The mafic metavolcanic rocks (mainly eclogites locally
126 interlayered with blueschists) occur irregularly distributed as differently sized pods, boudins, thin
127 layers or large massive blocks embedded in voluminous metasedimentary host rocks or less
128 abundant surrounded by metavolcaniclastic rocks (Gao and Klemd 2003). Blueschist occurrences

129 include prograde and retrograde varieties (Gao and Klemd 2001; Gao *et al.* 2007; van der Straaten
130 *et al.* 2008, 2012; Beinlich *et al.* 2010). Peak-metamorphic conditions of most eclogites and
131 prograde blueschists are similar (both lithologies occur locally with gradual transitions or intimately
132 intercalated) and range between 480 and 580 °C at 1.4–2.3 GPa at a regional scale (e.g., Klemd *et*
133 *al.* 2002; John *et al.* 2008). Moreover, relics of UHP conditions (e.g. coesite inclusions in garnet) or
134 thermodynamic modelling suggesting UHP conditions for both metasediments and eclogites have
135 been reported with peak P–T conditions of 570–630 °C at 2.7–3.3 GPa for eclogite-facies mica
136 schists and 470–510 °C at 2.4–2.7 GPa for eclogites from several localities (Lü *et al.* 2008, 2009;
137 Wei *et al.* 2009; Tian and Wei 2013). The juxtaposition of UHP and HP eclogite-facies rocks
138 juxtaposed on a meter scale is thought to reflect mixing of eclogite-facies rock from different depths
139 at the plate interface in a subduction channel-like setting (van der Straaten *et al.* 2008; Lü *et al.*
140 2009; Klemd *et al.* 2011). The timing of peak metamorphic conditions was determined by garnet
141 growth ages of ca. 315 Ma based on multi-point Lu-Hf isochron ages for both blueschists and
142 eclogites from various locations within the (U)HP-LT belt (Klemd *et al.* 2011). High-pressure veins
143 crosscutting a blueschist wall-rock formed contemporaneously at 317 ± 5 Ma (Rb-Sr) which is
144 consistent with metamorphic fluid release due to prograde transformations of blueschists to
145 eclogites (John *et al.* 2012). U-Pb SIMS ages of metamorphic zircon rims in eclogites are
146 indistinguishable within error at 319 ± 3 Ma (Su *et al.* 2010). The post-peak cooling was dated by
147 white mica geochronology (K-Ar, Ar-Ar, Rb-Sr) and gave ages between 310 and 311 Ma (Klemd *et*
148 *al.* 2005).

149 For the profiles, drill cores with a diameter of 2.54 cm and a length of about 10-15 cm were
150 taken to obtain a good spatial resolution. At both sample localities, the samples occur as loose,
151 meter-sized blocks, which have fallen from the steep mountain slopes as rock falls. The blocks
152 represent a mixture of various rock types that are now found within and partly covered by
153 quaternary deposits.

154 Profile 1 (JTS sequence; Figure 2a) represents the prograde transformation of blueschist into
155 eclogite due to fluid infiltration. The JTS sequence was studied in detail by Beinlich *et al.* (2010)
156 and John *et al.* (2012), and the following summary is based on these works. The massive blueschist
157 with the main mineral assemblage garnet + glaucophane + omphacite + phengite + quartz is cross-
158 cut by a carbonate-quartz vein, which is surrounded by an eclogitic reaction halo mainly composed
159 of omphacite and garnet. The vein represents a major former fluid pathway that shows fluid
160 infiltration from an external source and dehydration of the immediate wall rock. Important
161 petrographic observations of the fluid-induced eclogitization include replacement of sodic
162 amphibole by omphacitic clinopyroxene, increase in the modal abundances of quartz and carbonate

163 and decrease in the modal abundance of white mica with decreasing distance to the vein. The
164 successive breakdown of white mica towards the vein is responsible for a relative depletion in
165 large-ion lithophile elements (LILE: K, Rb, and Cs) in the eclogitic selvage compared to the host
166 blueschist. Enrichments in Ca, Pb and Sr and depletions in HFSE can also be attributed to the fluid-
167 induced eclogitization.

168 Profile 2 (FTS 9-1 sequence; Figure 2b) represents a gradual retrograde transition from eclogite
169 to blueschist caused by fluid-rock interaction during uplift in the subduction channel (van der
170 Straaten *et al.* 2008, 2012). The following description is based on the petrologic-geochemical
171 investigation by van der Straaten *et al.* (2012) on these samples. The eclogitic parts consist of a
172 fine-grained omphacite matrix with accessory rutile and porphyroblasts of garnet. The fluid-induced
173 blueschist-facies overprint caused replacement of the eclogite-facies assemblage by newly formed
174 glaucophane, paragonite, chlorite, calcite and titanite. The increase in the modal amounts of
175 glaucophane, white mica and calcite with increasing blueschist-facies overprint lead to a nearly
176 complete replacement of omphacite in the glaucophane schist.

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179 **2.2. Les Essarts Unit, Variscan Belt, Vendée, France**

180

181 Samples were taken along a ~100 m long profile from an approximately 1 km thick eclogite
182 lens via retrogressed eclogite and amphibolite into surrounding metasedimentary gneiss in the
183 quarry “La Gerbaudière” of the Les Essarts Unit, 25 km south of Nantes and west of St. Philbert de
184 Bouaine (Figure 1b). This unit constitutes a HP metamorphic basement complex of the Southern
185 Armorican Massif that is part of the Variscan belt (Matte 2001). Rocks of oceanic origin (eclogites,
186 amphibolites derived from eclogite, meta-plagiogranites and serpentinites) form several km-long
187 stretched and slightly boudinaged lenses surrounded by foliated ortho- and paragneisses that are
188 rich in white mica (Mauler *et al.* 2001). The eclogites have gabbroic protoliths with a crystallization
189 age of 1297 ± 60 Ma based on a zircon U-Pb upper intercept age (Peucat *et al.* 1982). The eclogite-
190 facies metamorphism was dated at 436 ± 15 Ma based on a zircon U-Pb lower intercept age (Peucat
191 *et al.* 1982). The primary HP mineral assemblage is omphacite + garnet + rutile \pm quartz \pm kyanite
192 \pm zoisite \pm magnesio-hornblende \pm pyrite \pm chalcopyrite and peak P-T conditions are 1.6-2.0 GPa
193 and 650-750 °C (Godard 2009). A major deformation event occurred during the eclogite-facies
194 metamorphism, followed by retrogression that transformed most of the eclogites into amphibolites,
195 in particular affecting the margins of the eclogite lenses. Retrogression is indicated by presence of
196 green amphibole and plagioclase-clinopyroxene symplectite along omphacite grain boundaries

197 (Mauler *et al.* 2001). The gneisses surrounding the eclogites with the main mineral assemblage
198 quartz + plagioclase + biotite + garnet + white mica are of continental origin and record two distinct
199 episodes of high-grade metamorphism (Godard 2009). The first event comprises intrusion of granite
200 and migmatization of cordierite-bearing metapelites ($T \sim 670^{\circ}\text{C}$, $P = 0.3 \text{ GPa}$) within the pre-
201 Variscan continental crust. The second event is an eclogite-facies overprint, cofacial with the
202 eclogitization of the adjacent oceanic mafic rocks at peak P-T conditions of $P > 1.6 \text{ GPa}$ and $T \sim$
203 700°C , which occurred during eo-Variscan subduction (Bernard-Griffiths and Cornichet 1985;
204 Godard 2009) with simultaneous deformation of eclogites and gneisses. Several coronitic and
205 pseudomorphic reactions caused the growth of high-pressure minerals (garnet, kyanite, phengite,
206 rutile) and the expense of the previous high-temperature parageneses (Godard 2009). The Les
207 Essarts Unit is interpreted as tectonic mélange of pre-Variscan oceanic and continental crusts that
208 were eclogitized during subduction and subsequently incorporated into the Variscan orogenic belt
209 (Godard 2001).

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211

212 [Figure 1 near here]

213 [Figure 2 near here]

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216 **3. Analytical methods**

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218 ***3.1. Nitrogen content and nitrogen isotopic compositions***

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220 Nitrogen concentrations and isotopic compositions of bulk rock powders were analysed at
221 Lehigh University. Sample preparation and analytical protocol follow the methods described in
222 Bebout *et al.* (2007). In brief, about 100-250 mg of sample powder and Cu/CuOx reagent are
223 evacuated for 24 h before sealing, with intermittent heating to $\sim 100^{\circ}\text{C}$. Nitrogen is extracted at
224 1000°C and transferred as N_2 into a Finnigan MAT 252 mass spectrometer using a Finnigan Gas
225 Bench II and a U-trap interface in which samples of N_2 are entrained in a He stream. Details
226 regarding the calculation of N concentrations in unknowns and reference materials analysed during
227 the course of this study can be found in Halama *et al.* (2010, 2014). The analytical uncertainties for
228 N concentrations are usually $<5\%$. For $\delta^{15}\text{N}$ values (referenced to the isotopic composition of

229 atmospheric N₂, “air”), uncertainties are 0.15‰ (1σ) for samples with > 5 μg/g N and 0.6‰ (1σ) for
230 samples with 1-5 μg/g N.

231

232 **3.2. Major and trace elements**

233

234 Major and trace element data of the JTS and FTS traverses were published in Beinlich *et al.* (2010)
235 and van der Straaten *et al.* (2012), respectively, and are reproduced in the supplemental dataset.
236 Major and trace elements of the Vendée traverse (supplemental dataset) were analysed by X-ray
237 fluorescence at Universität Heidelberg using a Siemens[®] SRS303 instrument equipped with a Rh-
238 tube. Major and minor elements were measured on fused glass discs with an accuracy of 0.5-1%.
239 Trace elements (Cr, Ni, Sr, Zr, Ba) were measured on pressed pellets with an accuracy of 5-10%.
240 Further details about the XRF methods are given in Pauly *et al.* (2016). Lithium concentrations
241 were determined at the University of Bristol with a sample-standard bracketing technique using a
242 ThermoElectron[®] Neptune MC-ICP-MS as described in Marschall *et al.* (2007b). Concentrations
243 were determined by intensity comparison with the bracketing standard (NIST L-SVEC) and have a
244 precision of approximately ±10%.

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246

247 **4. Results**

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249 In the profile representing the prograde blueschist-eclogite transformation (JTS sequence), N
250 concentrations successively decrease from the host blueschist (~26 μg/g) to the blueschist-eclogite
251 transition zone (BETZ; 19-23 μg/g) and the eclogitic selvage (12-16 μg/g; Figure 3a). The quartz-
252 carbonate vein has the lowest N concentrations (9.5 μg/g) and the highest δ¹⁵N_{air} value (+4.8‰) in
253 this sequence (Table 1). Nitrogen isotopic compositions of the eclogitic selvage (δ¹⁵N = +2.6 ±
254 0.2‰) are slightly elevated compared to the BETZ (+2.0 ± 0.2‰) and the host blueschists (δ¹⁵N =
255 +1.8 to +2.3‰). Overall, the profile shows a systematic decrease in [N] from the host wall rock
256 towards the vein, which is paralleled by LILE such as Rb (Figure 3a; supplemental dataset).
257 Excluding the vein, the overall range in δ¹⁵N in eclogites and blueschists is very limited (only about
258 1‰) with an average of +2.1±0.3‰ (n=9).

259 In the profile representing the retrograde eclogite-blueschist transition (FTS sequence), there is
260 a broad increase in N contents from the eclogite towards the blueschist, but the trend shows
261 significant scatter and there is also variability between adjacent samples from the same drill core
262 (3.1-3A and 3.1-3B). The overall range in N contents (8-27 μg/g) is comparable to the JTS

263 sequence, but the variability in $\delta^{15}\text{N}$ is larger ($\delta^{15}\text{N} = +1.0$ to $+5.4\%$). $\delta^{15}\text{N}$ varies unsystematically
264 with regard to distance along the profile (Table 1).

265 In the eclogite-gneiss profile, the country rock gneisses have high N contents (14-52 $\mu\text{g/g}$) and
266 positive $\delta^{15}\text{N}$ values (+2.9 to $+5.8\%$; Table 1). $\delta^{15}\text{N}$ values of both garnet amphibolites and
267 eclogites are within the range of the gneiss values, but [N] becomes increasingly lower towards the
268 eclogite with 11-24 $\mu\text{g/g}$ for the amphibolites and 10-14 $\mu\text{g/g}$ for the retrogressed eclogite (Figure
269 3b). The pristine eclogite is characterized by the lowest N concentrations (2.1-3.6 $\mu\text{g/g}$) and the
270 lightest N isotopic compositions ($\delta^{15}\text{N} = +2.1$ to $+3.6\%$). The elements Ba and Li show a similar
271 behaviour as N with successively decreasing concentrations from the gneisses to the eclogites
272 (Figure 3b; supplemental dataset).

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275 [Figure 3 near here]

276 [Table 1 near here]

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279 **5. Discussion**

280

281 **5.1. Residency of nitrogen**

282

283 Nitrogen occurs as ammonium (NH_4^+) in most silicate minerals, where it substitutes for K^+ due
284 to the similarity of these ions in charge and ionic radius. NH_4^+ is thus most strongly concentrated in
285 micas and alkali feldspars in many crustal rocks (Honma and Itihara 1981), as reflected by
286 correlations of N contents with concentrations of LILE (K, Rb, Cs, Ba) in several metasedimentary
287 suites (Bebout *et al.* 1999; Busigny *et al.* 2003; Sievers *et al.* 2016, this issue). Phengite (Si-rich
288 potassic white mica) is the main N carrier mineral in high-*P/T* metamorphosed mafic and ultramafic
289 rocks, but NH_4^+ may also occur in Ca-Na minerals where phengite is absent (Busigny *et al.*, 2011;
290 Halama *et al.*, 2010; 2012). The positive correlation of N with K, Ba, Rb and Cs (Figure 4) in both
291 Tianshan sequences points to a mineralogical control by phengite regarding the N concentrations in
292 the bulk rocks, because phengite is known to be the principal carrier for these elements in phengite-
293 bearing eclogites and high-*P/T* metapelites (e.g., Sorensen *et al.* 1997; Zack *et al.* 2001).

294 The JTS sequence shows the most striking correlation among N abundances and LILE
295 concentrations, with a systematic decrease from host blueschists via the BETZ towards eclogites
296 and the vein (Figure 4a). The key role of phengite as N host is underlined by the decreasing modal

297 occurrence of white mica (phengite + paragonite) towards the vein (Figure 5; Beinlich *et al.* 2010).
298 The somewhat larger scatter in the FTS sequence (Figure 4b) may be related to the generally much
299 smaller concentration variations compared to the JTS sequence. Moreover, paragonite (sodic white
300 mica) forms in response to the retrograde overprint in the FTS sequence. Although paragonite is
301 capable of incorporating significant amounts of N in the order of up to 100 $\mu\text{g/g}$ (Busigny *et al.*
302 2011), phengite frequently contains several hundreds of $\mu\text{g/g}$ (Sadofsky and Bebout 2000) and is
303 hence a more likely major N host. The unsystematic variations in modal abundances of these two
304 phases are therefore thought to contribute to the scattered trends in the FTS sequence. In the
305 eclogite-gneiss profile, there is a systematic, coupled increase in N and LILE as well as Li from
306 eclogites via retrogressed eclogites and amphibolites towards the surrounding gneisses (Figure 4c).
307 The low N contents in the eclogites are consistent with the lack of K-bearing phases. Any N present
308 is probably residing in omphacitic (Na-Ca) clinopyroxene, in agreement with observations from
309 natural metagabbros (Busigny *et al.* 2011) and experimental results that show the potential of
310 clinopyroxene to incorporate N at ultrahigh pressures (Watenphul *et al.* 2010). Additional N present
311 in retrogressed eclogites and amphibolites may be incorporated into plagioclase, for which N
312 concentrations of 2-45 $\mu\text{g/g}$ have been reported, substituting for Ca and Na (Honma and Itihara
313 1981), and to a lesser degree into amphibole (2-5 $\mu\text{g/g}$ N, Honma and Itihara 1981). In the gneisses,
314 N can be incorporated into muscovite and biotite, both of which can host large amounts (>1000
315 $\mu\text{g/g}$) of N (Sadofsky and Bebout 2000).

316

317

318 [Figure 4 near here]

319 [Figure 5 near here]

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322 ***5.2. Nitrogen elemental and isotopic characteristics***

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324 All three of the sample suites are characterized by a limited ($\leq 5\%$) variation in $\delta^{15}\text{N}$ and
325 positive $\delta^{15}\text{N}$ values, which distinguishes them from fresh MORB (Figure 6). Most of the $\delta^{15}\text{N}$
326 values of the mafic samples overlap with those of global eclogites, which were interpreted to
327 largely reflect the N isotope compositions of their protolith (altered oceanic crust, AOC) with or
328 without the effects of metamorphic dehydration (Halama *et al.* 2010). Metamorphic dehydration
329 generally causes a decrease in N concentrations and an increase in $\delta^{15}\text{N}$ values (Haendel *et al.* 1986;
330 Bebout and Fogel 1992), but the large compositional variability of AOC hinders the identification

331 of dehydration effects. At each location, some of the mafic samples have elevated N contents
332 relative to global eclogites, in particular the Tianshan blueschists and the Vendée amphibolites,
333 trending towards compositions of metasediments (Figure 6). In the prograde blueschist-eclogite JTS
334 sequence, the blueschists represent the rocks least affected by eclogitization-causing fluid overprint,
335 and hence may have inherited their signature during a previous metasomatic event, e.g. during
336 seafloor alteration or blueschist-facies metamorphism. The trend in the JTS sequence towards
337 relatively N-poor compositions is unlikely to be entirely due to a decreasing modal abundance of
338 white mica as suitable host mineral for N because the modal abundances of white mica are similar
339 in the host blueschists (8-11%) and the BETZ (12-15%), with only the eclogitic selvage having
340 lower contents (4-11%; Beinlich *et al.* 2010). Hence, the trend suggests that the fluid inducing the
341 eclogitization was relatively poor in N and probably not of sedimentary origin. This finding is in
342 agreement with the Ca and Sr isotope data pointing to a dehydrating oceanic lithosphere, i.e. AOC
343 or serpentinized slab mantle, as potential fluid source (John *et al.*, 2012). An estimate for the
344 average $\delta^{15}\text{N}$ of ultramafic rocks recycled into the mantle is $+3\pm 2\%$ (Halama *et al.* 2014), but
345 individual serpentinized peridotite samples have even more positive $\delta^{15}\text{N}$ values of up to $+15\%$
346 (Philippot *et al.* 2007).

347 In contrast, the blueschists of the FTS sequence are among the samples that are most strongly
348 affected by retrograde metasomatism. Their elevated N contents at moderately positive $\delta^{15}\text{N}$ are
349 consistent with a metasomatic overprint by a fluid that either originated from or equilibrated with
350 metasedimentary rocks. In the Vendée profile, the field evidence clearly demonstrates increasing
351 fluid-induced overprint of the eclogite lens by fluids derived from the surrounding metasedimentary
352 gneisses, producing the sequence fresh eclogite – retrogressed eclogite – amphibolite –
353 metasedimentary gneiss. This profile allows evaluation of the effects of the metasedimentary fluids
354 on [N] and $\delta^{15}\text{N}$ in the eclogite lens. Both the N concentrations and the $\delta^{15}\text{N}$ values increase in the
355 metasomatically overprinted mafic rocks compared to the pristine eclogite. These features can be
356 explained by assuming that the country rock paragneisses with high N contents and an adequate N
357 isotopic composition were the source lithology for the metasomatic fluids, corroborating the field
358 evidence. Hence, both the Tianshan FTS and the Vendée profile underline the sensitivity of the N
359 system to sediment-derived fluids. These fluids incorporated biogenic N that was originally present
360 as organic matter in the sediments. Granitic rocks from the Cornubian batholith similarly show high
361 N contents (6-139 $\mu\text{g/g}$) and positive $\delta^{15}\text{N}$ ($+5$ to $+10\%$) values (Boyd *et al.* 1993). These features
362 were interpreted to reflect inheritance of N of biological origin as the granites are essentially
363 derived from the anatexis of NH_4^+ -bearing metasediments that originally contained organic material
364 (Hall 1987; Boyd *et al.* 1993).

365

366

367 [Figure 6 near here]

368

369

370 **5.3. Fluid-rock interaction processes**

371

372 In this section, we focus on the prograde blueschist-eclogite JTS sequence because it shows a
373 relatively simple mineralogical control on N contents, resulting in clear correlations that can be
374 compared to various fluid-rock interaction processes potentially affecting the rocks. Busigny and
375 Bebout (2013) summarized four types of N exchange between mineral and fluid that can be
376 distinguished during metamorphism, and each of these will be evaluated in turn:

377

378 (1) Thermal decomposition: Thermal decomposition causes the complete breakdown of mineral
379 hosts due to increasing temperatures and the onset of partial melting. This leads to a decreasing
380 modal abundance of mica and loss of N if no other suitable host phases for N, such as K-feldspar
381 (incorporation of NH_4^+) or cordierite (incorporation of N_2 in channels of the mineral structure), are
382 present in the melting residue (Palya *et al.* 2011). Thermal decomposition can be excluded in the
383 studied profiles because there is no field or petrographic evidence for partial melting and estimates
384 of peak temperatures are too low for partial melting of mafic rocks to occur.

385

386 (2) Cation exchange: Cation exchange of NH_4^+ and K^+ between white mica and a fluid can release
387 NH_4^+ into the fluid if the rock equilibrates with a fluid rich in K^+ , thereby replacing NH_4^+ in white
388 mica by K^+ (Eugster and Munoz 1966; Busigny and Bebout 2013). A similar exchange may occur
389 between NH_4^+ and Rb^+ or Cs^+ . This process is expected to cause a negative correlation of NH_4^+
390 with K^+ (and Rb^+ , Cs^+). However, all investigated profiles show a positive correlation of K and N.
391 This is the opposite behaviour to what would be expected if cation exchange was the dominant
392 fluid-rock interaction process and we hence exclude cation exchange as major process.

393

394 (3) Continuous metamorphic devolatilization reactions: Devolatilization reactions during prograde
395 metamorphism cause changes in mica chemistry and mica modal abundances in the rock (Bebout
396 and Fogel 1992; Bebout *et al.* 2013). During devolatilization, isotopically light N is preferentially
397 fractionated into the metamorphic fluid. Consequently, residual mica records an increase in $\delta^{15}\text{N}$
398 with increasing degrees of devolatilization (Haendel *et al.* 1986; Bebout and Fogel 1992; Jia *et al.*

399 2006). To test the effects of metamorphic devolatilization, we calculated the composition of the
400 residual rock for batch devolatilization and Rayleigh distillation models (Figure 7a). In an open-
401 system Rayleigh distillation model, each fluid increment produced by phengite dehydration is
402 immediately removed from the rock. In contrast, the batch devolatilization model assumes that all
403 of the fluid released equilibrates with the rock and is lost in a single batch (Valley 1986).
404 The isotopic fractionation depends on the N speciation in the fluid (N_2 or NH_3). It is evident that
405 devolatilization models involving NH_3 cannot explain the observed trend in the JTS sequence
406 (Figure 7a). Busigny *et al.* (2003) modelled phengite chemical evolution during progressive
407 Rayleigh distillation for LILE, and we use this approach to test the applicability of continuous
408 metamorphic reactions on the prograde blueschist-eclogite JTS data set (Figure 7b, c). Different
409 partition coefficients between fluid and phengite for K, Rb, Cs and N cause fractionation between
410 these elements during devolatilization (Melzer and Wunder 2000; Busigny *et al.* 2003). Since all
411 these elements predominantly resided in phengite, their ratios in phengite reflect those of the whole
412 rock (Zack *et al.* 2001). Caesium has a larger preference for the fluid than both Rb and N,
413 producing a relatively sharp decrease in Cs abundances and curved Rayleigh distillation trends in
414 bivariate diagrams (Figure 7b, c). The linear correlations of the measured data suggest that
415 continuous metamorphic phengite dehydration via a Rayleigh distillation process in an open system
416 cannot have caused the coupled decrease in Rb-Cs and N-Cs, respectively. The coupled losses of
417 these elements which are observed with decreasing distance to the vein do not appear to obey a K_d -
418 controlled Rayleigh distillation process. However, a good fit to the JTS data is obtained for a N_2
419 batch devolatilization model, only the vein plots off the modelled trend (Figure 7a). Hence, the N
420 isotope data support a batch devolatilization process.

421

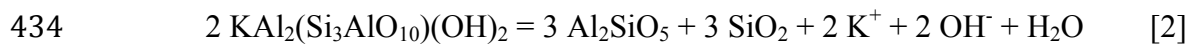
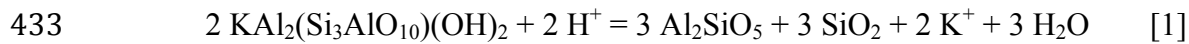
422

423 [Figure 7 near here]

424

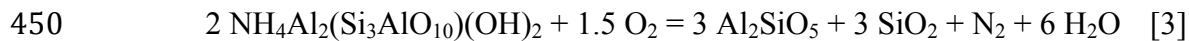
425

426 (4) Fluid-induced breakdown of white mica: It has been shown that the eclogitization adjacent to
427 the vein structure occurred due to fluid-mediated replacement processes during which the blueschist
428 continuously equilibrated with an external fluid characterized by a composition that differed
429 strongly from that of the wall rock blueschist (Beinlich *et al.* 2010; John *et al.* 2012). Consequently,
430 the blueschist mineral assemblage has been successively replaced by a new eclogite assemblage
431 (Putnis and Austrheim 2010; Putnis and John 2010). This process can be generalised by breakdown
432 reactions such as:

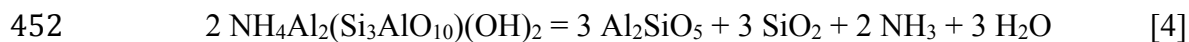


435 Once liberated from phengite, N and the LILE (formerly substituting for K in phengite) enter the
436 fluid, which mediates diffusive or advective transport towards the nearest transport vein leading to
437 long-distance element removal (Zack and John 2007). This process of fluid-induced decomposition
438 of white mica is in agreement with the coupled bulk losses of LILE and N. The combined stripping
439 of LILE and N from the blueschists requires infiltration of a K-poor fluid, which drives chemical
440 reactions towards reduced chemical potential gradients for fluid species by destroying phengite and
441 releasing LILE and N into the fluids (Breeding *et al.* 2004; John *et al.* 2012). Loss of Al_2O_3 in both
442 the BETZ (~2-9%) and in the eclogitic selvage (~12%) compared to the blueschist host (Beinlich *et al.*
443 *et al.* 2010) suggest release and removal of Al during phengite breakdown. The behaviour of Si is less
444 systematic, with some relative losses in BETZ samples but also gains in the eclogitic selvage
445 (Beinlich *et al.* 2010), likely related to infiltration from the vein-forming fluid.

446 If the fluids infiltrating the rock are highly oxidising, NH_4^+ will be partially oxidised to N_2 , which
447 will then be lost from the system in the fluid (Bebout and Fogel 1992; Svensen *et al.* 2008).
448 Oxidizing fluids are capable of destroying ammonium muscovite and forming kyanite and quartz by
449 the reaction (Eugster and Munoz 1966):



451 More reducing fluids may cause breakdown of ammonium muscovite by the reaction



453 Generally, fluid-rock interaction can be considered as an important mechanism to release large
454 amounts of specific elements that are hosted by a single mineral phase. Regarding the transport of
455 LILE and N, phengite mode and breakdown rate are the most important parameters of the rock for
456 storage and release, respectively, of these elements. The combined N elemental and isotope
457 systematics suggest a scenario of fluid-induced breakdown of white mica and batch devolatilization
458 of N in the system.

459

460

461 **5.4. Transfer and sources of nitrogen**

462

463 The prograde blueschist-eclogite transition of the JTS sequence, which is induced by
464 metasomatism, provides compelling evidence for removal of N due to phengite breakdown. Other
465 elements, such as Ca, Sr and Pb, were added by the fluid-induced overprint (Beinlich *et al.* 2010),
466 and consequently exhibit negative correlations with N contents (Figure 8). The degree to which N

467 potentially present in the fluid would have been able to exchange with the rock and alter [N] and
468 $\delta^{15}\text{N}$ depends on the compatibility of N in the available mineral hosts and the abundance of these
469 host phases. In the metasomatically formed eclogites of the JTS sequence, no other mineral except
470 phengite is able to incorporate significant amounts of N. The $\delta^{15}\text{N}_{\text{fluid}}$ is estimated as $\sim +7\text{‰}$ based
471 on vein composition and the $\text{NH}_4^+ - \text{N}_2$ fractionation factor at 527°C from Hanschmann (1981).
472 Positive $\delta^{15}\text{N}$ that overlap the vein composition were observed in AOC from the East Pacific Rise
473 (Busigny *et al.* 2005) and in various (meta)sedimentary rocks (Figure 9a). However, the
474 combination of a high- $\delta^{15}\text{N}$ fluid that introduced large amounts of externally-derived Ca and Sr, but
475 not LILE, is pointing towards AOC rather than (meta)sediments as the most likely fluid source.
476 This conclusion is consistent with Ca-Sr isotope data, which demonstrated that seawater-altered
477 lithospheric rocks were the dominant source for the metasomatic fluid that induced eclogitization in
478 the JTS sequence (John *et al.* 2012). In the $\delta^{15}\text{N} - \text{Rb/N}$ diagram (Figure 9a), where mixing
479 relationships appear as straight lines, an apparent mixing trend between the JTS rock with the
480 highest Rb/N ratio and the vein composition yields a decent fit to the data points. Our preferred
481 interpretation of this apparent mixing relationship is that up to $\sim 40\%$ of the initially present
482 phengite was destroyed by the fluid-induced overprint, in agreement with the observed decrease of
483 modal phengite abundance (Beinlich *et al.* 2010), causing successively decreasing Rb/N ratios
484 coupled to decreasing N contents. Changes in $\delta^{15}\text{N}$ in the overprinted eclogites compared to the
485 blueschists are minor and an externally-derived N isotope signature is not clearly discernible from
486 $\delta^{15}\text{N}$ variability due to protolith heterogeneities \pm devolatilization effects.

487 In contrast to the JTS sequence, both of the two profiles with a retrograde overprint, the FTS
488 sequence and the Vendée profile, show addition of N during metasomatism. For the FTS sequence,
489 the addition was not pervasive and systematic, as the [N]-distance relationships are scattered,
490 possibly related to the availability of fluid pathways within the rock and/or small-scale
491 heterogeneities. The straight line correlation on the $\delta^{15}\text{N} - \text{Rb/N}$ diagram (Figure 9a) points to a
492 mixing relationship, but the position of both eclogite and blueschist at the upper end of this trend
493 add a complexity likely related to the co-existence of phengite and paragonite, which precludes any
494 further conclusions.

495 Retrograde alteration in the Vendée mafic rocks was accompanied by increasing K/N ratios and
496 $\delta^{15}\text{N}$ values (Figure 9b). Any metasomatic fluid entering the eclogite lenses must have passed
497 through the surrounding paragneisses, which therefore constitute the most likely source for any
498 elements added to the eclogites. Retrogressed eclogites and amphibolites are enriched in N up to 10
499 times compared to the precursor eclogites and $\delta^{15}\text{N}$ has been changed by up to 4‰ . Original
500 protolith signatures and effects of prograde metamorphism were overprinted by the retrograde

501 metamorphism as N has been transported on length scales of at least several 10s of meters, although
502 the most pristine eclogites may still preserve the original signatures. The contribution by the
503 relatively N-rich, high- $\delta^{15}\text{N}$ paragneisses is exemplified by mixing relationships between two
504 different gneisses and eclogite where the whole-rock K/N ratios are considered to approximate
505 those of the fluid (Figure 9b). Given the large spread in K/N ratios in the gneisses, fluid-mediated
506 mixing can easily explain elevated K/N in retrograde overprinted eclogites. The complete overlap in
507 $\delta^{15}\text{N}$ between retrogressed eclogites/amphibolites and gneisses provides evidence for the great
508 sensitivity of the N isotope system to fluids that interacted with or are derived from
509 (meta)sediments. Amphibolites and retrogressed eclogites have isotopically almost fully
510 equilibrated with the gneisses, and heterogeneities, inherited from the eclogite precursor, were only
511 preserved in the inner parts of the eclogite lens. The fluid-mediated influx of N from the gneisses
512 into the eclogite lens was likely aided by transport of N via amphibole veins, which occur in the
513 eclogites and served as more effective transport pathway compared to the less permeable bulk rock.
514 The Vendée profile not only shows direct evidence for the derivation of N in a metasomatic fluid
515 from metasedimentary rocks, but, importantly, that this process can happen on length scales of 10s
516 of meters.

517

518

519 [Figure 8 near here]

520 [Figure 9 near here]

521

522

523 **6. Conclusions**

524

525 We investigated three profiles in metasomatically overprinted high-pressure metamorphic rocks
526 to determine the effects of fluid-rock interaction on N elemental and isotopic systematics. Positive
527 correlations of N with K, Ba, Rb and Cs in blueschists and eclogites demonstrate that phengitic
528 white mica is the major N host in metamorphic rocks with mafic precursors. During prograde
529 overprint of blueschists and transformation into eclogites, the observed straight line correlations
530 between N and LILE and near-constant ratios of N/K, N/Rb, N/Cs and Cs/Rb do not resemble
531 differential losses related to differing equilibrium partitioning during metamorphic devolatilization
532 via a Rayleigh distillation process, but instead indicate that fluid-mediated N mobilization and loss
533 from the rock is related to complete breakdown of white mica. Hence, N abundances are strongly
534 controlled by the stability and presence of white mica in HP metamorphic rocks, and external N

535 contributions to the whole rock budget remain insignificant as long as no other N host forms. Fluid-
536 induced breakdown of phengite in HP rocks can liberate large amounts of N that is released into the
537 fluid (Figure 10). The N isotopic compositions show only small variations that are consistent with a
538 batch devolatilization process coupled to the phengite breakdown. During fluid-induced retrograde
539 overprint of eclogites, the N system is highly sensitive to fluids that equilibrated with
540 metasedimentary rocks and can be used to trace the extent of N transport from host rocks into
541 eclogite lenses. This transport can occur over several tens of meters and affect both N
542 concentrations and isotopic compositions (Figure 10), as evidenced by a profile from
543 metasedimentary gneisses into an eclogite lens. Elevated N contents in retrogressed mafic HP rocks
544 suggest that plagioclase and amphibole are capable to incorporate N derived from metasomatic
545 fluids.

546

547

548 [Figure 10 near here]

549

550

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557

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784

784 **Figure captions**

785

786 **Figure 1:**

787 Locations and geological setting of the sampling areas. **A)** Simplified geological map of the
788 Chinese South Tianshan (modified after Gao *et al.* 1999). **B)** Geological map showing the Les
789 Essarts HP unit in the Southern Armorican Massif, France (modified after Mauler *et al.* 2001).

790

791 **Figure 2:**

792 Sketches and field photographs illustrating the sample profiles for **A)** the prograde blueschist-
793 eclogite transition (JTS sequence; Beinlich *et al.* 2010) and **B)** the retrograde eclogite-blueschist
794 transition (FTS sequence; van der Straaten *et al.* 2012). **C)** shows a map of the La Gerbaudière
795 quarry (Saint-Philbert-de Bouaine, Vendée) in 1999 with location of the sampling traverse
796 (modified after Mauler *et al.* 2001 and Godard 2001).

797

798 **Figure 3:**

799 Nitrogen elemental and isotopic variations in **A)** the prograde blueschist-eclogite transition (JTS
800 sequence, Tianshan) and **B)** the gneiss-eclogite traverse (Vendée). Additional trace element data for
801 the JTS sequence are from Beinlich *et al.* (2010), with a precision of <5% RSD (John *et al.* 2008;
802 van der Straaten *et al.* 2012). Uncertainties for element concentrations are smaller than the symbol
803 size.

804

805 **Figure 4:**

806 Elemental correlations of N with other trace elements in the three profiles studied. A) JTS sequence,
807 Tianshan, B) FTS sequence, Tianshan, C) Gneiss-eclogite traverse, Vendée.

808

809 **Figure 5:**

810 Modal content of white mica (phengite + paragonite) in rocks of the prograde blueschist-eclogite
811 transition (JTS traverse, Tianshan; data from Beinlich *et al.* 2010) plotted versus the N
812 concentrations.

813

814 **Figure 6:**

815 Nitrogen elemental and isotopic systematics of the analysed rocks compared to fresh MORB
816 (Busigny *et al.* 2005), eclogites (Halama *et al.* 2010), metasedimentary rocks (Bebout and Fogel
817 1992; Mingram and Bräuer 2001; Busigny *et al.* 2003) and altered oceanic crust (AOC; Busigny *et*

818 *al.* 2005; Li *et al.* 2007). Colours of individual symbols are the same as in Figures 2 (JTS and FTS
819 traverses) and 3b (Vendée traverse).

820

821 **Figure 7:**

822 Metamorphic dehydration models. **A)** Batch devolatilization (solid lines) and Rayleigh distillation
823 (dashed lines) models of N isotopic compositions and concentrations, using the most N-rich
824 blueschist of the JTS sequence (JTS-A) as initial composition. Isotopic fractionation by batch
825 devolatilization is described by the equation $\delta^{15}\text{N}_f = \delta^{15}\text{N}_i - (1-F)1000 \ln \alpha$, and fractionation
826 following Rayleigh distillation is given by the equation $\delta^{15}\text{N}_f = \delta^{15}\text{N}_i + 1000(F^{\alpha-1} - 1)$, where $\delta^{15}\text{N}_i$
827 and $\delta^{15}\text{N}_f$ are the initial and final isotopic compositions of the rock, α is the fluid–rock
828 fractionation factor and F is the N fraction that remains in the rock after devolatilization.
829 Fractionation factors used in the calculations are those tabulated in Haendel *et al.* (1986) based on
830 Hanschmann (1981) for 527 °C. Tick marks give the fraction of N remaining in the rock in 10%
831 steps. **B)** and **C)** show calculated curves of progressive phengite dehydration by Rayleigh
832 distillation using equations and methodology outlined in Busigny *et al.* (2003) and exchange
833 coefficients (K_D values) based on experimental conditions of 2.0 GPa and 600 °C (Melzer and
834 Wunder 2000), which represent a good approximation of the natural peak P-T conditions. Rayleigh
835 distillation is modelled by fixing the initial composition and applying $K_D^{\text{Cs-N}} = 0.14$ and $K_D^{\text{Cs-Rb}} =$
836 0.14. Tick marks give the fraction of remaining phengite after dehydration in 10% steps.

837

838 **Figure 8:**

839 Relationships between N, $\delta^{15}\text{N}$ and Pb, CaO in the prograde blueschist-eclogite JTS sequence. The
840 grey band indicates the average $\delta^{15}\text{N}$ value of the 9 samples from the profile, excluding the vein
841 ($\delta^{15}\text{N}_{\text{average}} = +2.1 \pm 0.3$).

842

843 **Figure 9:**

844 Potential mixing relationships in $\delta^{15}\text{N}$ –Rb/N and $\delta^{15}\text{N}$ –K/N space for the Tian Shan profiles (**A**)
845 and the Vendée profile (**B**). The field for altered oceanic crust (AOC) is based on data from the East
846 Pacific Rise (EPR; Busigny *et al.* 2005). Compositions of (meta)sedimentary rocks are average
847 values from five distinct locations (data from Busigny *et al.* 2003; Sadofsky and Bebout 2003,
848 2004; Li and Bebout 2005). Solid lines are calculated mixing curves with 10% tick marks.

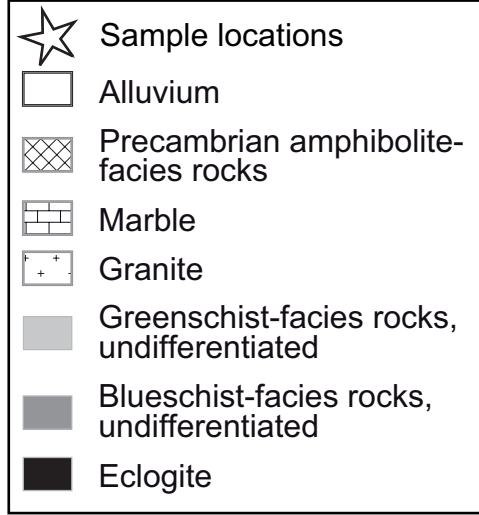
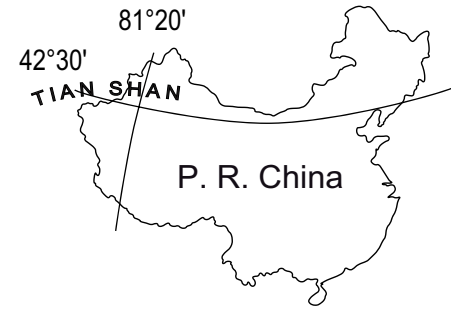
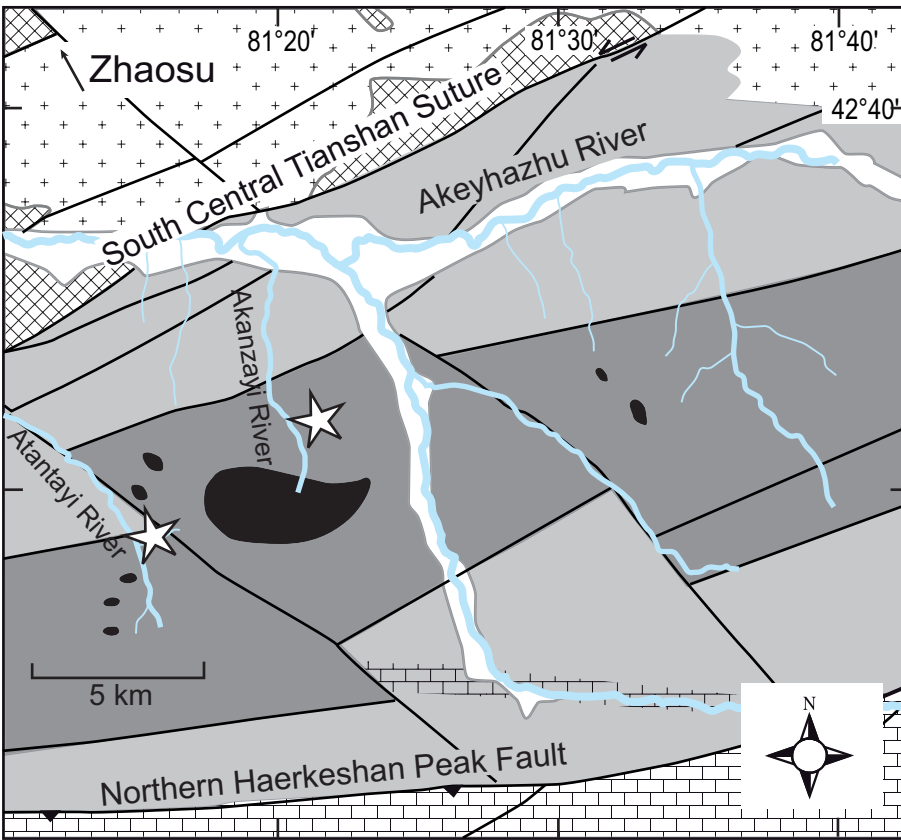
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850 **Figure 10:**

851 Summary figure illustrating the processes observed in the metamorphosed mafic rock sequences of
852 this study.

Fig. 1

A) Tianshan



B) South Armorican Massif

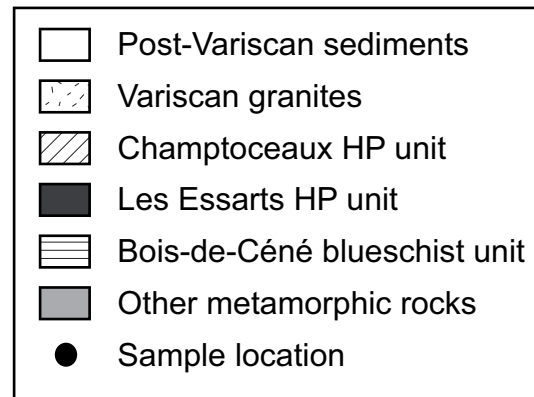
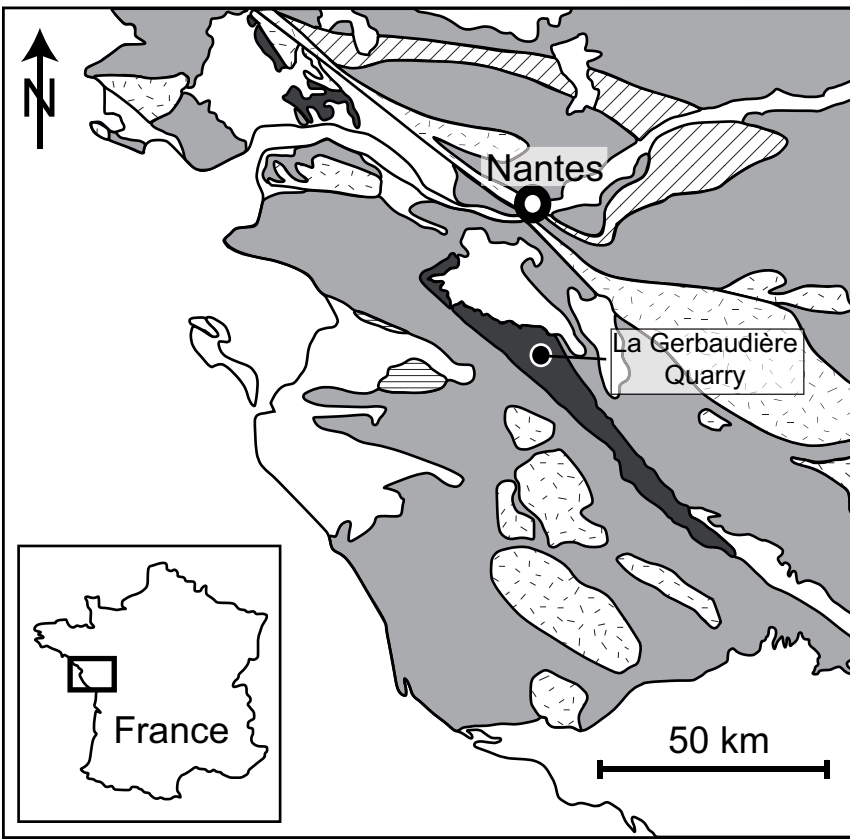
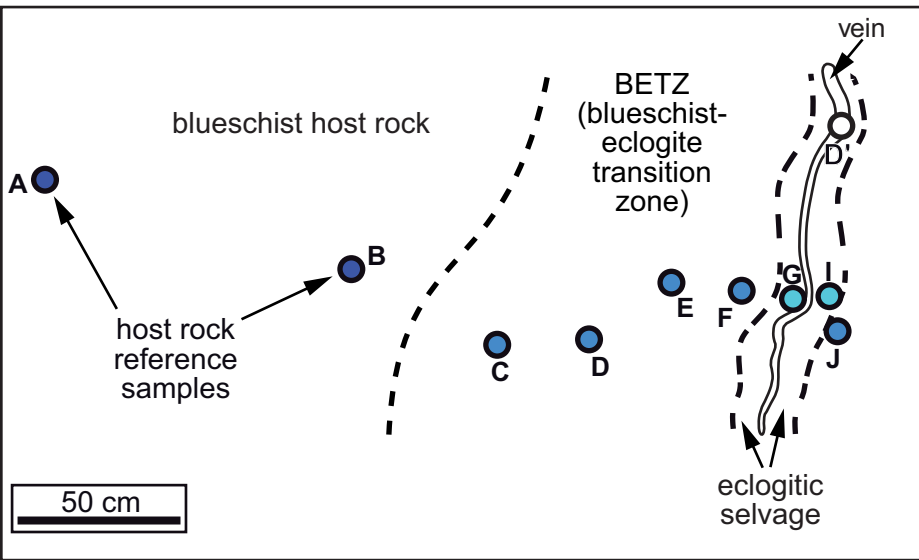
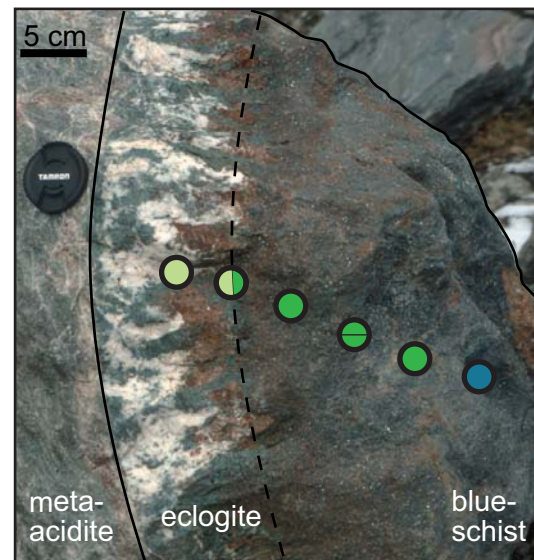
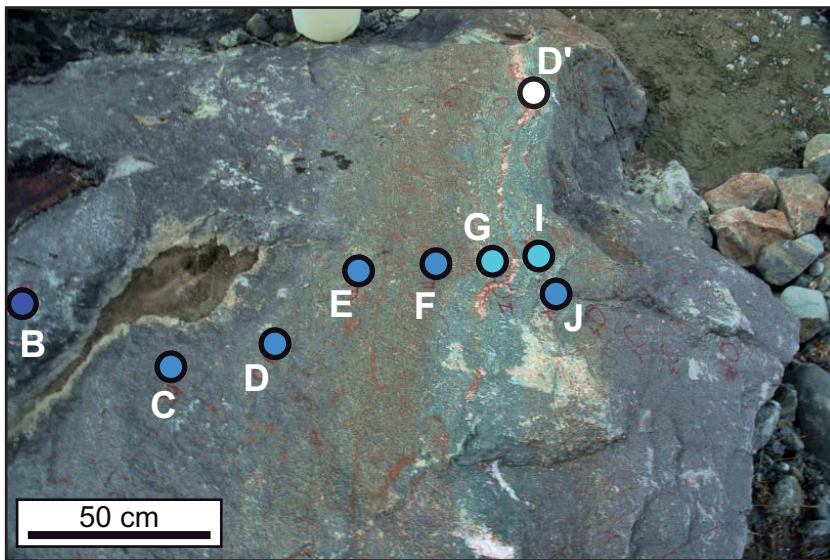
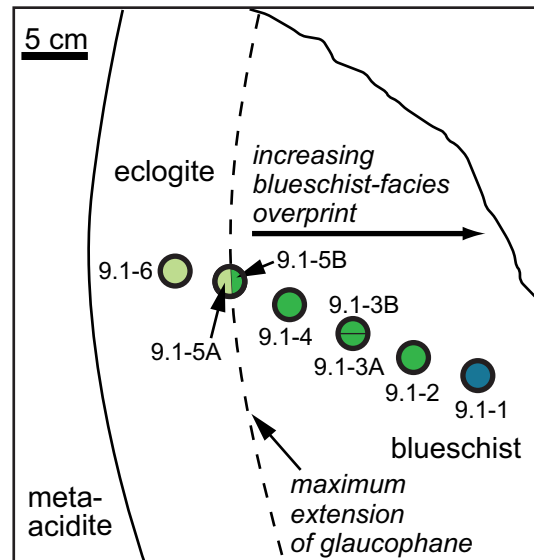


Fig. 2

A) JTS sequence



B) FTS sequence



C) Vendée traverse

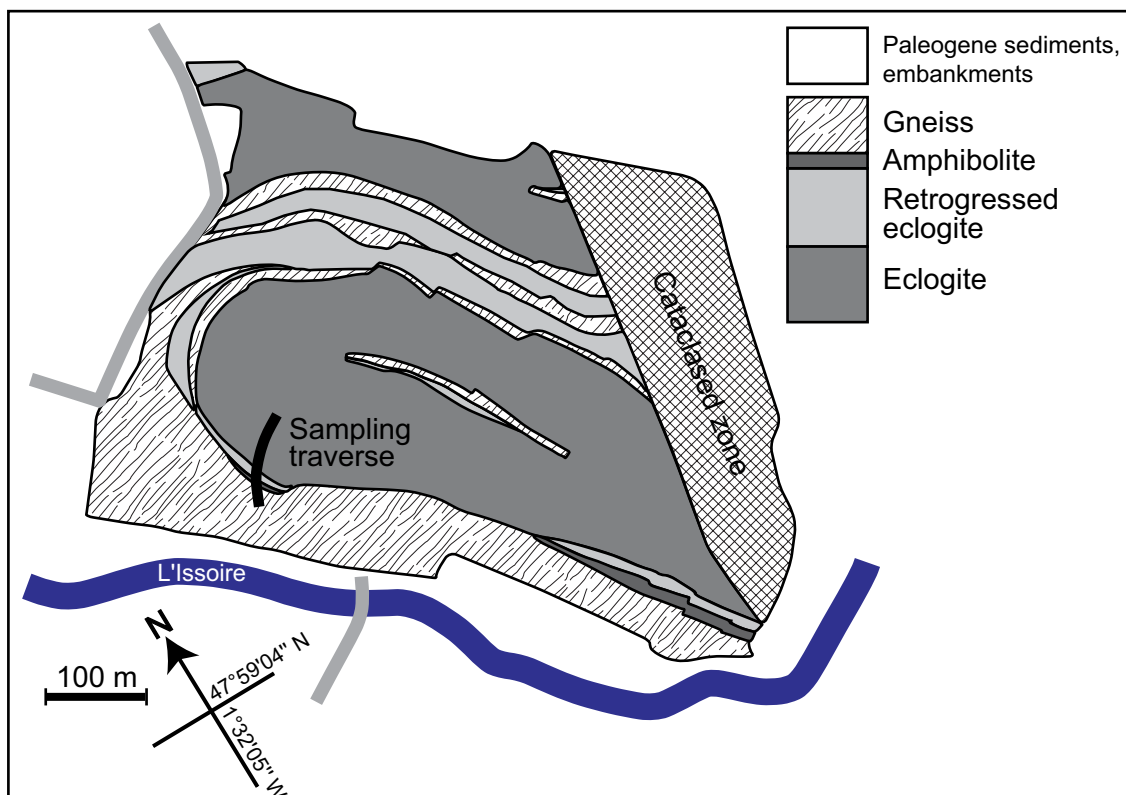
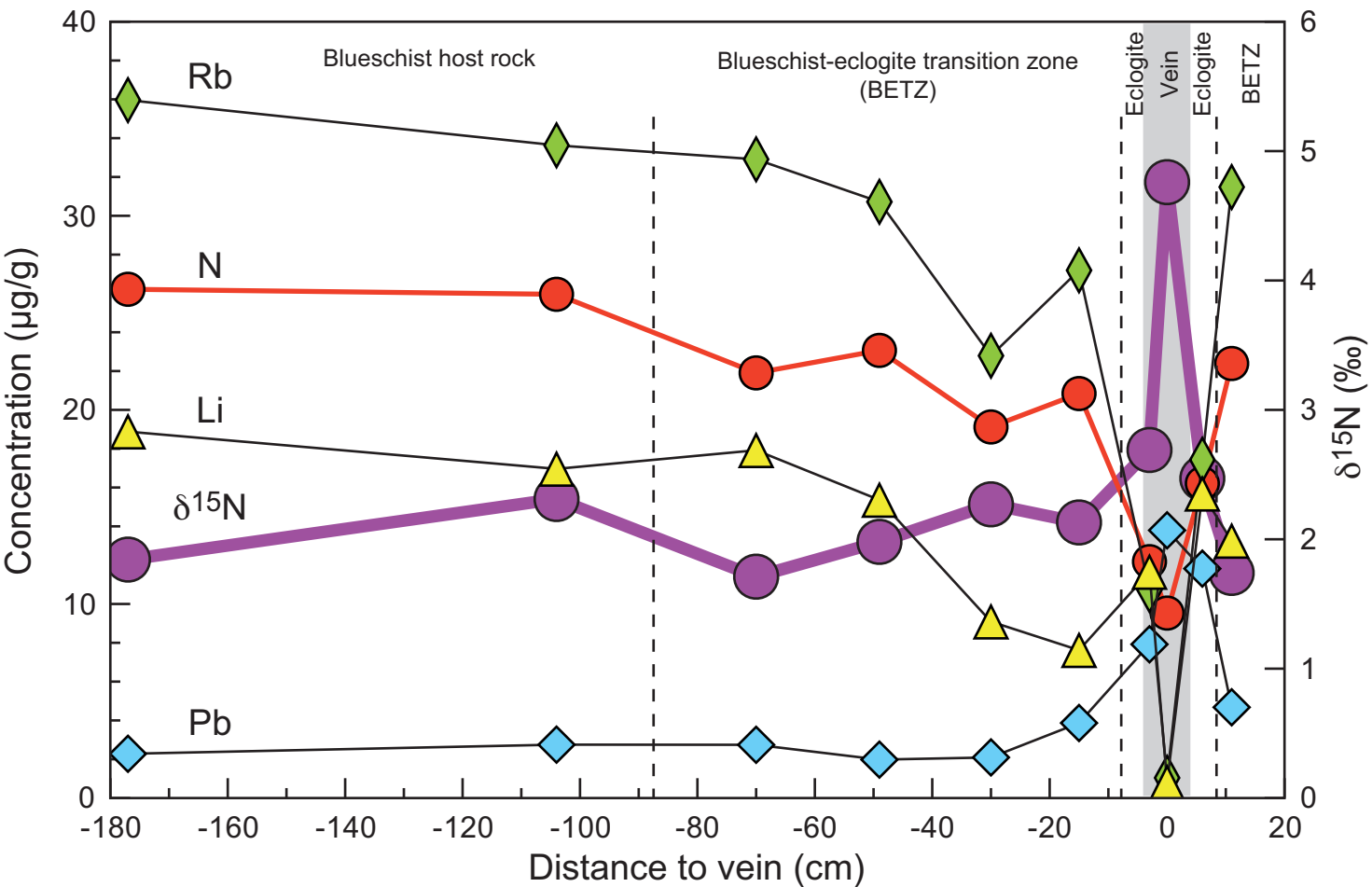


Fig. 3

A) JTS sequence



B) Vendée traverse

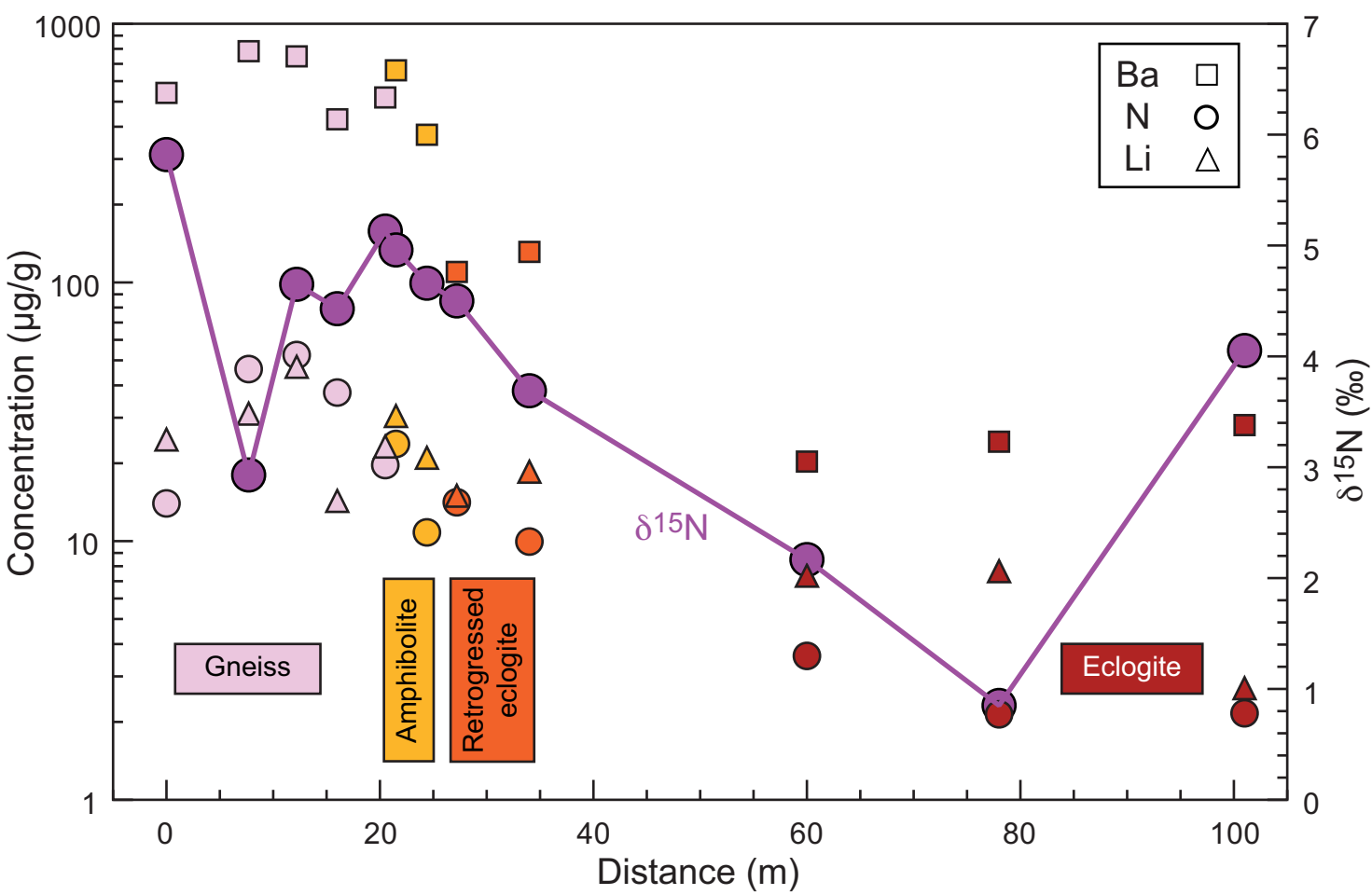


Fig. 4

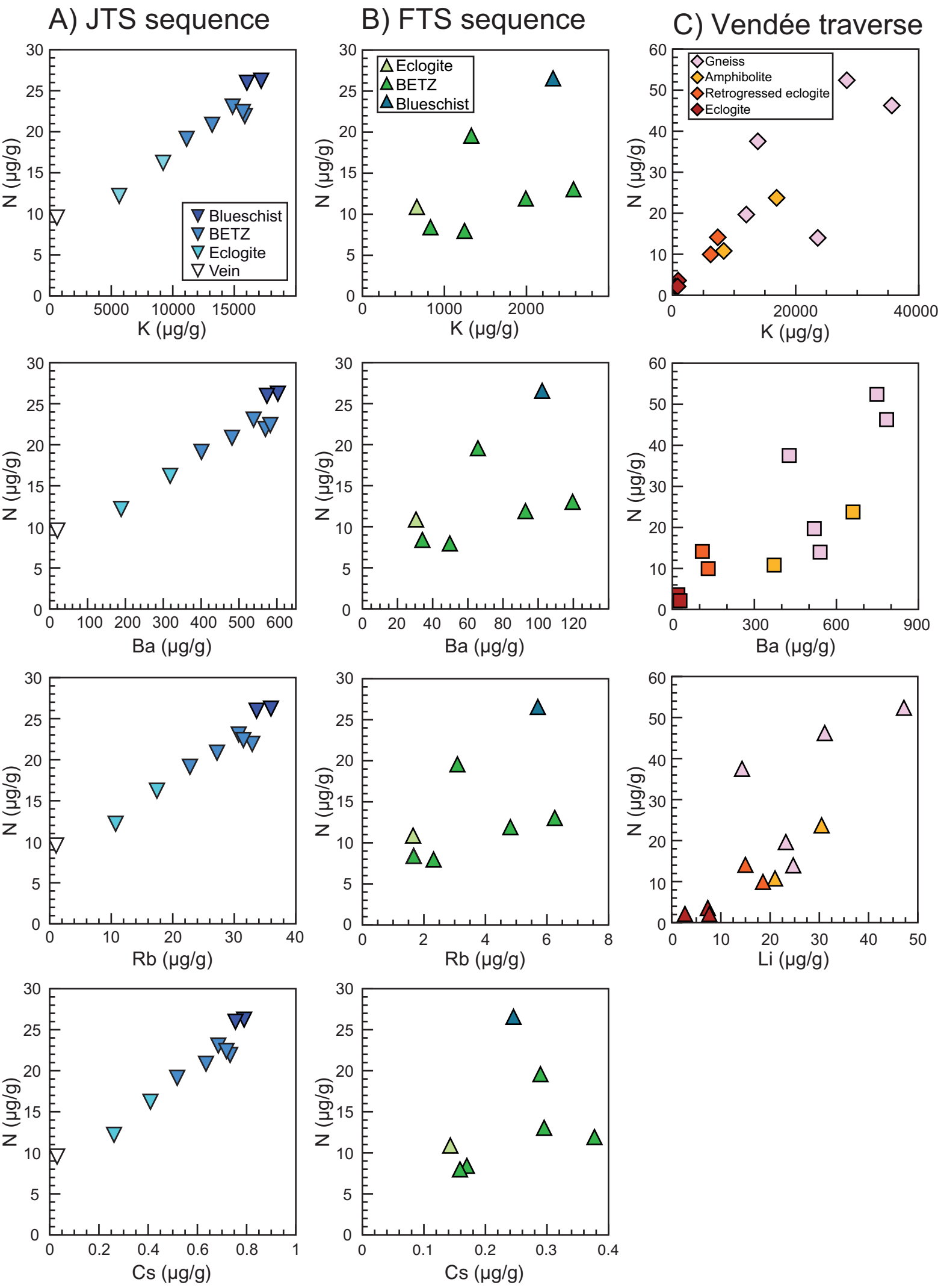


Fig. 5

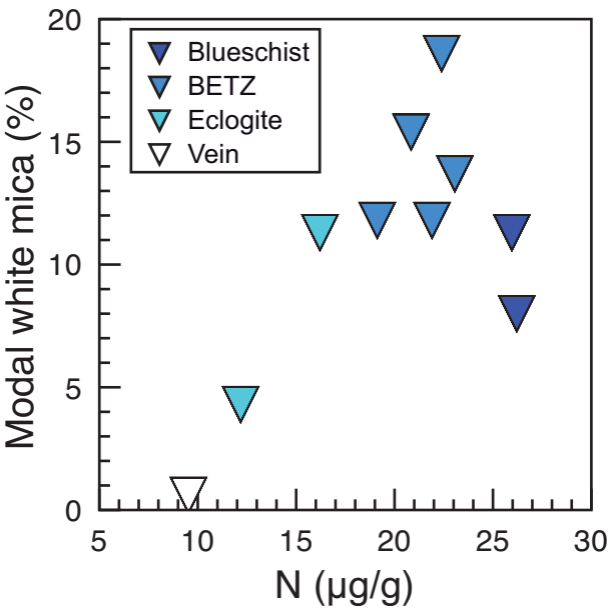


Fig. 6

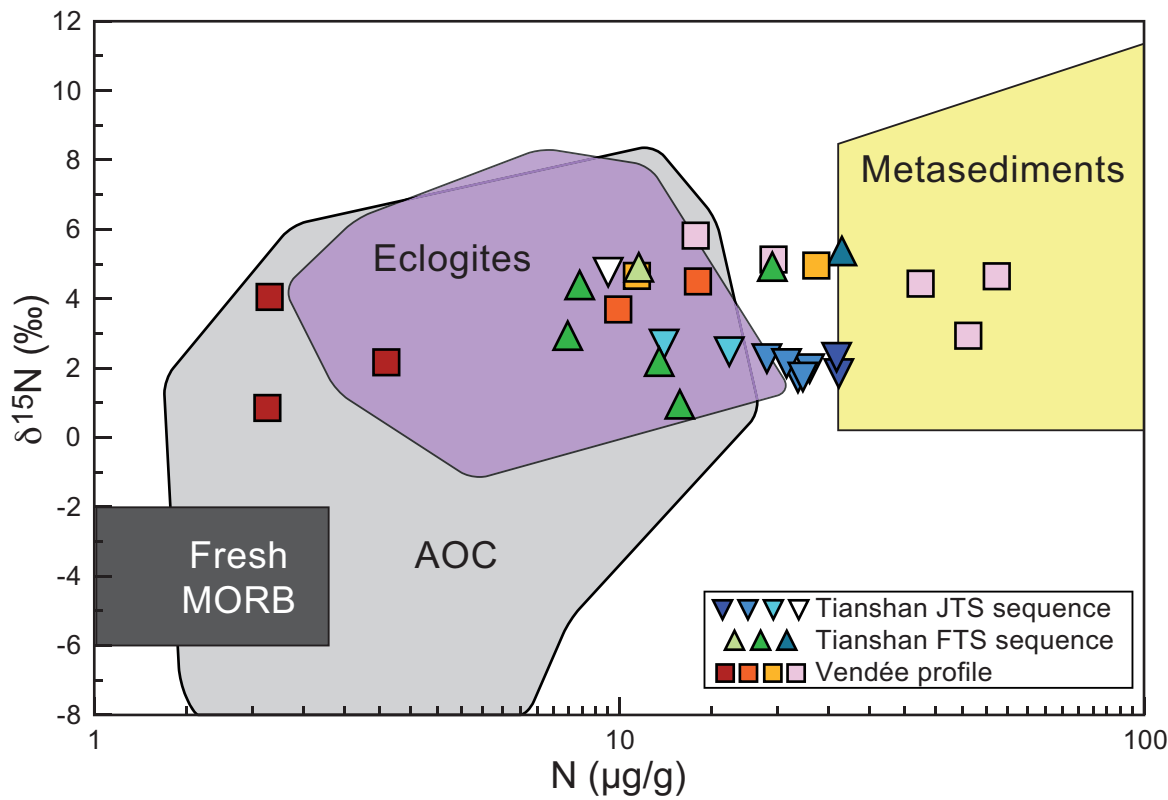


Fig. 7

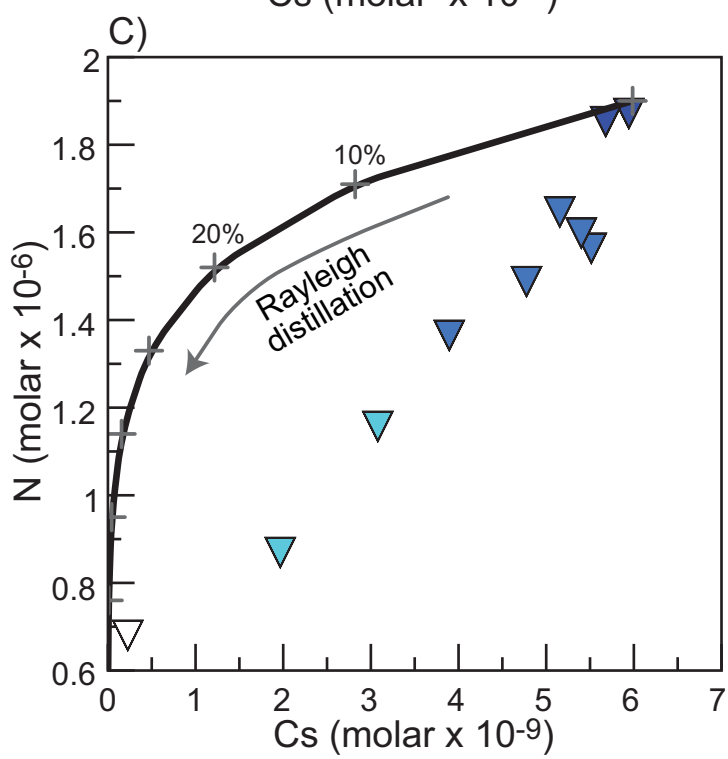
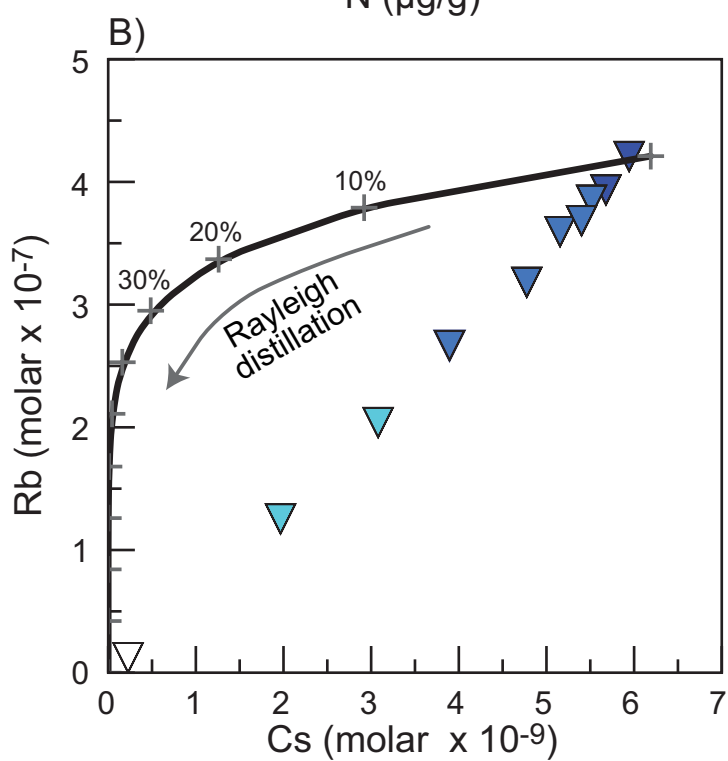
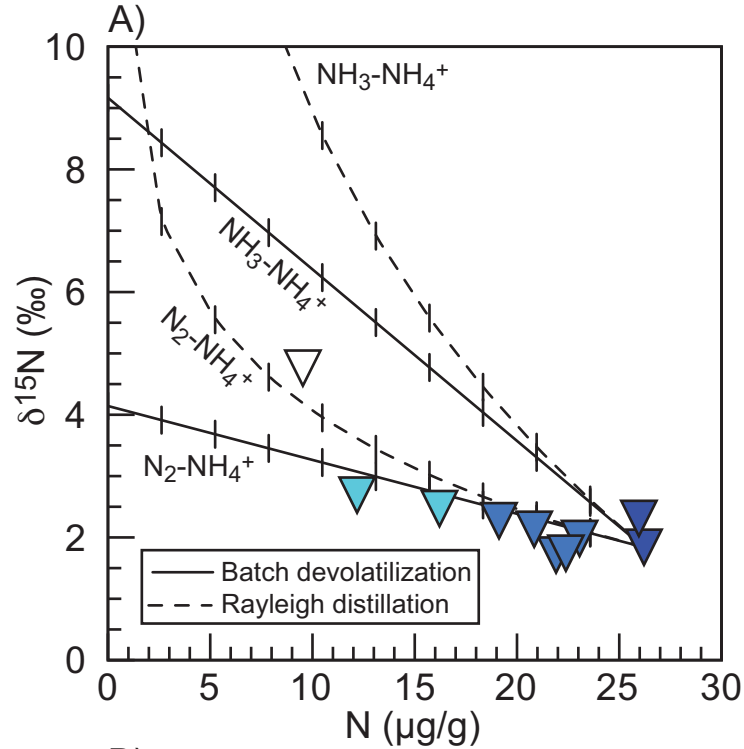


Fig. 8

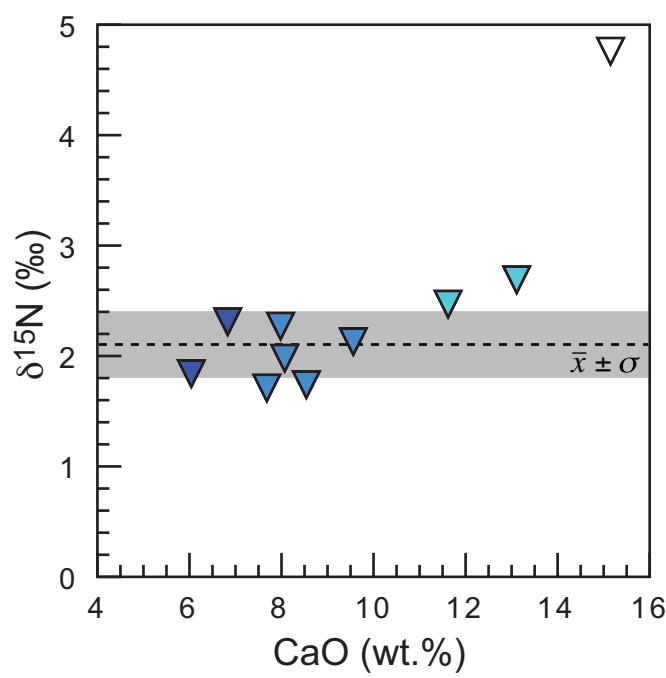
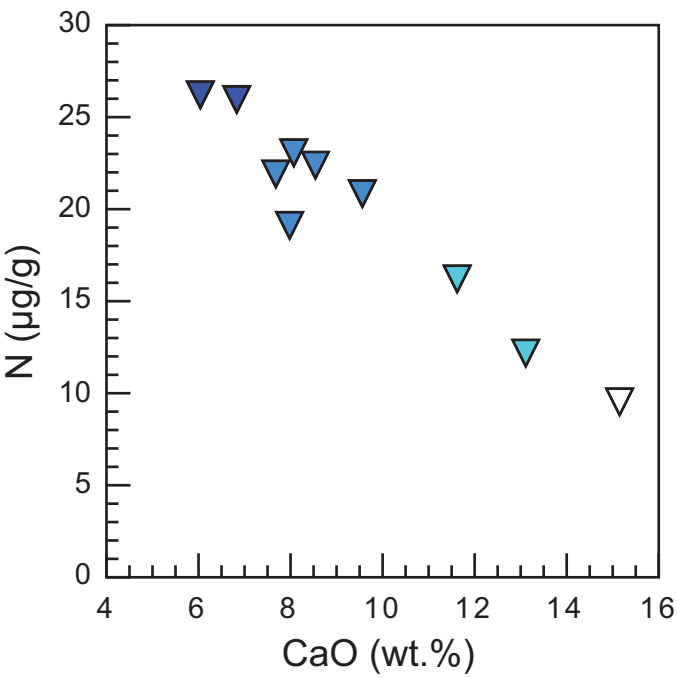
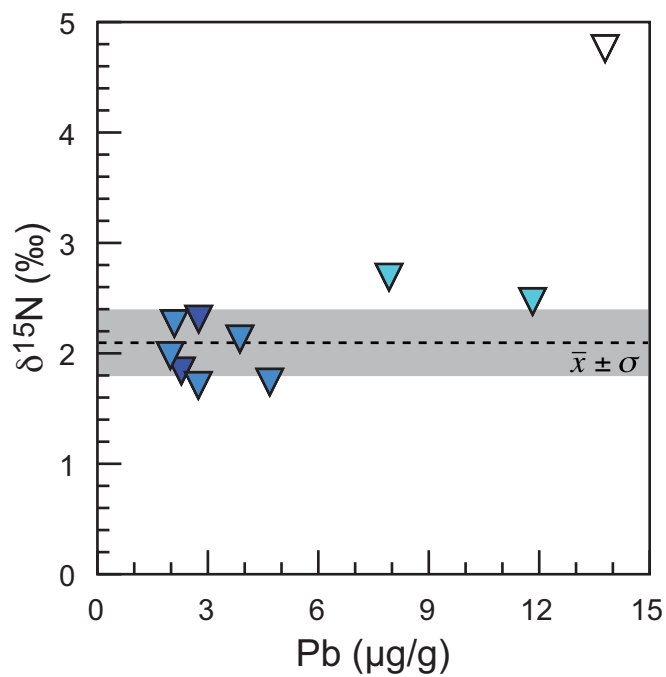
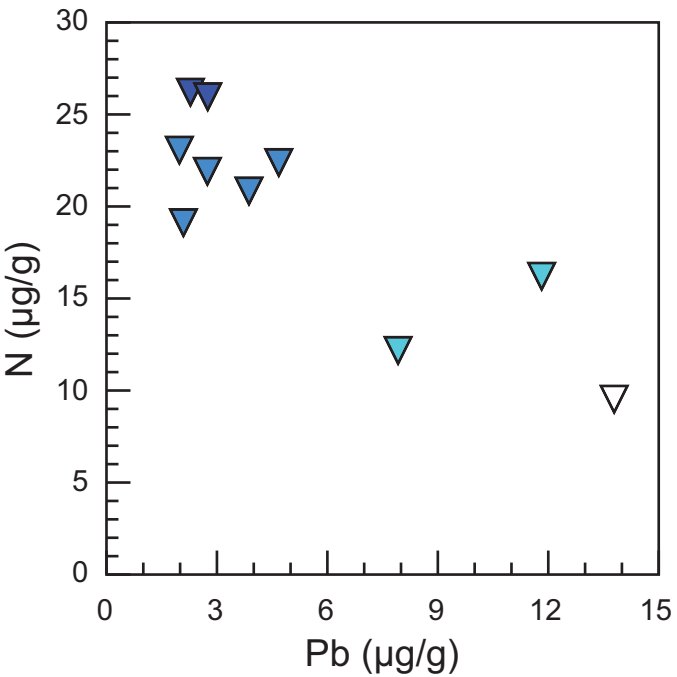
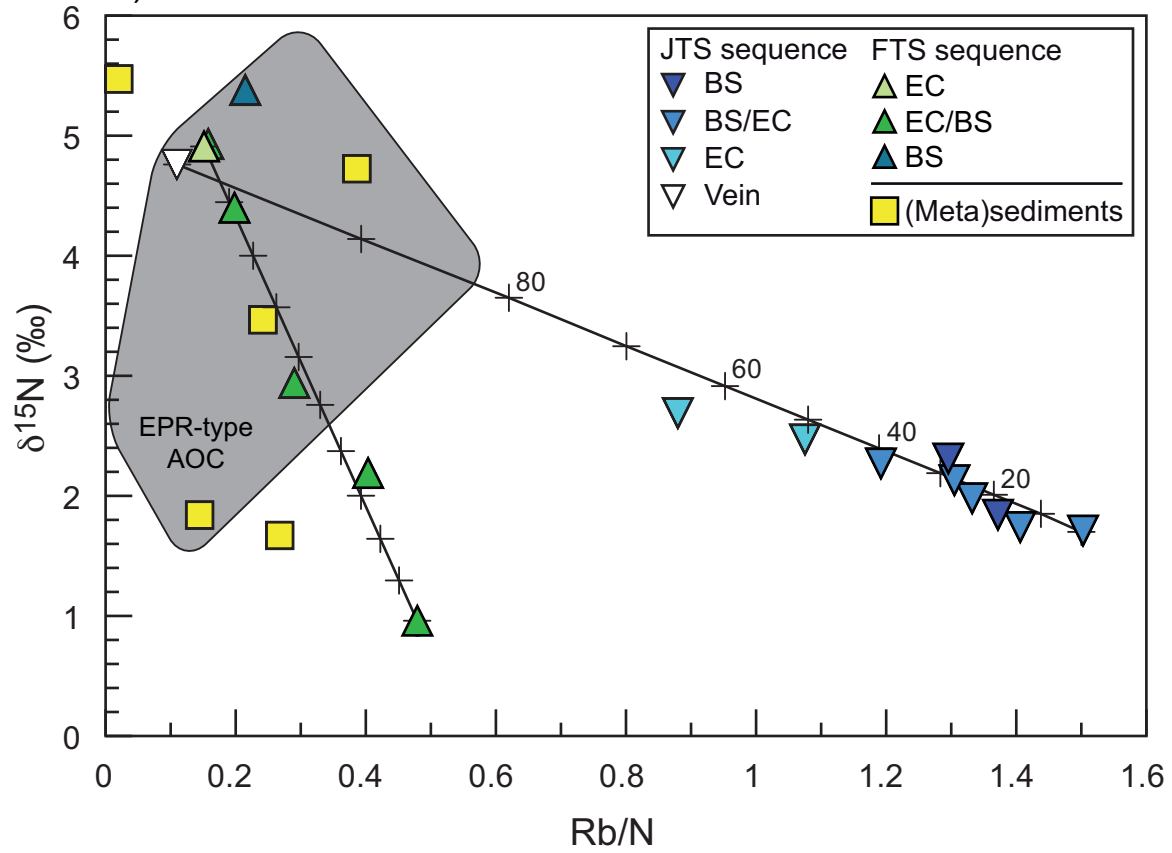


Fig. 9

A) Tianshan



B) Vendée

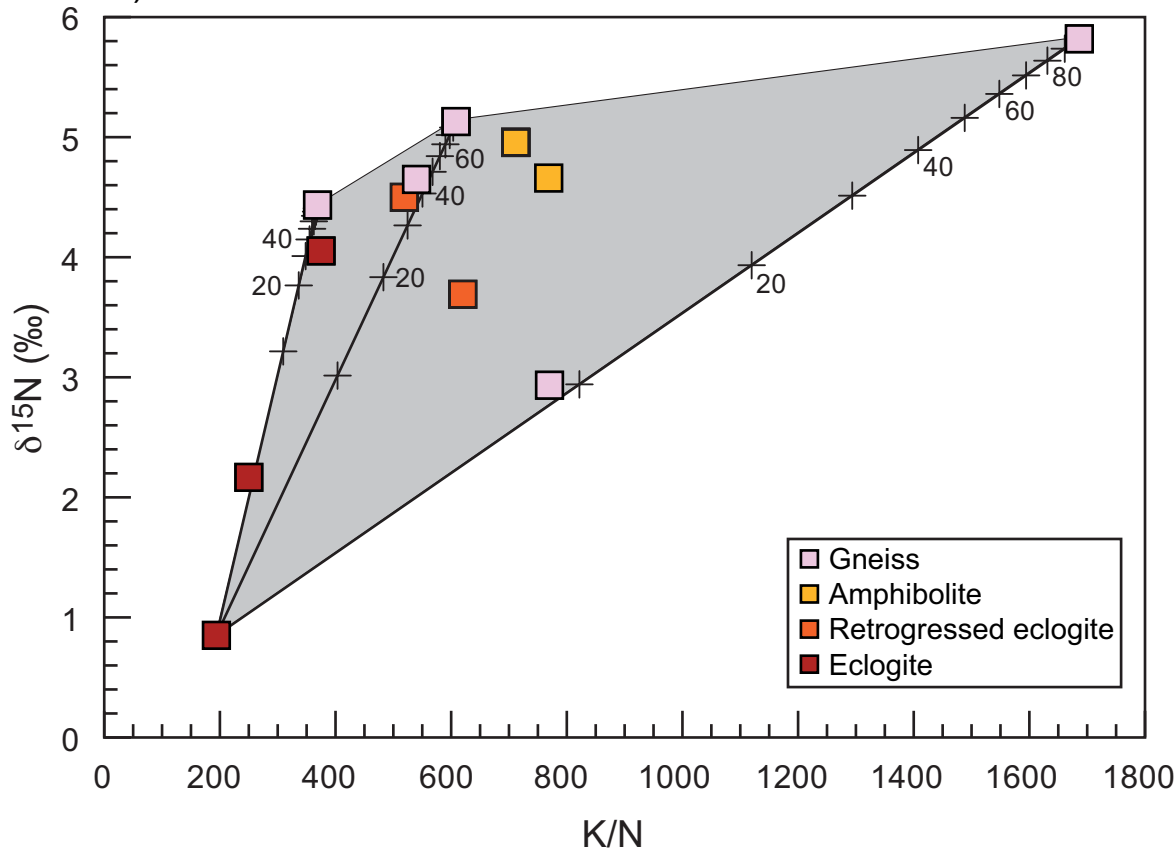
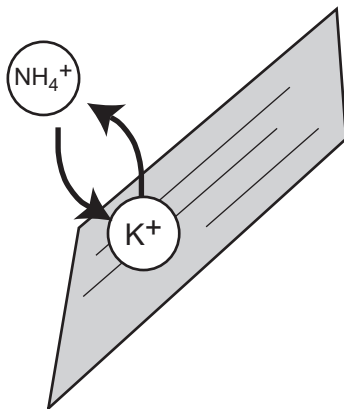


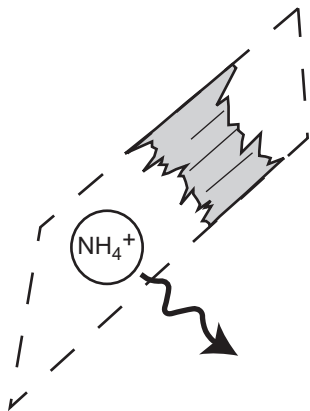
Fig. 10

Phengite growth



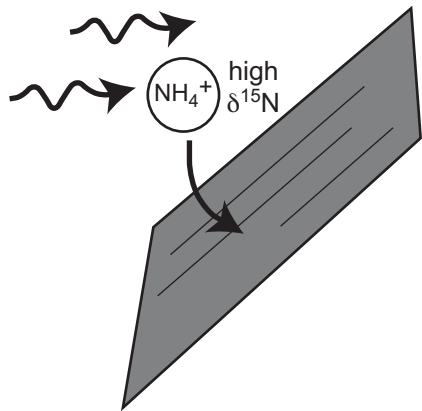
Phengite as major host of nitrogen
via incorporation of NH_4^+ for K^+

Phengite breakdown



Mobilisation of nitrogen and
release into fluid

Phengite re-equilibration



Exchange with high- $\delta^{15}\text{N}$
sediment-derived fluid

Table 1: Nitrogen concentration and isotope data of the three profiles investigated in this study

Sample #	Rock-type	N ($\mu\text{g/g}$)	$\delta^{15}\text{N}$ (‰)	Distance (m)
<i>Tian Shan, prograde blueschist-eclogite transformation:</i>				
JTS-A	blueschist	26.2	1.8	-1.77
JTS-B	blueschist	26.0	2.3	-1.04
JTS-C	bs/ec	21.9	1.7	-0.70
JTS-D	bs/ec	23.1	2.0	-0.49
JTS-E	bs/ec	19.1	2.3	-0.30
JTS-F	bs/ec	20.8	2.1	-0.15
JTS-G	eclogite	12.2	2.7	-0.03
JTS-D'	qz-carbonate vein	9.5	4.8	0
JTS-I	eclogite	16.2	2.5	0.06
JTS-J	bs/ec	22.4	1.7	0.11
<i>Tian Shan, retrograde eclogite-blueschist transformation (FTS 9-1 sequence)</i>				
FTS 9.1-1	blueschist	26.6	5.38	0
FTS 9.1-2	ec/bs	13.1	0.96	0.05
FTS 9.1-3 B	ec/bs	19.6	4.93	0.10
FTS 9.1-3 A	ec/bs	11.9	2.19	0.10
FTS 9.1-4	ec/bs	8.0	2.94	0.15
FTS 9.1-5 B	ec/bs	8.4	4.40	0.20
FTS 9.1-5 A	eclogite	10.9	4.91	0.20
<i>Vendée, gneiss-to-eclogite profile</i>				
G08-3-2	gneiss	14.0	5.8	0
G08-3-1	biotite gneiss	46.3	2.9	7.7
G08-3-3	garnet gneiss	52.4	4.6	12.2
G08-3-4	garnet gneiss	37.5	4.4	16.0
G08-3-5	gneiss	19.7	5.1	20.5
G08-3-6	garnet amphibolite	23.7	5.0	21.5
G08-3-7	garnet amphibolite	10.8	4.7	24.4
G08-3-8	retrogressed eclogite	14.1	4.5	27.2
G08-3-9	retrogressed eclogite	10.0	3.7	34
G08-3-10	eclogite	3.6	2.2	60
G08-3-11	eclogite	2.1	0.9	78
G08-3-12	eclogite	2.3	4.5	101
G08-3-12 repl.	eclogite	2.1	3.6	101
G08-3-12 avg.	eclogite	2.2	4.1	101

repl. = replicate analyses; avg. = average

Sample	JTS-A	JTS-B	JTS-C	JTS-D	JTS-E	JTS-F	JTS-J	JTS-G	JTS-I	JTS-D'	FTS 9-1.1	FTS 9-1.2	FTS 9-1.3B	FTS 9-1.3A	FTS 9-1.4	FTS 9-1.5B	FTS 9-1.5A	
Traverse	JTS	JTS	JTS	JTS	JTS	JTS	JTS	JTS	JTS	JTS	FTS	FTS	FTS	FTS	FTS	FTS	FTS	
Rock type	Blueschist	Blueschist	EC/BS	EC/BS	EC/BS	EC/BS	EC/BS	Eclogite	Eclogite	Vein	Blueschist	Blueschist	EC/BS	EC/BS	EC/BS	EC/BS	Eclogite	
Location	Host rock	Host rock	BETZ	BETZ	BETZ	BETZ	BETZ	Selvage	Selvage	Vein	Host rock	Host rock	BETZ	BETZ	BETZ	BETZ	Selvage	
Major elements (wt.%)																		
SiO ₂	47.66	48.71	47.16	49.03	48.53	41.83	49.29	45.4	53.55	52.43	47.23	39.43	36.43	42.03	41.17	43.65	49.75	
TiO ₂	3.76	3.55	3.54	3.64	3.34	3.58	3.99	3.45	3.23	0.54	0.65	0.75	0.44	0.58	0.68	0.59	0.64	
Al ₂ O ₃	15.44	14.4	14.29	14.51	14.32	14.42	14.63	11.84	12.01	4.57	13.26	12.77	9.48	12.15	12.60	11.93	12.52	
Fe ₂ O ₃	13.52	12.99	12.39	13.29	16.22	16.62	12.35	12.93	8.76	8.86	8.23	10.84	9.27	8.65	8.81	9.30	7.94	
MnO	0.19	0.2	0.16	0.2	0.29	0.28	0.14	0.19	0.05	0.12	0.11	0.35	0.23	0.17	0.22	0.24	0.20	
MgO	5.53	5.31	5.87	4.47	3.64	4.72	4.13	4.72	3.9	4.22	10.29	10.30	12.28	11.23	9.69	9.27	7.59	
CaO	6.04	6.83	7.68	8.07	7.98	9.56	8.54	13.11	11.62	15.15	6.66	9.86	11.90	8.67	11.12	11.72	12.28	
Na ₂ O	3.25	3.01	3.46	3.19	1.95	1.86	2.96	3.04	3.76	0.19	5.56	4.10	4.16	4.88	4.78	5.09	5.94	
K ₂ O	2.07	1.93	1.91	1.79	1.34	1.59	1.89	0.68	1.11	0.07	0.28	0.31	0.16	0.24	0.15	0.10	0.08	
P ₂ O ₅	0.70	0.67	0.65	0.69	0.62	0.57	0.55	0.52	0.6	2.66	0.01	0.01	0.01	0.05	0.01	0.01	0.01	
CO ₂	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7.34	11.76	n.a.	11.48	10.94	8.80	3.37	
H ₂ O = LOI-CO ₂	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.68	0.47	n.a.	1.34	0.50	0.34	0.10	
LOI	1.01	1.84	2.16	0.29	0.7	3.96	0.48	3.67	0.67	11.94	9.02	12.23	17.61	12.82	11.44	9.14	3.47	
Total	99.17	99.44	99.27	99.17	98.93	98.99	98.95	99.55	99.26	100.75	101.30	100.95	101.97	101.47	100.67	101.04	100.42	
Trace elements (µg/g)																		
Li	20.4	18.8	19.2	16.3	10.0	8.21	14.3	12.8	16.9	0.781	42.3	30.2	32.0	124	35.5	33.6	37.7	
Rb	36.0	33.6	32.9	30.7	22.8	27.2	31.5	10.7	17.4	1.04	5.70	6.25	3.09	4.81	2.31	1.67	1.65	
Sr	205	278	315	207	269	608	364	859	1117	2132	301	412	496	448	412	316	159	
Y	49.0	47.7	36.7	47.6	78.6	55.0	49.6	37.9	37.6	27.7	13.2	38.6	15.4	13.8	22.2	16.0	18.4	
Zr	382	333	340	311	303	301	342	290	279	36.3	26.7	28.6	16.2	22.7	26.7	23.5	26.2	
Cs	0.790	0.755	0.733	0.685	0.518	0.635	0.718	0.261	0.409	0.03	0.25	0.30	0.29	0.38	0.16	0.17	0.14	
Ba	603	574	570	539	401	481	583	189	318	20.1	102	120	65.7	92.8	49.7	34.1	30.5	
Pb	2.28	2.75	2.74	1.98	2.09	3.87	4.68	7.92	11.8	13.8	3.16	3.85	4.39	4.43	3.68	2.64	1.52	
Modal composition																		
Garnet	22.8	22.3	18.3	24.9	31.3	23.6	16.3	16.0	10.0	24.6								
Omphacite	16.9	17.5	29.7	34.1	30.9	26.9	39.5	50.0	50.0	5.0								
Glaucophane	36.4	28.2	23.8	6.4	2.8	1.0	0.3	0.3	-	1.5								
White mica	8.0	11.3	11.8	13.7	11.8	15.4	18.6	4.3	11.3	0.6								
Quartz	2.4	2.8	1.7	7.5	8.7	11.5	10.0	6.0	11.6	19.0								
Carbonate	0.9	5.2	4.7	0.9	2.6	12.1	0.7	7.3	1.7	38.0								
Others	12.7	12.6	10.0	12.5	11.9	9.5	14.6	15.9	15.4	11.3								

Sample	G08-3-2	G08-3-1	G08-3-3	G08-3-4	G08-3-5	G08-3-6	G08-3-7	G08-3-8	G08-3-9	G08-3-10	G08-3-11	G08-3-12
Rock type	Gneiss	Gneiss	Gneiss	Gneiss	Gneiss	Amphibolite	Amphibolite	RetEc	RetEc	Eclogite	Eclogite	Eclogite
Traverse distance (m)	0.0	7.7	12.2	16.0	20.5	21.5	24.4	27.2	34.0	60.0	78.0	101.0
Major elements (wt.%)												
SiO ₂	65.16	73.59	60.19	64.84	62.96	63.17	54.21	52.53	50.62	48.02	48.86	48.16
TiO ₂	0.66	0.27	1.19	0.91	0.76	0.80	0.98	0.28	0.33	1.23	1.21	1.29
Al ₂ O ₃	15.83	13.73	15.29	14.65	15.72	15.29	16.74	21.73	18.99	14.51	14.73	15.13
Fe ₂ O ₃	5.38	1.85	8.17	7.80	6.78	6.61	8.52	4.32	6.08	11.82	11.40	11.68
MnO	0.09	0.02	0.13	0.12	0.14	0.12	0.20	0.07	0.13	0.19	0.19	0.18
MgO	2.37	0.56	3.66	2.23	2.78	2.67	5.63	5.04	7.58	7.98	8.02	8.06
CaO	2.22	1.17	3.04	2.70	3.03	2.28	7.42	10.93	10.87	12.40	11.28	12.17
Na ₂ O	3.15	3.02	1.89	2.84	3.35	3.67	2.90	2.70	2.82	2.18	3.20	2.41
K ₂ O	2.84	4.29	3.41	1.67	1.44	2.04	1.00	0.88	0.74	0.11	0.05	0.10
P ₂ O ₅	0.20	0.10	0.19	0.11	0.16	0.10	0.13	0.02	0.02	0.10	0.10	0.10
LOI	1.45	0.82	2.23	1.41	1.96	2.08	1.91	1.56	1.78	0.72	0.41	0.52
Total	99.35	99.41	99.38	99.28	99.09	98.83	99.63	100.06	99.95	99.25	99.45	99.79
Trace elements (µg/g)												
Li	24.7	31.1	47.2	14.3	23.2	30.5	21.0	15.0	18.5	7.35	7.65	2.70
Cr	20.3	b.d.l.	72.2	35.1	30.3	42.9	169	52.7	147	258	202	215
Ni	b.d.l.	b.d.l.	5.0	10.2	3.1	2.8	28.7	b.d.l.	1.8	59.5	31.5	38.3
Sr	240	142	245	258	357	355	281	813	406	147	126	125
Zr	190	149	241	356	244	297	188	15.6	14.5	81.0	80.9	89.1
Ba	540	784	748	427	519	661	372	110	131	20.3	24.2	28.1

RetEc = Retrogressed eclogite

b.d.l. = below detection limit