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1 Nitrogen and carbon cycle perturbations through the Cenomanian- 2 Turonian Oceanic Anoxic Event 2 (~94 Ma) in the Vocontian Basin (SE 3 France)

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8

9 Abstract

10 Oceanic Anoxic Event 2, spanning the Cenomanian-Turonian boundary, was an episode of
11 major perturbations in global biogeochemical cycles, characterized by the widespread burial of organic
12 carbon in both oceans and epicontinental basins. In the Vocontian Basin (SE France), this event was
13 expressed by the deposition of the Niveau Thomel, a succession of interbedded dark shales, grey marls and
14 bioturbated carbonates as observed in the Lambruisse section. Analyses of the total organic carbon (TOC)
15 content, combined with the concentrations of redox-sensitive trace elements, revealed that conditions
16 fluctuated from oxic to suboxic-anoxic during the deposition of the Niveau Thomel. Transient periods of
17 deoxygenation were related to perturbations in nutrient cycling reflected by near-zero to negative $\delta^{15}\text{N}$
18 signatures indicative of increased diazotrophy.

19 The development of deoxygenated conditions in the Vocontian Basin was likely preconditioned by
20 hydrographically restricted conditions, as confirmed by Mo vs. U enrichments, reducing bottom-water
21 ventilation associated with water-column stratification. Intervals of reoxygenation were likely linked to
22 climate-induced changes. In particular, a phase of regional or global cooling associated with a drop in
23 $p\text{CO}_2$, called the Plenus Cold Event (PCE) resulted in vigorous reoxygenation of the Vocontian Basin.

24

25 **Keywords:** OAE 2; Anoxia; Redox; Trace elements; Nitrogen isotopes

26

27 1. Introduction

28

29 Several major perturbations of the global carbon cycle have been recognized. These episodes,
30 namely oceanic anoxic events (OAEs; Schlanger and Jenkyns, 1976), are characterized by a
31 widespread increase in organic matter (OM) content in the sedimentary record. The simultaneous
32 deposition of organic-rich sediments in both epicontinental and deep-sea sites has been attributed to
33 enhanced primary productivity in surface waters and/or to widespread oxygen-deficient conditions in
34 bottom waters (see Arthur and Sageman, 1994; Jenkyns, 2010).

35 Oceanic Anoxic Event 2 (OAE 2), spanning the Cenomanian-Turonian boundary (CTB; 93.9
36 Ma) has been described as the most intense and widespread OAE of the Cretaceous (e.g. Jenkyns,

37 2010). The consequence of this episode of massive burial of ^{13}C -depleted OM was a worldwide
38 positive excursion (+2 to 4‰) in the $\delta^{13}\text{C}$ signals of both carbonates and OM (Arthur et al., 1988;
39 Jenkyns et al., 1994; Kuypers et al., 2002; Tsikos et al., 2004; Erbacher et al., 2005; Sageman et al.,
40 2006; Jarvis et al., 2011). The interval encompassing this carbon isotope excursion used a
41 chemostratigraphic signature of OAE 2 (Kuypers et al., 2002), is thought to have lasted between 450
42 and 700 kyr (Sageman et al., 2006; Voigt et al., 2008; Meyers et al., 2012; Eldrett et al., 2015).

43 The mechanisms involved in the development of favourable conditions for OM accumulation
44 during OAE 2 are multiple and include an increase in primary productivity and OM export to depths,
45 associated with an expansion of the oxygen minimum zone and a more sluggish ocean circulation (e.g.
46 Schlanger and Jenkyns, 1986; Monteiro et al., 2012; Donnadieu et al., 2016).

47 Moreover, intense volcanic activity associated with the emplacement of large igneous
48 province(s) (LIPs) is thought to triggered OAEs (Sinton and Duncan, 1997; Jones and Jenkyns, 2001).
49 Ages reported for the Caribbean LIP (CLIP) (around 93–94 Ma; Snow et al., 2005) and for the High-
50 Arctic LIP (HALIP) (Cenomanian–Turonian age; Tegner et al., 2011; Kingsbury et al., 2017),
51 spanning the interval of OAE 2, support this inference. In addition, the isotopic compositions of
52 hydrothermally-derived metals such as Os (Turgeon and Creaser, 2008; Du Vivier et al., 2014, 2015),
53 Nd (MacLeod et al., 2008. Zheng et al., 2013) and Cr (Holmden et al., 2016), and geographically
54 restricted enrichments of Hg (Scaife et al., 2017; Percival et al., 2018), point to intense submarine
55 volcanic activity at the onset of OAE 2. A first consequence of this increased igneous activity was the
56 emission of large amounts of CO_2 to the atmosphere-ocean system (e.g. Sinninghe Damsté et al., 2008;
57 Barclay et al., 2010; van Bentum et al., 2012a). Higher sea-surface temperatures and a reduced
58 latitudinal thermal gradient in the already extreme warm Cenomanian–Turonian climate (Clarke and
59 Jenkyns, 1999; Pucéat et al., 2003; Bice et al., 2006; Forster et al., 2007; Friedrich et al., 2012;
60 O'Brien et al., 2017) may have further limited oxygen solubility in surface waters and favoured more
61 sluggish oceanic circulation.

62 The warm temperature and possibly accelerated hydrological cycle were associated with
63 enhanced continental weathering and runoff (Blättler et al., 2011; Pogge von Strandmann et al., 2013;
64 van Helmond et al., 2015), which may have increased nutrient input into the photic zone sustaining
65 higher primary productivity. Enhanced freshwater input and higher runoff may also have triggered
66 stratification of the water column and favoured oxygen-depletion in bottom waters in epicontinental
67 settings, at least seasonally (van Helmond et al., 2015).

68 A second consequence of LIP emplacement was increased concentrations of hydrothermal iron
69 and others trace metal micro-nutrients (Snow et al., 2005; Owens et al., 2012), which could have
70 further enhanced primary productivity if associated with the development of upwelling, as simulated
71 by some models (Trabucho Alexandre et al., 2010). Inputs of iron and trace metals into the photic zone
72 as the result of such processes would have promoted nitrogen fixation by cyanobacteria (e.g. Kuypers
73 et al., 2004) together with phosphorus released (linked to OM remineralization and instability of Fe-

74 Mn-oxyhydroxides) in stratified waters (Mort et al., 2007; Tsandev and Slomp, 2009; Kraal et al.,
75 2010; Poulton et al., 2015; Beil et al., 2019). In addition, oxidation of the reduced metals and sulfides
76 could have further to reduced free-oxygen concentration.

77 The overall anoxic water associated with OAE 2 were however interrupted by a reoxygenation
78 event, as indicated by repopulation of benthic fauna (Kuhnt et al., 2004; Friedrich et al., 2006; Eldrett
79 et al., 2014; van Helmond et al., 2016), a decrease in OM content, and changes in the concentrations of
80 redox-sensitive element observed in sediments (Hetzl et al., 2011; van Helmond et al., 2014a;
81 Dickson et al., 2016; Jenkyns et al., 2017; Danzelle et al., 2018). This event was contemporaneous
82 with a southern input of boreal waters as testimony by boreal marine fauna in the Northern
83 Hemisphere (Jefferies, 1962; Gale and Christensen, 1986; Kuhnt et al., 1986; Pearce et al., 2009;
84 Eldrett et al., 2014; van Helmond et al., 2014b) and Nd isotopes (Zheng et al., 2013, 2016). This event
85 is referred to as the Plenus Cold Event (PCE; Gale and Christensen, 1986) and was identified at
86 several European and Atlantic sites. It has been argued to reflect a decrease in $p\text{CO}_2$ resulting from
87 massive burial of organic carbon in sediments (Sinninghe Damsté et al., 2010; Jarvis et al., 2011).

88 In the Vocontian Basin (SE France), different phases of suboxic to anoxic conditions in
89 bottom waters have been recognized on the basis of congruent sedimentary enrichment in OM, which
90 is partially sulfurized (Raven et al., 2018; 2019), in varying iron sulfide concentrations, and in
91 enrichments in redox-sensitive trace-element (e.g. Mo, V, Zn; Danzelle et al., 2018). Local bottom-
92 water deoxygenation has been attributed to water column stratification forced by an upward migration
93 of sulfide-rich conditions from the sediments, at least up to the sediment-water interface. Anoxic
94 conditions could have further promoted deoxygenation by enhancing phosphorus recycling, leading to
95 a positive feedback loop between primary productivity in surface waters and deoxygenation in bottom
96 waters (Danzelle et al., 2018).

97 Expansion of sulfidic conditions in the Vocontian Basin could have been driven by an increase
98 in sulfate and CO_2 availability in the oceans, possibly linked to the pulses of volcanic activity at the
99 onset of OAE 2 (Adams et al., 2010). Oxygenation conditions during OAE 2 in the basin were
100 unstable, as highlighted by variations in OM concentrations over time (Crumière, 1989; Jarvis et al.,
101 2011; Danzelle et al., 2018). The contribution of other processes such as local/regional variations in
102 primary productivity or in the hydrological cycle however remains poorly constrained.

103 In this study, we investigated the interaction between the intensity in deoxygenated conditions
104 and variations in nutrient cycles by comparing changes in redox-sensitive elements with the carbon
105 and nitrogen cycles for the Lambruisse section. We also compare fluctuations of oxygenation with
106 climate to investigate the links between these processes, building on previous studies conducted in
107 both epicontinental (e.g. Voigt et al., 2008) and deep-ocean environments (e.g. Dickson et al., 2016).

108

109 **2. Geological setting**

110

111 **2.1. The Vocontian Basin through the CTB**

112

113 The Vocontian Basin was part of the northern continental margin of the Alpine realm of the
114 NW Tethys Ocean and was located at ~30°N (Philip et al., 1993). A north-south compressive regime
115 developed in the Late Cretaceous, which was responsible for a high rate of subsidence in the deeper
116 and eastern parts of the basin (Porthault, 1974; Grosheny et al., 2017), with a recently proposed
117 tectonic pulse around the CTB (Grosheny et al., 2017). This tectonic context provided space for the
118 gradual filling of the basin, dominated by a thick rhythmically bedded hemipelagic limestone–marl
119 succession. The paleodepth at the centre of the Vocontian Basin during CTB times is estimated to
120 have been a few hundred metres (Grosheny et al., 2006).

121 In the deepest part of the basin, a distinctive change in facies through the CTB interval is
122 characterized by a ~20–25 m interval composed of alternating dark organic-rich calcareous shale and
123 limestone (Crumière, 1989; Grosheny et al., 2006; Takashima et al., 2009; Jarvis et al., 2011). This
124 interval, named the Niveau Thomel, is the local sedimentary expression of OAE 2 recording the
125 globally recognized carbon isotope positive excursion (Morel, 1998; Takashima et al., 2009; Jarvis et
126 al., 2011; Gale et al., 2019).

127

128 **2.2 The Lambruisse section**

129

130 The Lambruisse section (44°02'05N; 06°28'00E) is one of the tectonically unaffected
131 successions of the deep eastern part of the Vocontian Basin (Fig. 1A), exposing the Niveau Thomel.
132 Based on lithology, four units can be distinguished within the Niveau Thomel, called TH1 to TH4
133 from the base to the top, following the description Jarvis et al. (2011) used for the Pont d'Issole
134 section (Fig. 2). The following description of the faunal content along the Lambruisse section is from
135 Takashima et al. (2009).

136 The base of the section (~17 m) preceding the Niveau Thomel is formed by an alternation of
137 highly bioturbated white and light grey limestones and grey marls. This pre-Thomel unit yields
138 abundant planktonic foraminifera. An interval at the base of the Niveau Thomel, estimated to be 4 m
139 thick, was unfavourable for lithological description or sampling. This interval corresponds to the
140 major part of TH1. The estimated thickness of TH1 (4 m of hidden and uppermost 1 m of exposed
141 dark shales) is in agreement with the 4.5–5 m thick TH1 described in Pont d'Issole section located at a
142 distance of ~4 km (Jarvis et al., 2011; Danzelle et al., 2018). These dark shales are devoid of benthic
143 foraminifera.

144 Unit TH2 (4.2 m) corresponds to a return to alternating light grey marly limestones and grey
145 limy marls, both highly bioturbated. This unit contains abundant planktonic and benthic foraminifera,
146 sponge spicules and radiolarians.

147 Unit TH3 (5.8 m) is composed of alternating dark laminated and non-bioturbated calcareous
148 shales and sparsely-bioturbated grey limy marls. Unlike the dark shales, the limy marls contain some
149 dwarf planktonic foraminifera, abundant radiolarians and sponge spicules.

150 Unit TH4 (7.2 m) is composed of alternating of moderately to highly bioturbated limestones
151 with dark shale and moderately bioturbated marls rich in radiolarians, planktonic and benthic
152 foraminifera. The top of TH4, and therefore of the Niveau Thomel, was placed at the top of the last
153 dark shale bed.

154 The top of the section (~14 m) is dominated by thick white highly-bioturbated limestone beds
155 rich in radiolarians, planktonic and benthic foraminifera. This interval also contains thin grey marl
156 intercalations and one 60 cm dark calcareous shale interbed, ~8.5 m above the top of the Niveau
157 Thomel.

158

159 **3. Methods**

160

161 A total of 91 samples were analyzed in this work. The approach included the analysis of
162 sedimentary OM by Rock-Eval analysis, carbonate carbon and oxygen isotope composition, organic
163 carbon and bulk nitrogen isotope composition, and of concentrations of major- and trace-elements of
164 bulk rock. Bulk-rock samples were powdered to ~10 μm using a ring and puck mill at Sorbonne
165 University's IStEP laboratory.

166

167 **3.1. Rock-Eval pyrolysis**

168

169 Following sequential pyrolysis and oxidation treatment (Espitalié et al., 1985a, b, 1986; Behar
170 et al., 2001) of 60 mg aliquots of powdered bulk sample, total organic carbon content (TOC wt%),
171 Hydrogen Index (HI) and Oxygen Index (OI) in samples were determined with a Rock-EvalTM 6 at the
172 Sorbonne University's IStEP laboratory of. Based on duplicates of the IFPEN 160000 standard,
173 reproducibility (1σ) was estimated at ± 0.05 wt% for TOC, ± 10 mg HC/g TOC for HI and ± 10 mg
174 CO_2/g TOC for OI. As HI and OI values are not reliable when TOC < 0.4 wt% (Espitalié et al., 1986;
175 Peters, 1986), the HI and OI presented in this paper are only reported for samples containing at least
176 0.4 wt% TOC.

177

178 **3.2. Carbon and oxygen isotope compositions of carbonate**

179

180 The stable carbon ($\delta^{13}\text{C}_{\text{carb}}$) and oxygen ($\delta^{18}\text{O}$) isotope compositions of carbonates were
181 determined in 50 powdered bulk-rock samples. Depending on the sample carbonate content, 60 to 200
182 μg aliquots were loaded in glass vials with 100% H_3PO_4 at 70°C. Carbon and oxygen isotopic
183 compositions were measured on a Thermo ScientificTM Delta VTM IRMS coupled with a Kiel VI

184 carbonate preparation device at the Biogeosciences Laboratory of the Bourgogne-Franche-Comté
185 University. All isotopic values are reported in the standard δ -notation (permil ‰) relative to V-PDB
186 (Vienna Pee Dee Belemnite) by calibration to $\delta^{13}\text{C}$ value of +1.95‰, and $\delta^{18}\text{O}$ value of -2.20‰ of the
187 NBS19 international standard. External reproducibility was checked by replicate analyses of both
188 NBS19 and in-house laboratory standards and was better than ± 0.08 ‰ for $\delta^{18}\text{O}$ and ± 0.04 ‰ for $\delta^{13}\text{C}$
189 (1σ).

190

191 **3.3. Carbon isotope composition of organic matter**

192

193 The stable carbon isotope composition of OM ($\delta^{13}\text{C}_{\text{org}}$) was determined on carbonate-free
194 residues collected from 83 samples at the Biogeosciences Laboratory. Decarbonation was carried out
195 by placing powdered samples in reaction tubes filled with 25 ml of 6N HCl solution for 12 hours at
196 room temperature. The dried residues were weighed (between 30 and 75 mg based on Rock-Eval
197 results) and poured into tin capsules. The capsules were combusted using a Vario MICRO cube
198 elemental analyser (Elementar GmbHTM) at 950°C coupled with an IsoPrime stable-isotope mass
199 spectrometer (IsoPrime, Manchester, UK). The isotopic results are reported in δ -notation relative to
200 the V-PDB and calibrated using USGS40 certified reference L-glutamic acid ($\delta^{13}\text{C}_{\text{org}} = -26.2$ ‰, TOC
201 = 40.82 wt%). Reproducibility (1σ) was better than ± 0.10 ‰ for $\delta^{13}\text{C}$, ± 0.10 wt% for C_{org}
202 concentration, based on replicated samples.

203

204 **3.4. Nitrogen isotope composition of bulk rock**

205

206 Stable nitrogen isotope compositions ($\delta^{15}\text{N}$) of the carbonate-free samples were determined on
207 the same 83 samples run in parallel to the $\delta^{13}\text{C}_{\text{org}}$ analyses using the same apparatus. The isotope
208 compositions are reported in δ -notation relative to AIR and calibrated using USGS40 certified
209 reference values ($\delta^{15}\text{N} = -4.5$ ‰, TN = 9.52 wt%). Reproducibility (1σ) was better than ± 0.30 ‰ for
210 $\delta^{15}\text{N}$, ± 0.02 wt% for N concentration, based on replicated samples.

211

212 **3.5. Concentrations of major and trace-element**

213

214 Concentrations of major (Al, Fe, Mn) and trace-elements (Mo, U, V, Zn) of 90 selected
215 samples were determined respectively with an ICP-OES (Thermo Fisher iCap 6500) and an ICP-MS
216 (7700X Agilent) at the spectrochemical laboratory of the Service d'Analyse des Roches et des
217 Minéraux of the Centre National de la Recherche Scientifique (Vandoeuvre-les-Nancy, France).
218 Sample preparation consisted in a fusion by LiBO_2 followed by acid digestion by HNO_3 (2%)
219 (Carignan et al., 2001). Analyses of international standards and replicate samples indicated levels of
220 accuracy and precision better than 1% for Al, Fe, Mn; 5% for Ba; 10% for Cu, Mo, Ni, Zn and 15%
221 for Co and U.

222 To distinguish major and trace elements of detrital origin from those representative of the
223 marine background, concentrations were normalized to Al (cf. Calvert and Pedersen, 1993; Morford et
224 al., 2001). Aluminium is a robust tracer of detrital input and it is not involved in or affected by
225 biological or diagenetic processes. In this study, element/Al (X/Al) ratios are expressed in terms of
226 enrichment factors (EF). This representation corresponds to the ratio between the X/Al values in the
227 sample and that in a reference, in this case average Upper Continental Crust (UCC) (Taylor and
228 McLennan, 1995; McLennan, 2001), and is expressed as $EF\ X = (X/Al)_{\text{sample}} / (X/Al)_{\text{UCC}}$. The purpose
229 of EF values is to easily quantify the enrichment ($EF > 1$) or depletion ($EF < 1$) of an element
230 compared to its detrital value ($EF = 1$).

231

232 **4. Results**

233

234 **4.1. Organic content**

235

236 As expected, the variation in organic content throughout the section is in accordance with
237 changes in facies, with dark intervals corresponding to the highest TOC values. TOC measurements,
238 obtained by Rock-Eval in this study (Fig. 2), resemble to those obtained using an elemental analyser
239 by Takashima et al. (2009).

240 In the pre-Thomel interval, mainly dominated by limestone beds, TOC never exceed 0.50
241 wt%. The organic content of the upper part of the TH1 is characterized by dm-scale fluctuations
242 between 0.25 wt% and 2.45 wt%. Unit TH2 represents an abrupt fall in the organic content (TOC
243 mostly lower than 0.30 wt%). One very thin organic-rich marl interbed (TOC = 1.50 wt%) is present
244 just before the TH2–TH3 boundary. In TH3, high frequency oscillations occurred between lower TOC
245 values ($0.20 < \text{TOC} < 0.75$ wt%) in the grey marls and higher TOC values ($1.25 < \text{TOC} < 3.10$ wt%)
246 in the dark shales. Unit TH4 marks a progressive return to low organic content ($\text{TOC} < 0.35$ wt%);
247 two dark shale beds observed at 36.50 m and at 39.60 m in this unit contain respectively 1.40 and 0.90
248 wt% TOC. Finally, two marly levels at the base and at the top of the post-Thomel dark calcareous
249 shale bed presents TOC values of 1.30 wt% (at 48.00 m) and 0.80 wt% (at 49.56 m) respectively.

250

251 **4.2. Stable carbon isotopes**

252

253 The stable carbon isotope composition of carbonates in the Lambruisse section, previously
254 documented by Takashima et al. (2009), were redetermined here to evaluate the differences between
255 the isotopic compositions of coexisting carbonate and organic carbon in order to investigate changes in
256 of the $\Delta^{13}\text{C}$ (defined as $\Delta^{13}\text{C} = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$) signal, as reported for the equivalent succession at
257 Pont d'Issole by Jarvis et al. (2011).

258

259 **4.2.1. Carbonate stable carbon isotopes**

260
261 The $\delta^{13}\text{C}_{\text{carb}}$ signal obtained in this work (Fig. 2) is consistent with that reported by Takashima
262 et al. (2009). In the pre-Thomel interval, $\delta^{13}\text{C}_{\text{carb}}$ remained relatively stable and only fluctuated slightly
263 around a mean of $2.38 \pm 0.08\text{‰}$ (1σ). As the lower part of TH1 was not exposed, the base of the first
264 build-up phase of the positive isotope excursion characterizing the onset of OAE 2 (Jarvis et al., 2006,
265 2011) could not be determined here. The $\delta^{13}\text{C}_{\text{carb}}$ curve presented by Takashima et al. (2009),
266 highlighted a $+0.70\text{‰}$ shift exactly at the base of the Niveau Thomel, confirming the temporal link
267 between the change in facies in the Vocontian Basin and the onset of OAE 2.

268 A major increase in $\delta^{13}\text{C}_{\text{carb}}$ is recorded from the top of TH1 to the middle of TH2 (from 2.8 to
269 4.0‰) which represents an acceleration in the positive excursion, also documented at Pont d'Issole
270 (Jarvis et al., 2011). The maximum value recorded in TH2 thus corresponds to peak "A" described by
271 Jarvis et al. (2006) in the Eastbourne section (England). The upper half of TH2 is marked by a trough
272 in the positive excursion, with $\delta^{13}\text{C}_{\text{carb}}$ values oscillating between 3.5 and 3.7‰ prior to a second
273 increase recorded at the TH2–TH3 boundary toward peak "B" ($\delta^{13}\text{C}_{\text{carb}} = 4.5\text{‰}$). An interval of
274 relatively constant and high $\delta^{13}\text{C}_{\text{carb}}$ values, termed the isotopic "plateau" (Paul et al., 1999),
275 corresponds to Unit TH3 and to the base of Unit TH4 (mean $\delta^{13}\text{C}_{\text{carb}} = 4.24\text{‰}$). The total amplitude of
276 the $\delta^{13}\text{C}_{\text{carb}}$ positive excursion, from pre-Thomel values to the maximum values recorded in TH3, thus
277 reached about 2‰ . The highest $\delta^{13}\text{C}_{\text{carb}}$ value corresponds to the peak "C" (4.5‰) and is located right
278 before the termination of OAE 2, which is underlined by a last small positive peak in the decreasing
279 phase. Based on the chemostratigraphic correlation with the $\delta^{13}\text{C}$ signals from the Eastbourne (Paul et
280 al., 1999) and Pueblo (Kennedy et al., 2005) sections, where the CTB was defined as the limit between
281 the *Neocardioceras judii* and *Watinoceras devonense* ammonite biozones, the CTB at Lambruisse was
282 placed in the small trough before peak "C", at 31.60 m. Unit TH4 marks a return to lower $\delta^{13}\text{C}_{\text{carb}}$
283 values that follows the positive excursion. However, two small positive peaks ($\sim +0.4\text{‰}$) can be
284 observed in this more stable interval of lower $\delta^{13}\text{C}_{\text{carb}}$ values, and correspond to two organic-rich
285 interbeds. The slight decrease in $\delta^{13}\text{C}_{\text{carb}}$ above the Niveau Thomel is interrupted at the top of the
286 section by a small ($\sim 0.4\text{‰}$) positive excursion in the vicinity of the last organic-rich interbed.

287

288 **4.2.2. Stable carbon isotopes of organic matter**

289

290 Changes in the carbon isotope composition of OM through the Lambruisse section resemble to
291 those of carbonate (Fig. 2). Higher resolution sampling (supplementary data) made it possible to
292 identify the transitions between the different phases depicted in the carbon isotope chemostratigraphic
293 signal more precisely. Below the Niveau Thomel, $\delta^{13}\text{C}_{\text{org}}$ values oscillate between -26.8 and -25.7‰
294 towards the onset of OAE 2 (Fig. 2). In the upper part of TH1, $\delta^{13}\text{C}_{\text{org}}$ values are relatively low ($-$
295 26.7‰ minimum), similar to the lowest pre-OAE 2 ones. A negative shift may be associated with Unit
296 TH1, as described in the Pont d'Issole section (Jarvis et al., 2011). $\delta^{13}\text{C}_{\text{org}}$ rises sharply at the TH1–
297 TH2 boundary, from -26.7‰ to a maximum of -24.3‰ at peak "A". This rise corresponds to the first

298 major step of the worldwide OAE 2 positive excursion. The trough in the positive excursion, between
299 peaks “A” and “B” in the $\delta^{13}\text{C}_{\text{org}}$ profile, has an amplitude of 1.5‰ (from -25.5‰ for the lowest TH2
300 value to -24.0‰ for peak “B”). Within the “plateau” phase, the $\delta^{13}\text{C}_{\text{org}}$ profile shows several small
301 peaks and troughs below 1.1‰ in amplitude and around a mean value of -24.7‰. The recovery phase
302 after peak “C” (-24.3‰) is similar in terms of amplitude (-1.7‰) to that of the $\delta^{13}\text{C}_{\text{carb}}$ signal (-1.5‰)
303 and is followed by positive $\pm 0.8\%$ peaks in TH4. The post-Thomel interval is first characterized by a
304 negative shift (-1.7‰) from -25.3‰ at the top of TH4 to -27.0‰ located in the dark shale interval at
305 48.00 m, followed by a positive shift toward -25.4‰ (at 50.50 m).

306

307 **4.2.3. Paired carbon isotope signal ($\Delta^{13}\text{C}$)**

308 The $\Delta^{13}\text{C}$ signal shows quite strong variability in the pre-Thomel interval between 28.0 and
309 29.2‰, with a mean value of 28.8 ($\pm 0.4\%$, 1σ) (Fig. 2). The top of TH1 is characterized by higher
310 values reaching 29.5‰ followed by a sharp negative shift at the base of TH2 with $\Delta^{13}\text{C}$ values
311 decreasing to 27.6‰. The entire TH2 is characterized by relatively low $\Delta^{13}\text{C}$ value with a mean of
312 28.3 ($\pm 0.4\%$, 1σ). The upper limit of TH2 corresponds to a transition toward higher values in the
313 entire TH3 Unit with a mean $\Delta^{13}\text{C}$ value of 29.1 ($\pm 0.3\%$, 1σ). The end of OAE 2 is marked by a
314 negative shift toward 28.1‰ at the base of TH4, followed by a positive shift at the end of TH4
315 reaching 29.4‰. The post-Thomel is characterized by $\Delta^{13}\text{C}$ reaching 30.0 ‰ in the dark shale bed at
316 48.00 m.

317

318 **4.3. Stable oxygen isotopes**

319

320 Stable oxygen isotope compositions through the Lambruisse section display a long-term
321 increase from the base of the section towards the base of TH3 (Fig. 2). Within this long-term trend, a
322 first increase in $\delta^{18}\text{O}$ values, from values of about -4.0‰ to about -3.5‰ is recorded prior to OAE 2,
323 approximately 5 m above the base of the section. Oxygen isotope compositions remain quite stable at
324 around -3.5‰, up to the base of the Niveau Thomel. A progressive positive shift is then recorded from
325 the upper TH1 ($\delta^{18}\text{O} = -3.5\%$) towards the base of TH3 ($\delta^{18}\text{O} = -2.7\%$), which yield the highest $\delta^{18}\text{O}$
326 values of the entire section. Beginning with this maximum and in units TH3 and TH4, $\delta^{18}\text{O}$ displays
327 an overall negative trend with superimposed oscillations. This decreasing trend culminates at about 1.5
328 m above the top of the Niveau Thomel ($\delta^{18}\text{O} = -4.7\%$) in the Turonian. The upper part of the section
329 shows highly fluctuating $\delta^{18}\text{O}$ values, with a possible increasing trend of about $\sim +1.0\%$.

330

331 **4.4. Stable nitrogen isotopes, N concentrations and C/N molar ratios**

332

333 First-order variations in $\delta^{15}\text{N}$ match the lithological units. The pre-Thomel unit presents
334 variable positive $\delta^{15}\text{N}$ values of $1.5 \pm 0.7\text{‰}$, associated with relatively low N concentrations ($0.09 \pm$
335 0.04 wt%, 1σ) and a relatively low carbonate-free C/N molar ratio (9.8 ± 3.2) (Fig. 3).

336 In the upper part of TH1, the $\delta^{15}\text{N}$ fluctuate considerably around a mean of $0.8 (\pm 0.9\text{‰}, 1\sigma)$,
337 to reach negative values of -0.3‰ . This interval also corresponds to higher but fluctuating N
338 sedimentary concentrations ranging from 0.08 to 0.21 wt% and higher C/N molar ratios varying
339 ranging from 7.1 to 18.6 . In TH2, the $\delta^{15}\text{N}$ profile first shifts towards more positive values from the
340 TH1–TH2 transition towards the middle of the unit ($\delta^{15}\text{N}$ up to $+2.5\text{‰}$), and then decreases towards
341 the top of TH2. Only one sample, located at $+25.80$ m in the only organic-rich level, shows a negative
342 $\delta^{15}\text{N}$ value (-0.2‰). This sample also has a higher concentration of N (0.16 wt%) and a higher C/N
343 ratio (17.14), than the rest of the unit ($\text{N} = 0.08 \pm 0.02\text{‰}, 1\sigma$ and $\text{C/N} = 8.5 \pm 2.4\text{‰}, 1\sigma$). Like TH1,
344 TH3 and the base of TH4 are characterized by high-frequency oscillations in the $\delta^{15}\text{N}$ signal between
345 $+2.1$ and -0.7‰ , N concentrations fluctuating between 0.06 and 0.23‰ , and a C/N ratio fluctuating
346 between 8.1 and 22.1 . Finally, the top of TH4 is characterized by a return to more positive $\delta^{15}\text{N}$ values
347 reaching $+2.7\text{‰}$, low N concentrations (< 0.10 wt%) and low C/N ratios (< 10). However, two
348 organic-rich marly beds in this interval yield lower $\delta^{15}\text{N}$ values, disrupting the general increasing
349 trend, with higher N concentrations, reaching 0.16 wt% in both cases. In those two intervals, C/N
350 ratios reach 19.4 and 15.4 , respectively. Finally, the last organic-rich bed, of Turonian age, at $+48.00$
351 m (with a TOC of 1.3 wt%) presents values ($\delta^{15}\text{N} = -0.8\text{‰}$; $\text{N} = 0.23\text{‰}$; $\text{C/N} = 21.7$) which are as
352 extreme as those in TH1 or TH3.

353

354 **4.5. Major and trace element geochemistry**

355

356 To evaluate the abundances and the authigenic (or biogenic) nature of the major- and trace-
357 elements measured through the Lambruisse section, the correlation coefficient (r-value) and associated
358 probability (p-value) for each element against Al were determined (Table 1). High r-values (> 0.7) for
359 U and V revealed that variations in these elements are highly influenced by the detrital content, with
360 the exception of some limited values above the X/Al regression line indicating sporadic authigenic
361 enrichments. Intermediate r-values obtained for Cu, Ni, Zn and TOC ($r < 0.7$) show they were
362 influenced by both redox/productivity conditions and detrital supply. Conversely, Ba is poorly
363 correlated with Al ($r < 0.4$) and fluctuations in the concentrations of these elements mainly reflect
364 authigenic variation. Molybdenum is also poorly correlated with Al ($r = 0.1$), but all sample values (n
365 $= 23$) correspond to TOC-rich levels. Phosphorus, a macronutrient for primary productivity, is not
366 presented here because phosphorus concentrations in only two samples were significantly above the
367 detection limit (i.e. 0.04‰).

368

369 **4.5.1. Redox-sensitive elements with minimal detrital influence**

370

371 Molybdenum, vanadium and uranium are commonly considered to be robust proxies for the
372 evaluation of redox conditions (e.g. Tribovillard et al., 2006). More specifically, reduced species of
373 these elements have the ability to form insoluble chemical precipitate in presence of sulfides, and to
374 form complex with OM. Variations in their enrichment factors (EF) broadly follow the TOC, resulting
375 in distinct values recorded between the relatively enriched dark shales (TOC > 1.0 wt%) compared to
376 the grey marl and carbonate intervals.

377 Measurable concentrations of Mo ([Mo] > 0.5 ppm) were only detected in the upper TH1,
378 TH3, the base of TH4, and in the post-Thomel organic-rich bed (Fig. 4). Significant enrichments are
379 observed in the dark shale packages of the TH3. The maximum Mo enrichment is recorded in the
380 middle TH3 (EF Mo up to 8.5). Those EF Mo peaks alternate at the dm-scale with near Upper Crust
381 values (EF ~1) or with samples showing depleted values.

382 Like Mo, V presented only limited and oscillating enrichments (EF V up to 4.7) in the Niveau
383 Thomel and post-Thomel organic-rich bed. However, in contrast to Mo, maximum enrichment in V is
384 observe at the base of TH4. Apart of these intermittent enrichments, the values for the large majority
385 of the section are very close to those of the UCC.

386 Even more limited uranium enrichments are recorded here than in crustal detrital background.
387 In the Niveau Thomel, EF U never exceeds 2.4 and the highest value is observed in the post-Thomel
388 organic-rich bed (EF U = 4.0).

389

390 **4.5.2. Redox-sensitive elements influenced by productivity**

391 Copper, nickel and zinc are micronutrients (e.g. Calvert and Pedersen, 1993) and are
392 consequently widely used as paleoproductivity proxies (e.g. Algeo and Maynard, 2004). Enrichment in
393 Cu, Ni and Zn in sediments indicates, first, scavenging by OM and/or by Fe-Mn-oxyhydroxides.
394 Reductive dissolution of these oxyhydroxides and OM decay in sediments may release Cu, Ni and Zn
395 into pore waters. Under bacterial sulfate reducing conditions (sulfidic), they may coprecipitate with
396 sulfides (e.g. Morse and Luther, 1999). Barium could also indicate of paleoproductivity because of its
397 incorporation in phytoplankton. However, barite is unstable under sulfidic conditions and a diagenetic
398 barite-front may be formed in the case of reoxygenation (e.g. McManus et al., 1998).

399 Zinc enrichments are scattered throughout the section. Background EF Zn values remain
400 around 2.0 from the base of the section to the top of the Niveau Thomel but reach 4.0 at the top of the
401 section. Within TH3, some intermittent enrichments are significant (EF up to 9.7) and stratigraphically
402 synchronous with the highest EF V values. In contrast to Mo, V and U, some Zn-enriched samples are
403 present below the Niveau Thomel (EF up to 6.1). Another difference from Mo, V and U
404 chemostratigraphy is the presence of a peak of EF Zn in TH2.

405 Nickel enrichments are low and never exceed 2.5 in the organic-rich intervals of the Niveau
406 Thomel. The highest EF Ni is recorded at the top of TH2 (EF = 3.8). Like for Zn, TH2 is marked by
407 progressive enrichment in Ni. Most EF Ni values above the Niveau Thomel remain stable around 1.5
408 but a relatively higher value (EF = 3.2) is recorded in the organic-rich interbed at the top of the
409 section.

410 Similarly, Cu is not specifically seen to be enriched in the organic-rich intervals, except in
411 TH3 (EF up to 5.7). A small enrichment is again visible in TH2 (EF up to 4.4). The main feature of the
412 EF Cu chemostratigraphy is a transition from near UCC background values (EF~1.2–2.7) in the
413 interval from the base of the section to the top of TH3, toward elevated EF Cu in TH4 and in the post-
414 Thomel deposits ($3.2 < \text{EF Cu} < 6.7$).

415 None or only scarce Ba enrichments are recorded in most of the section, except in two
416 intervals. The first is in TH2 (EF up to 5.3) synchronous with enrichments in Zn, Ni and Cu. Another
417 sharper peak occurs at the top of TH3 (EF up to 7.2) but is not associated with enrichments in TOC,
418 Mo, V, U, Zn, Ni or Cu.

419

420 **5. Discussion**

421

422 **5.1. Preservation of organic matter**

423

424 **5.1.1. Characterization of organic matter**

425

426 Organic matter concentrations in Units TH1 and TH3, described as “black shale” intervals by
427 Jarvis et al. (2011), are relatively modest compared to those recorded at sites on the southern margin
428 of the Central Atlantic, where the TOC reaches exceptionally high values in the OAE 2 section (up to
429 56 wt% at DSDP Site 367; Dickson et al., 2016). In the Vocontian Basin, maximum TOC values
430 recorded at Lambruisse (up to 3.1 wt%) resemble those at Pont d’Issole (3.5 wt%; Jarvis et al., 2011)
431 but are higher than those at Clot Chevalier (1.5 wt%; Gale et al., 2019).

432 The other shared characteristic of these Vocontian sites is that TOC values fluctuate greatly at
433 the scale of individual units but also within the organic-rich intervals, indicating that the conditions
434 which favoured OM burial in the basin were highly unstable throughout OAE 2. This resembles the
435 record in other epicontinental basins for example, the Briançonnais domain (Charbonnier et al., 2018),
436 Lower Saxony Basin (Hetzl et al., 2011) and the Western Interior Basin (e.g. Eldrett et al., 2014)
437 where similar TOC contents are recorded (up to 4.9, 2.5 and 5.6 wt%, respectively). Large variations
438 in TOC content during OAE 2 were also observed in Central Atlantic or Italian sites where values
439 respectively can reach 56 wt% and 26 wt% respectively (Tsikos et al., 2004; Scopelliti et al., 2008;
440 Hetzel et al., 2009; Dickson et al., 2016). The TOC fluctuations result therein from a combination of
441 global and local conditions (i.e. basin configuration and local primary productivity).

442 At Lambruisse, the origin of the OM was inferred by comparing HI and OI values in a
443 modified Van Krevelen diagram (Fig. 5). Samples with high TOC values (TOC > 1.0 wt%) in the
444 OAE 2 interval and in the Turonian dark shale beds present HI and OI values typical of Type II OM,
445 indicating that organic-rich intervals reflect marine primary production. The trend from the Type II
446 toward Type III poles in Fig. 5 suggests either OM oxidation or increased influence of terrestrial OM.
447 The two processes are not incompatible as the samples assigned to Type III had the lowest organic
448 content.

449 Analysis of the palynomorphs along the Pont d'Issole section by Jarvis et al. (2011) showed
450 that the low TOC intervals are associated with a high (> 0.7) proportion of marine to terrestrial
451 palynomorphs. Considering a preferential degradation of labile marine over terrestrial OM under well-
452 oxygenated conditions, intervals in which low TOC and HI values were measured are presumably
453 associated with a largely dominant marine OM downward flux. This inference is in accordance with
454 oxidized OM in low TOC intervals rather than a large proportion of terrestrial OM.

455

456 **5.1.2. Redox conditions and basin configuration**

457

458 The combination of enrichments in several elements that are highly sensitive to reduced
459 conditions (Mo, U, V) is an efficient tool for reconstructing redox conditions in the past (Algeo and
460 Maynard, 2004; Brumsack, 2006; Riquier et al., 2006; Tribovillard et al., 2006; Westermann et al.,
461 2014). Significant enrichment factors (EF > 3; cf. Algeo and Tribovillard, 2009) were only observed
462 with elevated TOC (> 1.0 wt%) (Fig. 4) similarly to Pont d'Issole (Danzelle et al., 2018), confirming
463 that higher OM concentrations are associated with better preservation conditions caused by depleted
464 oxygen concentrations, or that a higher flux of sedimentary OM caused oxygen depletion at
465 Lambruisse. What is more, the maximum enrichments measured (EF Mo = 8.5; EF V = 4.7; EF U =
466 2.1) are only moderate compared to the extremely organic-rich sections in the Central Atlantic or
467 Western Tethys, where EF often exceed 100 for Mo and 10 for V and U (e.g. Brumsack, 2006; Hetzel
468 et al., 2009, Westermann et al., 2014).

469 As observed at Pont d'Issole (Danzelle et al., 2018), Mo had higher enrichment factors than V
470 and U during OAE 2. During typical gradual oxygen depletion, U and V, reduced under denitrifying
471 conditions, can accumulate before Mo, which is enriched under sulfidic conditions (e.g. Tribovillard et
472 al., 2006). At Pont d'Issole, trace metal enrichments and degree of pyritization (DOP) data correlated
473 with TOC values revealed that the bottom waters oscillated between suboxic and anoxic conditions in
474 the organic-rich intervals (Danzelle et al., 2018). Similar enrichment factors at Lambruisse suggest
475 that higher enrichments are related to anoxic conditions in bottom waters. Tribovillard et al. (2004a)
476 demonstrated that the sulfurization of marine OM in sediments can preferentially capture Mo over
477 time. The highest peaks in Mo observed in TH1 and TH3 at Lambruisse correlated with intervals with

478 high DOP (Danzelle et al., 2018) and S/C values in the organic fraction characterizing the highly
479 sulfurized OM described at Pont d'Issole (Raven et al., 2018, 2019).

480 Molybdenum and uranium have not only been extensively studied to evaluate redox conditions
481 but also to reconstruct hydrographic conditions in the past (Algeo and Tribovillard, 2009; Algeo and
482 Rowe, 2012; Tribovillard et al., 2012; Westermann et al., 2014; Dickson et al., 2016, 2017). Because
483 of the different geochemical behaviour of Mo and U under anoxic conditions, the covariation between
484 their respective enrichments in sediments has been considered as a tool to evaluate the geometry of a
485 basin (Algeo and Tribovillard, 2009; Tribovillard et al., 2012). Uptake of authigenic U in sediments is
486 effective under suboxic conditions at the Fe(II)-Fe(III) redox boundary, while Mo only accumulates in
487 sediments in the presence of free H₂S (sulfidic conditions). In an environment characterized by gradual
488 oxygen depletion, U is thus enriched in sediments before Mo. As Mo readily accumulates when
489 sulfidic conditions are encountered in the sediments and in the water column, the EF Mo vs. EF U
490 trend from oxic to euxinic conditions displays a concave upward profile (Fig. 6). This trend only
491 applies to non-limited Mo and U contents, in open marine environments. Under restricted conditions,
492 characterized by a redox stratified water column, Mn and Fe oxyhydroxides formed in the upper oxic
493 part of the water column, which are unstable under sulfidic conditions, are partially recycled back into
494 the water column in their reduced soluble forms (Van Cappellen et al., 1998; Dellwig et al., 2010).
495 Recycling affects Mo behaviour in particular because it can be scavenged by Mn-oxyhydroxides
496 resulting in its transport from the water column to the sediments (Algeo and Tribovillard, 2009;
497 Dellwig et al., 2010). This process is called “particulate shuttle” effect (Fig. 6). In the case of sulfidic
498 conditions in sediments or in the lower part of the water column, the Mo transported by the Mn-
499 oxyhydroxides is delivered to the sulfidic zone and is fixed by sulfidation. Reduced Mn can diffuse
500 back to the oxic part of the water column and reform oxyhydroxides, repeating the process and leading
501 to a larger quantity of Mo fixed in sediments than U (Crusius et al., 1996).

502 The majority of the samples at Lambruisse presented higher Mo than U enrichments and are
503 located along a vector towards the particulate shuttle zone (Fig. 6), i.e., the most TOC enriched
504 samples are located farthest from the unrestricted marine trend. We therefore argue that the Vocontian
505 Basin was probably, at least weakly restricted, and that a deep chemocline at the sediment-water
506 interface episodically expanded into bottom waters, triggering a Mn cycle in the water column, as
507 proposed for Pont d'Issole (Danzelle et al., 2018). This interpretation is in agreement with the results
508 of a recent study by Grosheny et al. (2017). These authors propose that the Vocontian Basin was
509 affected by a short-lived compressive tectonic pulse at the CTB, leading to confinement of the basin at
510 that time.

511

512 **5.1.3. Productivity conditions**

513

514 The relationship between the enrichments in elements associated with primary productivity
515 and OM content is somewhat erratic. First, most of the enrichments during OAE 2 are low compared
516 to those in the southern Central Atlantic and Western Tethys sites (Brumsack, 2006) suggesting
517 moderate primary productivity at Lambruisse. During the carbon isotope plateau, only four near
518 concomitant peaks of Zn and Ni ($EF\ Zn > 4$; $EF\ Ni > 2$) are visible (Fig. 4). These peaks, which
519 coincide with the highest enrichments in V and U (Fig. 4), suggest a higher organic flux associated
520 with enhanced preservation due to the formation of sulfides (Tribovillard et al., 2006).

521 In contrast to Ni, Cu does not covary with TOC even though these two elements generally
522 display similar geochemical behaviour (Tribovillard et al., 2004b). The distinctive behaviour of Cu
523 can be attributed to its capacity to be scavenged from solution in deep water (Boyle et al., 1977). The
524 increasing trend of EF Cu through the carbon isotope plateau interval with the highest values observed
525 after the termination of OAE 2 (Fig. 4) could represent a deepening of the bottom water associated
526 with the end of the OAE 2 sea-level rise, rather than a long-term increase in primary productivity.

527 Enrichments in barium are low ($EF\ Ba$ dominantly < 3) even in organic-rich intervals (Fig. 4),
528 in stark contrasts with $EF\ Ba > 50$ observed in the Bonarelli level in Tethyan domain, which was
529 interpreted as representing high primary productivity (Turgeon and Brumsack, 2006), and confirms
530 that the Vocontian Basin did not experience intense eutrophication of the surface waters. The single
531 Ba peak in the carbon isotope plateau interval was found in a carbonate interbed overlying a dark shale
532 interval with the highest TOC value in the succession. This peak likely represents the diagenetic
533 formation of barite ($BaSO_4$) either under the form of a front or of nodules (McManus et al., 1998).
534 This suggests that the oxygenation front, and the dissolved sulfate, may have migrated downwards in
535 the sediments, inducing precipitation of the dissolved Ba accumulated in the pore waters. This
536 interpretation is coherent with a reoxygenation following the interval presenting the highest TOC and
537 EF Mo values of the Niveau Thomel indicating more intense sulfate-reducing conditions within the
538 sediments, confirming the difficulty to employ Ba as a paleoproductivity proxy.

539 In contrast to the rest of the OAE 2 interval, the PCE is a phase of relative enrichment in Ni,
540 Cu, Ba and to a lesser degree in Zn, culminating in the only organic-rich bed of PCE at +25.80 m
541 ($TOC = 1.48\ wt\%$), probably the result of a short-lived increase in primary productivity. Jenkyns et al.
542 (2017) and Sweere et al. (2018) proposed that those elements contained in sulfides and/or in organic
543 matter, were released due to increasing aerobic biodegradation during the PCE. Moreover, enhanced
544 mixing of the entire water column could have promoted the recycling of these elements from bottom
545 waters towards the surface waters, favouring continued primary productivity throughout OAE 2
546 (Forster et al., 2007; Parente et al., 2008).

547

548 **5.2. Perturbation of the nitrogen cycle**

549

550 The chemostatigraphy of the nitrogen isotope signal revealed occurrences of negative $\delta^{15}\text{N}$
551 excursions in the organic-rich intervals, in OAE 2 (towards -0.7‰) and in the post-OAE 2 interval
552 (towards -0.8‰) (Fig. 3). This relationship is clearly displayed by a $\delta^{15}\text{N}$ vs. TOC crossplot (Fig. 7A).
553 As the HI parameter is positively correlated with TOC (Fig. 5), given a predominantly marine-origin
554 for the OM, the relationship between $\delta^{15}\text{N}$ and HI (Fig. 7B) indicates that sedimentary $\delta^{15}\text{N}$ variations
555 are not influenced by a changing contribution of continental OM and, therefore, reflect changes in the
556 oceanic biogeochemical N cycle.

557 Nitrogen isotope compositions of sediments was widely used as as an indicator of nitrogen
558 biogeochemistry and for the reconstruction of redox conditions in the past (e.g. Ader et al., 2014,
559 2016; Algeo et al., 2014) and particularly during OAE 2 (Kuypers et al., 2004; Arnaboldi and Meyers,
560 2007; Ohkouchi et al., 2006; Jenkyns et al., 2007; Junium and Arthur, 2007; Blumenberg and Wiese,
561 2012; Higgins et al., 2012; Algeo et al., 2014; Ruvalcaba Baroni et al., 2015; Zhang et al., 2019). The
562 nitrogen cycle is dominated by biologically induced mechanisms that depend on the oxygenation state
563 of the water column and of the sediments. Transitions between the oxidized and reduced forms of N
564 are associated with isotopic fractionation (e.g. Thomazo et al., 2011). Under oxygenated conditions in
565 the water column, ammonium (NH_4^+) released by remineralized OM is oxidized to nitrite (NO_2^-) and
566 nitrate (NO_3^-) through nitrification processes, and can be assimilated by photosynthetic organisms.
567 Denitrifying bacterial using the NO_3^- for oxidizing the OM, particularly within the oxygen-minimum
568 zone, involves a large fractionation that results in a ^{15}N -enriched residual reservoir of NO_3^- as observed
569 in present-day oceans with $\sim+7\text{‰}$ average isotopic composition (Tesdal et al., 2013), which is in
570 agreement with the $\sim5\text{‰}$ average composition of NO_3^- in the oceans (Sigman et al., 2005).

571 Under oxygen-depleted environments, NH_4^+ can accumulate because of its incomplete
572 oxidation. In stratified basins, segregation takes place between a nitrate reservoir in the oxygenated
573 part of the water column and an ammonium reservoir in the anoxic part. In this case, loss of nitrogen
574 occurs at the chemocline due to the combined effect of bacterial denitrification process and anaerobic
575 oxidation of ammonia (anammox process), converting NO_3^- into gaseous species (N_2 and N_2O). If
576 denitrification processes occurring at the redoxcline progress to completion, the subsequent deficit of
577 N in the photic zone promotes the development of atmosphere- N_2 fixers (diazotrophs), including
578 cyanobacteria (Sigman et al., 2005). A dominance of N fixation by diazotrophs drives $\delta^{15}\text{N}_{\text{NO}_3^-}$ of
579 surface waters toward 0‰ (Quan and Falkowski, 2009) resulting in sedimentary $\delta^{15}\text{N}$ values close to
580 0‰ during in the modern anoxic Black Sea or generally during the anoxic periods of the Phanerozoic
581 (Ader et al., 2014; 2016; Algeo et al., 2014). In expanded oxygen minimum zones as observed in
582 today's upwelling settings, or as proposed within the late Neoproterozoic ocean (Ader et al., 2014;
583 2016), a part of the NO_3^- is partially or quantitatively denitrified, inducing an increasing of the $\delta^{15}\text{N}$
584 composition of the residual NO_3^- pool toward a $+12\text{‰}$ value (Tesdal et al., 2013).

585 At Lambruisse, intervals characterized by anoxic conditions consistently record low $\delta^{15}\text{N}$
586 values (Fig. 3). Those intervals represent therefore periods of increased diazotrophy compensating a

587 decreasing in the N bioavailability that would have resulted from the establishment of a stratification
588 of the water-column during those periods. The frequent oscillations of $\delta^{15}\text{N}$ values observed in TH1
589 and TH3 imply that this stratification was relatively unstable. The relationship between $\delta^{15}\text{N}$ and TOC
590 (Fig. 7A) and HI (Fig. 7B) indicates that the burial of marine organic matter in the sediments (TOC >
591 1.0 wt% and HI > 200 mg HC/g TOC) was mainly enabled by its preservation under anoxic bottom
592 waters. This relationship between N_2 fixation in surface waters and bottom water deoxygenation is
593 confirmed by the negative correlation between $\delta^{15}\text{N}$ and EF V (Fig. 7D).

594 In addition, $\delta^{15}\text{N}$ was negatively correlated with the $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ molar ratio of the carbonate-free
595 samples (Fig. 7C). While the highest $\delta^{15}\text{N}$ values are consistent with “normal” marine OM (C/N = ~5-
596 8; Redfield ratio = 6.625), ^{15}N depletion is associated with increased $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ values towards typical
597 terrestrial OM (C/N > 25; Meyers, 1994). The dichotomy between high $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ values measured and
598 the presence of an interpreted dominant marine-derived OM with low $\delta^{15}\text{N}$, which characterize phases
599 of perturbation of the nitrogen cycle, has been explained by a complete denitrification occurring at the
600 redoxcline located within the water-column, combined with cyanobacterial nitrogen fixation in the
601 photic zone (e.g. Junium and Arthur, 2007). Experiments on denitrifying bacteria demonstrated the
602 preferential degradation of proteinaceous compounds, rich in N, as a source of carbon, leaving the OM
603 depleted in N and resulting in the high C/N preserved ratio (van Mooy et al., 2002). Besides, algal
604 biomass could presents a C/N ratio in excess of the Redfield-ratio as observed in modern settings with
605 N-limited surface-waters (e.g. Copin-Montégut, 2000). Another explanation for elevated $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ is
606 that a part of the ammonium accumulated in the clay fraction exceeded its retention capacity and
607 migrated out the sediments. Conversely, low $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ could be attributed to preferential preservation
608 of organic N as clay-adsorbed ammonium.

609 At Lambruisse, elevated $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ was observed in the dark shale intervals and the lowest
610 $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ within carbonates (Fig. 3). The impact of the clay fraction on the $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ ratio is therefore
611 minimal. Thus we consider that, at Lambruisse, the elevated $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ ratios, coherent with low $\delta^{15}\text{N}$
612 values, reflect the alteration of a Redfield-ratio organic matter pool, caused by intense denitrification
613 in the water-column and sediments.

614

615 **5.3. Integration of the Vocontian Basin in the regional nitrogen cycle**

616 During OAE 2, the development of cyanobacteria in the photic zone is deduced from the
617 preservation of methylhopanoids in the Central Atlantic (Kuypers et al., 2004; van Bentum et al.,
618 2012b), Lower Saxony Basin (Blumenberg and Wiese, 2012) and Levant Basin (Sepúlveda et al.,
619 2009). Thus, low $\delta^{15}\text{N}$ values associated with OAE 2 may be related to increasing cyanobacterial N_2
620 fixation at global scale (Kuypers et al., 2004; Ohkouchi et al., 2006; Junium and Arthur, 2007).

621 The similarity between the $\delta^{15}\text{N}$ vs. TOC trend at diverse OAE 2 sites and at Lambruisse
622 suggests that the scenario leading to diazotrophy in the photic zone is also consistent in the Vocontian

623 Basin (Fig. 8). However, this interpretation is challenged because bacterial N₂ fixation (involving the
624 enzyme nitrogenase) is only accompanied by a 0 to -2‰ fractionation from a slightly positive isotope
625 composition of dissolved N₂ (Zhang et al., 2014). Measured δ¹⁵N values lower than -2‰, particularly
626 those detected in the southern Central Atlantic (Fig. 8) (Kuypers et al., 2004; Junium and Arthur,
627 2007; Higgins et al., 2012; Ruvalcaba Baroni et al., 2015), have been explained by a change in the
628 metal at the active site of the nitrogenase, from a classic Mo-nitrogenase to Fe- or V-nitrogenase,
629 causing higher fractionation (Zerkle et al., 2008; Zhang et al., 2014). A change in biological nitrogen
630 fixation could be related to a decrease of the global Mo concentration in seawater due to its uptake by
631 sediments deposited in euxinic basins, as proposed for OAE 2 (Goldberg et al., 2016; Dickson et al.,
632 2017). Another explanation for extreme negative δ¹⁵N values involves a biological partial assimilation
633 of NH₄⁺ by phytoplankton in a sustained upwelling of bottom waters in the photic zone, which fuelled
634 the primary productivity in N (Junium and Arthur, 2007; Higgins et al., 2012; Ruvalcaba Baroni et al.,
635 2015). This NH₄⁺ contribution proposed for southern Central Atlantic sites is compatible with the
636 presence upwelling currents in this area (Trabucho Alexandre et al., 2010).

637 A high rate of phosphorus recycling during OAE 2 (Mort et al., 2007; Kraal et al., 2010), also
638 suggested in the Vocontian Basin (Danzelle et al., 2018), has been interpreted as a consequence of OM
639 decay and reductive dissolution of Fe-Mn-oxyhydroxides on which P is adsorbed (e.g. Ingall and
640 Jahnke, 1994; Van Cappellen and Ingall, 1994; Dellwig et al., 2010). A positive feedback loop
641 between primary productivity, increasing the oxygen demand in the water column, and P release in
642 deoxygenated conditions and diffused back in the water column is interpreted as a requirement for
643 maintaining anoxic conditions. In addition, phosphorus recycling combined with effective N loss due
644 to intense denitrification process could have favoured N₂ fixation (Deutsch et al., 2004; Planavsky,
645 2014).

646

647 **5.4. Paired carbon isotopes constraints on the carbon cycle**

648

649 The relationship between the surficial global carbon cycle reflected in the OAE 2 sedimentary
650 carbon isotope excursion and the long-term variations in TOC recorded at Lambruisse reveals a
651 synchronicity between the global and the local expression of OAE 2. Variations in Δ¹³C result from:
652 (1) variations in the origin of OM with different initial δ¹³C composition; or (2) variations in the
653 kinetic fractionation associated with photosynthesis by primary producers, mostly controlled by the
654 concentration of dissolved CO₂ in the ocean (Hayes et al., 1999).

655 At Lambruisse, chemical characterization of OM demonstrates an overwhelming dominance
656 of marine-derived material (Fig. 5). This inference is in accordance with the palynology analysis of the
657 Pont d'Issole section (Jarvis et al., 2011) indicating low terrestrial OM inputs, even during organic-
658 poor intervals. Thus the Δ¹³C record through the Lambruisse section could be interpreted as a pCO₂
659 indicator. The rising phase in Δ¹³C at the base of the Niveau Thomel, recorded at Pont d'Issole (Jarvis
660 et al., 2011), and represented at Lambruisse by the shift from lower Δ¹³C values in the Pre-Thomel to

661 higher values in TH1 (Fig. 2), is interpreted as a consequence of the onset of CO₂ outgassing due to the
662 emplacement of the Caribbean LIP at that time, also demonstrated by a drop in the Os isotope
663 composition characterizing the hydrothermal activity of this LIP (Du Vivier et al., 2014).

664 The PCE interval is accompanied by low $\Delta^{13}\text{C}$ in the Lambruisse section (Fig. 2) as observed
665 elsewhere in the Vocontian Basin (Pont d'Issole, Jarvis et al., 2011; Clot Chevalier, Gale et al., 2019),
666 in the European Anglo-Paris and Saxony basins (Voigt et al., 2006; Jarvis et al., 2011) and in the
667 Tarfaya basin (Moroccan Atlantic margin, Kuhnt et al., 2017). This event could be associated with a
668 drop in marine and atmospheric CO₂ concentrations, explained by the massive quantities of organic
669 carbon trapped in the sediments which act as a negative retroaction process for the carbon cycle (c.f.
670 Jarvis et al., 2011).

671 The second rise after the PCE which culminate at around the CTB (Fig. 2), in parallel with the
672 termination of the Os isotope excursion (Du Vivier et al., 2014), argues for continuous CO₂ outgassing
673 during OAE 2. The termination of OAE 2 would mark a short drop in $p\text{CO}_2$ (Fig. 2) which could be
674 one consequence of the second phase of carbon burial mostly corresponding with the TH3 unit.

675 Finally, the maximum $\Delta^{13}\text{C}$ values, observed during the Turonian (Fig. 2) indicate a
676 continuous rise in the $p\text{CO}_2$ after the termination of OAE 2, implying that $p\text{CO}_2$ variations are not the
677 only trigger of OAE 2. Thus, the burial of organic carbon, and subsequent cooling was not responsible
678 for the termination of OAE 2, as proposed for the PCE. Robinson et al. (2019), proposed that a global
679 sea-level rise combined with reduced nutrient delivery and hence reduced nutrient availability due to
680 their sequestration in black shales would have favoured a decrease in productivity-supported or
681 productivity-driven anoxic conditions.

682

683 **5.5. Variations in paleotemperatures inferred from carbonate $\delta^{18}\text{O}$**

684 Bulk carbonate $\delta^{18}\text{O}$ compositions were analyzed to assess changes in seawater temperature in
685 the Vocontian Basin, and to compare them with the variations in $p\text{CO}_2$ identified from $\Delta^{13}\text{C}$ values.
686 The absence of a positive correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ($r^2 = 0.07$) throughout the Lambruisse
687 section argues for the absence of a diagenetic alteration under meteoric conditions. Although $\delta^{18}\text{O}$
688 values can nevertheless shift to lower values during limited diagenesis, original trends may be
689 preserved, making it possible to assess changes in seawater temperature, at least qualitatively (i.e.
690 Jenkyns et al., 1994).

691 The absence of a clear $\delta^{18}\text{O}$ trend in the pre-OAE 2 interval suggests that sea-surface
692 temperature remained relatively stable (Fig. 2). A positive $\delta^{18}\text{O}$ trend in TH2, with maximum values
693 culminating at the TH2 – TH3 transition, around $\delta^{13}\text{C}$ peak “B”, is interpreted here as a cooling phase
694 associated with the PCE (Fig. 2). This interpretation implies the existence of a temporal lag in the
695 record of maximum $\delta^{18}\text{O}$ values, in contrast to Boreal sections like Eastbourne (England; Paul et al.,
696 1999), Gröbern (Germany; Voigt et al., 2006) or in the Western Interior Basin at Pueblo (Colorado;

697 Desmares et al., 2016) where the thermal minimum inferred from $\delta^{18}\text{O}$ is located around peak “A” (in
698 PCE). Although quite erratic, the $\delta^{18}\text{O}$ signal roughly defines a long-term decrease after PCE, which
699 we interpret as a general warming trend culminating at the top of the Niveau Thomel. This warming is
700 coherent with the stratigraphic position of the early Turonian thermal maximum identified at Pont
701 d’Issole and elsewhere in Europe (Jarvis et al., 2011), as well with the $p\text{CO}_2$ rise inferred from $\Delta^{13}\text{C}$
702 values (Fig. 2).

703 The absence of a large $\delta^{18}\text{O}$ positive excursion during the PCE in the Vocontian Basin is
704 interpreted as less temperature sensitivity to variations in $p\text{CO}_2$ at subtropical latitudes than in the
705 Boreal basins (Jarvis et al., 2011). We can also speculate that in the semi-enclosed Vocontian Basin,
706 presumably characterized by a water-column stratification during OAE 2, variations in the evaporation
707 vs. precipitation ratio may have affected the $\delta^{18}\text{O}$ composition of seawater, and consequently of
708 carbonates.

709 Other sea temperature indicators in the Vocontian Basin confirm a cooling phase during the
710 PCE. In the slope domain of the Vocontian Basin at Les Lattes, belemnites with a Boreal affinity have
711 been reported within the stratigraphic interval of the PCE (Gale and Christensen, 1996). Grosheny et
712 al. (2017) also described changes in the coiling-direction ratio of the planktonic foraminifera
713 *Muricohedbergella delrioensis*, indicating that the transient cooling associated with the PCE was
714 marked by the southward migration of Boreal species. What is more, sea-surface temperatures (SST)
715 based on TEX_{86} values have been reported from the Cassis section in the South-Provençal Basin
716 (Heimhofer et al., 2018), located immediately south of the Vocontian Basin (Fig. 1B). Most of the
717 OAE2 interval is characterized by elevated SST of $\sim 37 \pm 2^\circ\text{C}$, interrupted by lower SST during the
718 PCE reaching $\sim 27^\circ\text{C}$ at the end of this cooling episode. Based on the analysis of palynomorph
719 abundances throughout this section, Heimhofer et al. (2018) described a mixed-forest vegetation,
720 dominated by conifers indicating relatively humid conditions, during most of OAE2. Conversely, the
721 PCE interval corresponds to a more open angiosperms-rich vegetation, likely representing the
722 development of a savanna-type environment associated with a drier climate.

723

724 **5.6. Global vs. local forcing mechanisms**

725

726 In the Vocontian Basin, variations in the oxygen concentration in the sediments and in the
727 water column over time were affected by both global and local forcing mechanisms at different
728 timescale. During OAE 2, those variations are particularly evidenced at the scale of the lithological
729 units. TH1 and TH3 periods (Fig. 9A) are distinctive to TH2 that broadly corresponds to PCE (Fig.
730 9B).

731 The tectonic confinement of the Vocontian Basin through the CTB (Grosheny et al., 2017)
732 combined with the observation that black shales are restricted to the deepest part of the basin argues in
733 favour of a semi-enclosed geometry of the Vocontian Basin. The EF Mo vs. EF U values measured at

734 Lambruisse are consistent with intermittent or weak particulate shuttle characterizing a fluctuating
735 redoxcline within bottom waters (Tribovillard et al., 2012). During OAE 2, water-mass restriction is
736 proposed as a major control for the establishment of anoxic conditions in different basins and
737 particularly in the Central Atlantic where the most oxygen depletion was recorded (e.g. Monteiro et
738 al., 2012).

739 The hypothesis that OAE 2 was triggered by a pulse of volcanic activity is widely supported in
740 the literature (e.g. Turgeon and Creaser, 2008; Du Vivier et al., 2014; Adams et al., 2010; Jenkyns et
741 al., 2017). A negative excursion of Os isotopes triggered ~50 kyr before OAE 2, which ended at the
742 carbon isotope peak “B”, was recorded at Pont d’Issole and worldwide (Du Vivier et al., 2014). An
743 increase in $p\text{CO}_2$ is reflected in the increase in the $\Delta^{13}\text{C}$ record at the base of the Niveau Thomel
744 (Jarvis et al., 2011) and has been linked to a global warming phase (Voigt et al., 2006; Forster et al.,
745 2007; Sinninghe Damsté et al., 2010). The excess carbon in the ocean-atmosphere system was then
746 regulated by the high rate of carbon burial in the form of OM, as recorded in the TH1 unit, and was
747 further consumed as a reactant in the silicate weathering reaction (Blättler et al., 2011; Pogge von
748 Strandmann et al., 2013). This would have led to the global transient cooling of the PCE, marked in
749 Lambruisse by a drop in $\Delta^{13}\text{C}$ values followed by an increase in measured carbonate $\delta^{18}\text{O}$ values.
750 Export of OM and associated oxygen consumption would have resulted in gradual oxygen depletion in
751 bottom waters, marked by the enhanced preservation of OM and by enrichments in redox sensitive
752 trace element (Mo, U, V, Zn). The inflow of boreal waters, associated with the PCE, could have
753 promoted more efficient vertical mixing of the water column and intense reoxygenation of bottom
754 waters in the Vocontian Basin.

755 Another consequence of volcanic activity is the degassing of large quantities of sulfate in the
756 sulfate-poor Cenomanian oceans (Adams et al., 2010; Gomes et al., 2016). This would have promoted
757 a higher rate of bacterial sulfate-reduction in sediments not limited by the availability of either sulfate
758 or organic compounds (Poulton et al., 2015). Elevated rates of pyritization in the Vocontian Basin
759 would have inhibited the burial of P sorbed onto Fe-oxyhydroxides, leading to significant P recycling
760 in the water column (Danzelle et al., 2018). The resulting imbalanced N/P ratio would have been
761 further strengthened by intermittent phases of enhanced water-column denitrification, in parallel with
762 the oscillations in oxygenation of bottom waters, and favoured the development of nitrogen fixing
763 cyanobacteria, thereby increasing primary productivity during OAE 2.

764

765 **6. Conclusions**

766

767 Our new data suggest that the development and evolution of OAE 2 in the Vocontian Basin
768 could have resulted from a combination of exogenous mechanisms (volcanism, climate, tectonic)
769 perturbing the hydrology of the Vocontian Basin and biogeochemical cycling. The moderately
770 elevated concentrations of redox-sensitive trace elements and TOC reflect the establishment of

771 suboxic to anoxic conditions in the bottom waters in units TH1 and TH3. A relative higher enrichment
772 in Mo than in U is consistent with the semi-enclosed geometry of the Vocontian Basin which favours
773 the development of a stratified water body. The absence of noticeable enrichments in elements such as
774 Ba, Ni and Cu suggests that surface waters in the Vocontian Basin did not experience eutrophic
775 conditions, but rather episodic phases of moderately enhanced productivity.

776 Low sedimentary $\delta^{15}\text{N}$ values correlated with phases of bottom-water deoxygenation indicate
777 periods of perturbation in the N cycle, characterized by the development of N_2 -fixing cyanobacteria in
778 the photic-zone. N_2 -fixation indicates partial loss of bioavailable N caused by a high water-column
779 denitrification rate, and a redoxcline located in the water column.

780 Phases of enhanced weathering conditions on land during periods of elevated $p\text{CO}_2$,
781 supporting P transport and possible P recycling from deoxygenated bottom waters, would have led to
782 low N/P availability for primary productivity, further favouring atmospheric N_2 fixation. Additional
783 cyanobacterial production and the resulting increased export of marine OM would have acted as a
784 positive feedback loop sustaining deoxygenation of the bottom waters.

785 The Plenus Cold Event, representing a cooler and drier climate phase, is characterized by a
786 long-term reoxygenation of the Vocontian Basin. The massive burial of organic carbon during the
787 early phase of OAE 2 may have led to lower $p\text{CO}_2$ at the global scale. This cooling phase may have
788 modified ocean circulation and led to efficient mixing of the water column and ventilation of bottom
789 waters.

790

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792

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1297 **Figures and table captions**

1298 **Figure 1**

1299 (A) Paleogeographic map at the Cenomanian of the Vocontian Basin and the South-Provençal Basin
1300 presenting the extension of the facies deposits (after Crumière et al., 1990). (B) Location of the
1301 Vocontian Basin sections referred to in the text (after Crumière et al., 1990).

1302

1303 **Figure 2**

1304 Stratigraphic succession, TOC content and carbon- and oxygen-isotope compositions through the
1305 Lambruisse section. Descriptions of the lithological units (TH1 to TH4) forming the Niveau Thomel
1306 are provided in the text. OAE 2 interval is represented by the light grey band determined on the base
1307 of the positive carbon isotope excursion (characterized by three maxima A, B, C). Blue band
1308 represents the Plenius Cold Event (PCE) placed by stratigraphic correlation with European sections
1309 (Jarvis et al., 2011). Horizontal dark grey bands highlight the intervals of dark shale characterized by
1310 TOC values higher than or equal to 1.0 wt%.

1311

1312 **Figure 3**

1313 Evolution of the N concentration, C_{org}/N_{bulk} molar ratio and nitrogen isotope composition of the
1314 decarbonated fraction through the Lambruisse section.

1315

1316 **Figure 4**

1317 Evolution of the enrichment factors $[EF X = (X/Al)_{sample}/(X/Al)_{UCC}]$ of the redox-sensitive trace
1318 elements (RSTE) with minimal detrital influence (Mo, V, U) and those associated with primary
1319 productivity (Zn, Ni, Cu, Ba) through the Lambruisse section.

1320

1321 **Figure 5**

1322 Modified Van Krevelen diagram presenting Hydrogen Index (HI) versus Oxygen Index (OI) and the
1323 associated type of OM at Lambruisse. Only samples having TOC > 0.4 wt% are plotted.

1324

1325 **Figure 6**

1326 EF Mo versus EF U for the Lambruisse (this study), Pont d'Issole (Danzelle et al., 2018) and Clot
1327 Chevalier (Gale et al., 2019) sections. Diagonal dashed lines represent the 3/1; 1/1 and 0.3/1 (Mo/U)
1328 ratios of present-day seawater. Area of yellow to red color gradient corresponds to the evolution of EF
1329 Mo vs. EF U under suboxic to euxinic conditions in modern unrestricted marine environments, based
1330 on eastern tropical Pacific locations (Tribouillard et al., 2012). Grey area corresponds to the values
1331 typical of "Particulate Shuttle" effect characteristic of weakly restricted basins (Tribouillard et al.,
1332 2012).

1333

1334

1335

1336 **Figure 7**

1337 Nitrogen isotopes compositions versus (A) TOC, (B) HI, (C) C_{org}/N_{bulk} molar ratio and (D) EF V at
1338 Lambruisse. Greenish arrows represent the broad inverse trends observed.

1339

1340 **Figure 8**

1341 (A) Palaeogeographic reconstruction at 90 Ma after Blakey (2011) with the location of the Lambruisse
1342 section in the Vocontian Basin and other sites discussed in the compilation of nitrogen isotope signals
1343 during OAE 2. (B) Nitrogen isotope compositions versus TOC for Lambruisse and compiled OAE 2
1344 sites from the Lower Saxony Basin (Wunstorf section, Blumemberg and Wiese, 2012; Ruvalcaba
1345 Baroni et al., 2015), Central Atlantic (DSDP Site 367, Kuypers et al., 2004; Bass River section, DSDP
1346 Sites 386, 641, ODP Site 1276, Ruvalcaba Baroni et al., 2015), Western Tethys (Gorgo a Cerbara
1347 section, Ohkouchi et al., 2006) and Eastern Tethys (Gongzha section, Zhang et al., 2019) showing a
1348 general similar negative trend supporting a global perturbation of the N cycle. Diagram (C) is a zoom
1349 of (B) with TOC restrained to 0 to 10 wt% (greyish area).

1350

1351 **Figure 9**

1352 Schematic representation of the biogeochemical cycles and hydrological conditions during the
1353 deposition of the (A) TH1 and TH3 units and (B) PCE interval within the semi-enclosed Vocontian
1354 Basin. Processes labelled as 1 and 2 represent denitrification and anammox, respectively.
1355 Representation of the vegetation on land is derived from Heimhofer et al. (2018).

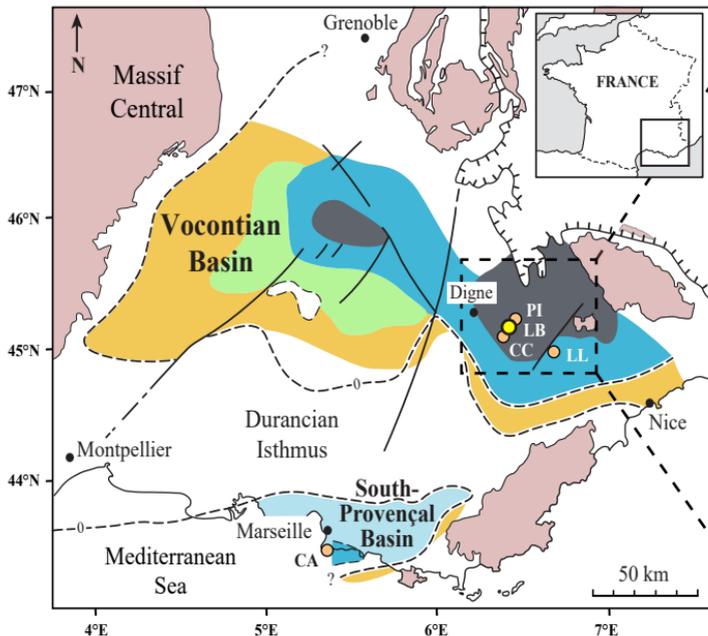
1356

1357 **Table 1**

1358 Correlation coefficients (r-values, Pearson correlation) of selected trace elements with respect to Al of
1359 the n samples analyzed and level of significance of correlations (p-values, expressed in %) associated.

1360

A



Basement

Sandstones, locally calcareous
with shelly fossils

Glaucinitic sandstones

Marls and marly limestones

Rudistid limestones

Dark shales :
Niveau ThomelPenninic thrust
front

Cretaceous faults

Borders of the basin

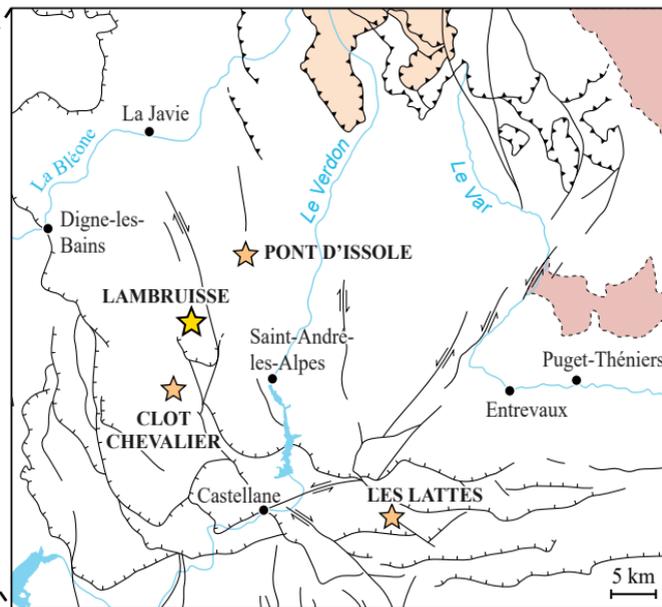
● LB Lambruisse

● Other sections referred:

PI Pont d'Issole LL Les Lattes

CC Clot Chevalier CA Cassis

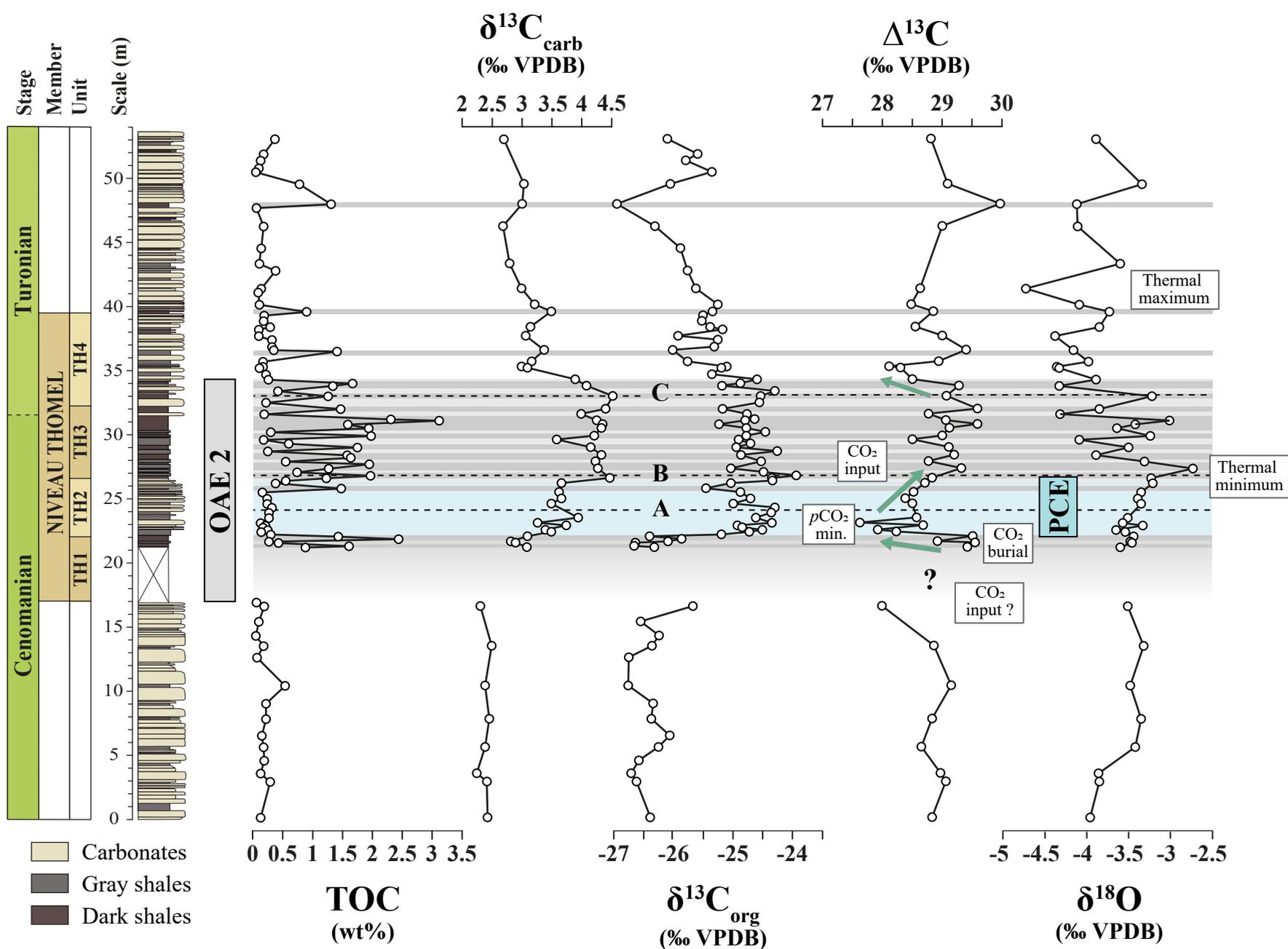
B

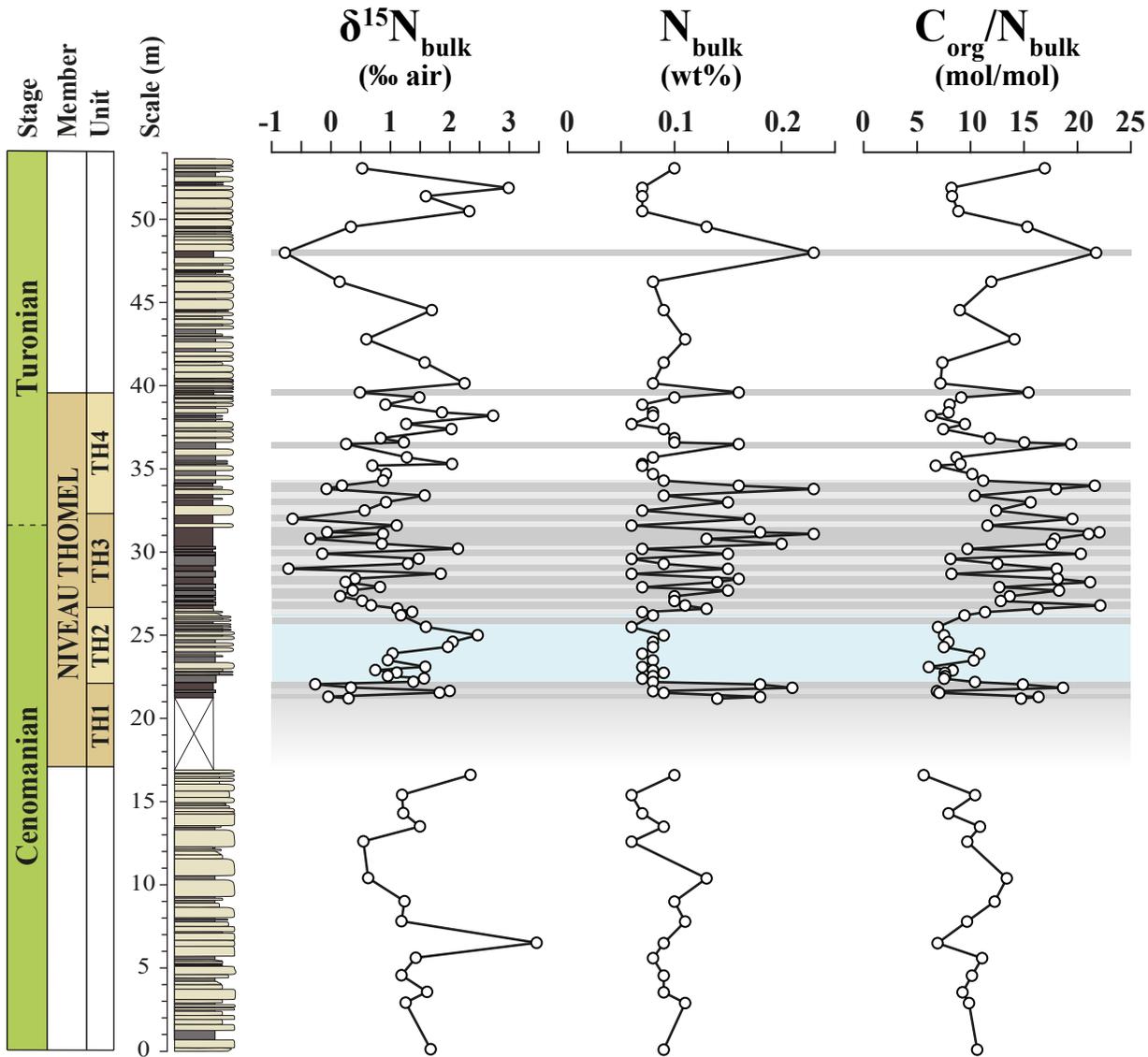


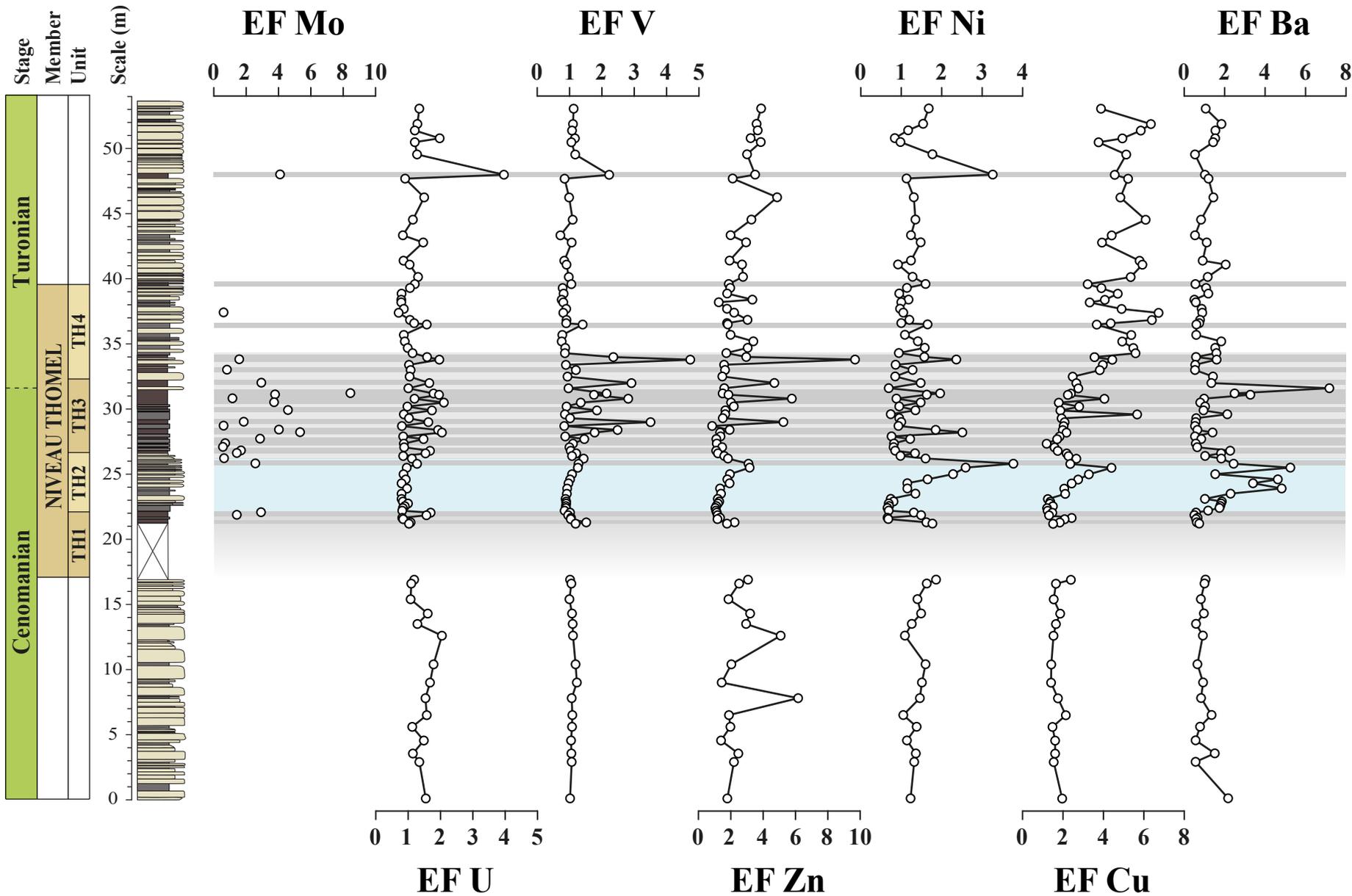
Basement

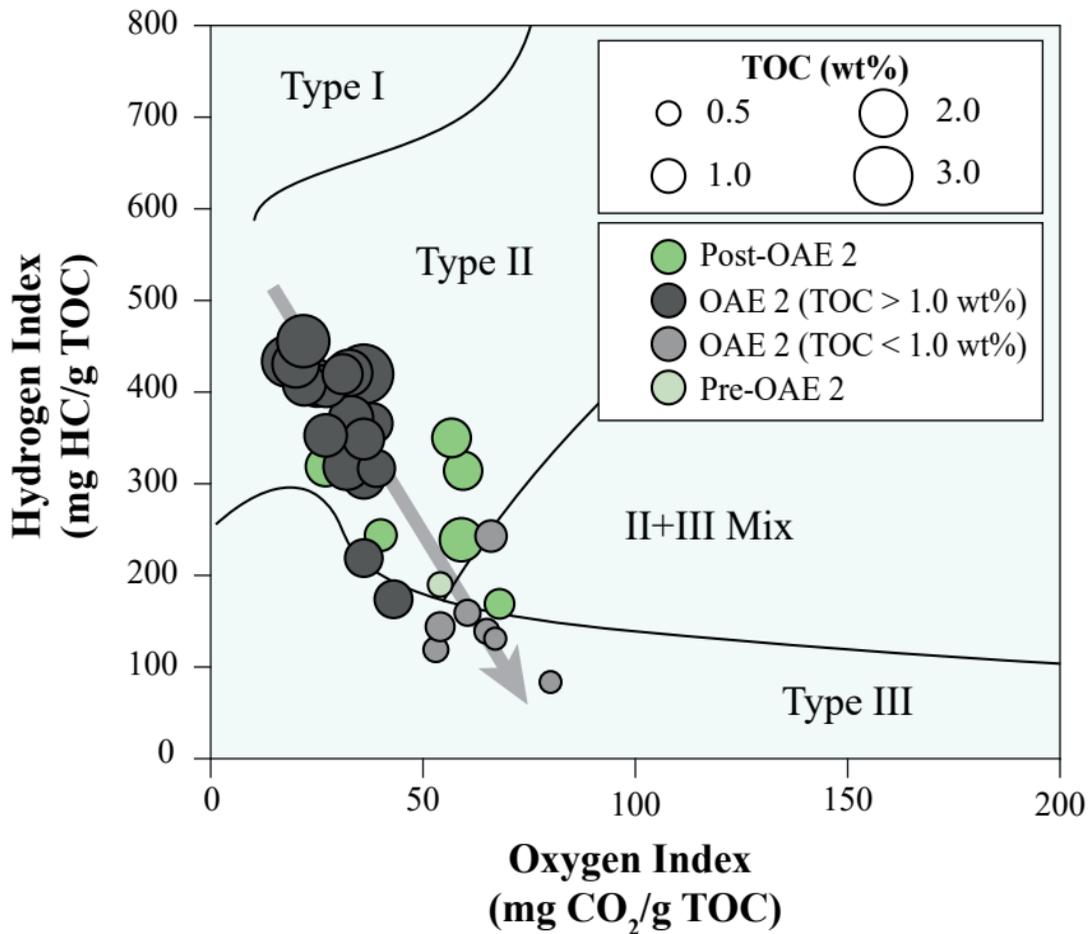
Sub-briançonnais
unitsPenninic thrust
frontDigne-Castellane
thrusts

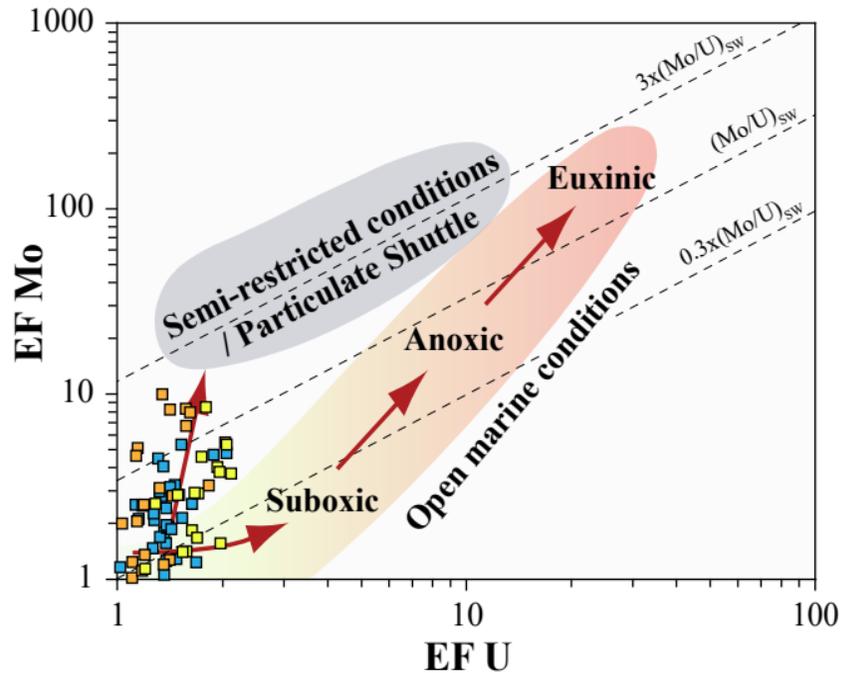
Transverse faults











Vocontian Basin sections

- **Lambruisse**
 (This study)
- **Pont d'Issole**
 (Danzelle et al., 2018)
- **Clot Chevalier**
 (Gale et al., 2019)

