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3 **Nitrogen cycle in the Late Archean ferruginous ocean**

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42 **Abstract**

43  
44 The Hamersley Group comprises a Late Archean sedimentary succession, which is  
45 thought to record the prelude to the atmospheric oxygenation in the Paleoproterozoic, the so-  
46 called Great Oxidation Event (GOE), at ~2.4 Ga. We studied drill-core samples of sedimentary  
47 rocks from the upper Mount McRae Shale and Brockman Iron Formation deposited before the  
48 GOE at ~2.5 Ga in order to characterize the environments and ecosystems prevailing during their  
49 deposition. The rocks from the Mount McRae Shale and Brockman Iron Formation represent,  
50 respectively, proximal euxinic conditions and distal ferruginous depositional environments, thus  
51 providing an opportunity to examine lateral variability in the open-marine basin. We analyzed the  
52 concentration and isotopic composition of carbon in carbonate and organic matter, bulk nitrogen  
53 content and its isotopic composition as well as major element concentrations. The  $\delta^{13}\text{C}_{\text{carb}}$  values  
54 and carbonate content range from -3.2 to -10.7 ‰ and 0.1 to 58 wt%, respectively. Organic  
55 carbon content also varies over a large range from 0.05 to 4.6 wt% with a near constant  $\delta^{13}\text{C}_{\text{org}}$   
56 value of  $-28.7 \pm 0.8$  ‰. Negative  $\delta^{13}\text{C}_{\text{org}}$  excursions (down to -31 ‰) are generally correlated with  
57 high organic matter content. Bulk nitrogen shows highly variable concentration, between 1.3 and  
58 785 ppm, and  $\delta^{15}\text{N}$  values between 0.4 and 13.4 ‰.

59 The  $\delta^{13}\text{C}_{\text{carb}}$  values reflect a diagenetic carbonate origin, with negative values typical for Fe-  
60 rich carbonates formed by organic matter mineralization with ferric oxyhydroxides. In contrast,  
61  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  values record primary isotope signatures derived from ancient living organisms.  
62 The relatively constant  $\delta^{13}\text{C}_{\text{org}}$  values at around -28.7 ‰ are interpreted as reflecting  
63 photoautotrophs utilizing a large pool of dissolved inorganic carbon. Inverse stratigraphic co-  
64 variation between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values was observed for the Brockman Iron Formation. We

65 propose that N and C biogeochemical cycles were coupled by Fe redox cycling in the water  
66 column and in sediments of the Late Archean ocean. Several models for biogeochemical N  
67 cycling linked to the redox structure of the water column are considered. Under fully anoxic  
68 conditions, the dominant N species available for assimilation by micro-organisms in the photic  
69 zone could be ammonium ( $\text{NH}_4^+$ ). Highly positive  $\delta^{15}\text{N}$  values would reflect the assimilation of  
70  $\text{NH}_4^+$  enriched in  $^{15}\text{N}$  by partial oxidation to nitrite, followed by quantitative removal of the  
71 produced nitrite by denitrification or anamox processes. Ammonium oxidation could have been  
72 driven by (i)  $\text{O}_2$  produced locally via oxygenic photosynthesis, or (ii) microbial oxidation utilizing  
73 Fe(III)-oxyhydroxides formed in the water column. Under redox-stratified conditions, N  
74 assimilated by primary producers could have been in the form of  $\text{NO}_3^-$ , based on modern and  
75 Phanerozoic analogues. The positive  $\delta^{15}\text{N}$  values would have resulted in this case from partial  
76 denitrification of  $\text{NO}_3^-$  coupled to anaerobic microbial oxidation of Fe(II) to Fe(III). We conclude  
77 that similar positive  $\delta^{15}\text{N}$  signatures may record very different N biogeochemical cycles under  
78 anoxic, stratified and fully oxic conditions in the ocean. Interpretation of the N isotopes in terms  
79 of N biogeochemical cycle thus requires independent constraints on the redox structure of the  
80 ocean.

81

82 *Keywords:* nitrogen; carbon; isotopes; Archean ocean; banded iron formation

83

## 84 **1. Introduction**

85

86           One of the most important changes in Earth's surface history is the oxygenation of the  
87 atmosphere-ocean system (Holland, 1984, 2009). The oxygenation imparted major modifications  
88 to the geochemical cycles of many redox-sensitive elements, such as C, O, N, S, and base metals,  
89 with dramatic implications for the development and evolution of life (Anbar and Knoll, 2002). It  
90 is now well established that the first irreversible oxygenation of the atmosphere, the so called  
91 Great Oxidation Event (GOE), occurred between 2.4 and 2.3 Ga (Holland, 2002; Bekker et al.,  
92 2004; Guo et al. 2009), although transient oxygenation could have occurred earlier. Recent  
93 studies of the Mount McRae Shale, Western Australia suggested that atmospheric oxygenation  
94 started at 2.5 Ga, based on Mo and Re concentrations and isotopic compositions (Anbar et al.,  
95 2007), and C and S isotope values of whole-rock shale samples (Kaufman et al., 2007). Nitrogen  
96 isotope (Garvin et al., 2009) and Fe speciation (Reinhard et al., 2009; Raiswell et al., 2011)  
97 studies of the same sample set also argued for surface ocean oxygenation at that time. Earlier  
98 oxygenation of the surface ocean at ~2.67 Ga was proposed based on N isotope composition of  
99 shales from the Campbellrand-Malmani carbonate platform, South Africa (Godfrey and  
100 Falkowski, 2009). Besides the question of timing, the secular trend of O<sub>2</sub> accumulation in the  
101 atmosphere-ocean system is also highly debated. Two secular trends have been proposed: (1)  
102 gradual O<sub>2</sub> increase and accumulation (e.g., Holland, 2006; Murakami et al., 2011), and (2)  
103 oscillatory variations in O<sub>2</sub> level in association with the early Paleoproterozoic glacial events and  
104 the Lomagundi carbon isotope excursion (Bekker and Kaufman, 2007; Bekker and Holland,  
105 2012). The Late Archean may also have been characterized by transient and local low-levels of  
106 oxygen, so-called "whiffs" of oxygen (Anbar et al., 2007).

107 Nitrogen isotopes represent a unique tool for exploring the secular evolution of oxygen  
108 because (i) N biogeochemistry is mainly controlled by redox reactions and (ii) N is present in all  
109 sedimentary rocks, providing a continuous record in different geological settings. In contrast to  
110 the Archean, the modern N cycle in the ocean is relatively well understood (see reviews in  
111 Brandes et al., 2007; Sigman et al., 2009). The main reservoir of N at the Earth's surface is the  
112 atmosphere with a present  $\delta^{15}\text{N}$  value of 0 ‰ (N isotope composition is expressed as  $\delta^{15}\text{N} =$   
113  $[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{standard}} - 1] \times 1000$ , where the standard is atmospheric  $\text{N}_2$ ). Nitrogen enters the  
114 oceanic cycle through atmospheric  $\text{N}_2$  fixation by aerobic and anaerobic autotrophs with minor N  
115 isotope fractionation (<3 ‰; e.g., Wada et al., 1975; Minagawa and Wada, 1986). After the death  
116 of these autotrophic organisms, organic matter mineralization releases N as ammonium ( $\text{NH}_4^+$ ),  
117 with very little isotopic fractionation (Prokopenko et al., 2006; Möbius, 2013). In the presence of  
118 free  $\text{O}_2$ ,  $\text{NH}_4^+$  is oxidized into nitrate ( $\text{NO}_3^-$ ) during a two-step biological process called  
119 nitrification, which is associated with significant N isotope fractionation  $\sim 16$  ‰ (Sigman et al.,  
120 2009). This fractionation is rarely fully expressed in modern marine environments since the  
121 transformation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  is generally complete. In  $\text{O}_2$ -depleted environments such as  
122 oxygen-minimum zones or anoxic sediments, nitrates are partially reduced by denitrification or  
123 anammox (i.e., anaerobic ammonium oxidation) into gaseous  $\text{N}_2$  or  $\text{N}_2\text{O}$ . During denitrification,  
124  $^{14}\text{N}$  is preferentially released relative to  $^{15}\text{N}$ , leaving residual marine  $\text{NO}_3^-$  enriched in the heavy  
125 isotope (average marine  $\delta^{15}\text{N}_{\text{NO}_3^-} \sim +5$  ‰; e.g., Altabet and François, 1994). The heavy isotope  
126 signature of  $\text{NO}_3^-$  is transferred by assimilation to organisms living in the water column or in the  
127 diagenetic realm and then recorded in sedimentary organic matter. Accordingly, assuming a  
128 steady-state system, the N isotope composition of organic matter in modern marine environment  
129 reflects mainly the relative proportion of N denitrification (in the water column and in sediments)

130 and N fixation. In O<sub>2</sub>-free environments such as the Early Archean oceans, the nitrification and  
131 thus subsequent denitrification are unlikely, and dissolved N species may have been dominated  
132 by NH<sub>4</sub><sup>+</sup> (Holland, 1984, 2002; Beaumont and Robert, 1999; Papineau et al., 2005). Accordingly,  
133 N cycle and isotope composition of Archean ocean and sediments may have been significantly  
134 different from those of the modern world (Canfield et al., 2010).

135         Most of the N in the Earth exosphere is contained as N<sub>2</sub> in the atmosphere (presently ~  
136 3.98 × 10<sup>21</sup> g). Based on data from fluid inclusion in cherts (Sano and Pillinger, 1990) and  
137 geochemical modeling (Tolstikhin and Marty, 1998), the N isotope composition of the  
138 atmosphere is believed to have remained largely constant during the last 3 Ga with δ<sup>15</sup>N values of  
139 about 0‰. The use of N isotope compositions of Precambrian sedimentary rocks as a tracer of  
140 NO<sub>3</sub><sup>-</sup>, and thus O<sub>2</sub>, content was proposed in the pioneering work of Beaumont and Robert (1999).  
141 In their study, the authors analyzed cherts of various ages and suggested a dramatic change in the  
142 N biogeochemical cycle between 3 and 2 Ga. Negative δ<sup>15</sup>N values were observed in cherts older  
143 than ~2.4 Ga and interpreted as reflecting N<sub>2</sub> fixation or NH<sub>4</sub><sup>+</sup> assimilation (Beaumont and Robert,  
144 1999; Papineau et al., 2005), a result compatible with low NO<sub>3</sub><sup>-</sup> concentrations (if any) under  
145 anoxic conditions in the early Earth oceans. However, this interpretation was questioned since  
146 some of these cherts were deposited in hydrothermal settings and may have recorded N isotope  
147 signatures of chemoautotrophic organisms specific to these environments (Pinti and Hashizume,  
148 2001; Pinti et al., 2001, 2009). If this was the case, their N isotope signature would not reflect  
149 phototrophic organisms living in the photic zone of the upper ocean and the N isotope  
150 composition of seawater nitrogen compounds. Two recent N-isotope studies of Archean  
151 sedimentary sequences from Western Australia and South Africa suggested earlier oxygenation  
152 of the Earth's surface ocean starting at 2.5 Ga (Garvin et al., 2009) and 2.67 Ga (Godfrey and

153 Falkowski, 2009), respectively. Both studies identified  $\delta^{15}\text{N}$  shifts from near 0 ‰ to positive  
154 values, up to 7.5 ‰, and interpreted these trends as evidence for coupled nitrification-  
155 denitrification, pathways typical of a surface ocean containing free  $\text{O}_2$ . According to their  
156 interpretations, denitrification had to be partial so that N isotope fractionation can be expressed.  
157 Bulk rock N isotope analyses of  $\sim 2.72$  Ga carbonates from the Tumbiana Formation, Western  
158 Australia revealed extreme  $\delta^{15}\text{N}$  values up to +50.4 ‰, possibly recording the onset of  
159 nitrification coupled to consumption of its products (nitrite and nitrate) via biological  
160 denitrification (Thomazo et al., 2011). Such extreme N isotope compositions could only be  
161 expressed under oxygen-limited conditions so that partial nitrification would be associated with  
162 complete denitrification (Thomazo et al., 2011). High  $\delta^{15}\text{N}$  values, up to +20 ‰, were also  
163 observed in  $\sim 2.7$  Ga carbonaceous shales from the Western Abitibi Greenstone Belt (Canada) and  
164 Penhalonga Formation (Botswana). These values were explained by an Archean  $^{15}\text{N}$ -enriched  
165 atmosphere resulted from secondary accretion of C1 chondrite-like material (Jia and Kerrich,  
166 2004a, 2004b). However, discrete N isotope excursions in time seem more likely than a long-  
167 term evolution in composition of the atmosphere since other datasets illustrate very small, if any,  
168 N isotope variations in the atmosphere through time (e.g., Sano and Pillinger, 1990; Tolstikhin  
169 and Marty, 1998; Marty et al., 2012).

170 Previous studies of N isotopes in Precambrian rocks either (1) focussed on samples of  
171 different lithologies and ages from different areas (e.g., Beaumont and Robert, 1999; Papineau et  
172 al. 2005, 2009; Pinti et al., 2001, 2009; Jia and Kerrich, 2004b), or (2) analyzed stratigraphic  
173 sequences of organic-rich shales (i.e., Garvin et al., 2009; Godfrey and Falkowski, 2009) or  
174 carbonates (Thomazo et al., 2011). However, no study has presented so far a stratigraphic dataset  
175 for a drill-core section of banded iron formation, which is one of the common Archean



176 sedimentary rocks. In this work, we analyzed the N isotope composition of drill core samples of  
177 organic carbon-poor and Fe-rich sediments from the Brockman Iron Formation, Western  
178 Australia, one of the best preserved banded iron formations in the world (Trendall and Blockley,  
179 1970). The unit contains the products of redox reactions, including Fe oxidation in the water  
180 column either by oxygenic or anoxygenic photosynthesis (e.g., Cloud, 1973; Konhauser et al.,  
181 2002; Kappler et al., 2005; see also review in Bekker et al., 2010). Systematic N isotope study of  
182 banded iron formations has never been performed before since they contain only small amounts  
183 of N, requiring high-sensitivity techniques based on static mass-spectrometry. The Brockman  
184 Iron Formation was deposited immediately above the Mount McRae Shale, which was  
185 extensively studied previously to constrain the redox state of the atmosphere-ocean system  
186 (Anbar et al., 2007; Kaufman et al., 2007; Garvin et al., 2009; Reinhard et al., 2009; Raiswell et  
187 al., 2011). Accordingly, we build on these previous studies and continue to explore the  
188 Hamersley Group in order to constrain environmental changes for the time period between ~2.5  
189 and 2.46 Ga. In addition, samples from the Brockman Iron Formation were also selected because  
190 they contain stilpnomelane, an Fe-rich mica-like silicate that may have preserved N isotope  
191 signatures since  $\text{NH}_4^+$  commonly substitutes for  $\text{K}^+$  in K-bearing minerals (e.g., Honma and  
192 Itihara, 1981; Boyd et al., 2001; Busigny et al., 2003a; Papineau et al., 2005). We found that N  
193 concentrations are significantly higher in stilpnomelane-rich shale samples associated with  
194 banded iron formation than in previously analyzed banded iron formation and chert samples  
195 (Pinti et al., 2001, 2007, 2009). Nitrogen isotope analyses of our samples from the Mount McRae  
196 Shale and Brockman Iron Formation were coupled with C isotope analyses of organic matter and  
197 carbonates and measurements of major element concentrations. Both elemental and isotopic data  
198 are used to separate primary signatures from late diagenetic and metamorphic overprints. Finally,

199 our results are compared to existing data in the literature and previously proposed models in order  
200 to further develop and test existing models for the N biogeochemical cycle and redox structure of  
201 the early Earth oceans before the GOE.

202

## 203 **2. Geological setting and sample description**

204

205 The rocks analyzed in our study belong to the Late Archean to early Paleoproterozoic  
206 Hamersley Group (Western Australia), and include samples from the Mount McRae Shale and  
207 Brockman Iron Formation (Fig. 1). They are composed of laminated and well-preserved  
208 sediments that accumulated in relatively deep-water, marine environments below the wave base  
209 (Pickard et al., 2004; Kaufman et al., 2007). For the Mount McRae Shale, regional sequence  
210 stratigraphic analysis indicates the presence of two depositional cycles; each sequence starts with  
211 carbonate and siliciclastic turbidite and breccia and deepens upwards to either semi-pelagic shale  
212 or banded iron formation (Krapež et al., 2003). Bulk shale analyses of Re-Os isotopes gave an  
213 age of  $2501 \pm 8$  Ma for the Mount McRae Shale (Anbar et al., 2007) consistent with a high-  
214 precision SHRIMP  $^{207}\text{Pb}$ - $^{206}\text{Pb}$  zircon age of  $2504 \pm 5$  Ma for a tuff layer in the same unit  
215 (Rasmussen et al., 2005). The Mount McRae Shale contains large amounts of organic C and  
216 pyrite, which are mainly accompanied by quartz, siderite, dolomite, ankerite/ferroan dolomite,  
217 chlorite, mica, K-feldspar, albite and minnesotaite (Krapež et al., 2003; Pickard et al., 2004;  
218 Raiswell et al., 2011). The upper part of the Mount McRae Shale, the Colonial Chert Member, is  
219 transitional to the Brockman Iron Formation (Trendall and Blockley, 1970). The Brockman Iron  
220 Formation is composed of four stratigraphic units in ascending order: Dales Gorge, Whaleback  
221 Shale, Joffre, and Yandicoogina Shale members (Trendall and Blockley, 1970; Krapež et al.,

222 2003). Depositional ages of  $\sim$ 2.48 and 2.46 Ga have been established for the Dales Gorge  
223 Member and the Whaleback Shale Member, respectively, based on U-Pb SHRIMP analyses of  
224 zircons from tuffaceous layers (Trendall et al., 2004). The Brockman Iron Formation contains  
225 alternating hematite-magnetite-chert (BIF) and chert-carbonate-silicate (S) decimeter to meter  
226 thick macrobands (Trendall and Blockley, 1970; Krapež et al., 2003; Fig. 1). Macrobands are  
227 divided into mesobands (10 to 50 mm in thickness) and laminated microbands (0.2 to 2 mm  
228 thick), composed of Fe-oxides, Fe-silicates, Fe-carbonates and chert in variable proportions with  
229 minor amounts of pyrite and organic carbon. Banded iron formations of the Brockman  
230 Supersequence have long been considered as pure marine chemical precipitates but were recently  
231 proposed to reflect episodic density flows (Krapež et al., 2003; Pickard et al., 2004; Rasmussen et  
232 al., 2013). Whole-rock major and trace element analyses suggest two dominant sources for BIF  
233 and S macrobands, with a major hydrothermal influence and a mafic provenance for BIF and a  
234 strong influence of continental and submarine weathering for S macrobands (Krapež et al., 2003;  
235 Pickard et al., 2004; Pecoits et al., 2009).

236 In the present work, we selected 31 samples from the Rio Tinto Exploration drill-core  
237 WLT-10, collected at 22.73°S and 116.75°E, approximately 100 km WNW from Paraburdoo  
238 township close to the south-western margin of the preserved extent of the basin, at depths ranging  
239 from 124 to 387 m (Fig. 1; see Table 1 for description of the samples). The samples are  
240 uniformly distributed through the uppermost part of the Mount McRae Shale to the unit J3 of the  
241 Joffre Member, spanning a depositional period of  $\sim$ 40 Ma. The units have experienced only  
242 minimal deformation and mild metamorphism (from 100°C to  $<$ 300°C; Becker and Clayton,  
243 1976; Smith et al., 1982; Kaufman et al., 1990), and carry primary chemical and isotopic  
244 signatures. The samples represent different lithologies of the Mount McRae Shale and Brockman

245 Iron Formation, thus allowing global changes in C and N biogeochemical cycles to be  
246 distinguished from local variations related to either diagenetic or source-rock effects.

247

### 248 **3. Analytical techniques**

249

250 For each drill-core sample, uniform layers of 0.5 to 2 cm thick were selected, cut and  
251 powdered to <60  $\mu\text{m}$ . Carbon and N isotope analyses together with major element analyses were  
252 performed on the same homogeneous powders. For C isotope analysis of carbonates, 3.26 to  
253 109.09 mg of rock powder was loaded in a vacutainer tube. The tube was then flushed with  
254 helium. Rock powder was treated with 100% phosphoric acid at 80°C for 2 hours and then at  
255 130°C for another 2 hours. This treatment secured complete dissolution of carbonate (McCrea,  
256 1950). Calcite and dolomite are expected to react at 80°C, while ankerite and siderite react at  
257 130°C (Rosenbaum and Sheppard, 1986). Tests on samples subsequently heated to 150°C  
258 produced no detectable  $\text{CO}_2$ . For each temperature step, C isotope composition of  $\text{CO}_2$  was  
259 measured using a continuous-flow mass-spectrometer (AP-2003) operated with helium as a  
260 carrier gas. The isotopic data are reported in conventional  $\delta$  units (in per mil) with respect to the  
261 V-PDB standard. Analytical error on  $\delta^{13}\text{C}$  values is better than  $\pm 0.1$  ‰. Carbonate content in  
262 samples was estimated from the ion intensity of the  $\text{CO}_2$  peak in the mass-spectrometer with a  
263 precision better than  $\pm 10\%$  ( $2\sigma$ ). Two to four replicate analyses of each sample were performed  
264 for  $\delta^{13}\text{C}_{\text{carb}}$  measurements, but only the average values are presented herein.

265 Total organic C content (TOC) and its C isotope composition were determined on  
266 carbonate-free samples. Carbonates from powdered samples were removed using 6N HCl at 80°C  
267 for 2 hours. The residue of decarbonation was rinsed with milliQ water several times until it

268 reached neutral pH, centrifuged and dried for 2 days at 50°C. Mass balance was used to estimate  
269 the amount of removed carbonate. Aliquots of dried decarbonated samples (50 to 100 mg for the  
270 Brockman Iron Formation samples and <10mg for the Mount McRae Shale samples) were then  
271 loaded into quartz tubes together with CuO wires, sealed under vacuum and combusted at 950°C  
272 for 6 hr (Duma combustion; cf., Bekker et al., 2001, Ader et al., 2006, 2009; Thomazo et al.,  
273 2009a; Sansjofre et al., 2011). The produced CO<sub>2</sub> was purified on a vacuum line and quantified  
274 manometrically; TOC content reproducibility was better than ±0.3 wt%. Carbon isotope  
275 composition of the purified CO<sub>2</sub> was then measured on a Delta<sup>plus</sup>XP mass-spectrometer with a  
276 precision better than ±0.1 ‰. Results are reported using the δ<sup>13</sup>C notation in per mil relative to V-  
277 PDB.

278         The procedure used for measurement of nitrogen content and its isotopic composition in  
279 rocks has been thoroughly described in previously published papers (Busigny et al., 2005; Ader  
280 et al., 2006) and is only summarized herein. Nitrogen was extracted from samples by combustion  
281 in quartz tubes sealed under vacuum. Before sample combustion, the powders were degassed  
282 under vacuum at 300°C for 12hrs. This degassing temperature is different from that previously  
283 used (450°C; Busigny et al., 2005; Ader et al., 2006) and was preferred for two reasons: (1) the  
284 Mount McRae Shale and Brockman Iron Formation have experienced a maximum burial  
285 temperature of 300°C (Smith et al., 1982; Kaufman et al., 1990), and (2) stilpnomelane, a  
286 potential N-bearing mineral phase, starts to break down at 450°C (Miyano and Klein, 1989).  
287 Nitrogen generated by combustion was then separated from other volatiles (mainly H<sub>2</sub>O and CO<sub>2</sub>)  
288 using purified Cu, CuO, and CaO (Kendall and Grim, 1990). It was quantified as dinitrogen (N<sub>2</sub>)  
289 with a capacitance manometer on ultra-high vacuum line and its isotope analysis was performed  
290 on a triple-collector static vacuum mass-spectrometer, allowing measurement of nanomole

291 quantities of N<sub>2</sub>. Nitrogen isotope composition is expressed in the  $\delta^{15}\text{N}$  notation in per mil relative  
292 to atmospheric N<sub>2</sub>. The quantity of N contributed by the analytical blank is low ( $0.65 \pm 0.30$  nmol  
293 N<sub>2</sub>) and its isotope composition is  $-3.7 \pm 2.7$  ‰ ( $2\sigma$ ). The precisions for sample nitrogen content  
294 and its isotope composition are better than 8% and 0.5 ‰, respectively.

295 Whole-rock concentrations of major elements were measured using ICP-AES at the  
296 Service d'Analyse des Roches et des Mineraux (SARM) of the Centre de Recherches  
297 Petrographiques et Geochimiques (CRPG) of Vandoeuvre, France. Analytical precision for major  
298 element concentrations is available at <http://helium.crpg.cnrs-nancy.fr/SARM/pages/roches.html>  
299 and typically better than 10%.

300

## 301 **4. Results**

302

### 303 *4.1. Major element concentrations linked to petrology*

304

305 Correlations observed between some major elements (Fig. 2) supports the identification of  
306 lithologies established during drill-core sampling and petrographic study. This shows a diversity  
307 of chemical compositions between several mineralogical end-members. Positive correlation  
308 among Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and K<sub>2</sub>O (Fig. 2a and 2b) indicates that these elements are contained in the  
309 same phases, mostly stilpnomelane, but also mica and K-feldspar. Only one sample (DGM307-6)  
310 shows strong enrichment in SiO<sub>2</sub> (73 wt%) with no associated enrichment in Al<sub>2</sub>O<sub>3</sub> (0.2 wt%).  
311 This sample is identified as a chert based on petrography. For all samples, an inverse correlation  
312 between Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> (Fig. 2c) indicates that Fe-silicates do not represent one of the dominant  
313 Fe-bearing phases, in contrast to Fe-oxides (hematite and magnetite) and Fe-carbonates (siderite

314 and ankerite). It should be noted that our samples from the Mount McRae Shale differ from those  
315 of the Brockman Iron Formation in containing dolomite as a dominant carbonate phase while Fe-  
316 rich carbonates were not found by electron microprobe analysis. In contrast to the relationship  
317 between  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$ , the best-fit line for  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  does not pass through the origin on the  
318 graph (Fig. 2a). Indeed,  $\text{SiO}_2$  is at 10 to 20 wt%, when  $\text{Al}_2\text{O}_3$  concentration is close to 0 wt%. This  
319 observation, coupled with petrography, indicates that most of our samples contain quartz (chert).  
320 Samples from the Brockman Iron Formation are strongly enriched in Fe with  $\text{Fe}_{\text{Total}}$  (expressed as  
321  $\text{Fe}_2\text{O}_3$ ) concentrations ranging from 6.7 to 78.2 wt% and averaging  $33.8 \pm 15.5$  wt% (n=26). This  
322 differs significantly from the Mount McRae Shale samples, which have  $\text{Fe}_{\text{Total}}$  concentrations  
323 between 2.3 and 6.2 wt% (average is  $3.8 \pm 1.6$  wt%, n=5). This contrast is also reflected in Fe/Ti  
324 molar ratios (Fig. 3). Fe-enrichment of the Brockman Iron Formation likely reflects  
325 contemporaneous anoxic and ferruginous conditions in the deep ocean (cf., Bekker et al., 2010),  
326 while the depositional environment of some portions of the Mount McRae Shale has been  
327 interpreted as anoxic and sulfidic (e.g., Reinhard et al., 2009; Raiswell et al., 2011).

328 To conclude, samples from the Brockman Iron Formation are mostly composed of  
329 potassium- and aluminum-rich silicates, Fe-oxides, quartz and carbonates in variable proportions.  
330 According to mineralogy and major element composition, our samples were divided into five  
331 rock types: organic-rich shale from the Mount McRae Shale, and stilpnomelane-rich mudrock,  
332 banded iron formation and chert from the overlying Brockman Iron Formation. Stilpnomelane-  
333 rich mudrocks were furthermore subdivided based on their carbonate content into carbonate-rich  
334 (>10 wt%) and carbonate-poor (<10 wt%) varieties.

335

336 4.2. Carbon content and its isotope composition

337  
338 Carbonates contained in samples from the Mount McRae Shale were completely extracted  
339 at temperature below 80°C and no signal was detected at 130°C, confirming that they contain no  
340 siderite. About half of our samples from the Brockman Iron Formation were fully decarbonated at  
341 80°C, while the other half still contained carbonate, which was extracted at 130°C. This clearly  
342 points to the presence of siderite in half of these samples (Rosenbaum and Sheppard, 1986).  
343 However, for both extraction temperatures (80°C and 130°C),  $\delta^{13}\text{C}_{\text{carb}}$  values are nearly identical  
344 within  $\pm 0.5\text{‰}$ . Thus, only bulk carbonate content and average  $\delta^{13}\text{C}_{\text{carb}}$  values will be considered in  
345 the following discussion. For the Brockman Iron Formation, the bulk carbonate content varies  
346 greatly from less than 0.1 up to 83 wt%. The range of carbonate content in the Mount McRae  
347 Shale from 8 to 57 wt% is smaller but still significant. The  $\delta^{13}\text{C}_{\text{carb}}$  values measured in samples  
348 from the Brockman Iron Formation (-10.7 to -5.1 ‰) are lower than those measured in samples  
349 from the Mount McRae Shale (-5.6 to -3.2 ‰). The chemostratigraphic profile of C isotope  
350 composition in carbonates shows significant variations, with intervals of increasing and  
351 decreasing  $\delta^{13}\text{C}_{\text{carb}}$  values (Fig. 4).

352 Depth profiles of  $\text{C}_{\text{org}}$  content and  $\delta^{13}\text{C}_{\text{org}}$  values within the core are shown on Fig. 4. Data  
353 for the Mount McRae Shale from Garvin et al. (2009) are also plotted for comparison. A strong  
354 contrast is noticeable between samples from the Mount McRae Shale and Brockman Iron  
355 Formation. The Mount McRae Shale is enriched in organic C with concentrations ranging from  
356 1.7 to 16.1 wt% (average =  $5.7 \pm 3.8$  wt%,  $1\sigma$ ), while samples from the Brockman Iron  
357 Formation contain between 0.05 and 1.9 wt% of  $\text{C}_{\text{org}}$  (average =  $0.7 \pm 0.5$  wt%,  $1\sigma$ ). This contrast  
358 is even more pronounced in  $\text{C}_{\text{org}}$  isotope values, which roughly show a bimodal distribution with



359 the sharp transition from the Mount McRae Shale to the Brockman Iron Formation (Fig. 4). The  
360 Mount McRae Shale has markedly negative  $\delta^{13}\text{C}_{\text{org}}$  values, averaging  $-37.6 \pm 2.8 \text{ ‰}$  ( $1\sigma$ ), in  
361 contrast to the Brockman Iron Formation with a mean  $\delta^{13}\text{C}_{\text{org}}$  value of  $-28.7 \pm 0.8 \text{ ‰}$  ( $1\sigma$ ). The  
362 heaviest C isotope composition ( $-26.4 \text{ ‰}$ ) is found in the chert DGM307-6 of the Brockman Iron  
363 Formation, and corresponds to the lowest  $\text{C}_{\text{org}}$  content (0.05 wt%). The organic carbon content of  
364 our complete sample set shows an inverse trend with Fe/Ti molar ratio (Fig. 3a), indicating that  
365 Fe enrichment is associated with organic C depletion. Organic carbon contents also roughly  
366 correlate with  $\delta^{13}\text{C}_{\text{carb}}$  values with the most negative  $\delta^{13}\text{C}_{\text{carb}}$  values corresponding to the lowest  $\text{C}_{\text{org}}$   
367 contents (Fig. 5).

368

#### 369 *4.3. Nitrogen content and isotope composition*

370

371 Depth profiles of N content and  $\delta^{15}\text{N}$  values within the drill-core are shown in Fig. 4.  
372 Nitrogen content shows a similar stratigraphic pattern to that of  $\text{C}_{\text{org}}$  content (Fig. 4). This is also  
373 illustrated by the positive correlation between these parameters (Fig. 6a). Samples from the  
374 Mount McRae Shale are enriched in N with concentrations ranging between 385 and 786 ppm  
375 (average =  $495 \pm 169$  ppm,  $1\sigma$ ). In contrast, samples from the Brockman Iron Formation are  
376 characterized by significantly lower N contents from 1.3 to 186 ppm (average =  $55 \pm 50$  ppm,  
377  $1\sigma$ ). Like organic C, N content decreases with increasing Fe/Ti molar ratio, indicating that Fe  
378 enrichment is associated with low N concentrations (Fig. 3b).  $\text{C}_{\text{org}}/\text{N}$  molar ratios for the Mount  
379 McRae Shale vary from 45 to 127 (average =  $70 \pm 35$ ,  $1\sigma$ ). On the average, they are lower  
380 compared to samples from the Brockman Iron Formation (mostly between 19 and 895, the  
381 average is  $242 \pm 200$ ,  $1\sigma$ ). Only one sample of the Brockman Iron Formation shows an

382 exceptionally high  $C_{org}/N$  ratio of 2251 (sample DGM288-2, Table 3). This high value is  
383 geologically relevant and is not an analytical artefact from incomplete carbonate dissolution,  
384 since this sample shows a  $\delta^{13}C_{org}$  value of  $-29\text{‰}$ , indistinguishable from other samples (even minor  
385 carbonate contamination would significantly increase the measured  $\delta^{13}C$  value). The depth profile  
386 of N isotope composition shows large variations in  $\delta^{15}N$  values. These variations are independent  
387 of rock lithology, with N isotope values of organic-rich shale, carbonate-rich and carbonate-poor  
388 stilpnomelane mudrock, banded iron formation and chert fitting to the broad trend (Fig. 4). The  
389  $\delta^{15}N$  values range from 4.4 to 5.7 ‰ for the Mount McRae Shale (average =  $4.9 \pm 0.6 \text{‰}$ ,  $1\sigma$ ) and  
390 from 0.4 to 13.4 ‰ for the Brockman Iron Formation (average =  $7.5 \pm 2.7 \text{‰}$ ,  $1\sigma$ ). Pinti et al.  
391 (2001) analyzed one banded iron formation sample, containing magnetite, quartz and chlorite,  
392 from the Dales Gorge Member of the Brockman Iron Formation and found N content and  $\delta^{15}N$   
393 value of 1.9 ppm and 11.5 ‰, respectively, within the range of the present data. In our sample  
394 set, N isotope values do not show any correlation with N content,  $C_{org}/N$  ratios (Fig. 7), or  $\delta^{13}C_{org}$   
395 values. The chemostratigraphic profile shows a generally inverse correlation between  $\delta^{15}N$  and  
396  $\delta^{13}C_{carb}$  values (Fig. 4). However, a plot of  $\delta^{15}N$  versus  $\delta^{13}C_{carb}$  values does not clearly show any  
397 correlation between these two parameters ( $r^2 = 0.31$ ; Fig. 7c), suggesting that they are only  
398 indirectly linked to each other.

399

## 400 **5. Discussion**

401

402 Before any discussion about paleoenvironmental implications of our results can take  
403 place, it is important to establish whether measured C and N contents and isotope compositions

404 preserved a primary signature, i.e., one generated in the water column, or one that has been  
405 produced by later processes such as diagenesis or low-grade metamorphism.

406

### 407 *5.1. Evidence for primary C isotope composition of organic matter*

408

409 In sedimentary rocks, large variations in organic carbon content may reflect changes in (1)  
410 primary productivity (i.e., production of microbial photoautotrophic biomass), (2) degree of  
411 recycling of organic matter in the water column and in sediments during diagenesis, (3) extent of  
412 thermal maturation of carbonaceous materials associated with sediment burial, and (4)  
413 sedimentation rate resulting in organic matter dilution or concentration. These controls are further  
414 explored below. Thermal maturation of organic molecules releases carbon (in the form of  
415 hydrocarbons; e.g., CH<sub>4</sub>), preferentially enriched in <sup>13</sup>C, and may lead to a significant decrease in  
416 C<sub>org</sub> content associated with an increase in δ<sup>13</sup>C values of the residual organic matter (Hayes et al.,  
417 1983). This isotope effect is small for metamorphic grades lower than the upper greenschist  
418 facies (typically <2‰) and can thus be neglected in the present case since the Mount McRae  
419 Shale and Brockman Iron Formation have experienced metamorphic temperatures <300°C  
420 (Becker and Clayton, 1976; Smith et al., 1982; Kaufman et al., 1990, 2007). An important  
421 observation for our samples is the relationship between C<sub>org</sub> content and Fe/Ti molar ratios (Fig.  
422 3a). Because Ti is immobile in any kind of aqueous fluid, the sedimentary flux of Ti mostly  
423 reflects detrital contributions. If we assume a constant Fe/Ti molar ratio for the detrital source,  
424 then an increase in Fe/Ti molar ratio in the sedimentary rocks will track an increase in the flux of  
425 authigenic Fe (e.g., Dauphas et al., 2007a, 2007b). Accordingly, Fig. 3a shows that C<sub>org</sub> content is  
426 inversely proportional to the flux of authigenic Fe to the sediment. Previous studies of Archean

427 sedimentary rocks also identified an inverse relationship between  $C_{\text{org}}$  and Fe contents and  
428 proposed that it reflects the role of Fe-oxyhydroxides in mineralization of organic matter (e.g.,  
429 Walker, 1984; Beukes et al., 1990; Kaufman et al., 1990; Bekker et al., 2010). In this scenario,  
430 ferric iron precipitate acts as an electron acceptor during early diagenesis for organic matter  
431 oxidation. This explanation is supported by the inverse correlation between  $C_{\text{org}}$  contents and Fe/Ti  
432 molar ratios (Fig. 3a), implying that  $C_{\text{org}}$  content was likely influenced to variable degree by  
433 organic-matter mineralization. An important question is whether this mineralization process  
434 imparted any modification to the C isotope composition of organic matter. If mineralization was  
435 associated with C isotope fractionation, then  $\delta^{13}\text{C}$  values should show some correlation with  $C_{\text{org}}$   
436 contents. This is not the case and in contrast to large variations in  $C_{\text{org}}$  content,  $\delta^{13}\text{C}_{\text{org}}$  values of the  
437 Brockman Iron Formation show only moderate variability and can be regarded as constant at  
438 about  $-28.7 \pm 0.8 \text{ ‰}$  ( $1\sigma$ ). The possibility of a modern contamination — related to sampling or  
439 analytical procedures — with a source having a homogeneous  $\delta^{13}\text{C}$  value seems unlikely, since  $C_{\text{org}}$   
440 contents would be similar in all of the samples and would not show a stratigraphic trend (Fig. 4).  
441 The remarkable isotopic constancy for the whole range of lithologies suggests that modification  
442 of the  $\delta^{13}\text{C}_{\text{org}}$  values was minor after sediment deposition. We therefore argue that the C isotope  
443 composition of organic matter measured in our study represents the primary organic carbon  
444 signature of the microorganisms thriving in the water column. The constancy of  $\delta^{13}\text{C}_{\text{org}}$  values also  
445 indicates that C was assimilated from a homogeneous pool of dissolved inorganic carbon, with  
446 constant (or near constant) C isotope composition. The few samples of the Brockman Iron  
447 Formation significantly diverging from the mean  $\delta^{13}\text{C}_{\text{org}}$  value may have organic matter generated  
448 via at least two different metabolic pathways imposing different carbon isotope fractionations.  
449 The chert sample (DGM307-6) has a particularly low  $C_{\text{org}}$  content and high  $\delta^{13}\text{C}_{\text{org}}$  value of 0.05

450 wt% and -26.4 ‰, respectively, and could have been affected by intense loss of organic matter  
451 during diagenesis. Three samples in our study have  $\delta^{13}\text{C}_{\text{org}}$  values significantly lower than the  
452 average  $\delta^{13}\text{C}_{\text{org}}$  value of  $-28.7 \pm 0.8$  ‰ (samples DGM287, DGM288-1, and MR387). These lower  
453  $\delta^{13}\text{C}_{\text{org}}$  values are associated with high  $\text{C}_{\text{org}}$  contents ( $> 1\text{wt}\%$ ; see Table 2). On the stratigraphic  
454 profile (Fig. 4), they fit well with  $\delta^{13}\text{C}_{\text{org}}$  values previously measured for the Mount McRae Shale,  
455 having even more negative values down-section (as low as -41.6 ‰; data from Kaufman et al.,  
456 2007 and Garvin et al., 2009). These negative  $\delta^{13}\text{C}$  values have been related to the activity of  
457 methanotrophic organisms (Kaufman et al., 2007). Accordingly, our samples with markedly  
458 negative  $\delta^{13}\text{C}_{\text{org}}$  values may also contain some organic matter derived from methanotrophic  
459 microbes.

460

## 461 *5.2. Carbonate precipitation during diagenesis*

462

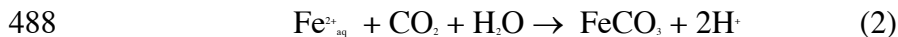
463 Sedimentary carbonates record the isotopic composition of dissolved inorganic carbon  
464 (DIC) pool from which they precipitated with a positive offset of  $\sim 1$  ‰ due to thermodynamic  
465 isotope equilibrium (e.g., Morse and Mackenzie, 1990; for siderite see Zhang et al., 2001, and  
466 references therein). Their  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  values can be used to deduce the isotope fractionation  
467 associated with carbon assimilation ( $\Delta^{13}\text{C} = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$ ), which is a proxy for metabolic  
468 processes (e.g., Hayes et al., 1999; Bekker et al., 2001, 2008; Thomazo et al., 2009b; Bekker and  
469 Kaufman, 2007; Sansjofre et al., 2011).

470 In our samples of the Brockman Iron Formation,  $\delta^{13}\text{C}_{\text{org}}$  values show little variation over  
471 the stratigraphic profile (Fig. 4). It implies that living organisms thrived in a homogeneous pool  
472 of dissolved inorganic carbon with a constant  $\delta^{13}\text{C}$  value. In contrast,  $\delta^{13}\text{C}_{\text{carb}}$  values show large

473 variability among the samples, implying that not all carbonates precipitated from the same pool  
474 of dissolved inorganic carbon as that utilized by organic matter. A portion (if not all) of the  
475 carbonates could have precipitated from either (1) a deep layer of the stratified water column  
476 (Beukes et al., 1990), or (2) sediment porewaters during diagenesis (Walker, 1984). Petrographic  
477 and geochemical data supports the second scenario. Petrographic observations show that many  
478 carbonates in the Brockman Iron Formation cement matrix minerals, indicating that they formed  
479 after sedimentary components were deposited. Another argument derives from the rough  
480 correlation between  $C_{org}$  contents and  $\delta^{13}C_{carb}$  values (Fig. 5). Low  $C_{org}$  content might reflect  
481 mineralization of organic matter during sediment diagenesis (see discussion in section 5.1).  
482 Correlation between  $C_{org}$  contents and  $\delta^{13}C_{carb}$  values then may indicate that the more organic matter  
483 was mineralized, the more negative  $\delta^{13}C$  values were imprinted on carbonates. This can be  
484 explained by a two-stage process: (1) organic matter degradation via ferric-oxyhydroxide  
485 reduction, which increases ferrous iron and  $CO_2$  content in solution as in the following reaction:



487 (2) precipitation of iron-rich carbonates from sediment pore-waters such as:



489 Based on this model, we could expect a correlation between  $\delta^{13}C_{carb}$  value and the amount or  
490 proportion of siderite (or other Fe-carbonate) in our samples, as represented by the carbonate  
491 fraction extracted at the temperature of  $\sim 130^\circ C$  (Table 3). Such a correlation is not observed  
492 possibly because many carbonates are not pure siderites but mixed Fe-Ca-Mg carbonates, which  
493 may have formed during diagenesis or later by carbonate recrystallization during sediment burial.  
494 In any case, it does not contradict the possibility of diagenetic carbonate formation during organic  
495 matter degradation via ferric-oxyhydroxide reduction, but it suggests that diagenetic Fe-

496 carbonates are not exclusively siderites. A similar mechanism for carbonate precipitation was  
497 also inferred based on  $\delta^{13}\text{C}$  data obtained for carbonates and organic matter from the Late Archean  
498 Transvaal Supergroup in South Africa (Fischer et al., 2009). It was also proposed based on  
499 coupling of Fe and C isotope values in the Late Archean carbonate-bearing iron formations  
500 (Heimann et al., 2010; Craddock and Dauphas, 2011), suggesting that this process could have  
501 been common during the Late Archean.

502

### 503 *5.3. Preservation of N isotope signature in organic matter*

504

505 Like for carbon, it is important to determine if N isotope composition reflects a signature  
506 of organisms living in the water column or was affected by late modifications related to post-  
507 depositional processes. This is crucial since late-stage hydrothermal processes have been invoked  
508 for iron formation in some localities within the Hamersley Province (Webb et al., 2003).  
509 Correlation between N and  $C_{\text{org}}$  contents suggests that N originated from organic matter (Fig. 6a).  
510 Since organic C is likely predominantly derived from primary producers, the same origin might  
511 equally apply to N. Samples from the Brockman Iron Formation have  $C_{\text{org}}/\text{N}$  molar ratios  
512 averaging  $242 \pm 200$  ( $1\sigma$ ), which is similar to the average  $C_{\text{org}}/\text{N}$  molar ratio of the previously  
513 measured Archean cherts from various localities including Western Australia, South Africa and  
514 Northern America ( $200.7 \pm 137$ ,  $1\sigma$ ,  $n=59$ ; Beaumont and Robert, 1999; Ueno et al., 2004, Pinti  
515 et al., 2007, 2009). Similarly to carbon content, nitrogen content is negatively correlated with  
516 Fe/Ti molar ratio, suggesting that N was also removed from the sediment by organic matter  
517 mineralization (Fig. 3b; see discussion on organic carbon content in section 5.1). The lowest N

518 content corresponds to the chert sample DGM307-6 that contains ~1.3 ppm N, and is similar to  
519 some other Archean chert samples in nitrogen content (Pinti et al., 2001, 2007, 2009).

520 Nitrogen content shows a broad positive correlation with  $K_2O$  content (Fig. 6b). This  
521 suggests that part of the nitrogen released to sediment porewaters during organic matter  
522 mineralization, was substituted in the form of  $NH_4^+$  for  $K^+$  in K-bearing minerals, because of their  
523 similar charge and ionic radius (Honma and Itihara, 1981; Busigny et al., 2003a; Rouchon et al.,  
524 2005). In other words, C and N were likely supplied from the same organic material but  
525 diagenetic evolution induced a loss of N from organic matter with partial incorporation as  $NH_4^+$   
526 into K-minerals. Since N is preferentially released from organic matter during diagenesis and  
527 metamorphism with respect to C, C/N ratio can be used as a proxy to evaluate the effect of these  
528 processes on N content and its isotopic composition (Ader et al., 2006; Boudou et al., 2008).  
529 Decrease in C/N ratio with increasing  $K_2O$  content confirms that part of the N released from  
530 organic matter was fixed as  $NH_4^+$  in K-silicates and was then protected from diagenesis and early  
531 metamorphism (Fig. 6c). One banded iron formation sample (DGM364), plotting away from the  
532 general  $K_2O$ -N trend, represents particularly high N content with respect to its  $K_2O$  and  $C_{org}$   
533 contents (83.9 ppm N, 0.12 wt%  $K_2O$ , and 0.59 wt%  $C_{org}$ ; Fig. 6a and b). This sample shows the  
534 highest  $Fe_{total}$  concentration, having 78.16 wt%  $Fe_2O_3$ . It might indicate that N was predominantly  
535 bound with Fe oxides, as was earlier suggested by Pinti et al. (2007). Since N isotopes could be  
536 fractionated during organic matter degradation, it is important to evaluate whether N isotope  
537 signature of our samples records paleo-ecosystem and paleo-environmental (e.g., redox)  
538 conditions. Organic matter degradation occurs (1) in the water column and in the sediment during  
539 early diagenesis, and (2) during thermal maturation associated with burial diagenesis and  
540 metamorphism. In oxic environments, early diagenesis may impart a shift in  $\delta^{15}N_{org}$  values



541 towards more positive values with a magnitude reaching  $\sim 3$  ‰ (e.g., Altabet and Francois, 1994;  
542 Lehmann et al., 2002; Gaye et al., 2009; Möbius et al., 2010). In contrast, organic matter  
543 degradation under anoxic and suboxic conditions either preserves original nitrogen isotope values  
544 or slightly lowers  $\delta^{15}\text{N}_{\text{org}}$  values with a shift smaller than 1 ‰ (e.g., Lehmann et al., 2002; Thunell  
545 et al., 2004; Möbius et al., 2010). In the case of the Brockman Iron Formation, the deep waters of  
546 the basin were clearly anoxic as indicated by (i) the particularly high Fe content in the sediments  
547 requiring high dissolved Fe(II) concentrations, and (ii) REE patterns lacking a negative Ce  
548 anomaly and with a pronounced positive Eu anomaly reflecting a source of reduced, high-  
549 temperature fluids similar to modern, mid-ocean ridge hydrothermal systems (e.g., Klein and  
550 Beukes, 1989; Alibert and McCulloch, 1993; Beukes and Gutzmer, 2008; Planavsky et al., 2010).  
551 Accordingly,  $\delta^{15}\text{N}$  values of our samples were probably not or only slightly modified during early  
552 diagenesis in this anoxic depositional setting. Effect of thermal maturation associated with burial  
553 diagenesis and metamorphism on N isotope composition can be tested using tracers such as N  
554 concentration and C/N ratio. Studies on coal with variable maturity showed that as metamorphic  
555 grade increases, organic N content decreases and  $C_{\text{org}}/N_{\text{org}}$  ratio increases, while  $\delta^{15}\text{N}$  values remain  
556 largely unaffected (Ader et al., 1998, 2006; Boudou et al., 2008). However, if N present in form  
557 of  $\text{NH}_4^+$  in silicate minerals is lost during metamorphism then the residual  $\delta^{15}\text{N}$  values could be  
558 increased by up to a few per mil (Bebout and Fogel, 1992; Mingram and Braüer, 2001; Bebout et  
559 al., 1999; Busigny et al., 2003b; Jia, 2006). In our sample set, N contents and C/N ratios do not  
560 show any significant correlation with  $\delta^{15}\text{N}$  values (Fig. 7a and b), thus suggesting that  $\delta^{15}\text{N}$  values  
561 are not controlled by N loss during sediment burial and metamorphism. In support of this  
562 statement, the stratigraphic trend of  $\delta^{15}\text{N}$  values within the drill-core shows smooth alternating  
563 rises and falls of  $\delta^{15}\text{N}$  values suggesting either a secular or local control over N isotope variations

564 (Fig. 4) rather than that imposed by post-depositional modification. We conclude that the  $\delta^{15}\text{N}$  and  
565  $\delta^{13}\text{C}_{\text{org}}$  values of our samples from the Brockman Iron Formation and Mount McRae Shale mostly  
566 reflect primary organic matter composition.

567

#### 568 *5.4. Implications for ancient N biogeochemical cycle*

569

570 In this section, the elemental concentrations and isotopic variations of N-C<sub>org</sub>-C<sub>carb</sub>-Fe in the  
571 Mount McRae Shale and Brockman Iron Formation are integrated to explore several models of N  
572 biogeochemical cycle in the Late Archean ocean. For all herein discussed models, we assume the  
573 following lateral distribution of sedimentary facies from proximal to distal, deep-sea  
574 environments (cf., Beukes et al., 1990; Bekker et al., 2010): (1) organic matter-rich, sulfidic  
575 shales deposited under euxinic conditions, (2) iron-rich shales and carbonates, and (3) banded  
576 iron formations and chert in deeper settings (Fig. 8). Nutrients sustaining organic productivity  
577 were predominantly supplied from the continents or by coastal upwelling currents, resulting in  
578 higher organic productivity in proximal facies. Part of the Mount McRae Shale was deposited  
579 under euxinic conditions (Reinhard et al., 2009; Raiswell et al., 2011), where accumulation of  
580 free H<sub>2</sub>S in the water column in excess of dissolved Fe<sup>2+</sup> might have resulted from either riverine  
581 delivery of SO<sub>4</sub><sup>2-</sup> produced by oxidative continental weathering or atmospheric supply of sulphate  
582 aerosols generated in the anoxic atmosphere by UV photolysis (Bekker et al., 2010), combined  
583 with bacterial SO<sub>4</sub><sup>2-</sup> reduction associated with the remineralisation of organic matter. The Mount  
584 McRae Shale high organic productivity, reflected in its elevated C<sub>org</sub> concentrations, is associated  
585 with markedly negative  $\delta^{13}\text{C}_{\text{org}}$  values (Figure 4) suggesting high methanotrophic contributions to  
586 the organic matter (Kaufman et al., 2007). Methanotrophs have two specific requirements. First, a

587 flux of methane, likely derived from preferential organic matter mineralization by methanogens  
588 under low oxygen conditions. For the Mount McRae Shale, the low Fe/Ti ratios (Figure 3)  
589 indicate that ferric iron availability was limited, therefore favouring methanogenesis as the  
590 dominant degradation pathway in the deeper part of the water column and in the sediment  
591 porewaters. Second, methanotrophic organisms require oxidant availability so that methane is  
592 oxidized via either anaerobic, with, for example, sulphate as an electron acceptor, or aerobic  
593 oxidation (Hayes et al., 1983; Thomazo et al., 2009a). The upper part of the water column in the  
594 Mount McRae Shale depositional environment therefore should have contained either dissolved  
595 oxygen or another oxidant such as sulphate, nitrate, or Fe- and Mn-oxyhydroxides. In contrast to  
596 the Mount McRae Shale, the biomass in the Brockman Iron Formation depositional setting was  
597 probably dominated by photosynthetic organisms, either oxygenic or anoxygenic.  
598 Chemoautotrophic organisms living in hydrothermal systems were also proposed as the main  
599 source of organic matter for Archean cherts (Pinti and Hashizume, 2001; Pinti et al., 2001, 2009).  
600 This source of organic carbon and nitrogen seems unlikely for our samples from the Brockman  
601 Iron Formation both because of their geological setting (no evidence for active hydrothermal  
602 systems at the depositional site of this unit) and their  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values, which are not as  
603 negative as those typical of chemoautotrophs (e.g.,  $\delta^{15}\text{N}$  values as low as -5 ‰ and  $\delta^{13}\text{C}$  values  
604 lower than -40 ‰). The  $\delta^{13}\text{C}$  values of our samples ( $-28.7 \pm 0.8$  ‰; Fig. 4) are compatible with  
605 primary producers living in the photic zone of the water column. The ferric iron flux to the  
606 depositional site of the Brockman Iron Formation was obviously higher than that to the  
607 depositional site of the Mount McRae Shale, as illustrated by their Fe/Ti ratios (Fig. 3). This  
608 suggests that anaerobic respiration using iron oxyhydroxide reduction may have been the  
609 dominant degradation pathway for organic matter, which is energetically more favourable than

610 methanogenesis. Iron oxyhydroxide reduction would have increased dissolved Fe(II) and DIC  
611 concentrations in porewaters, likely inducing Fe-rich carbonate precipitation with low  $\delta^{13}\text{C}_{\text{carb}}$   
612 values (see discussion in section 5.2). The chemostratigraphic profiles presented in Figure 4 show  
613 roughly inverse trends for  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values in the Brockman Iron Formation. Since  $\delta^{13}\text{C}_{\text{carb}}$   
614 values likely reflect a diagenetic origin of Fe-rich carbonates,  $\delta^{15}\text{N}$  variations might be also  
615 interpreted as resulting from organic matter degradation. However, the discussion presented  
616 above in section 5.3 as well as a weak direct correlation between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values (Fig. 7c)  
617 suggest that  $\delta^{15}\text{N}$  values more likely represent the primary signature of organic matter in the water  
618 column, i.e. the N isotope composition of photosynthetic organisms. It seems likely therefore that  
619 N and  $\text{C}_{\text{carb}}$  isotope compositions were linked by indirect processes.

620         According to previous studies, two possible scenarios can be considered for the redox  
621 structure in the water column of the Late Archean oceans. In the first case, the water column is  
622 stratified with a thin oxygenated (oxic or disoxic) upper layer overlying an anoxic and  
623 ferruginous lower layer (e.g., Beukes and Gutzmer, 2008). This scenario is traditionally invoked  
624 to explain deposition of banded iron formations, where upwelling dissolved Fe(II) is oxidized  
625 with  $\text{O}_2$  produced through photosynthetic activity of cyanobacteria (Cloud, 1973; Klein and  
626 Beukes, 1989). The second scenario infers a fully anoxic water column (e.g., Planavsky et al.,  
627 2010) with banded iron formation deposition controlled by one or several of the following  
628 processes: metabolic Fe(II) oxidation, UV photooxidation, or quantitative consumption of  
629 produced  $\text{O}_2$  (e.g., Bekker et al., 2010). In both models for iron formation deposition, nitrogen  
630 from the atmosphere was initially introduced into the ocean by  $\text{N}_2$ -fixing organisms, such as  
631 cyanobacteria, under either aerobic or anaerobic conditions. Nitrogen assimilated by these  
632 organisms is not strongly fractionated in the modern ocean ( $\delta^{15}\text{N} \approx 0 \text{ ‰}$ ; e.g., Minagawa and

633 Wada, 1986), but can have negative values (as low as -3 ‰) when N<sub>2</sub>-fixing organisms are grown  
634 in Fe-enriched media (Zerkle et al., 2008). After death of N<sub>2</sub>-fixing bacteria, they would sink  
635 through the water column and would be incorporated into sediments resulting in δ<sup>15</sup>N values of  
636 sedimentary organic matter around 0 ‰. Nitrogen from their nucleic and amino acids can be  
637 partially released as ammonium (NH<sub>4</sub><sup>+</sup>) by mineralization in the water column or in sediments.  
638 Further processing of NH<sub>4</sub><sup>+</sup> will depend on local redox conditions. The positive δ<sup>15</sup>N values of the  
639 Mount McRae Shale and Brockman Iron Formation indicate that N<sub>2</sub>-fixing organisms were not  
640 the only source of organic matter to the sediment. Positive δ<sup>15</sup>N values of this magnitude in  
641 Precambrian rocks can be caused by three different pathways: (1) partial assimilation of  
642 ammonium (Papineau et al., 2009), (2) partial nitrification of ammonium, followed by complete  
643 denitrification of the produced nitrite (Thomazo et al., 2011), and (3) quantitative oxidation of  
644 ammonium to nitrate, followed by partial denitrification in the water column (Godfrey and  
645 Falkowski, 2009; Garvin et al., 2009). The cases 1 and 2 require global anoxic conditions for  
646 ammonium to be stable in the water column under open-marine conditions. In contrast, case 3  
647 requires an oxic photic zone for nitrate stability, with limited denitrification under suboxic  
648 conditions, similar to an oxygen minimum zone of the modern ocean. For all 3 cases, the rises  
649 and falls of δ<sup>15</sup>N values in the Mount McRae Shale and Brockman Iron Formation would be  
650 produced by variations in the relative proportion of N<sub>2</sub>-fixation and <sup>15</sup>N-enriched NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup>  
651 assimilation. The Mount McRae Shale has lower δ<sup>15</sup>N values (the average is 3.8 ± 1.7 ‰, n = 82;  
652 Garvin et al., 2009) than the Brockman Iron Formation (the average is 7.5 ± 2.7 ‰, n = 26; Fig.  
653 4). The lower δ<sup>15</sup>N values of the Mount McRae Shale might reflect a stronger contribution of N<sub>2</sub>-  
654 fixation with respect to NO<sub>3</sub><sup>-</sup> or NH<sub>4</sub><sup>+</sup> assimilation, lowering δ<sup>15</sup>N values towards 0 ‰ (Zerkle et al.,  
655 2008), which is characteristic of marine areas with high organic productivity. In contrast, a lower

656 organic productivity at the depositional site of the Brockman Iron Formation would have left  
657 more dissolved  $\text{NO}_3^-$  or  $\text{NH}_4^+$  available for assimilation, resulting in less intense  $\text{N}_2$ -fixation and  
658 higher  $\delta^{15}\text{N}$  values of the biomass. In the following sections, the three cases will be further  
659 explored and their applicability to the Mount McRae Shale and Brockman Iron Formation will be  
660 evaluated.

661

#### 662 *5.4.1. Nitrogen cycle in fully anoxic and ferruginous ocean*

663

664 Under fully anoxic conditions (Fig. 8), dissolved  $\text{NH}_4^+$  would accumulate in the water  
665 column and would be readily assimilated by living organisms. Ammonium assimilation favours  
666 light N isotope, rendering the residual  $\text{NH}_4^+$  enriched in  $^{15}\text{N}$  (Papineau et al., 2009; Hadas et al.,  
667 2009). Assuming a maximum fractionation factor of 27 ‰ for  $\text{NH}_4^+$  assimilation (Sigman et al.,  
668 2009) and an initial ammonium  $\delta^{15}\text{N}$  value of 0 ‰, a Rayleigh distillation model requires that  
669 70% of the initial ammonium has to be assimilated and transferred to the sediment before  
670 producing organic matter with  $\delta^{15}\text{N}$  values of +5 ‰, similar to those found in the Mount McRae  
671 Shale and Brockman Iron Formation (Fig. 4). However, the cumulated fraction of organic matter  
672 with nitrogen assimilated via such a distillation process would have a mean  $\delta^{15}\text{N}$  value around -20  
673 ‰, which is not found in either the Mount McRae Shale or Brockman Iron Formation. Thus,  
674 partial assimilation of ammonium (case 1 hypothesis) is unlikely to explain the present results.

675 The second hypothesis is based on a partial oxidation of  $\text{NH}_4^+$ , followed by complete  
676 removal of the nitrite product (Thomazo et al., 2011). Partial oxidation of  $\text{NH}_4^+$  leads to the  
677 production of isotopically light nitrite with a fractionation of 10 to 40 ‰ (Casciotti et al., 2003),  
678 while residual  $\text{NH}_4^+$  becomes progressively enriched in heavy isotope. The light isotope is then

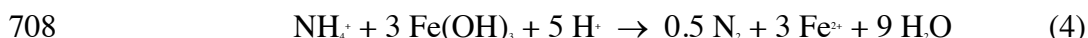
679 removed from the system by quantitative denitrification of nitrite to nitrogen gas ( $N_2$ ). This  
680 sequence of reactions occurs under anoxic conditions, but requires a flux of  $O_2$  that is fully used  
681 up. This is rarely observed in modern environments because of their highly oxygenated state.  
682 However, a recent study of particulate organic matter in Lake Kinneret, Israel, found  $^{15}N$ -  
683 enrichment up to 15-30 ‰ due to partial nitrification of  $NH_4^+$  (Hadas et al., 2009), demonstrating  
684 the feasibility of this process. If the positive  $\delta^{15}N$  values observed in the Mount McRae Shale and  
685 Brockman Iron Formation are inherited from partial oxidation of  $NH_4^+$ , then this process also has  
686 to explain the  $\delta^{15}N$ - $\delta^{13}C_{carb}$  co-variations observed along the chemostratigraphic profile (Fig. 4). One  
687 possibility is that  $O_2$  produced by oxygenic photosynthesis was utilized for both Fe oxidation and  
688 partial  $NH_4^+$  oxidation. If this is the case, the flux of Fe-oxyhydroxides, leading to organic matter  
689 mineralization and Fe-carbonate precipitation, will roughly correspond with the degree of partial  
690  $NH_4^+$  oxidation. Based on this scenario, an increase in  $\delta^{15}N$  values would track an increase in the  
691  $O_2$  production in the upper ocean. It is important to note that application of this model to the  
692 open-marine depositional site of the Mount McRae Shale and Brockman Iron Formation requires  
693  $NH_4^+$  stability in the water column and thus generally anoxic conditions, with some “oxygen  
694 oases” generated by blooms of oxygenic photosynthesizers (Fig. 8a), inducing partial  $NH_4^+$   
695 oxidation.

696 If  $O_2$  was entirely absent from this system, an alternative electron acceptor for  $NH_4^+$   
697 oxidation could have been ferric oxyhydroxides ( $Fe(OH)_3$  in Fig. 8b) that were generated in  
698 anoxic, ferruginous Archean oceans. Microbial oxidation of  $NH_4^+$  with Fe(III) under anaerobic  
699 conditions was recently demonstrated in wetland soils (Clément et al., 2005; Shrestha et al.,  
700 2009), tropical upland soil slurries (Yang et al., 2012), and a sludge from a cattle waste treatment  
701 plant (Sawayama, 2006), and was also shown to be thermodynamically feasible (Clément et al.,

702 2005). This reaction may have been important in the Archean biogeochemical N cycle and can be  
703 written as,



705 Following  $\text{NH}_4^+$  oxidation,  $\text{NO}_3^-$  would be reduced to  $\text{N}_2$  by denitrification or anammox processes,  
706 since it is unstable under anaerobic conditions. Direct  $\text{NH}_4^+$  oxidation to  $\text{N}_2$  is also energetically  
707 feasible, yielding up to 245 kJ/mol (Yang et al., 2012), through the following reaction:



709 Although the N isotope fractionation associated with  $\text{NH}_4^+$  oxidation with Fe(III) is not known, it  
710 is reasonable to assume fractionations similar to those imposed by  $\text{O}_2$ -driven nitrification process  
711 (10 to 40 ‰; Casciotti et al., 2003), thus enriching the residual  $\text{NH}_4^+$  in  $^{15}\text{N}$ . This scenario could  
712 also provide an explanation for the roughly inverse trends of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values (Fig. 4). The  
713 highest flux of Fe-oxyhydroxides would correspond to the highest rate of ammonium oxidation,  
714 resulting in both an increase in  $\delta^{15}\text{N}$  values and early diagenetic organic matter mineralization  
715 with ferric iron. The latter process in turn would induce Fe-carbonate precipitation with negative  
716  $\delta^{13}\text{C}_{\text{carb}}$  values.

717

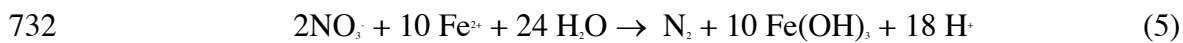
#### 718 *5.4.2. Nitrogen cycle in a redox-stratified ocean*

719

720 In the oxic upper layer of a stratified water column (Fig. 8c),  $\text{NH}_4^+$  would be quantitatively  
721 oxidized to  $\text{NO}_3^-$  by nitrification, thus preventing any nitrogen isotope fractionation. In oxygen-  
722 minimum zones, or at redox boundaries, partial denitrification would increase the  $\delta^{15}\text{N}$  value of  
723 residual  $\text{NO}_3^-$  (see review in Sigman et al., 2009). Assimilation of this residual  $\text{NO}_3^-$  by living  
724 organisms would transfer positive N isotope signature to the sedimentary deposit. Such a scenario



725 of a redox-stratified ocean has been proposed in previous studies to explain positive  $\delta^{15}\text{N}$  values in  
726 Archean sedimentary rocks (Garvin et al., 2009; Godfrey and Falkowski, 2009). This scenario  
727 can be extended to the sedimentary sequence of the Brockman Iron Formation if it can explain  
728 the coupling between N and Fe biogeochemical cycles in the water column, which is required to  
729 establish the  $\delta^{15}\text{N}$ - $\delta^{13}\text{C}_{\text{carb}}$  co-variation (Fig. 4). One possibility is that partial denitrification of  $\text{NO}_3^-$   
730 was mediated by anaerobic microbial oxidation of Fe(II) to Fe(III) (Shen et al., 2006). The  
731 corresponding reaction can be written as,



733 The existence of anaerobic nitrate-dependant microbial Fe(II)-oxidation has been demonstrated  
734 by laboratory experiments (Straub et al., 1996), but data on N isotope fractionations associated  
735 with this process are still lacking. If partial denitrification via this process increases  $\delta^{15}\text{N}$  values of  
736 residual  $\text{NO}_3^-$ , as it does in modern marine oxygen-minimum zones (Sigman et al., 2009), then  
737 assimilation of the  $^{15}\text{N}$ -enriched residual  $\text{NO}_3^-$  would generate a pool of organic matter with  
738 positive  $\delta^{15}\text{N}$  values. According to this reaction, the higher fluxes of  $\text{Fe}(\text{OH})_3$  to the sediment,  
739 possibly inducing diagenetic Fe-carbonate precipitation, would be associated with more positive  
740  $\delta^{15}\text{N}$  values in the sedimentary organic matter. Dissolved  $\text{NO}_3^-$  would be in contact with  $\text{Fe}^{2+}$  only  
741 at the redox boundary between upper oxygenated and lower anoxic layers in a stratified water  
742 column (Fig. 8c). Away from the redox boundary,  $\text{Fe}^{2+}$  would be immediately oxidized to  $\text{Fe}^{3+}$   
743 under fully oxic conditions, and  $\text{NO}_3^-$  would be quantitatively denitrified under anoxic conditions.  
744 Although redox-stratified water column allows for an inverse relationship between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{carb}}$   
745 values, as in the Brockman Iron Formation (Fig. 4), the feasibility of this model can be  
746 questioned. Based on this scenario, the flux of Fe oxyhydroxides to the sediments has to be  
747 balanced by  $\text{NO}_3^-$  denitrification. The reaction (5) presented above indicates that 1 mole of  $\text{NO}_3^-$  is

748 required for the oxidation of 5 moles of  $\text{Fe}^{2+}$ . However, considering the large flux of Fe associated  
749 with deposition of banded iron formation,  $\text{NO}_3^-$  denitrification would have led to extensive,  
750 probably quantitative, loss of dissolved  $\text{NO}_3^-$  to gaseous  $\text{N}_2$ . As a result of its low concentration,  
751 the residual pool of partially denitrified  $\text{NO}_3^-$  at the redox boundary would have a negligible  
752 impact on the  $\text{NO}_3^-$  inventory of the upper oxygenated ocean and, more specifically, on the N  
753 isotope composition of the  $\text{NO}_3^-$ -assimilating organisms. The feasibility of this redox-stratified  
754 model should be further tested with a detailed dispersion-reaction model coupling N-C-Fe  
755 biogeochemical cycles in the water column.

756

## 757 **6. Conclusion**

758

759 We propose herein that N and Fe biogeochemical cycles in the Late Archean open-marine  
760 basin of the Hamersley Province were linked via redox reactions in the water column, and are  
761 recorded by inverse co-variations between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values in the Brockman Iron Formation.  
762 Like in the Phanerozoic, N was probably introduced to the ocean mainly via  $\text{N}_2$ -fixation leading  
763 to  $\delta^{15}\text{N}$  values close to 0 ‰ in organic matter and  $\text{NH}_4^+$  released during mineralization of organic  
764 matter. Several scenarios based on different redox structures of the water column can satisfy the  
765 literature and our own N isotope data. If the water column was anoxic,  $\text{NH}_4^+$  would have been the  
766 dominant species of dissolved nitrogen available for assimilation in the photic zone. Positive  $\delta^{15}\text{N}$   
767 values in this case would represent partial oxidation of  $\text{NH}_4^+$ , by either (1)  $\text{O}_2$ -controlled  
768 nitrification, or (2) microbial oxidation with ferric oxyhydroxides, and subsequent quantitative  
769 denitrification of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  products. If the water column was redox-stratified, with an oxic  
770 layer covering anoxic deep waters, N assimilated by primary producers would have been mostly

771 in the form of  $\text{NO}_3^-$  like in the Phanerozoic oceans. In this case, the positive  $\delta^{15}\text{N}$  values would  
772 have been produced by partial denitrification of  $\text{NO}_3^-$  coupled to anaerobic microbial oxidation of  
773 ferrous to ferric iron. Accordingly, similar positive  $\delta^{15}\text{N}$  values may record very different N  
774 biogeochemical cycles under anoxic, redox-stratified, or fully oxic conditions in the oceans. We  
775 emphasize therefore that N isotopes alone cannot be used to constrain the redox structure of the  
776 ancient oceans, but can still be useful to address this question if utilized in combination with  
777 other elemental and isotopic tracers.

778 As a perspective, we also point out the need to determine experimentally N isotope  
779 fractionations associated with microbial redox reactions involving N and Fe cycles, such as  $\text{NH}_4^+$   
780 oxidation by ferric oxyhydroxides and/or denitrification of  $\text{NO}_3^-$  mediated by anaerobic oxidation  
781 of Fe(II) to Fe(III). This may help future studies for seeking ancient traces of life in the Archean  
782 geological record.

783

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794 No. XXX.

795

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**Table 1**

Stratigraphic unit, depth in the drill core, rock type and mineralogical description of the samples from the Mount McRae Shale and Brockman Iron Formation analyzed in this study.

Stratigraphic unit	Sample #	Depth, m	Rock type	Mineralogy
<i>Brockman Iron Formation</i>				
Joffre Member	J1-124-1	124.7	stilp-rich mudrock	stilp, qtz, K-fdsp, carb (5%), chl, sulfide
Joffre Member	J1-138-1	138.7	calcareous stilp-rich mudrock	stilp, qtz, K-fdsp, carb (30%), chl, sulfide
Joffre Member	J1-148-2	148.2	calcareous stilp-rich mudrock	Fe-carb (37%; siderite), stilp, biot, minor chl, sulfide
Joffre Member	J1-148-3	148.2	stilp-rich mudrock	stilp, sulfide, carb (3%)
Joffre Member	J1-162-1	162	stilp-rich mudrock	stilp, qtz, fdsp, sulfide*
Whaleback Shale	WS188	188	stilp-rich mudrock	stilp, qtz, fdsp, chl, biot, carb (9%)
Whaleback Shale	WS196	196.8	calcareous stilp-rich mudrock	stilp, carb (30%), K-fdsp, qtz, rare biot, sulfide
Dales Gorge Member	DGM236	236.6	calcareous stilp-rich mudrock	stilp, carb (40%), qtz, fdsp, chl, biot, rare sulfide
Dales Gorge Member	DGM243	243	calcareous stilp-rich mudrock	K-fdsp, biot, qtz, stilp, carb (20%), rare sulfide
Dales Gorge Member	DGM258-1	258.3	calcareous stilp-rich mudrock	stilp, carb (25%), Fe-ox, rare biot, sulfide
Dales Gorge Member	DGM258-2	258.3	calcareous stilp-rich mudrock	stilp, carb (45%), Fe-ox, rare biot, sulfide
Dales Gorge Member	DGM268	268.8	calcareous stilp-rich mudrock	stilp, carb (14%), minor qtz, fdsp, sulfide
Dales Gorge Member	DGM271-2	271.8	stilp-rich mudrock	stilp (40%), chl (60%)
Dales Gorge Member	DGM287	287	calcareous stilp-rich mudrock	qtz, K-fdsp, biot, carb (10%), chl, org. mat., sulfide
Dales Gorge Member	DGM288-1	288	calcareous stilp-rich mudrock	stilp, Fe-carb (53%, siderite)
Dales Gorge Member	DGM288-2	288	BIF	chert, carb (83%, siderite)
Dales Gorge Member	DGM302	302.6	calcareous stilp-rich mudrock	Fe-carb (42%), stilp, biot, minor chl, sulfide
Dales Gorge Member	DGM307-4	307.9	BIF	Fe-ox, carb (20%), minor stilp, sulfide
Dales Gorge Member	DGM307-6	307.9	Fe-carb-rich chert	chert, carb (23%, ankerite)
Dales Gorge Member	DGM325	325.6	calcareous stilp-rich mudrock	stilp, chl, biot, carb (20%), sulfide
Dales Gorge Member	DGM337	337.9	calcareous stilp-rich mudrock	stilp, chl, biot, carb (30%, ferroan dolomite), sulfide
Dales Gorge Member	DGM350	350.85	stilp-rich mudrock	stilp, qtz, chl, K-fdsp, carb (10%)
<i>Mount McRae Shale</i>				
Colonial Chert	CC364	364	BIF	Fe-ox, Fe-carb (35%; siderite), minor stilp, chl, sulfide
Colonial Chert	CC367	367.7	calcareous stilp-rich mudrock	stilp, chl, carb (11%), minor fdsp, sulfide
Colonial Chert	CC373	373.9	stilp-rich mudrock	stilp, chl, carb (8%), minor fdsp, sulfide
Colonial Chert	CC376	376.5	stilp-rich mudrock	stilp, chl, carb (3%), minor fdsp
Mc Rae Shale	MR379	379.9	organic-rich marl	carb (40%; dolomite), qtz, K-fdsp, biot, org. mat., sulfide
Mc Rae Shale	MR381	381	organic-rich marl	carb (50%; dolomite), qtz, K-fdsp, biot, org. mat., sulfide
Mc Rae Shale	MR382	382.3	calcareous black shale	qtz, K-fdsp, biot, carb (8%; dolomite), org. mat., sulfide
Mc Rae Shale	MR383	383.8	organic-rich marl	carb (60%; dolomite), qtz, K-fdsp, biot, org. mat., sulfide
Mc Rae Shale	MR387	387.4	organic-rich marl	carb (60%; dolomite), qtz, K-fdsp, biot, org. mat., sulfide

Column 4 includes 4 types of rocks : organic-rich marls, stilpnomelane-rich mudrocks, calcareous (i.e. &gt;10% carb) stilpnomelane-rich mudrocks, banded iron formation (BIF), and one chert rich in Fe-carbonates.

Column 5: mineralogy from thin section and SEM analyses. The values in brackets indicate the proportion of carbonates as determined from H<sub>2</sub>PO<sub>4</sub> decarbonation (see details in the analytical section). Abbreviations: stilp: stilpnomelane; qtz: quartz; K-fdsp: potassic feldspar; carb: carbonates; chl: chlorite; biot: biotite; Fe-ox: Fe-oxides (hematite and/or magnetite), org. mat.: high organic matter content; Fe-carb: Fe-rich carbonate.

**Table 2**

Major element concentrations in samples from the Mount McRae Shale and Brockman Iron Formation (in wt.%).

Sample #	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI	Total
J1-124-1	55.02	12.72	14.51	0.03	2.62	1.14	0.25	11.36	0.08	0.05	2.78	100.55
J1-138-1	30.02	2.99	41.38	0.64	5.67	0.44	0.41	1.47	0.09	0.08	17.11	100.31
J1-148-3	44.14	4.85	35.21	0.12	5.44	0.28	0.70	2.48	0.14	0.07	7.00	100.41
J1-148-2	25.02	2.99	41.98	0.60	6.79	1.28	0.38	1.54	0.07	0.07	19.72	100.44
J1-162-1	45.57	6.72	31.45	0.05	5.85	0.04	0.59	3.90	0.12	0.07	6.19	100.53
WS188	36.29	9.25	31.22	0.16	6.82	1.39	0.27	4.26	0.16	0.31	9.80	99.93
WS196	33.56	7.85	19.78	0.33	6.11	9.41	0.26	5.90	0.34	0.11	15.78	99.44
DGM236	29.59	5.29	28.57	0.53	5.51	6.04	0.18	4.06	0.17	0.13	19.24	99.30
DGM243	46.38	12.46	11.21	0.22	3.66	5.77	0.11	10.48	0.26	0.10	9.98	100.63
DGM258-1	29.37	3.14	43.02	0.47	5.20	0.81	0.27	2.33	0.11	0.09	14.49	99.30
DGM258-2	23.10	2.71	38.85	0.57	5.94	5.68	0.21	2.00	0.14	0.07	19.85	99.11
DGM268	37.66	7.29	26.23	0.36	7.79	4.27	0.67	2.91	0.32	0.13	12.22	99.84
DGM271-2	29.53	15.37	35.16	0.07	11.54	-	0.14	0.51	0.17	0.06	7.67	100.21
DGM287	51.28	12.40	13.24	0.13	5.94	3.04	-	5.60	0.50	0.17	8.37	100.65
DGM288-1	14.01	1.38	45.55	0.73	9.18	1.92	0.23	0.62	0.03	0.18	26.47	100.29
DGM288-2	8.96	0.74	43.81	0.86	10.53	2.40	0.13	0.37	0.01	0.24	31.11	99.16
DGM302	24.53	2.38	45.34	0.29	5.65	1.07	0.45	0.97	0.09	0.11	19.85	100.73
DGM307-4	14.26	1.42	64.78	0.18	3.75	4.20	0.29	0.56	0.03	1.95	9.64	101.06
DGM307-6	73.13	0.19	6.71	0.11	2.32	6.86	-	0.05	0.00	-	10.53	99.90
DGM325	33.24	4.38	37.21	0.37	5.87	2.18	0.76	1.67	0.21	0.09	14.11	100.08
DGM337	29.06	6.63	26.82	0.12	8.95	8.80	0.69	1.09	0.29	0.08	17.90	100.43
DGM350	49.65	3.43	25.88	0.13	7.32	0.67	0.65	1.29	0.01	0.07	9.97	99.05
CC364	4.56	0.18	78.16	0.13	3.12	3.19	-	0.12	0.01	0.17	10.54	100.19
CC367	34.64	7.77	29.92	0.08	10.09	3.09	0.53	1.07	0.28	0.11	12.13	99.70
CC373	37.77	6.68	31.94	0.05	9.34	0.65	0.71	1.38	0.24	0.08	10.34	99.18
CC376	38.67	7.90	30.37	0.04	10.77	0.63	0.64	1.37	0.29	0.09	8.71	99.48
MR379	35.82	9.58	6.19	0.28	8.33	13.15	-	4.98	0.33	0.06	21.31	100.03
MR381	31.89	7.71	4.60	0.38	8.44	16.53	-	4.51	0.27	0.05	24.94	99.34
MR382	59.32	14.03	2.31	0.07	2.94	2.35	0.21	9.34	0.46	0.07	8.75	99.85
MR383	29.01	8.71	2.71	0.39	10.37	16.77	0.11	6.03	0.12	0.03	26.32	100.55
MR387	27.90	7.55	3.28	0.28	10.18	17.55	-	3.91	0.23	0.04	29.21	100.13

**Table 3**

Carbonate and organic carbon contents and their C isotopic compositions, bulk N content and its isotopic composition, C/N and Fe/Ti molar ratios in samples from the Mount McRae Shale and Brockman Iron Formation

Sample #	C <sub>carb 40°C</sub> , wt%	C <sub>carb 130°C</sub> , wt%	C <sub>carb total</sub> , wt%	δ <sup>13</sup> C <sub>carb total</sub> , ‰	C <sub>org</sub> , wt%	δ <sup>13</sup> C <sub>org</sub> , ‰	N <sub>bulk</sub> , ppm	δ <sup>15</sup> N, ‰	C <sub>org</sub> /N <sub>bulk</sub>	Fe/Ti
J1-124-1	4.4	bdl	4.4	-8.6	0.14	-28.27	87.4	9.5	18.9	188.4
J1-138-1	11.7	21.3	33.1	-8.6	0.41	-28.70	16.7	8.1	285.9	465.0
J1-148-3	1.5	1.7	3.2	-7.9	0.52	-28.64	46.5	9.5	129.9	258.9
J1-148-2	12.4	24.5	36.9	-8.3	0.35	-28.22	40.3	8.6	102.5	617.4
J1-162-1	0.1	bdl	0.1	bdl	0.28	-28.74	121.3	7.4	26.7	273.5
WS188	4.6	3.9	8.5	-7.8	0.66	-28.98	8.6	5.1	894.6	200.1
WS196	32.5	bdl	32.5	-5.1	0.42	-27.62	173.3	6.0	28.4	58.4
DGM236	25.2	14.7	39.9	-8.1	0.70	-28.34	54.0	9.0	150.4	167.1
DGM243	17.9	bdl	17.9	-9.3	0.93	-29.04	100.0	9.2	108.8	43.6
DGM258-1	11.6	15.0	26.6	-7.4	0.49	-28.48	63.2	13.4	90.5	384.1
DGM258-2	29.8	16.2	46.0	-7.2	1.06	-28.61	62.8	11.6	196.2	285.7
DGM268	13.3	1.0	14.3	-5.5	1.39	-29.24	113.9	4.2	142.7	81.5
DGM271-2	0.1	bdl	0.1	bdl	0.67	-28.62	31.2	7.6	250.6	204.4
DGM287	9.7	bdl	9.7	-6.1	1.93	-31.29	186.1	4.8	120.9	26.5
DGM288-1	21.5	31.7	53.1	-7.0	1.44	-29.95	40.6	0.4	415.0	1469.3
DGM288-2	-	83.3	83.3	-6.8	1.20	-28.92	6.2	5.8	2250.9	5475.9
DGM302	24.7	18.2	42.9	-8.0	0.28	-28.70	6.0	6.3	547.3	487.5
DGM307-4	14.7	6.7	21.3	-7.9	0.18	-28.29	6.0	8.0	348.4	2491.4
DGM307-6	22.7	bdl	22.7	-7.8	0.05	-26.43	1.3	7.9	421.4	1678.0
DGM325	11.8	11.3	23.1	-9.0	0.29	-28.76	24.2	8.8	138.7	179.8
DGM337	29.6	2.0	31.6	-9.2	0.41	-28.41	10.7	9.9	443.5	94.1
DGM350	4.4	5.8	10.1	-10.7	0.22	-29.22	7.6	11.1	345.1	2876.0
CC364	20.4	15.2	35.6	-9.2	0.59	-28.16	83.9	6.7	81.5	7816.4
CC367	9.1	1.2	10.3	-5.9	1.22	-28.48	38.8	3.2	367.4	105.4
CC373	3.7	4.6	8.3	-9.2	0.70	-28.85	30.4	7.0	267.0	133.1
CC376	1.7	1.2	2.9	-10.5	0.62	-28.63	61.7	6.9	117.8	104.7
MR379	40.0	bdl	40.0	-4.2	1.74	-28.83	384.7	5.4	52.8	18.5
MR381	51.1	bdl	51.1	-3.9	2.64	-28.59	385.5	5.7	80.0	16.9
MR382	8.0	bdl	8.0	-3.7	3.05	-29.39	785.5	4.4	45.2	5.1
MR383	56.0	bdl	56.0	-3.2	1.92	-29.15	497.5	4.4	45.0	23.5
MR387	57.9	bdl	57.9	-5.6	4.58	-30.48	420.1	4.6	127.2	14.2

bdl: below detection limit.

C<sub>org</sub>/N<sub>bulk</sub> and Fe/Ti are molar ratios.

1097 **Figure captions**

1098  
1099 **Fig. 1.** Geological map of the Hamersley Province and stratigraphic divisions of the upper part of  
1100 the Hamersley Group showing the location of the drill-core WLT-10 and stratigraphic position of  
1101 the geological units discussed in this work (modified from Krapež et al., 2003). The boundary  
1102 between the Chichester Range and Hamersley Range megasequences is the unconformity at the  
1103 base of the Mount Sylvia Formation (Blake and Barley, 1992).

1104  
1105 **Fig. 2.** Major element concentrations (in wt%) of the samples analyzed in our study, including  
1106 organic-rich shales from the Mount McRae Shale, and stilpnomelane-rich mudrocks, banded iron  
1107 formations and chert from the Brockman Iron Formation. Samples are marked as "calcareous" if  
1108 their total carbonate content is higher than 10 wt%.

1109  
1110 **Fig. 3.** Organic carbon content (in wt%) and whole-rock nitrogen content (in ppm) versus Fe/Ti  
1111 molar ratio in samples from the Mount McRae Shale (organic-rich shales) and Brockman Iron  
1112 Formation (all other lithologies). Low Fe/Ti molar ratio indicates a predominantly detrital Fe  
1113 flux, while high Fe/Ti molar ratio points to a higher flux of authigenic Fe.

1114  
1115 **Fig. 4.** Variations in organic C and whole-rock N contents and isotopic compositions, and C  
1116 isotope values of whole-rock carbonate as a function of the depth in the drill-core for samples  
1117 from the Mount McRae Shale (organic-rich shales) and Brockman Iron Formation (all other  
1118 lithologies). Data of Garvin et al. (2009) for the Mount McRae Shale are also plotted for  
1119 comparison. See the main text for further discussion. Since samples of Garvin et al. (2009) were  
1120 collected from other drill-core (ABDP-9) at a different location in the Hamersley Province  
1121 (21°59'29.5"S, 117°25'13.6"E), the depths reported in their paper were adjusted (shifted down by  
1122 275 m) in order to obtain a continuous profile of C and N contents and  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  values.

1123  
1124 **Fig. 5.** Organic C content versus C isotope composition of carbonates in samples from the Mount  
1125 McRae Shale (organic-rich shales) and Brockman Iron Formation (all other lithologies). A  
1126 positive trend (albeit with large deviations) suggests that organic matter mineralization was  
1127 associated with precipitation of secondary carbonates during diagenesis.

1128  
1129 **Fig. 6.** Nitrogen content as a function of organic carbon content (A) and whole-rock potassium  
1130 content (B) in samples from the Mount McRae Shale (organic-rich shales) and Brockman Iron  
1131 Formation (all other lithologies). (C) C/N molar ratio versus whole-rock potassium content.  
1132 Positive correlation in (A) suggests that N was derived from organic matter and in (B) that N was  
1133 at least partially in form of  $\text{NH}_4^+$  substituting for  $\text{K}^+$  in stilpnomelane. Decrease in C/N molar ratio  
1134 with increasing  $\text{K}_2\text{O}$  content indicates that  $\text{NH}_4^+$ , released from organic matter via mineralization,  
1135 was partially trapped in stilpnomelane.

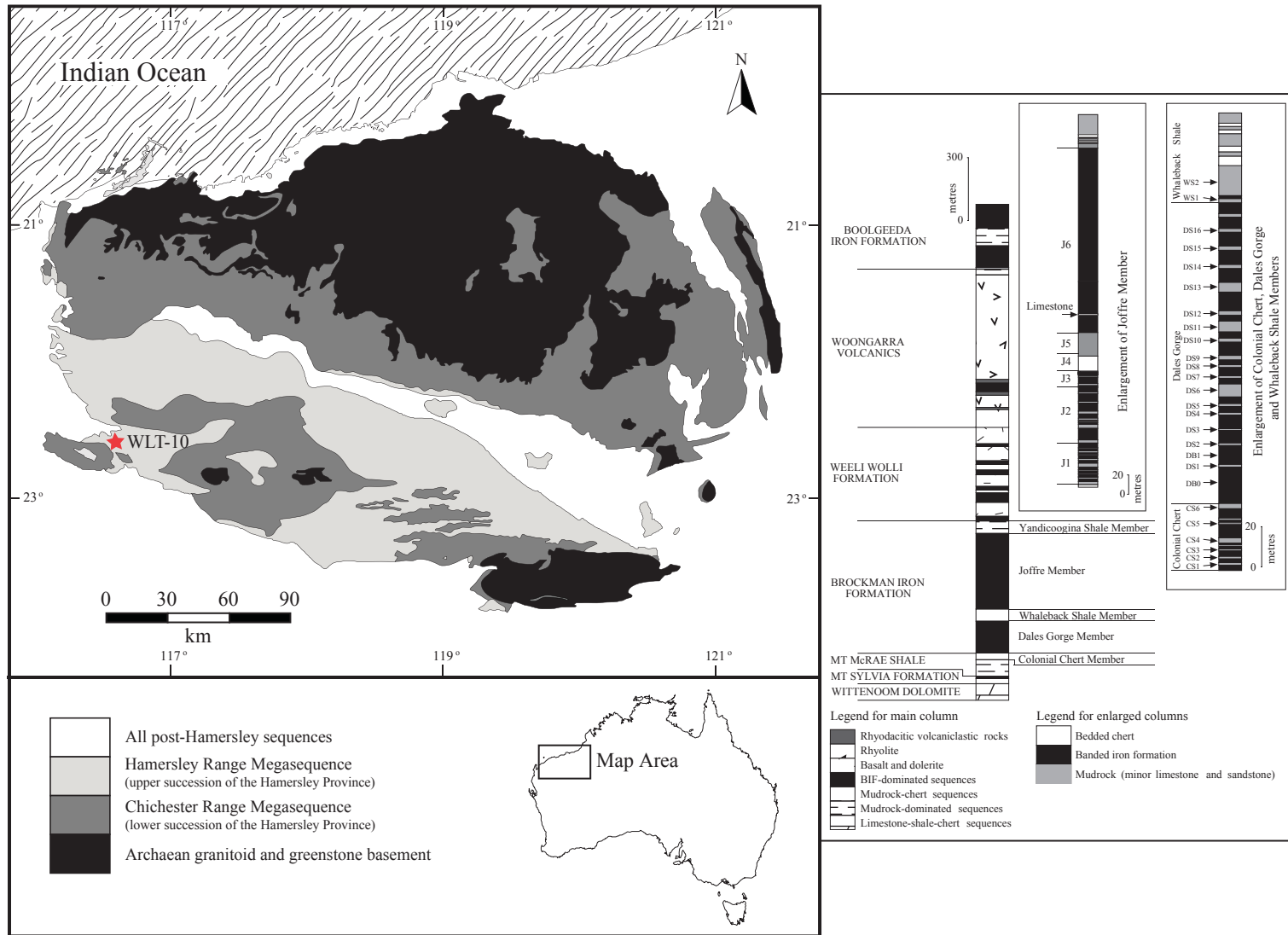
1136  
1137 **Fig. 7.** Nitrogen isotope composition versus  $\text{C}_{\text{org}}/\text{N}$  molar ratio (A), N concentration (B), and C  
1138 isotope values of carbonate (C) in samples from the Mount McRae Shale (organic-rich shales)  
1139 and Brockman Iron Formation (all other lithologies). Decoupling among these parameters  
1140 suggests that N loss related to diagenesis did not induce any systematic N isotope shift,  
1141 supporting preservation of primary  $\delta^{15}\text{N}$  values.

1142  
1143 **Fig. 8.** Schematic models illustrating N biogeochemical cycle in (A) anoxic water column with  
1144 local  $\text{O}_2$  production (noted as “oxygen oases”), (B) fully anoxic water column, and (C) redox-  
1145 stratified water column. In these models, high productivity is restricted to proximal facies due to  
1146 a higher nutrient supply as recorded by organic-rich shales of the Mount McRae Shale, while  
1147 lower productivity is typical for distal environments as represented by the Brockman Iron  
1148 Formation. High productivity in the Mount McRae Shale depositional environment likely limited  
1149  $\text{NH}_4^+$  and  $\text{NO}_3^-$  availability for biological assimilation, thus inducing larger contribution of  $\text{N}_2$ -  
1150 fixing bacteria to the biomass resulting in lower  $\delta^{15}\text{N}$  values. Co-variation of  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values  
1151 in the Brockman Iron Formation (Fig. 4) requires a connection between N and Fe biogeochemical  
1152 cycles in the water column (see the main text for further details). Under anoxic conditions  
1153 (models A and B), the dominant N species available for biological assimilation in the photic zone  
1154 would be  $\text{NH}_4^+$ . Positive  $\delta^{15}\text{N}$  values under these conditions may reflect partial consumption of  
1155  $\text{NH}_4^+$  by  $\text{O}_2$ -driven nitrification (A) or microbial oxidation utilizing Fe(III) oxyhydroxides (B)  
1156 formed in the water column. Under redox-stratified conditions (model C), N in the form of  $\text{NO}_3^-$   
1157 would be assimilated by primary producers. Highly positive  $\delta^{15}\text{N}$  values would be expected under

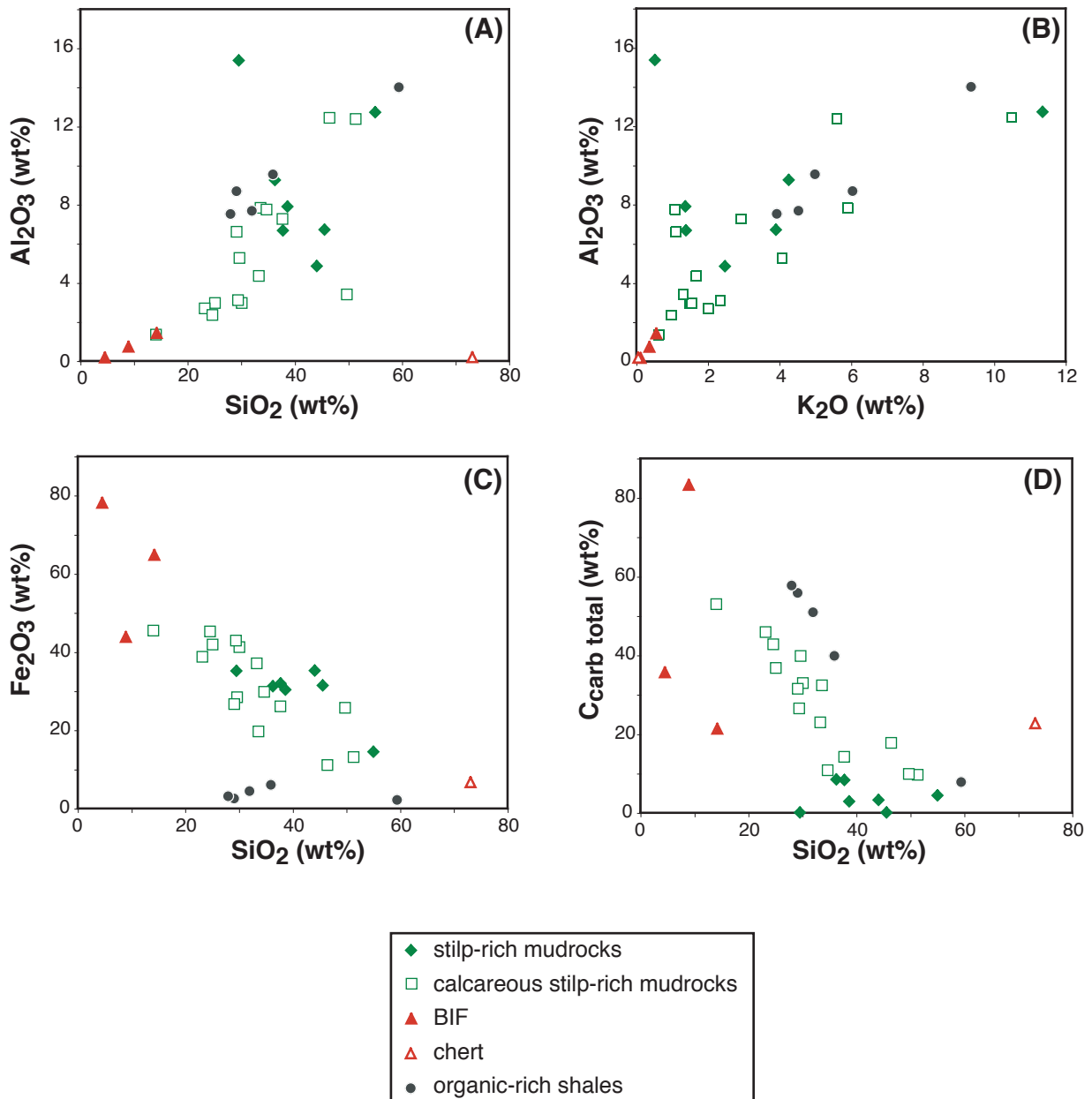
1158 high denitrification conditions, related to high rates of microbial Fe(II) oxidation at the redox  
1159 boundary.



# Figure 1



# Figure 2



**Figure 3**

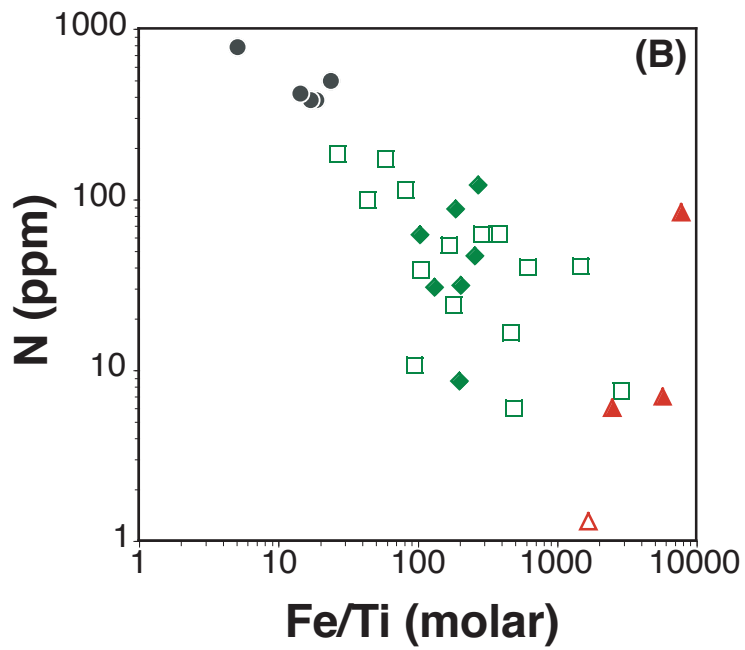
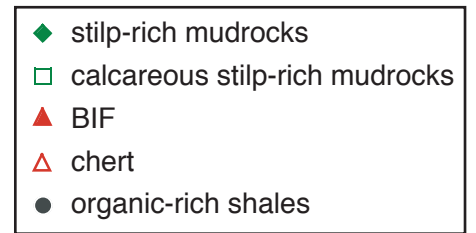
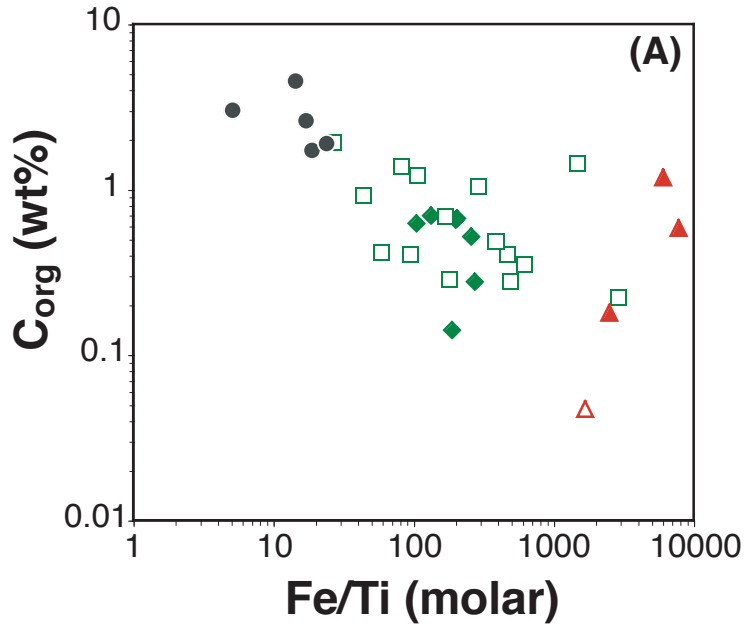
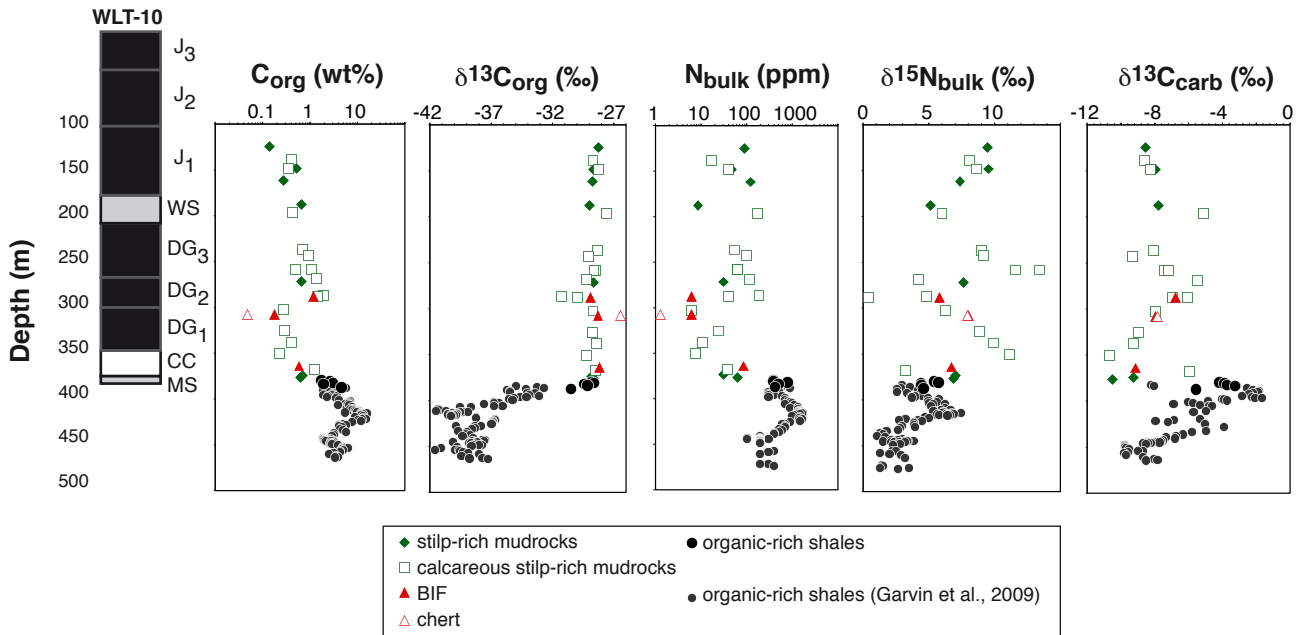
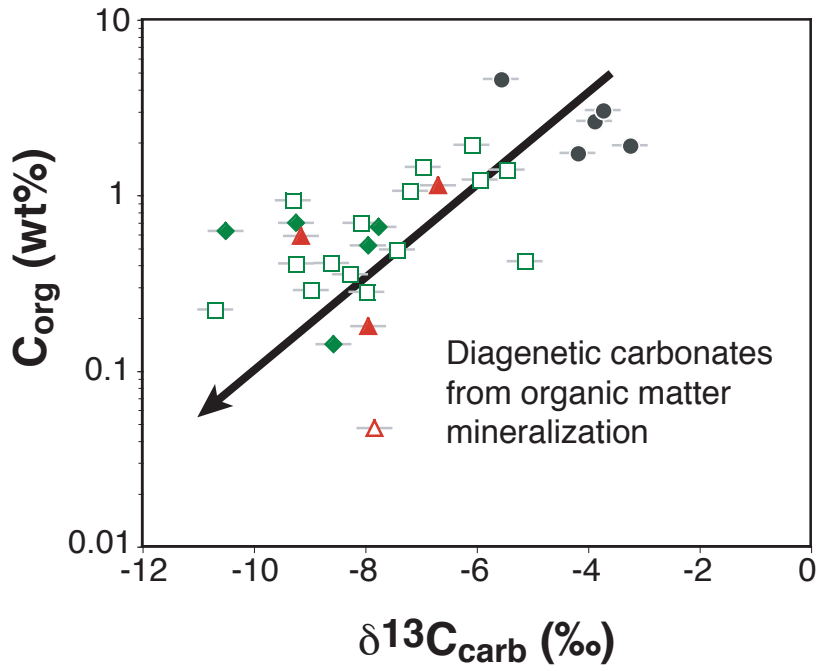


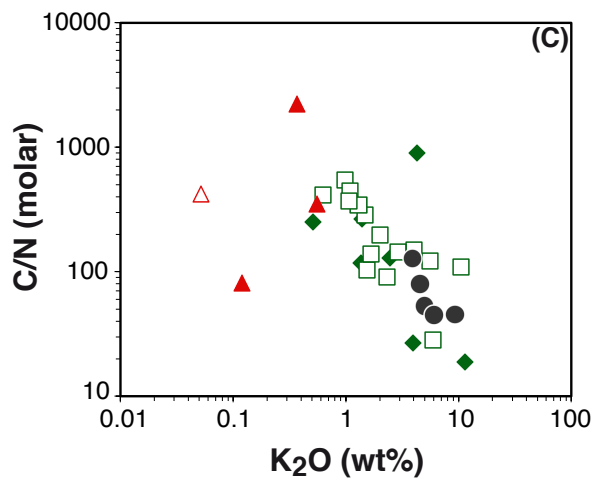
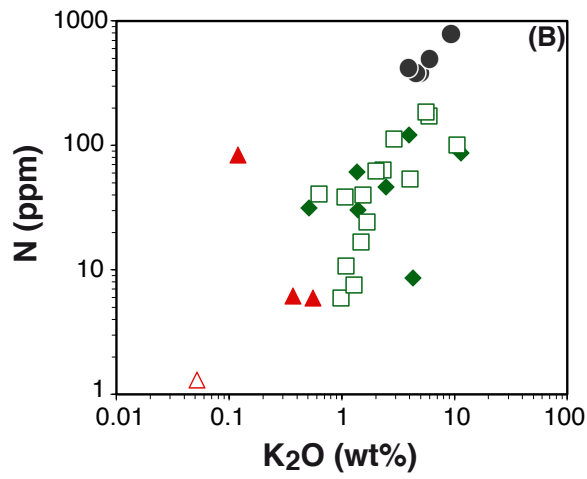
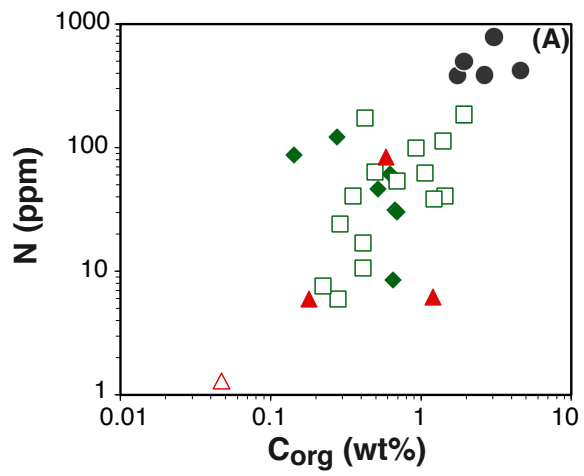
Figure 4



**Figure 5**



- ◆ stilp-rich mudrocks
- calcareous stilp-rich mudrocks
- ▲ BIF
- △ chert
- organic-rich shales



**Figure 6**

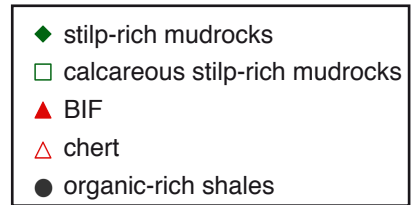
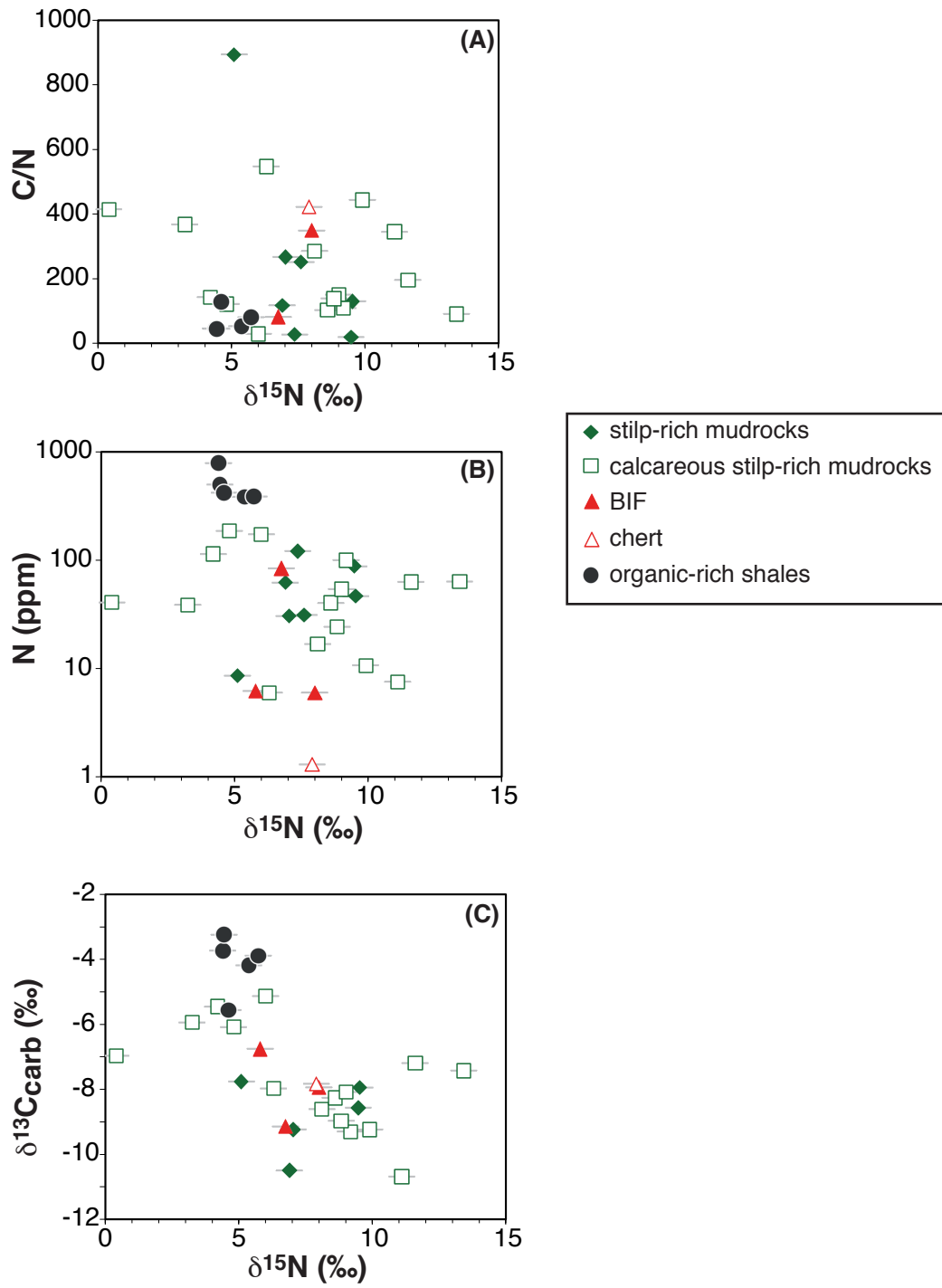
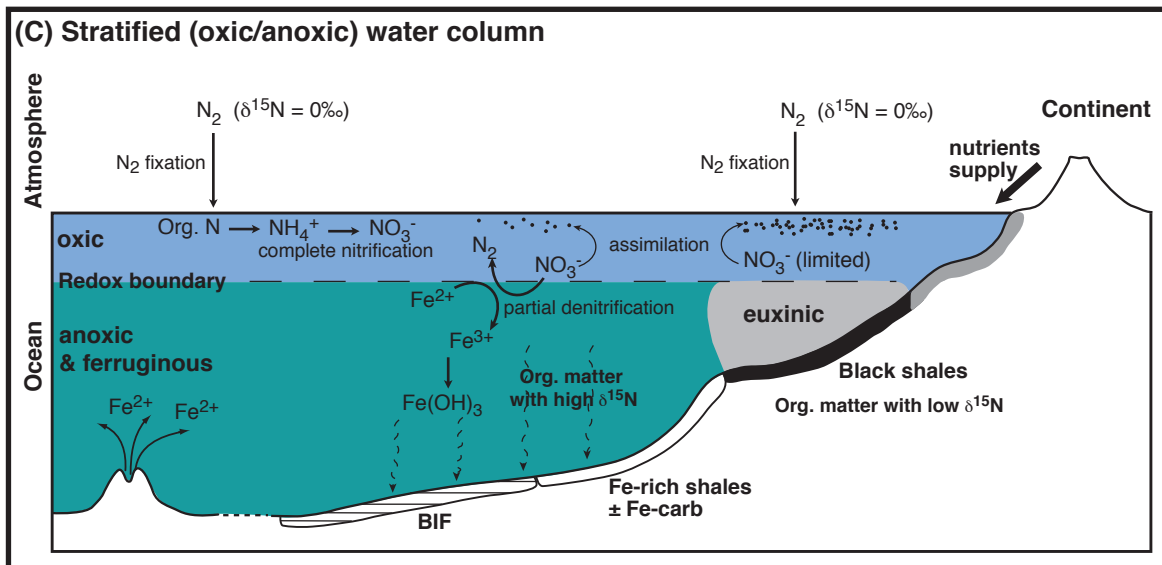
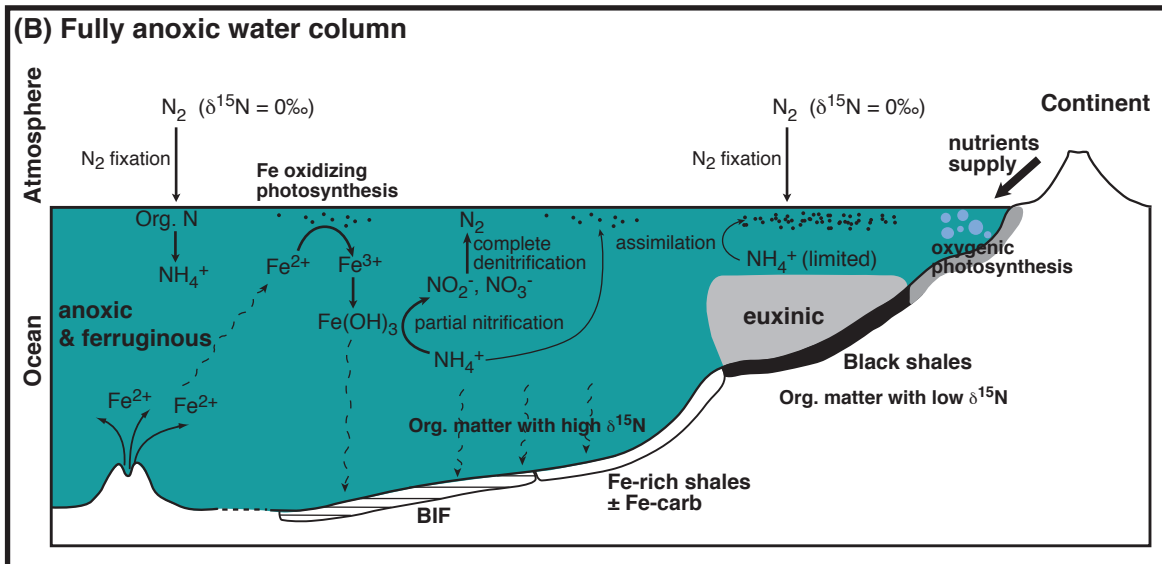
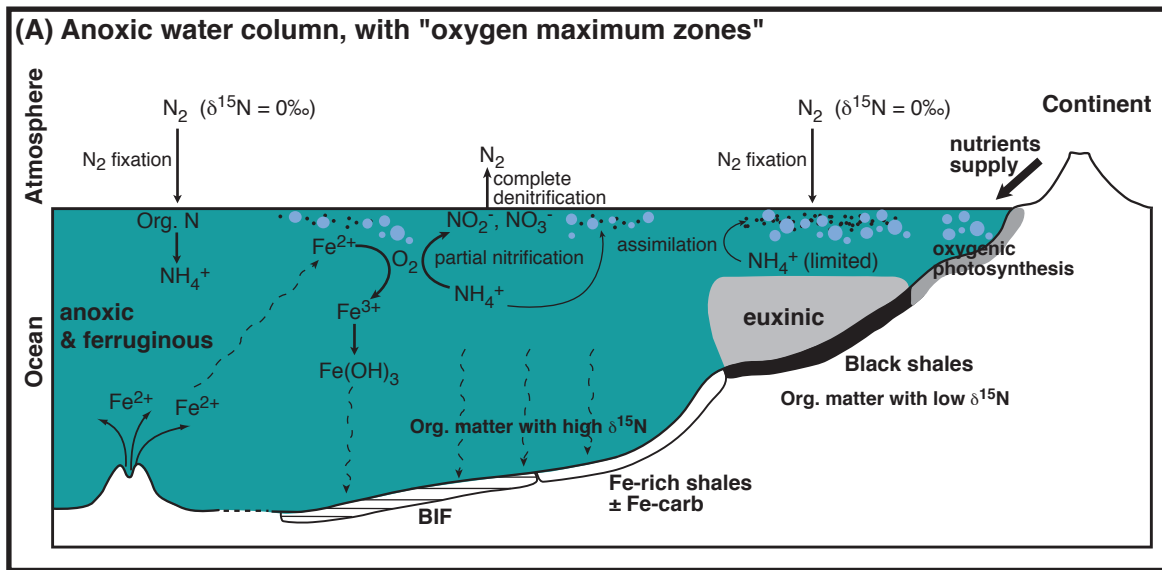


Figure 7



# Figure 8



- |  |  |
|--|--|
| <p>← Brockman Iron Formation →</p> <ul style="list-style-type: none"> <li>- low nutrients</li> <li>- low productivity</li> <li>- high <math>\delta^{15}N</math></li> </ul> | <p>← Mount Mc Rae Shale →</p> <ul style="list-style-type: none"> <li>- high nutrients</li> <li>- high productivity</li> <li>- low <math>\delta^{15}N</math></li> </ul> |
|--|--|