Biogenic nitrogen and carbon in Fe-Mn-oxyhydroxides from an Archean chert, Marble Bar, Western Australia

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[1] To quantify and localize nitrogen (N) and carbon (C) in Archean rocks from the Marble Bar formation, Western Australia, and to gain insights on their origin and potential biogenicity, we conducted nuclear reaction analyses (NRA) and carbon and nitrogen isotope ratio measurements on various samples from the 3460-Myr-old Fe-rich Marble Bar chert. The Marble Bar chert formed during the alteration of basaltic volcanoclastic rocks with Fe- and Si-rich hydrothermal fluids, and the subsequent precipitation of magnetite, carbonates, massive silica, and, locally, sulfides. At a later stage, the magnetite, sulfides, and carbonates were replaced by Fe-Mn-oxyhydroxides. Nuclear reaction analyses indicate that most of the N and C resides within these Fe-Mn-oxyhydroxides, but a minor fraction is found in K-feldspars and Ba-mica dispersed in the silica matrix. The N and C isotopic composition of Fe-oxides suggests the presence of a unique biogenic source with $\delta^{15}N_{\text{AIR}}$ values from $+6.0 \pm 0.5\%$ to $7.3 \pm 1.1\%$ and a $\delta^{13}C_{\text{PDB}}$ value of $-19.9 \pm 0.1\%$. The C and N isotope ratios are similar to those observed in Proterozoic and Phanerozoic organic matter. Diffusion-controlled fractionation of N and C released during high combustion temperatures indicates that these two elements are firmly embedded within the iron oxides, with activation energies of $18.7 \pm 3.7$ kJ/mol for N and $13.0 \pm 3.8$ kJ/mol for C. We propose that N and C were chemisorbed on iron and were subsequently embedded in the crystals during iron oxidation and crystal growth. The Fe-isotopic composition of the Marble Bar chert ($\delta^{56}\text{Fe} = -0.38 \pm 0.02\%$) is similar to that measured in iron oxides formed by direct precipitation of iron from hydrothermal plumes in contact with...
with oxygenated waters. To explain the N and C isotopic composition of Marble Bar chert, we propose either (1) a later addition of N and C at the end of Archean when oxygen started to rise or (2) an earlier development of localized oxygenated environments, where biogeochemical cycles similar to modern ones could have developed.

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1. Introduction

[2] A significant portion of nitrogen (N) in sedimentary rocks is of biological origin, mainly occurring as ammonium (NH₄⁺) [Boyd, 2001]. Ammonium can be found as (1) exchangeable NH₄⁺ representing organic nitrogen that has been decomposed in sediments most recently or (2) fixed NH₄⁺ derived from the decomposition of organic substances during diagenesis. In the first form, NH₄⁺ is adsorbed on clay surfaces, while as fixed NH₄⁺, it is bound to the lattice of mica and feldspars minerals, replacing K⁺ ions [Honma and Ithara, 1981]. The $^{15}$N/$^{14}$N ratio (expressed as $\delta^{15}$N of the fixed NH₄⁺ is mainly constrained by the N-isotopic composition of the organic nitrogen prior to diagenesis. Thus $\delta^{15}$N of lattice-bound, or diagenetic, NH₄⁺ has the potential to function as a paleoindicator [Shen et al., 2006].

[1] Compared to other bioindicative elements such as (organic) carbon or sulfur, nitrogen is characterized by its non-reactive chemical behavior and its high volatility. The first characteristic, largely owing to the exceeding stability of N₂ molecules, which strictly limits inorganic transmission of N from the atmosphere to the biosphere via *atmospheric N fixation*, may lead to construction of a simpler biological flux model of N from the atmosphere to the sediment [Shen et al., 2006]. The latter suggests that N isotopic information in old sedimentary rocks can be biased by various post-sedimentary geological events [Boyd and Philippot, 1998; Dauphas and Marty, 2004]. A correct interpretation of the Precambrian nitrogen $^{15}$N/$^{14}$N isotopic ratio in terms of biogenesis requires (1) detection of the mineral or organic sites where N resides; (2) assessment of the speciation of N; and (3) knowledge of the post-depositional events potentially affecting N-hosting minerals.

[4] Recent studies on Precambrian sediments [Boyd and Philippot, 1998; Beaumont and Robert, 1999; Pinti et al., 2001; Jia and Kerrich, 2004; van Zuilen et al., 2005; Papineau et al., 2005; Ueno et al., 2004; Nishizawa et al., 2005; Shen et al., 2006] showed the high potential of N as a biomarker. Yet, they also showed its limitations which are mainly due to our poor understanding of the origin of N in sediments and of the geochemical behavior of nitrogen during early diagenesis [Freudenthal et al., 2001; Lehmann et al., 2002] weathering [Busigny et al., 2005] and metamorphism [Busigny et al., 2003].

[5] Most studies of the Precambrian nitrogen cycle have been focused on cherts. The Precambrian cherts have often been considered as chemical precipitates from a warm and silica-saturated Archean ocean [Siever, 1992]. However, an increasing number of studies have provided evidence that the cherts are, in fact, “replacement cherts,” that is, sediments (often volcanoclastic) that have been post-depositionally silicified by pervasive hydrothermal or diagenetic fluids [de Wit et al., 1982; Paris et al., 1985; Sugitani, 1992; Kato and Nakamura, 2003; Hofmann, 2005; Orberger et al., 2006c; see also Perry and Lefiicariu, 2003]. Post-depositional alteration [Rouchon et al., 2004], and metamorphism [Boyd and Philippot, 1998] of these cherts can also alter their primary
biogenic N (and C) isotopic signature [Dauphas and Marty, 2004; Pinti et al., 2001].

[6] Ammonium in mica is not the only form of N in ancient rocks [Honma, 1996; Rouchon et al., 2005; Papineau et al., 2005; Boyd and Philippot, 1998]. Sano and Pillinger [1997] found ammonium or ammonia in fluid inclusions and suggested the occurrence of N₂ in fluid inclusions and de Ronde et al. [1997] found ammonium or ammonia in hydrothermal fluid inclusions in Archean ironstones of South Africa. Pinti et al. [2001] and, more recently, Nishizawa et al. [2005] have shown that magnetite from banded iron formations (BIFs) contain significant amounts of N in unknown form [Shen et al., 2006; Cloquet et al., 2006]. Recent data by Orberger et al. [2005, 2006c] indicate that biogenic apatite and sulfides host significant amounts of organic C and N in Paleozoic black shales.

[7] The objective of this study is to investigate in detail the sources and fate of nitrogen and carbon in a Precambrian chert using quantitative micro- and nanometric scale in situ analyses of N and C by nuclear reaction analysis (NRA hereafter) [Gallien et al., 2004; Rouchon et al., 2005; Orberger et al., 2005] combined with stepped-combustion extraction and isotopic analysis of N by mass spectrometry [Yamamoto et al., 1998; Pinti et al., 2001]. We focus on the search of geochemical and isotopic “fingerprints,” providing signs of ancient life. The studied sample is an Eoarchean chert (A458) from the Pilbara Craton, Western Australia. It is composed of (1) a replacement chert, representing a silicified basaltic rock; (2) iron oxide bands alternating with silica bands with astromatolitic texture; and (3) a pure chert precipitate.

2. The 3.5 Ga Chert A458 From Marble Bar–Towers Formation

[8] The Marble Bar chert sample A458 (Australiasian Map Grid 50, 782100mE, 7654600mN; Geographical 21°11’17.3760” lat, 119°43’1.2397” long) belongs to the A-section of the Towers Formation (Figure 1a), a 45 m-thick sequence of ferruginous cherts directly overlying Fe-rich, K-poor, MOR-like tholeiitic basalts in Marble Bar, Western Australia (Figure 1b) [Kato and Nakamura, 2003]. The estimated depositional age of the Marble Bar Chert Unit is between 3474 and 3433 Ma [Thorpe et al., 1992]. These cherts have been interpreted as precipitates from a high-temperature Fe- and Si-rich hydrothermal solution emanating from a Mid Ocean Ridge [Kato and Nakamura, 2003].

[9] Orberger et al. [2006b] provide a detailed mineralogical and geochemical description of the sample. In brief, the sample A458 is a composite chert consisting of a dark gray part (zone I), a microbanded iron layer a few millimeters thick (zone II), and a light gray part (zone III, Figure 2a). Prior to silification, the precursor rock of zone I had a porphyritic or porphyroclastic texture, typical of volcaniclastic rocks. Precursor minerals were most likely pyroxenes, amphiboles and feldspars, suggesting a basaltic protolith (Figure 2c) [Orberger et al., 2006b]. The presence of euhehdral Fe-sulfides point to a reducing environment during silicification (Figure 2c). Zone II is composed of alternating, millimeter-size iron-manganese oxyhydroxide (named FeMnOH hereafter) and quartz bands with a stromatolitic texture (Figure 2b). The iron bands are formed of skeletal goethite aggregates and euhehdral rhombic-shaped phenocrysts of FeMnOH. The phenocrysts have an inner euhehdral core with a vermicular texture and a heterogeneous composition reflected by bright and dark microbands under scanning electron microprobe (Figure 2e). A euhehdral filamentous overgrowth zone is separated from the inner crystal by K-Al silicates, possibly illite (Figure 2e). Magnetite inclusions in the silica bands intercalated with the FeMnOH bands (Figure 2d) indicate that these layers were originally composed of magnetite and Ca-Mg-carbonates.

[10] Focused Ion Beam-Transmission Electron Microscope (FIB-TEM) investigations at the GFZ-Potsdam showed that each microband of FeMnOH is composed of nanometric filaments, each of them consisting of euhehdral hematite crystals with an average size of 100 nm [Orberger et al., 2006a, 2006b]. The vermicular microscopic textures and filamentous, clustered nanotextures of the hematite can possibly be related to microbial activity. Similar nanotextures were observed in ferrihydrite formed by the activity of Fe-oxidizing bacteria growing in near-neutral pH groundwater [Banfield and Zhang, 2001]. Electron microprobe analyses showed that the FeMnOH phenocrysts contain traces of Ca and Mg, which were left from precursor carbonates. Zone III represents a chert precipitate composed of microcrystalline quartz, intergrown with micro- metric K-Al-silicates (Figure 2d), and, occasionally, barite, Ba-rich mica and/or Fe-sulfides. The latter have a texture similar to the FeMnOH
bands. The chert is cut by millimeter-scale quartz veins, also containing FeMnOH, with textures similar to those observed in the main FeMnOH bands (Figures 2a and 2b).

Orberger et al. [2006b] proposed a model of the chert formation, in which the Fe-microbands were initially composed of magnetite, Ca-Mg-carbonates and sulfides, precipitated from a reducing, hot ($\sim$215$^\circ$C), hydrothermal fluid. Subsequently, oxidizing fluids infiltrated the chert along selective permeable zones such as the magnetite-carbonate layer (zone II) and the crosscutting quartz veins (zone III). During this episode, magnetite was oxidized to FeMnOH and carbonates were dissolved, and, replaced by FeMnOH.

3. Analytical Techniques

3.1. NRA Analytical Procedure for N and C Determinations

The CEA-CNRS Pierre Süe Laboratory nuclear microprobe [Khodja et al., 2001] was used to achieve in situ N and C determination in chert A458. The analysis chamber allows performing simultaneously measurements of the light element abundances ($^{12}$C, $^{14}$N, $^{16}$O, $^{28}$Si, $^{27}$Al and $^{32}$S) by Nuclear Reaction Analysis, as well as the determination of heavier element abundances such as Ni, Fe, Zn, Ca and K by X-ray [Mosbah et al., 1993; Gallien et al., 2004]. A 1.9 MeV deuteron ($^{2}$H$^+$) incident beam was used to achieve the maximum sensitivity for nitrogen detection. The deuteron beam was focused to $3 \times 3$ $\mu$m$^2$ whose intensity is close to 0.8 nA. Nuclear reaction light product were detected using a 130 mSr, 1500 m$^2$ depletion depth annular silicon surface barrier detector located at 170$^\circ$. X-rays were measured using a 95 $\mu$m, collimated high-purity germanium detector with a 50 $\mu$m Mylar filter to stop most charged particles. Backscattered particles are stopped in the Mylar screen, but higher energy charged particles derived from nuclear reactions can pass. These analytical conditions led to a counting rate of few hundred particles per seconds, depending on the mineral composition.
A subsample \((4 \times 2.5 \times 0.5 \text{ cm}^3)\) was cut (Figure 2a), polished with aluminum oxide powder, cleaned in an ultrasonic bath and coated with gold, to avoid contamination. Signals only from 1 to \(\sim 9 \mu\text{m}\) depth were used for N and C quantification. The first micron was discarded to avoid surface contamination. Point analyses were performed on K-Al silicates, sulfides and quartz, while scanning mode was used for highly heterogeneous FeMnOH in order to select the most suitable (in terms of size and thickness) area for N and C determination. The MPAWIN data acquisition software was run in the “listcard-coincident” mode and the generated data files were processed with the homemade RISMIN.
special care is taken to extract data (X-ray and NRA spectra) corresponding to a homogeneous phase, to correct for matrix effects. When performing NRA analyses on minerals, the spectrum is the sum of several \((d, p)\) or \((d, a)\) nuclear reactions (fundamental and excited states) for all “light” elements \((Z < 17, \text{isotopes included}).\) With respect to our analytical conditions (beam energy, detection angle), the lack of NRA cross-section data for the contributing isotopes the following standards must be used for quantification: \(\text{Al}_2\text{O}_3, \text{SiO}_2, \text{Mg, FeS}_2, \text{UO}_2, \text{CaPO}_4\text{(OH)}_6, \text{TiN}\) and \(\text{CaCO}_3\). The overall spectrum is fitted and backgrounds are determined especially for C measurements. The numbers of counts extracted from a defined region of NRA spectrum (related to a specific nuclear reaction) is linearly correlated to the concentration of the element analyzed and the accumulated charge. Quantification can be achieved by taking into account the matrix effect, in both the standard and the sample. The “matrix effect” in ion beam analyses (in this case NRA) is caused by the slowing-down of the particles through the matter [Khodja et al., 2001]. This effect can be quantified if the composition of the standard and of the sample is well known, which is the case [Orberger et al., 2006b].

Analyses were done on larger scanned areas of approximately \(100 \times 100 \mu\text{m}^2\) but generally 10% to 70% of the spectral data is retained, corresponding to homogeneous mineral phases. The totality of the analyzed spectrum is retained for the smaller scans of \(20 \times 20 \mu\text{m}^2\) and \(5 \times 5 \mu\text{m}^2\) spots (Table 1). During a few hours measurement, beam current fluctuation effects on scanned areas are minimized using a high scanning rate (1 kHz). Quantitative N microanalysis requires high a microbeam current (800 pA, \(5 \times 5 \mu\text{m}^2\)) to reach \(20 \mu\text{C}-\text{accumulated charge in a realistic time (7 hours). The detection limit of N and C by NRA is about 100 ppm.}

### 3.2. Mass Spectrometric Techniques for Nitrogen Isotope Determinations

Following NRA measurements, N and Ar isotopic abundances, and C and H\(_2\text{O}\) elemental abundances in mineral phases containing N and C (mainly FeMnOH; see Results), were measured at the Department of Earth and Space Sciences of Osaka University. An iron-rich portion of A458 was crushed to about 1-10 \(\mu\text{m}-\text{size grains and iron-bearing particles separated by a heavy liquid (}\rho = 2.66 \text{g/cm}^3\text{), sodium polytungstate (SPT). The red-colored portion with density higher than 2.66 g/cm}^3\) was used in this study hereafter (referred to as A458.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Mineral Phases</th>
<th>C, at. %</th>
<th>N, at. %</th>
<th>C, eq. ppm</th>
<th>N, eq. ppm</th>
<th>C/N, atomic</th>
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<tbody>
<tr>
<td>PB4581f max Fe-Mn oxide bands</td>
<td>1.59</td>
<td>0.51</td>
<td>6049</td>
<td>2241</td>
<td>3.1</td>
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<td>PB4581f min</td>
<td>0.80</td>
<td>0.11</td>
<td>3010</td>
<td>497</td>
<td>7.0</td>
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<tr>
<td>PB4581l max Fe-Mn oxide bands</td>
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<td>0.35</td>
<td>7550</td>
<td>1549</td>
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<tr>
<td>PB4581l min</td>
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<td>3437</td>
<td>206</td>
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<td>PB4581m max Fe-Mn oxide bands</td>
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<td>0.24</td>
<td>4306</td>
<td>1065</td>
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<td>PB4581m min</td>
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<td>0.08</td>
<td>3439</td>
<td>355</td>
<td>11.3</td>
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<td>0.12</td>
<td>5108</td>
<td>525</td>
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<td>PB4581g min</td>
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<td>0.45</td>
<td>3983</td>
<td>1973</td>
<td>2.3</td>
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Micro-scans (20 \(\times\) 20 \(\mu\text{m}^2\))

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<th>Sample Number</th>
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<th>C, at. %</th>
<th>N, at. %</th>
<th>C, eq. ppm</th>
<th>N, eq. ppm</th>
<th>C/N, atomic</th>
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<tr>
<td>PB4581gB max microscan of PB458g</td>
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<td>0.22</td>
<td>4786</td>
<td>985</td>
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<tr>
<td>PB4581gB min</td>
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<td>0.11</td>
<td>2833</td>
<td>492</td>
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<tr>
<td>S8-458-Fe Fe oxide</td>
<td>4.00</td>
<td>0.08</td>
<td>15436</td>
<td>333</td>
<td>52.8</td>
<td></td>
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<tr>
<td>S8-458-Qz Quartz around Fe oxide</td>
<td>1.03</td>
<td>0.01</td>
<td>6203</td>
<td>79</td>
<td>91.2</td>
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Spots (5 \(\times\) 5 \(\mu\text{m}^2\))

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<th>Mineral Phases</th>
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<th>N, at. %</th>
<th>C, eq. ppm</th>
<th>N, eq. ppm</th>
<th>C/N, atomic</th>
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<td>PB458803 Fe oxide</td>
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<td>113</td>
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<td>PB4581103 Fe oxide</td>
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<td>PB458503 K-Al-silicates</td>
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<td>4189</td>
<td>1778</td>
<td>2.7</td>
<td></td>
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*The C and N values for Fe-Mn-oxides have been calculated using a Fe\(_2\text{O}_3\) matrix [Gallien et al., 2004]. Calculations based on a FeO(OH) basis increase the C, N amounts of 10%. Maximum and minimum values in scans give the variation of concentration with the penetration depth. Nitrogen in sulfides of porphyric zone I, cryptocrystalline quartz of zone III, near quartz veins and in quartz from vein filling of zone IV are lower than detection limits. Carbon amount in quartz has been estimated to be 0.04 at%.
iron-rich separate). The iron-rich separate was washed with 60°C ultrapure water for two days in order to totally dissolve the residual SPT on the grain surfaces. The washing procedure is critical to obtain reliable data, since SPT contains significant amounts of nitrogen enriched in $^{15}$N ($\delta^{15}$N $\geq$ 20%). Complete removal of the SPT by the current washing procedure was verified by measuring N of an industrially produced silica powder essentially free of nitrogen, which was treated by the SPT following exactly the same procedures with the samples. Prior to the N isotope analyses, the separated powder was loaded directly (without polishing and electro-conductive coating) on a low-vacuum type SEM-EDX (JSM-5510LV + JED-2300, JEOL). Major elements were determined by scanning a broad area ($\sim$1 mm$^2$). Major element oxide abundances are: Fe$_2$O$_3$ (54 wt.%); SiO$_2$ (43 wt.%); MnO (1.5 wt.%); MgO (0.8 wt.%); Al$_2$O$_3$ (0.4 wt.%); CaO (0.07 wt.%); K$_2$O (0.05 wt.%). Finally, after repeated washing with acetone and ethanol, a 5.86 mg aliquot of the dried sample wrapped in an annealed platinum foil was loaded into the mass spectrometry system.

The mass spectrometry system includes a quadrupole mass spectrometer (QMG-420, Balzers$^8$) with an inlet system consisting of an all-metal vacuum line to extract nitrogen from the sample, loaded in a double-walled quartz glass tube, by step combustion. Yamamoto et al. [1998] and Pinti et al. [2001] described in detail the analytical infrastructure; thus only recent improvements of the system are described below. Condensable impurities (e.g., hydrocarbons, H$_2$O and CO$_2$) were removed from the sample gas using a liquid nitrogen trap, consisting in a capillary tube made of Pyrex glass. Tests using 40 picomoles (about 10$^{-6}$ Torr) of atmospheric standard air N$_2$ showed that several% of the N$_2$ was adsorbed onto the Pyrex tube’s wall. Isotopic ratios of the standard air N$_2$ correlated well with degree of adsorption, suggesting isotopic fractionation during adsorption, with $^{15}$N enrichment in the adsorbed fraction. Interestingly, the degree of N$_2$ adsorption was dependent on the thickness of the glass tube, possibly through its minute effect on the temperature gradient between the inner and outer surface of the tube. Adsorption of N$_2$ has been avoided by using a new double-walled tube, where dry N$_2$ gas of an atmospheric pressure was encapsulated between the inner and outer tubes, a slight modification of the earlier method that significantly improved the quality of our N isotopic measurements.

The reproducibility of nitrogen isotopic measurements, estimated through the repeated (n = 42) analysis of the standard gas over the period of a month, is 0.9‰ (1σ), which now seems to be limited by uncertainties in the reduction of hydrocarbons (C$_2$H$_6$) and subsequent isobaric interferences at m/z ratios of 28 and 29 [Hashizume and Sugitara, 1990]. The reproducibility for $^{40}$Ar/$^{36}$Ar ratios measured in the same standard air was 1.0‰ (1σ). The blanks of N$_2$ and Ar, determined by performing the extraction and purification procedures without any sample, were typically 1–2 picomoles (N$_2$) and 5–20 femtomoles ($^{40}$Ar) at a combustion temperature of 1000°C. The N isotopic ratio ($^{15}$N/$^{14}$N) is expressed in the conventional delta notation, which is defined as follows: $\delta^{15}$N $\equiv$ $\{(^{15}$N/$^{14}$N)$_{\text{sample}}/^{15}$N/$^{14}$N$_{\text{air}}\} - 1$ $\times$ 1000, where ($^{15}$N/$^{14}$N)$_{\text{air}}$ = 3.653 $\times$ 10$^{-3}$.

Amounts of carbon and hydrogen, converted to CO$_2$ and H$_2$O, were quantified by a pressure gauge (crystal gauge M-320XG, ANELVA), followed by examination of the gas species by a gas chromatography mass spectrometer (GC/MS: quadrupole mass spectrometer, SUN200, FAM, attached with a GC, 6890, Agilent) connected to the gas extraction line. The detection limit of the CO$_2$ and H$_2$O pressures by the crystal gauge is 0.1 Pa, which, in our analytical setup, corresponds to 8 ppm of C and 1.3 ppm of H.

### 3.3. Mass Spectrometric Analyses of Carbon Isotopes

A total of 100 mg of rock was reduced to 10–20 μm grain-sized powders with an agate mortar and loaded in a quartz tube with copper oxide. The quartz tube was then sealed under vacuum and the sample combusted at 850°C for 30 min. The produced gas phase was then analyzed for the $^{13}$C/$^{12}$C ratio using a stable isotope mass spectrometer SIRA 19 of GV Instruments at the Université Paris SUD. Analogous to N, the C-isotope ratios are reported as ‰ deviation relative to the Pee Dee Belemnite (PDB) international standard. Total uncertainties on the measurement are of ±0.1‰.

### 3.4. MC-ICP-MS Techniques for Fe Isotopes Determinations

The Fe isotopic composition of the microband iron layers of chert A458 was determined with the goal to understand the origin of these precipitates and its relation with incorporated N and C. All the digestion procedure was done in a class 1000 clean laboratory at GEOTOP, using sub-
boiled acids and Teflon beakers. After a bulk digestion in a mixture of 3 mL concentrated HNO$_3$ – 1 mL concentrated HF overnight on a hot plate, the sample was evaporated to dryness and then dissolved in a 3 mL concentrated HNO$_3$-0.2 mL concentrated HClO$_4$ mixture and warmed during 24h on a hot plate. After evaporation, the sample is diluted in a 3 mL of concentrated HCl – 0.2 mL of concentrated HClO$_4$, warmed again during 24h and evaporated to dryness. Iron was isolated from the matrix using AGMP-1 anion exchange resin in HCl media, following the procedure described by Dauphas et al. [2004].

Iron isotopes were measured using the Multi-collector-ICP-MS Micromass$^\text{\tiny I}$ Isoprobe at the GEOTOP-UQAM-McGill Research Center. Mass bias corrections were performed using the standard-sample-standard (bracketing) technique with the IRMM014 international isotopic standard as reference. The long-term reproducibility obtained with this technique is on the order of 0.05‰ per atomic mass unit (2σ) and the blank (<50 ng/g) was always negligible compared to the total amount of Fe in the sample. Precision and accuracy were verified by repeat analyses of three reference materials: basalt (BCR 1), granite (AC-E) and BIF from Isua (IF-G). The Fe isotopic composition is expressed in the conventional delta notation ($\delta^{56}\text{Fe} \equiv \left\{\left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{sample}} / \left(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\right)_{\text{IRMM014}} - 1\right\} \times 1000$), where the ($^{56}\text{Fe}/^{54}\text{Fe}$)$_{\text{IRMM014}}$ is equal to 15.69858. The $\delta^{56}\text{Fe}$ values measured for the reference materials were $+0.63 \pm 0.09$‰ (2σ, N = 3) for IF-G; $+0.33 \pm 0.20$‰ (2σ, N = 2) for AC-E; and $+0.14 \pm 0.05$‰ (2σ, N = 2) for BCR 1, respectively. Those values are very similar to those previously published [Beard et al., 2003; Butler et al., 2005; Dauphas and Rouxel, 2006; Poitrasson et al., 2004; Rouxel et al., 2005].

4. Results

To detect the nitrogen- and carbon-hosting mineral phases, NRA was performed on the following:
Figure 4. N versus C concentration measured both by NRA (expressed as ppm equivalent) and by mass spectrometry (QMS; expressed as ppm of FeMnOH). Data from NRA measurements for analyses S8-458-Fe are not reported here because of the anomalously large amount of C. While the NRA data do not show a relation between N and C, this relation is significant using QMS data (see text for details about the 300 and 600 °C combustion steps).
Table 2. C, N, and Ar Elemental and Isotopic Analyses by QMS of FeMnOH in Chert A458a

<table>
<thead>
<tr>
<th>Temp. Comb., °C</th>
<th>H2O, ppm</th>
<th>C, ppm</th>
<th>N, ppm</th>
<th>C/N atomic</th>
<th>δ15N, %</th>
<th>±</th>
<th>40Ar*, ±10^-8 ccSTP/g</th>
<th>±</th>
<th>40Ar/36Ar ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>867</td>
<td>133</td>
<td>0.92</td>
<td>169</td>
<td>10.5</td>
<td>1.6</td>
<td>1.1</td>
<td>2.6</td>
<td>318/49</td>
</tr>
<tr>
<td>400</td>
<td>1524</td>
<td>485</td>
<td>6.01</td>
<td>94</td>
<td>7.1</td>
<td>1.1</td>
<td>12.8</td>
<td>5.5</td>
<td>494/84</td>
</tr>
<tr>
<td>500</td>
<td>164</td>
<td>180</td>
<td>3.49</td>
<td>60</td>
<td>9.7</td>
<td>1.13</td>
<td>18.2</td>
<td>6.2</td>
<td>693/134</td>
</tr>
<tr>
<td>600</td>
<td>152</td>
<td>164</td>
<td>5.28</td>
<td>36</td>
<td>7.3</td>
<td>0.9</td>
<td>74.1</td>
<td>16.9</td>
<td>1058/173</td>
</tr>
<tr>
<td>700</td>
<td>21</td>
<td>125</td>
<td>2.40</td>
<td>61</td>
<td>3.1</td>
<td>0.8</td>
<td>165.3</td>
<td>30.1</td>
<td>3705/622</td>
</tr>
<tr>
<td>800</td>
<td>b.l.</td>
<td>94</td>
<td>1.80</td>
<td>61</td>
<td>4.4</td>
<td>1.0</td>
<td>86.1</td>
<td>12.8</td>
<td>2153/277</td>
</tr>
<tr>
<td>900</td>
<td>b.l.</td>
<td>41</td>
<td>1.15</td>
<td>42</td>
<td>10.1</td>
<td>1.1</td>
<td>21.1</td>
<td>4.6</td>
<td>1344/246</td>
</tr>
<tr>
<td>1000</td>
<td>b.l.</td>
<td>16</td>
<td>0.74</td>
<td>25</td>
<td>10.2</td>
<td>1.1</td>
<td>17.1</td>
<td>3.3</td>
<td>825/161</td>
</tr>
<tr>
<td>1100</td>
<td>b.l.</td>
<td>b.l.</td>
<td>0.16</td>
<td>-</td>
<td>13.0</td>
<td>1.8</td>
<td>3.5</td>
<td>1.6</td>
<td>353/31</td>
</tr>
<tr>
<td>1200</td>
<td>b.l.</td>
<td>b.l.</td>
<td>0.08</td>
<td>-</td>
<td>20.3</td>
<td>7.4</td>
<td>5.5</td>
<td>2.5</td>
<td>339/34</td>
</tr>
<tr>
<td>1200</td>
<td>b.l.</td>
<td>b.l.</td>
<td>0.01</td>
<td>-</td>
<td>b.l.</td>
<td>0.1</td>
<td>1.8</td>
<td>303/84</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2729</td>
<td>1237</td>
<td>22.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>404.9</td>
<td></td>
</tr>
</tbody>
</table>

aFeMnOH separates weight is 5.86 mg. b.l., blank level.

[24] 1. FeMnOH from the iron bands (Figures 2a and 2b) of zone II and in the crosscutting veins.

[25] 2. Quartz veins and microcrystalline quartz of zone III; quartz filling of zone IV.

[26] 3. Dispersed K-Al-silicates (likely K-feldspars or mica) from the microcrystalline quartz matrix of zone III (Figure 2c).

[27] 4. Fe-sulfides from the chert precipitate (zone III).

[28] N and C were predominantly found in FeMnOH (zone II) and in K-Al-silicates. Microcrystalline quartz does not contain detectable amounts of N. However, the C content in quartz could be estimated to be 0.04 at%, between 2 and 12% of the C content in iron oxides (Table 1). A total of four 100 × 100 μm² NRA scans, three 20 × 20 μm² microscans and five 5 × 5 μm² spots showed detectable amounts of C and N (Table 1, reported as atom (at)% and equivalent ppm).

[29] The amount of N and C measured in FeMnOH ranged between 0.025 to 0.51 at% and between 0.30 to 1.59 at%, respectively (Table 1), but one scan on quartz (sample S8-458-Qz) shows anomalously high carbon concentration of 4.0 at% (1.5 wt% equivalent; Table 1). It is noteworthy that the bulk NRA-based N and C concentrations determined by large-scan analyses are significantly higher than those resulting from small-scan or spot measurements. In particular, nitrogen shows a substantial decrease in concentration from an average of 0.24 at% in larger scans of 100 × 100 μm² to 0.11 at% in 20 × 20 μm² scans to solely 0.03 at% in 5 × 5 μm² spots. Carbon decreases only from 1.2 at% in 100 × 100 μm² scans to 0.58 at% in 5 × 5 μm² spots (Table 1).

[30] The C/N atomic ratio varies by more than one order of magnitude from 2.3 to 91 (Table 1), with the S8-458 sample having the highest C/N ratio. The two K-rich silicates contain twice as much C and N as the iron oxides but with constant C/N atomic ratios of 2.7 to 2.8 (Table 1). Variations in the C/N ratios are largely due to variations in N contents (Figure 3), and no clear correlation exists between the amounts of C and N measured by NRA (Figure 4a). However, a significant co-variation exists between the concentrations of C and N from FeMnOH as measured by mass spectrometry (Table 2; Figure 4b; except for the step at 300 and 600°C). The C and particularly the N concentrations measured by mass spectrometry, however, differ significantly from those measured by NRA. The total amount of C extracted from FeMnOH is 1237 ppm (0.33 at% equivalent), and it is thus only half of that measured by NRA. Mass spectrometrically determined N amounts of 22 ppm (0.005 at% equivalent) (Table 2) are more than one order of magnitude lower than estimates for the same sample based on NRA (Table 1). This discrepancy will be discussed later.

[31] In Figure 5, we reported concentrations of C, H2O, N and radiogenic 40Ar*, as well as the δ15N values from FeMnOH as measured by mass spectrometry. Nitrogen is released at 400°C, together with C and H2O and again at 600°C (Figure 5). The 40Ar* is released mostly at 700°C. δ15N values were observed at the 400°C and 600°C step not significantly different, with +7.1 ± 1.1‰ and +7.3 ± 0.9‰ respectively. At temperatures higher than 600°C, N release from the sample constantly declines, concomitant with an increase in the δ15N values from +3.1‰ at 700°C to +20‰ at 1200°C. The combustion pattern of N for the chert
A458, between 700°C and 1200°C, is characteristic of a diffusion-controlled fractionation [Boyd et al., 1993]. When N₂ is released from the sample reservoir, the degree of ¹⁵N-enrichment is proportional to the log of the fraction f of N₂ remaining in the reservoir. The fraction f can be calculated from the total amount of N released during incremental combustion. Figure 6 depicts the change in δ¹⁵N as a function of the log(f). The δ¹⁵N value correlates well with the yield of N (Figure 6) and the reaction/diffusion rate ratio, k(15)/k(14), for the respective species (molecules or atoms), or fractionation factor can be estimated from: δ¹⁵N ≈ 1000 × [k(15)/k(14) − 1] × ln(N/N_initial). The slope of the trend in the data yield apparent estimates of k(15)/k(14) of 0.997, indicating a slightly faster release of ¹⁴N (3%). The N released between 700°C and 1200°C, had an average δ¹⁵N value of +6.0 ± 0.5‰, slightly lower than the δ¹⁵N value of N released at 400°C (+7.1 ± 1.1‰) and at 600°C (+7.3 ± 0.9‰).

Figure 5. Combustion release pattern for elemental C, H₂O, N, and ⁴⁰Ar* concentrations reported together with the nitrogen isotopic composition (expressed with the δ¹⁵N notation) for the FeMnOH separates.
However, given the relatively large errors, the difference cannot be considered significant. The bulk $^{13}$C value measured in the FeMnOH is $-19.9 \pm 0.1\%$.

[32] The $^{40}$Ar* and N are not correlated suggesting that radiogenic $^{40}$Ar* trapping sites differ from those of N. Finally, Figure 7 shows the Arrhenius plots (the log of the element’s amount extracted at each combustion temperature versus the inverse of the extraction temperature) for N and C. Except for the data corresponding to the N released at 1000°C, all data points follow a linear trend, and the slope of the correlation line yield estimates on the activation energy ($E_a$) of the rate-determining process. For nitrogen, $E_a$ is equal to $18.7 \pm 3.7$ kJ/mol, which does not differ significantly from the $E_a$ calculated for carbon ($13.0 \pm 3.8$ kJ/mol).

5. Discussion

5.1. Localization of N and C at the Mineral Scale

[33] The large discrepancies with regards to N and C content determined by NRA versus mass spectrometry can most likely be explained in terms of the various intra and inter-crystalline N reservoirs being differently targeted by the two methods. In minerals, volatile elements can (1) be dissolved within grains; (2) be adsorbed on grain boundaries or cleavages; or (3) occur as a separate phase in host minerals, in dislocations or inclusions [Robert and Halbout, 1990]. The N and C extracted and analyzed by mass spectrometry are likely bound or dissolved within the crystal structure of the FeMnOH and originate most likely from a common source (see next paragraph). However, the N and C measured by NRA represent a mix between two components. This is clearly illustrated in Figure 3, where the bulk N (calculated as at% equiv.) and the C/N ratio determined by mass spectrometry is plotted together with NRA data. The first end-member component is likely the one bound to, or dissolved in, the FeMnOH. The second end-member is N-rich and its addition has the effect to decrease both the 1/N and the C/N ratio (Figure 3). From the mixing line in Figure 3, the C/N ratio of the N-rich end-member is suggested to be about 6, which is consistent with addition of modern organic contamination (C/N values from 3 to 30) adsorbed
on grain surfaces or due to microscopic distinct phases dispersed within these grains. At first sight, an adsorbed component does not seem plausible, given that during NRA, the first micron-size layer is discarded to avoid measuring recent organic contamination. However, combustion experiments in Archean cherts showed that this component deeply permeates the samples and is totally removed only at 400–450°C [Pinti et al., 2001, 2003]. The adsorbed N component accounts for the 18 to 32% of the total N released amount in iron separates [Pinti et al., 2001]. In some case up to 72% of the total released N in Archean metasediments derives from this recent adsorbed component (D. L. Pinti et al., manuscript in preparation, 2007). Thus, while the adsorbed component would not be detected by mass spectrometry (1) because a strict mineral separation was done before analyses and (2) because of overnight pre-combustion of the sample at low temperature that eliminates mostly any adsorbed component, NRA-based N and C determination would include the contribution from contaminant N and C adsorbed below 1μm underneath the surface layer. The fact that two different sources of N and C are targeted by the NRA analyses can explain the inconsistent relation between N and C (Figure 4a). The relation between N and C is rather good during the stepwise combustion because these two species are extracted from a single source (Figure 4b).

5.2. C and N Origin in Iron Layers

The diffusive release of N and C only at relatively high combustion temperatures (Figures 5 and 6) indicates that these elements are firmly embedded in the Fe-oxides, and shielded from the oxygen, which can act to facilitate the release of volatile species. This suggests that N and C were incorporated during the FeMnOH formation, potentially yielding environmental information.

The relatively constant C/N ratio measured by stepwise combustion (Figure 4b) suggests a common organic source of these elements. In Figure 4b, the 300°C and 600°C step data have different C/N ratios. At 300°C, released gases may be contaminated by superficial components, relatively rich in C (as observed by Pinti et al. [2001] in other samples), while at 600°C, C/N ratios are probably affected by a second, more N-enriched, organic phase, that admixed to the primary N and C-rich organic phase. It is possible that this second source of organic N is enclosed in quartz, as has been observed in some other cherts [Pinti et al., 2001]. At the temperature of phase transition between α-quartz and β-quartz (573°C), this quartz-bound organic phase would instantaneously be released [Sano and Pillinger, 1990].

The measured C/N ratios, the δ¹⁵N and δ¹³C values, all point out to an organic source for N and C. The C/N ratios measured by mass spectrometry range from 53 (integrated value of C/N 700 – 1200°C) to 94 (at 400°C step), within the values measured in Archean and Proterozoic kerogens (Figure 8). The corresponding δ¹⁵N values (δ¹⁵N 700 – 1200°C = +6.0 ± 0.5%; δ¹⁵N 400°C = +7.1 ± 1.1%) are at the high end for the Eo-Paleoarchean (Figure 9). Beaumont and Robert [1999] showed that ¹⁵N-depleted organic matter dominates this period with δ¹⁵N values between −6‰ to around 0‰. Compilation of all published data since then by Shen et al. [2006]
showed that two distinct populations characterize Eo-Paleoarchean with $\delta^{15}N$ values centered at $3.6\%$ and $+4.3\%$, respectively. The measured $\delta^{15}N$ values in chert A458 are, however, more common during Neoarchean (3.2 to 2.5 Ga; $\delta^{15}N_{mean} = +10.8\%$ [Shen et al., 2006]), Proterozoic (2.5 to 0.6 Ga; $\delta^{15}N_{mean} = +5.6\%$; Shen et al., 2006) (Figure 9) or modern times ($\delta^{15}N = +8.0 \pm 2.7\%$ [Shen et al., 2006]).

The $\delta^{13}C$ value measured in the iron bands of chert A458 suggests also an organic origin. Organic matter in modern marine sediments shows a $\delta^{13}C$ value around $20\%$ [Peters et al., 1978], compatible with the value found in chert A458, while Archean kerogens show $\delta^{13}C$ values centered on $-30\%$ [Beaumont and Robert, 1999]. Several authors [e.g., Lindsay et al., 2005; van Zuilen et al., 2003] have claimed that abiotic processes could produce C with an isotopic signature close to values typical for biologically produced carbon. For example, high-molecular weight organics and kerogen could be abiotically produced by Fischer-Tropsch type reactions during hydrothermal serpentinization of the surrounding basalts. However, recent experiments carried out by McCollom and Seewald [2006] showed that the produced organics have a $\delta^{13}C$ value much lower ($-50\%$) than those observed in this study. However, if the carbonaceous matter formed biogenically during greenschist facies metamorphism ($\sim300^\circ C$), and in isotopic equilibrium with the mantle-derived CO$_2$, then the $\delta^{13}C$ value of this material could be as low as $-17\%$ [van Zuilen et al., 2006], quite close to $-19.9 \pm 0.1\%$, the value found in chert A458. However, the C/N ratios reported by van Zuilen et al. [2006] for abiotic organic compounds from 500 to 4000, would clearly be distinguishable from C/N ratios in biogenic organic matter. Furthermore, in chert A458 the C is intrinsically linked to N (Figure 4b). An abiotic production of N as ammonia through the
Haber-Bosch process is a very slow reaction and requires high temperatures (400–500°C) and pressures (from 200 bar to several MPa) [Asperger, 2003]. There is no indication for such conditions being applicable to the studied samples.

[38] The unusual vermicular internal texture of the FeMnOH (Figure 2d) and the non-stoichiometry of this phase [Orberger et al., 2006b] suggest a microbially mediated crystallization of the iron oxyhydroxides, analogous to some iron formations from modern mid-ocean hydrothermal vents [e.g., Boyd and Scott, 2001]. FIB-TEM investigations [Orberger et al., 2006a] showed that the vermicular texture of the FeMnOH is produced by nanofilaments composed of aligned hematite nanoclusters, commonly observed in biologically mediated precipitation of hematite [Orberger et al., 2006a, 2006b]. Within these filaments, carbon nodules of a few nanometers wide have been observed. Electron Energy Loss Spectroscopy (EELS) analyses showed that these C-rich nodules contain also traces of nitrogen [Orberger et al., 2006a]. Further investigations have to be carried out to explain the nature and the origin of these nodules and to confirm that these nodules are the ultimate host of the measured N and C.

[39] So, how is the N (and C) bound in iron oxides? Nitrogen can be adsorbed within the porous structure of Fe-MnOx. The activation energy for the chemisorption of N and C on iron oxides is generally between 20 and 80 kJ/mol [Burakowski and Wierzchon, 1998], which is consistent with our observations (see Results). The stepwise-heating release temperature of noble gases trapped in a diffusion-controlled isotopic fractionation indicate that part of N and C is deeply embedded in the iron oxides.

[40] K-Al-silicates from zone III show C/N ratios of 2.7–2.9, characteristic of those measured in K-AI-silicates from Archean cherts [Rouchon et al., 2005]. The N isotopic composition in these silicates was not analyzed because of the separation difficulties related to its fine intergrowth with microcrystalline quartz matrix of zone III (Figure 2c). However, Pinti et al. [2001] measured the N isotopic composition of the A458 on a selected aliquot of pure quartz, which may be representative for zone III. A nitrogen release peak at 1200°C was observed, associated with a release of radiogenic 40Ar* which could indicate the occurrence of NH4 bounded in K-feldspars [Boyd et al., 1993]. This component has a δ15N value of +12.1 ± 2.9‰, but it is still unclear whether its isotopic value has been affected by post-depositional devolatilization [Pinti et al., 2001].

5.3. Organic Nitrogen and Carbon: Pristine or Later Addition?

[41] If the N and C in the Marble Bar chert is originally derived from the degradation of organic matter, the question arises when and how they were incorporated into the chert. This study shows that both N and C are part of the mineral structure of the iron oxides, implying their incorporation at the time of the FeMnOH precipitation.

[42] The iron isotopic composition of the two microbanded iron layers (δ56Fe = −0.38 ± 0.02‰) is similar to that measured in hot (>300°C) hydrothermal fluids from mid-ocean ridges (δ56Fe = −0.5 to −0.2‰) [e.g., Sharma et al., 2001; Severmann et al., 2004]. The hydrothermal origin of the these iron oxide-rich microbands in chert A458 is also confirmed by the enrichment in Mn and most of the REE and the occurrence of pronounced Eu anomalies [Orberger et al., 2006b].

[43] These low-temperature FeMnOH deposits can form at the mid-ocean ridges through two different mechanisms: (1) the reaction of basalts in the upper oceanic crust with oxygenated deep-seawater and the subsequent low-temperature formation of secondary minerals including Fe oxyhydroxides, smectite, and celadonite [Alt, 1995] and (2) the direct precipitation of iron oxides from the hydrothermal plume when it enters oxygenated waters. Present-day examples of the first case are composed mainly of silica (quartz), and Fe-oxyhydroxides showing variable δ56Fe values between −1.6 and +0.3‰ [Rouxel et al., 2003]. These variations have been interpreted to result from the effects of Rayleigh distillation kinetics on the Fe-isotope fractionation during Fe-oxyhydroxide precipitation and/or during partial oxidation of hydrothermal
Fe\(^{2+}\). In contrast, Fe-oxyhydroxide-rich sediments precipitated directly from the hydrothermal plume (case 2 above) display \(\delta^{56}\)Fe values that are indistinguishable from the \(\delta^{56}\)Fe values found for high-temperature hydrothermal fluids (−0.5 to −0.2\%), indicating that the original isotopic composition of the vent fluid is preserved when Fe(II)\(_{aq}\) oxidation in seawater is complete [Dauphas and Rouxel, 2006].

Our \(\delta^{56}\)Fe data are consistent with both scenarios, yet we prefer on the basis of the close similarity of the \(\delta^{56}\)Fe values found from this study and those of hot hydrothermal fluids as well as other characteristics that the FeMnOH precipitated directly from a hydrothermal plume. Supporting evidence comes from the Th/U ratio of the Marble Bar chert which is close to unity. Cloquet et al. [2006] showed that BIFs produced by direct precipitation from a hydrothermal effluent have Th/U ratios ranging from 0.2 to 1.2, thus consistent with our value. Residual iron oxides derived from weathering show higher Th/U ratios (up to 10) due to the higher mobility of U rather than Th, during alteration processes [Cloquet et al., 2006]. Finally, the N isotopic composition of FeMnOH from Marble Bar chert does not match with those expected from basalt weathering. Indeed, Busigny et al. [2005] showed that Fe-oxyhydroxide facies in altered basalt from modern oceanic crust contain NH\(_3\) located in secondary minerals such as K-bearing celadonite and smectite and showing \(\delta^{15}\)N values ranging from −3.8\% to −2.7\%. The decoupling between radiogenic \(^{40}\)Ar* and N indicates clearly that K-bearing minerals are not the principal host of N in the Marble Bar chert. All these evidences support a direct precipitation of FeMnOH from a hot hydrothermal effluent at Marble Bar, rather than the product of ancient or modern basalt weathering.

The determination of the absolute age of FeMnOH formation has obviously important implications for the age of the organic matter and its biogenic traces. On the basis of earlier work of Barley [1993], the silicification of the sedimentary sequences of the Warrawoona group in Pilbara Craton by pervasive hydrothermal fluids is produced within 300 Myr from the age of their formation. Because the iron isotope composition of the FeMnOH seems to exclude the secondary origin by recent weathering, we consider that these iron oxides precipitated during the main hydrothermal pulses which produced the Marble Bar cherty units. The Marble Bar’s FeMnOH could theoretically be dated by the K-Ar method, since traces of K (0.01 to 0.09 wt% [Orberger et al., 2006b]), and radiogenically produced \(^{40}\)Ar* (Table 2) are found. However, we consider that N in FeMnOH most likely predates the formation of Ar-bearing phases because of the following: (1) The K concentration in Fe is heterogeneous. Laser ablation ICP-MS analyses on two iron microbands located in the lower part of the sample (Figure 2a) found that K in the Fe-microbands varied significantly, ranging from 63 ± 37 ppm to 1420 ± 621 ppm. (2) The absence of relationship between N and \(^{40}\)Ar* indicates the decoupling of these two elements.

This study is limited to one sample, yet the occurrence of a primitive organic N with a positive \(\delta^{15}\)N value in chert A458 has important implications on the continuing debate on the evolution of the nitrogen biogeochemical cycle and its relation with past changes of the redox state of the primitive oceans and atmosphere [Shen et al., 2006, and references therein]. As mentioned above, Eo-Paleoarchean organic matter is characterized by N with \(\delta^{15}\)N values between −7\%o to 0\%o [Beaumont and Robert, 1999; Pinti et al., 2001, 2003; Ueno et al., 2004; Papineau et al., 2005; Hashizume et al., 2006]. This nitrogen could derive from the mantle, and metabolized by chemosynthetic communities living close to hydrothermal systems, in fully agreement with the depositional environments of the N-host rocks [Pinti and Hashizume, 2001]. A \(^{15}\)N-enriched composition like in chert A458 is usually found in later periods, from Neoarchean to Proterozoic, and beyond, when the oceans were progressively oxygenated and the biological production of oceanic nitrates (NO\(_3\)) with characteristic \(\delta^{15}\)N values around +7\%o was enhanced [Peters et al., 1978].

Positive \(\delta^{15}\)N values in earlier Archean times are difficult to explain. One explanation could be that the nitrogen isotopic composition of the pristine organic matter was sensibly \(^{15}\)N-depleted (\(\delta^{15}\)N values of ≈−6\%) and then it has been fractionated toward higher values during incorporation in iron oxides. Shen et al. [2006] have indeed noticed that the N isotopic composition in banded iron formations is extremely high, from +20\%o to +35\%o. This has been confirmed by recent work on a Neoarchean BIFs from the Dharwar craton, India by Cloquet et al. [2006] that showed \(\delta^{15}\)N values as high as +22\%. However, the cause of this fractionation is still unclear [Shen et al., 2006]. The alternative hypothesis is that the N isotopic composition reflects biological fractionation.
ation similar to that produced in the modern oxygenated ocean by the assimilation-nitrification-denitrification cycle. Recent geochemical studies on Marble Bar unaltered samples recovered from the Archean Biosphere Drilling Project (ABDP) borehole suggest that the iron oxides within Marble Bar cherts are derived from reactions with oxygenated waters [Ohmoto et al., 2004]. These environmental conditions, although localized, could have enhanced the presence of nitrifiers. It is clear that such a hypothesis would have dramatic consequences on the ongoing debate of the oxygenation of the Earth [e.g., Holland, 2002], and further investigations are needed to unequivocally determine the age of the N (and C) incorporation in Marble Bar cherts.

6. Conclusions

[48] In this contribution, we identified the mineralogical sites where bioindicative elements, such as N and C, reside within a rock. We have done this by using a combination of new developed in situ analytical methods for detecting N and C at mineral scale and routine measurements of their isotopic composition using the stepwise combustion method. Such a work is the first step toward a correct interpretation of the N and C sources and fate during rock diagenesis, weathering and metamorphism and of their isotopic composition in term of biogenicity.

[49] Analyses on separate mineral phases from a well-studied Archean chert of Marble Bar, Western Australia confirmed that N and C is tightly retained within iron oxides. This is an important finding, because biogenic N and C, encapsulated within iron oxide mineral sites, could be better protected from post-depositional weathering and metamorphic events. This may help in preserving their pristine isotopic composition, yielding important environmental information. This study showed that the N and C isotopic composition ($\delta^{15}N \approx +6\%$ and $\delta^{13}C \approx -20\%$) and the C/N elemental ratio (C/N = 52) in FeMnOH of the Marble Bar chert are similar to that of organic matter preserved in modern marine sediments. The Fe isotopic composition of these oxides also permits to suggest a direct precipitation of Fe-oxides from reactions of Fe-rich hydrothermal plumes with locally oxygenated waters. These reactions likely took places during the earlier hydrothermal pulses affecting the Marble Bar Formation, rather than derived from modern basalt weathering. This has important consequences on the interpretation on the isotopic composition of N and C which point out the possibility to have in early times, oasis of oxygenated waters where biosynthesis of N and C worked in a way similar to modern times.

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