Mechanisms of nitrogen isotope fractionation at an ancient black smoker in the 2.7 Ga Abitibi greenstone belt, Canada

A.N. Martin[1,*], E.E. Stüeken[2], J.A.-S. Michaud[1], C. Münker[3], S. Weyer[1], E.H.P. van Hees[4], and M.M. Gehringer[5]

[1]Institut für Mineralogie, Leibniz Universität Hannover, 30167 Hannover, Germany
[2]School of Earth and Environmental Sciences, University of St Andrews, St Andrews KY16 9TS, UK
[3]Institut für Geologie und Mineralogie, Universität zu Köln, 50674 Köln, Germany
[4]Department of Chemistry, Oakland University, Rochester, Michigan 48309, USA
[5]Department of Microbiology, University of Kaiserslautern, 67663 Kaiserslautern, Germany

ABSTRACT

The biological nitrogen (N) cycle on early Earth is enigmatic because of limited data from Archean (meta-)sediments and the potential alteration of primary biotic signatures. Here we further investigate unusual ^{15}N enrichments reported in 2.7 Ga meta-sediments from the Abitibi greenstone belt, Canada, purportedly related to a ^{15}N-enriched Archean atmosphere. Given that sediments from this region are contemporaneous with large-scale volcanogenic massive sulfide deposits, we utilize Cu and Zn contents to trace the effects of hydrothermal circulation on N isotope fractionation. We show that high $\delta^{15}N_{bulk}$ values as high as +23‰ are associated with Cu-Zn mineralization, whereas unmineralized organic-rich shales exhibit much lower $\delta^{15}N_{bulk}$ and $\delta^{15}N_{kerogen}$ values. Moreover, we find a large offset between $\delta^{15}N_{bulk}$ and $\delta^{15}N_{kerogen}$ of as much as 17‰ and relate this to the addition of organic-bound N during the late-stage emplacement of organic-rich veins. We conclude that the previously reported high $\delta^{15}N$ values are most parsimoniously explained by biotic and abiotic mechanisms rather than a ^{15}N-enriched atmosphere. Crucially, both mechanisms require the presence of NH_4^+ in hydrothermal fluids, supporting the hypothesis that hydrothermal discharge was an important nutrient source for Neoarchean marine life.

INTRODUCTION

Nitrogen (N) composes 78% of Earth's modern atmosphere as N_2 but must be chemically transformed to become bioavailable (Galloway et al., 2004). All N redox transformations, including biological N_2 fixation (BNF), ammonification, nitrification, and denitrification, fractionate stable N isotopes ($\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard}]$; Zerkle and Mikhail, 2017). Relative to the modern atmosphere ($\delta^{15}N = 0‰$), the marine nitrate reservoir is slightly enriched ($\sim+5‰$), largely reflecting the balance between BNF and denitrification, and is archived in marine sediments via organisms that assimilate dissolved nitrate as a nutrient and transfer it into sediments via biomass burial (Sigman and Fripiat, 2019). While BNF likely dates to the Mesoarchean (Stüeken et al., 2015a), additional fixed N may have been supplied by hydrothermal vents, but limited N isotope data from such systems in the Archean leaves fundamental uncertainties regarding the early N cycle.

Phanerozoic $\delta^{15}N$ values typically range from 0‰ to +10‰, likely reflecting climatically driven variations in the balance between BNF and denitrification (Algeo et al., 2014). In contrast, $\delta^{15}N$ values as high as +50‰ are found in Neoarchean rocks such as the 2.7 Ga Tumbiana Formation (Pilbara craton, Western Australia), which could represent either partial ammonium (NH_4^+) oxidation under low atmospheric O_2 levels (Thomazo et al., 2011) or NH_3 volatilization in a high-pH lacustrine environment (Stüeken et al., 2015b). Curiously high $\delta^{15}N$ values as high as $\sim+20‰$ are also found in the 2.7 Ga Abitibi greenstone belt (Canada; Fig. 1), both in silicate-bound N ($\delta^{15}N_{bulk}$) from volcanogenic massive sulfide (VMS) deposits (Kerrich et al., 2006) and kerogen-bound N ($\delta^{15}N_{kerogen}$) from shales reported to be distal from VMS and gold deposits (Jia and Kerrich, 2004). These data were attributed by Kerrich et al. (2006) to a ^{15}N-enriched Archean atmosphere possibly caused by input from primitive, ^{15}N-rich meteorites. However, this explanation conflicts with $\delta^{15}N$ values of $\sim0‰$ in 3.2–2.7 Ga Archean sediments (Stüeken et al., 2015a) and fluid inclusions in 3.5–3.0 Ga hydrothermal quartz (Marty et al., 2013; Avice et al., 2018), suggesting that the atmospheric $\delta^{15}N$ composition has remained stable over the past ~3.5 billion years.

Here we explore whether hydrothermal processes may explain the elevated $\delta^{15}N$ values in the Abitibi greenstone belt by utilizing Cu and Zn as tracers of hydrothermal circulation. Like Kerrich et al. (2006), we investigate samples from the ca. 2.72 Ga Kidd Creek VMS deposit but expand on the study of organic-rich shales from the younger ca. 2.68 Ga Timiskaming assemblage (Jia and Kerrich, 2004) by targeting additional organic-rich shales from the western Abitibi greenstone belt. This includes the ca. 2.72 Ga Kidd-Munro and ca. 2.71 Ga Tisdale assemblages that were deposited during volcanic hiatuses and distal to Cu-Zn mineralization at Kidd Creek (Thurston et al., 2008), corresponding to the Tully, Hoyle, Halliday, and Tisdale localities (Fig. 1; see Table S1 in the Supplemental Material[1] for details of cores).

RESULTS

Major element compositions of Abitibi greenstone belt meta-sediments determined by X-ray fluorescence (see the Supplemental Material for details regarding all analytical pro-

A.N. Martin ⬥ https://orcid.org/0000-0002-0268-0471
*a.martin@mineralogie.uni-hannover.de

Figure 1. (A, B) Maps of the regional setting (A) and volcano-sedimentary assemblages (B) of the study area, Abitibi greenstone belt, Canada (U-Pb ages and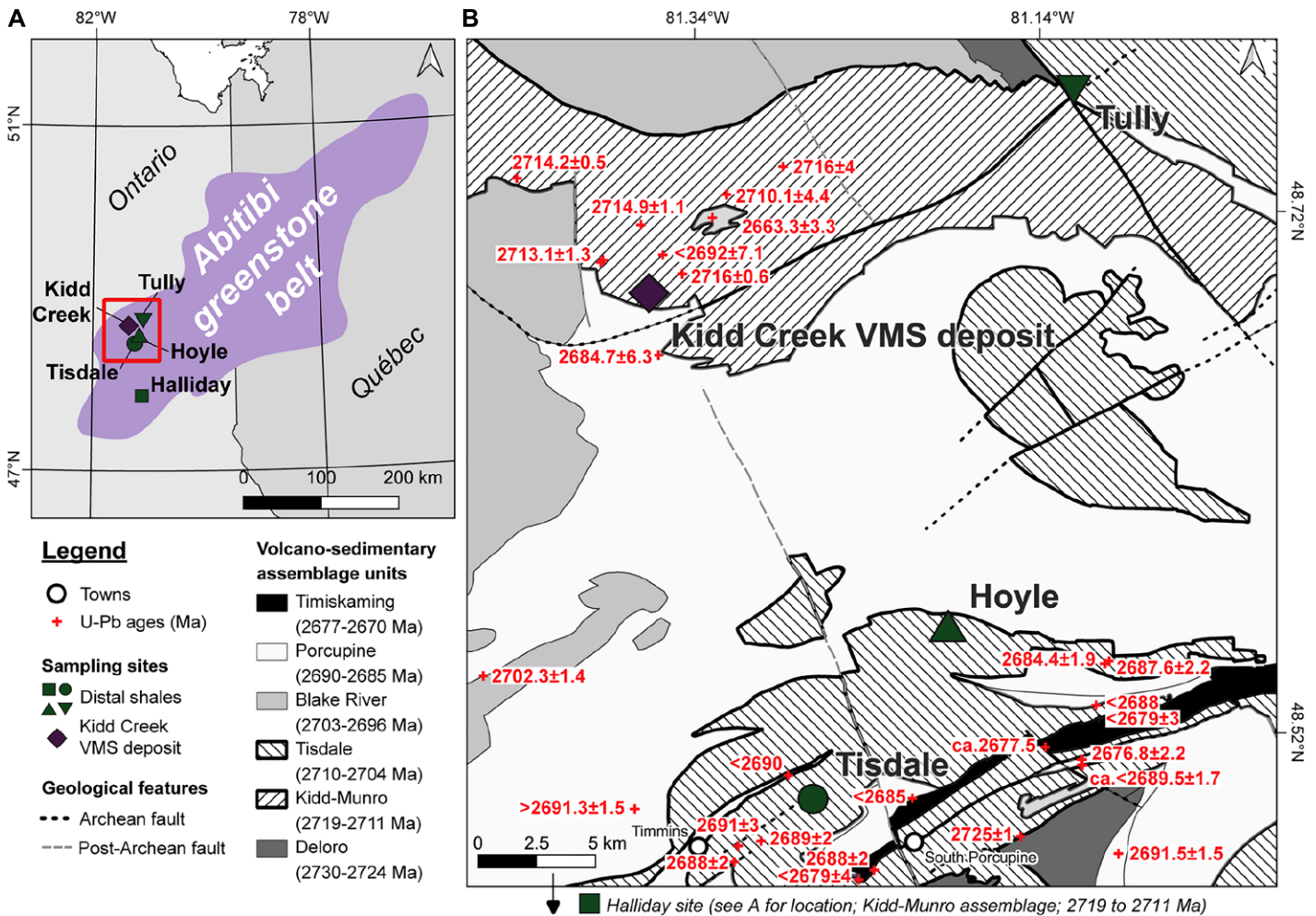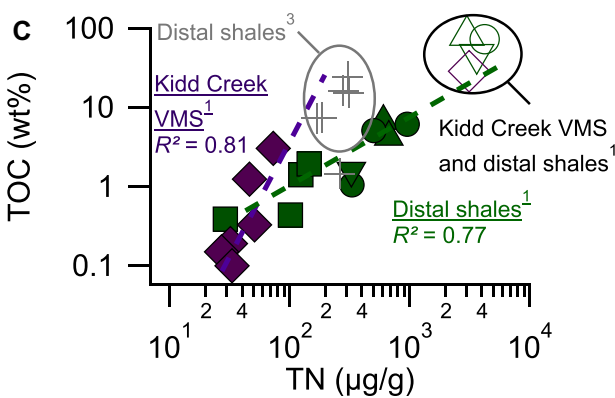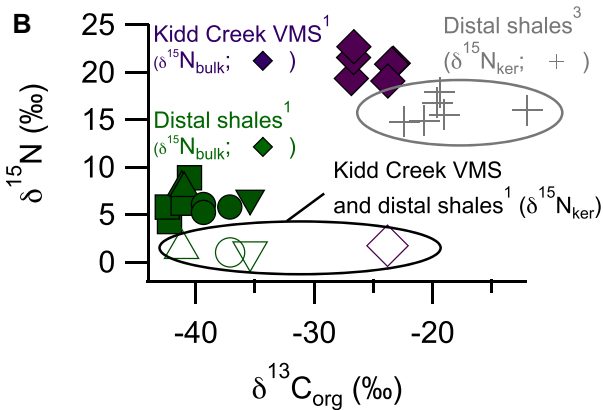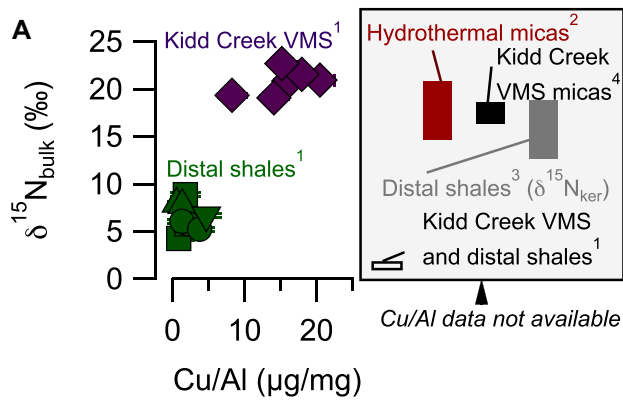 spatial data from Ayer et al., 2005). VMS—volcanogenic massive sulfide. (C) Histograms of silicate-bound N ($\delta^{15}N_{bulk}$) and organic-bound N ($\delta^{15}N_{kerogen}$) in (sub–)greenschist facies Archean sedimentary rocks (compiled by Stüeken et al., 2016).

cedures; Table S2) were mostly characterized by upper-crustal compositions with loss-on-ignition values as high as 12.5 wt%, except the highly siliceous Halliday samples that derive from a silicified debris flow (see the Supplemental Material for detailed petrographic descriptions and Figs. S1 and S2 for thin-section images). Copper and Zn contents measured by inductively coupled plasma–mass spectrometry (ICP-MS)

were around one order of magnitude greater for the Kidd Creek VMS samples compared to shales from the Tully, Hoyle, and Halliday localities (average: ~1000 versus 100 μg/g for Cu and ~10,000 versus 1000 μg/g for Zn; Table S3). Moreover, Cu and Zn contents are highly correlated ($R^2 = 0.96$; Fig. S3), and the effect of Cu-Zn mineralization is also reflected in the higher Cu/Al for the Kidd Creek samples

(Fig. 2A; Zn plots not shown owing to identical trends as for Cu). Thus, the shales from the Tully, Hoyle, and Halliday localities are collectively considered as "distal" to hydrothermal activity.

Stable isotope measurements by elemental analyzer–isotope ratio mass spectrometry (EA-IRMS) yielded $\delta^{15}N_{bulk}$ and $\delta^{13}C_{org}$ (organic carbon) values from +5.8‰ to +22.7‰ and −23.3‰ to −42.4‰, respectively (Fig. 2B;

Figure 2. Plots of δ¹⁵N versus Cu/Al ratios (A), δ¹⁵N versus δ¹³C$_{org}$ (organic carbon) (B), and total organic carbon (TOC) versus total nitrogen (TN) contents (C) for Abitibi greenstone belt meta-sediments including selected literature data. Purple and green dashed lines show the regression lines for the Kidd Creek VMS samples and distal shales, respectively. Error bars represent 1 s.d.; error bars not shown are hidden by markers. ker—kerogen.

Samples in this study (filled markers = bulk; hollow = kerogen)
◆ Kidd Creek VMS **Distal shales:** ■ Halliday ▲ Hoyle ● Tisdale ▼ Tully
References 1: this study; 2: Jia and Kerrich (2000); 3: Jia and Kerrich (2004); 4: Kerrich et al. (2006).
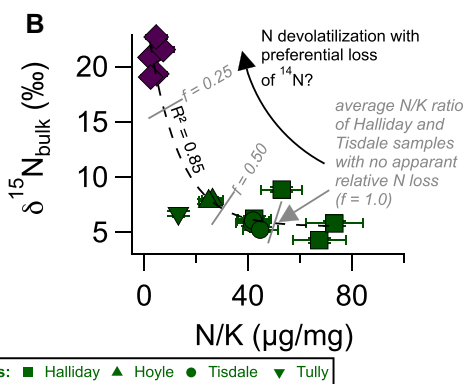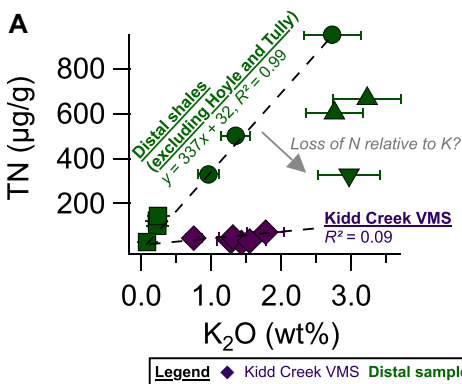

Figure 3. Plots of total nitrogen (TN) vs. K$_2$O contents (A) and δ¹⁵N versus N/K ratios (B) for Abitibi greenstone belt meta-sediments. VMS—volcanogenic massive sulfide; f—fraction of nitrogen remaining. Error bars represent 1 s.d.; error bars not shown are hidden by markers.

Legend ◆ Kidd Creek VMS **Distal samples:** ■ Halliday ▲ Hoyle ● Tisdale ▼ Tully

Table S3). The δ¹⁵N$_{bulk}$ values for the Kidd Creek VMS samples (average: +20.8‰; $n = 6$) are similar to values reported by Kerrich et al. (2006) and significantly higher ($p_{two-tailed} = 0.003$) than those of the distal shales (average: +6.5‰; $n = 10$). Similarly, the δ¹³C$_{org}$ values of the Kidd Creek VMS samples (average: −25.1‰) are significantly higher ($p < 0.001$) than those of the distal shales (average: −40.0‰).

The average total nitrogen (TN) and total organic carbon (TOC) contents of the distal shales (378 μg/g and 2.9 wt%, respectively) are higher than those of the Kidd Creek VMS samples (44 μg/g and 0.8 wt%, respectively; Fig. 2C). There are no correlations between δ¹⁵N$_{bulk}$ and N contents or C/N ratios (Fig. S4) nor between δ¹³C$_{org}$ and TOC or C/N ratios (Fig. S5). The sulfur contents of samples varied from 0.2% to 9.7% (Table S2), but there are no significant differences ($p > 0.05$) between sample groups nor correlations with δ¹³C$_{org}$ or δ¹⁵N values (Fig. S6).

The δ¹⁵N$_{kerogen}$ and δ¹³C$_{org}$ values from the Kidd Creek VMS deposit and distal shales ranged from +1.1‰ to +1.8‰ and −23.8‰ to −41.2‰, respectively ($n = 4$; Table S2). Our δ¹⁵N$_{kerogen}$ and δ¹³C$_{org}$ are much lower than those reported by Jia and Kerrich (2004) in the Timiskaming shales (Fig. 2B), but unfortunately, C/N ratios for the kerogen isolates from this previous work are not available for comparison with our data.

DISCUSSION

The association of elevated δ¹⁵N$_{bulk}$ values with Cu-Zn mineralization in Abitibi greenstone belt meta-sediments (Fig. 2A) requires consideration of hydrothermal explanations in addition to invoking a ¹⁵N-enriched Archean atmosphere (cf. Kerrich et al., 2006). To explore this, we first consider N speciation in hydrothermal systems before discussing potential abiotic and biotic mechanisms for generating N isotope fractionation in meta-sediments.

Origin and Speciation of N in Meta-Sediments

An organic origin for N in our samples is supported by the correlation between TN and TOC contents. A strong correlation ($R^2 \sim 0.8$) is found when considering all samples or sample groups separately (Fig. 2C), and the C/N ratios cover the typical range found in Archean sedimentary rocks and kerogen extracts (35–600; Hayes et al., 1983). The C/N ratios of the Kidd Creek VMS samples are higher and more similar to those of the Timiskaming shales reported by Jia and Kerrich (2004) compared to those of our distal shales, possibly suggesting a higher degree of N loss in the former.

Although originally sourced from organic matter (OM), N now likely occurs as NH$_4^+$ in K-bearing minerals. This is supported by the correlation between N and K contents in the distal shales (excluding the Hoyle and Tully sam-
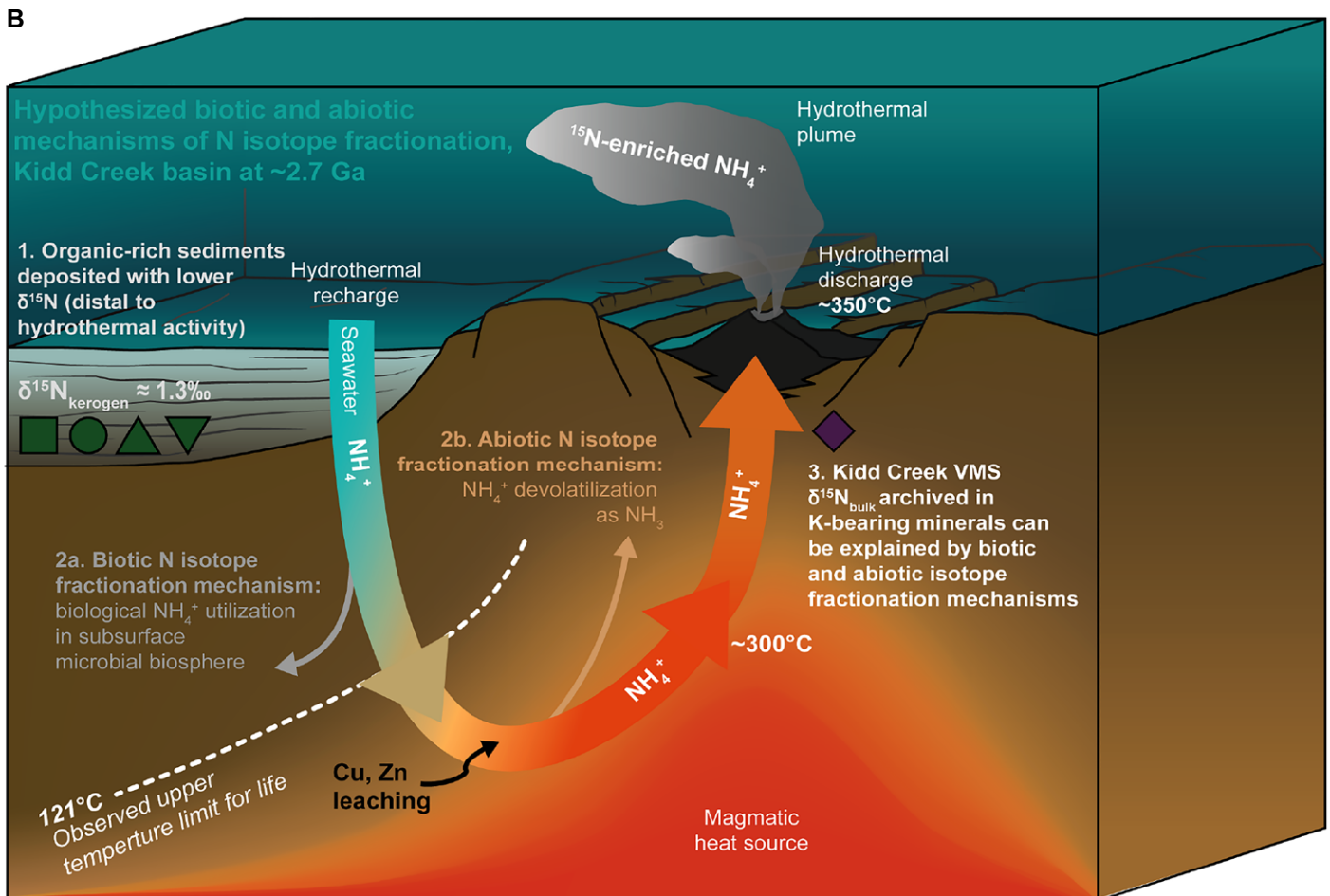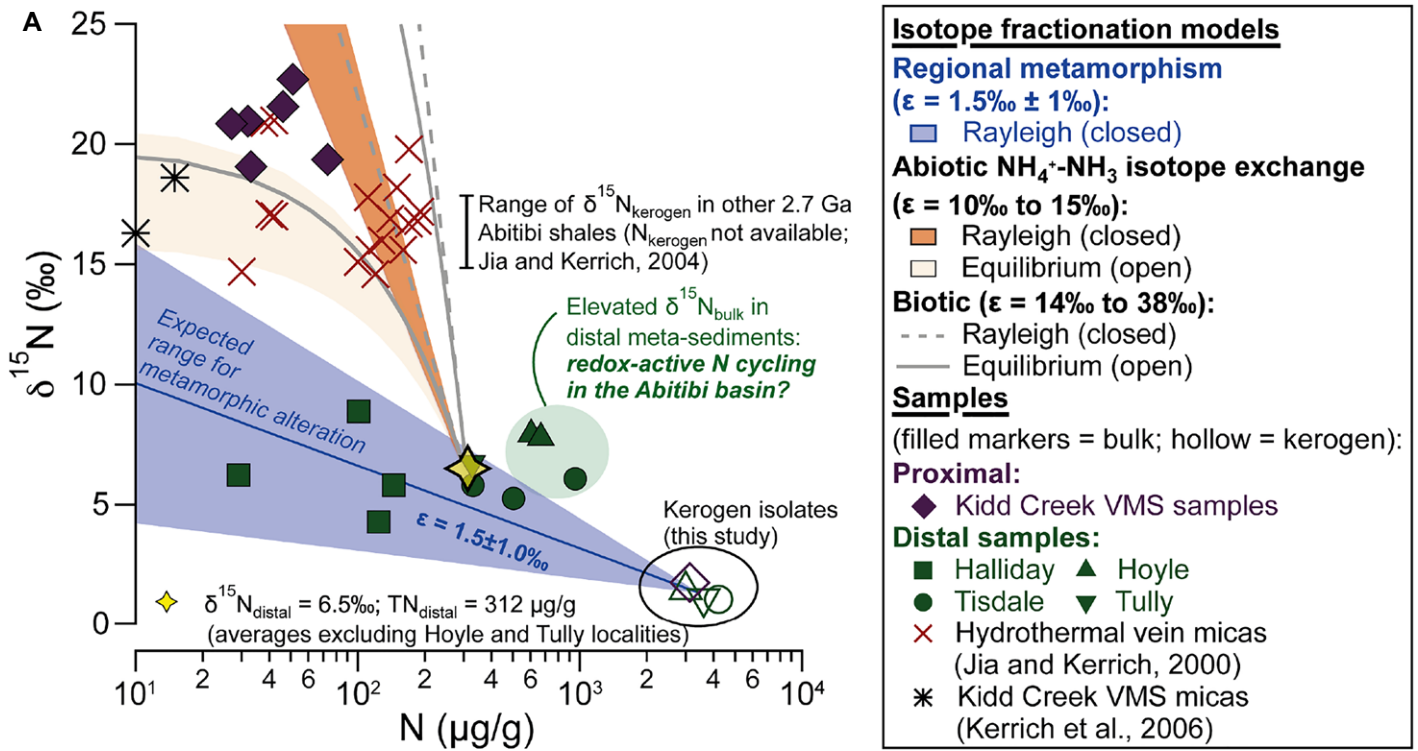
Figure 4. (A) Proposed N isotope fractionation models considering the effects of regional metamorphism, abiotic NH_4^+-NH_3 isotope exchange, and biological utilization of NH_4^+ in a hydrothermal vent system. (B) Schematic diagram illustrating the processes linked with N isotope fractionation models in the Abitibi basin. TN—total nitrogen; VMS—volcanogenic massive sulfide. See main text for discussion and references regarding the chosen isotopic fractionation factors (ε).

ples; Fig. 3A) due to the similar ionic radii of NH_4^+ (1.6 Å) and K^+ (1.5 Å) allowing NH_4^+-K^+ exchange in phyllosilicates. The Hoyle, Tully, and Kidd Creek VMS samples plot below the regression line in Figure 3A, indicating N volatilization without concomitant K loss, as further demonstrated by the relationship between N/K and $\delta^{15}N$ (Fig. 3B). Mechanisms of N loss to explain the elevated $\delta^{15}N$ values in the Kidd Creek VMS samples are discussed in the following.

Abiotic N Isotopic Fractionation Mechanisms

The offset between $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{bulk}$ in the distal shales is diagnostic of metamorphic alteration where kerogen-bound N becomes isotopically lighter while silicate-bound N becomes heavier (Stüeken et al., 2017), as measured in many Precambrian meta-sediments (e.g., Godfrey and Falkowski, 2009; Godfrey et al., 2013; Stüeken et al., 2015a). The offset in the distal shales ($-4.8‰$ to $-6.5‰$) is slightly larger than expected for internal partitioning driven by sub–greenschist facies metamorphism ($\sim-3‰$ to $-4‰$), indicating additional N loss during metamorphic alteration. The unusually large offset in the Kidd Creek VMS sample ($-17.3‰$) cannot be explained by these processes and is discussed later.

Nitrogen is typically volatilized from silicates during metamorphism at (sub–)greenschist facies conditions as N_2 (Bebout and Fogel, 1992), yielding meta-sediments with moderately elevated $\delta^{15}N$ values. The isotope fractionation factor (ε; assuming $\varepsilon \approx 1000\ln\alpha$, whereby α represents the ratio of the heavy to light isotope (R) in two substances A and B, i.e., $\alpha = R_A/R_B$) associated with this process is $1.5‰ \pm 1.0‰$ (Bebout and Fogel, 1992); note that no fractionation factors are available for kerogen isolates to our knowledge, which are likely distinct from those of bulk-rock systems given that kerogen can become isotopically depleted during low-grade metamorphism (Stüeken et al. 2017). A Rayleigh distillation model was preferred to a batch volatilization model (cf. Bebout and Fogel, 1992) to calculate the $\delta^{15}N$ value of the residual rock during the sequential release of infinitesimally small amounts of fluid, each in equilibrium with the rock prior to release, given as:

$$\delta^{15}N = \delta^{15}N_0 - 1000\left(F^{\alpha-1} - 1\right), \quad (1)$$

where α is the isotope fractionation factor and F is the fraction of remaining N. The initial N isotope composition ($\delta^{15}N_0$) represents the average value of the kerogen isolates ($+1.3‰ \pm 0.3‰$; ± 1 s.d.), which is consistent with a primary sedimentary N isotope signature of $\sim 0‰$ in the Archean (Stüeken et al., 2015a). This model can explain the $\delta^{15}N_{bulk}$ values of most distal shales but not those of the Kidd Creek VMS samples (blue shaded area in

Fig. 4A), which eliminates N loss via N_2 as a likely explanation for these high $\delta^{15}N_{bulk}$ values.

A significantly higher N isotope fractionation factor of $+10‰$ to $+15‰$ is expected when N is released from minerals as NH_3 rather than N_2 at temperatures found in black smokers (~ 300 °C), as constrained by theoretical (Scalan, 1958; Hanschmann, 1981) and empirical methods (Haendel et al., 1986). Our data can indeed be explained by NH_4^+-NH_3 isotope exchange reactions at ~ 300 °C (brown shaded areas in Fig. 4A) assuming that hydrothermal fluids were sufficiently reducing to stabilize NH_4^+; however, this is reasonable considering that (1) the acid dissociation constant pK_a, for the $NH_4^+ \rightleftharpoons NH_3 + H^+$ reaction, moves to lower pH with increasing temperature (Li et al., 2012), and (2) elevated NH_4^+ concentrations are found around modern hydrothermal vents (e.g., Lilley et al., 1993). Moreover, elevated $\delta^{15}N$ values in oceanic meta-gabbros are associated with coupled Cu-N cycling during hydrothermal fluid circulation, indicating that such abiotic N isotope fractionation mechanisms may occur in various geological settings (Busigny et al., 2011).

Alternatively, NH_4^+ and/or NH_3 may thermally decompose into H_2 and N_2, which is kinetically controlled and enriches ^{15}N in the residual NH_3-NH_4^+ (Li et al., 2009). However, the gas-phase decomposition of NH_3 to N_2 is slow below 500 °C, which is likely not exceeded in hydrothermal systems or during sub–greenschist facies metamorphism. Thus, we prefer an abiotic explanation featuring isotopic exchange between NH_4^+ and NH_3.

Biological NH_4^+ Utilization Pathways

Early microbial life at ancient hydrothermal vents might also have enriched the local N reservoir in ^{15}N via partial NH_4^+ utilization, as supported by $\delta^{15}N$ values as high as $+17‰$ at modern seafloor vents (Sylvan et al., 2017). Our measured $\delta^{15}N$ range can be explained using the isotopic fractionation factors (ε) determined for microbial NH_4^+ oxidation ($+14‰$ to $+38‰$; Mariotti et al., 1981; Casciotti et al., 2003) and NH_4^+ assimilation ($+14‰$ to $+27‰$; Hoch et al., 1992; Fig. 4A). In this scenario, NH_4^+ may be leached from a previously deposited sediment pile by progressively heated fluids as microbes farther along the flow path partially utilize NH_4^+ before the ^{15}N-rich residual NH_4^+ reaches the hot zone, exchanges with K^+ in phyllosilicates, and is archived (Fig. 4B).

Microbial N isotope fractionation should also yield ^{15}N-poor biomass and sediments, as found around modern hydrothermal vents (e.g., Levesque et al., 2005). This may be stored away from the discharge zone, along unsampled fluid flow paths, but may also partially explain the unusually large $-17‰$ offset between $\delta^{15}N_{kerogen}$ and $\delta^{15}N_{bulk}$ in the Kidd Creek VMS sample,

which is typically $<-4‰$ with metamorphism as high as greenschist facies (Stüeken et al. 2017). Contact metamorphism (cf. Godfrey et al., 2013) is rejected as an explanation for this offset here because the typically associated mineralogical assemblages, e.g., muscovite-biotite-garnet, cordierite-andalusite, or hornblende-hornfels (Pattison and Vogl, 2005), are absent in our samples (Figs. S1 and S2). However, foliation planes in the Kidd Creek VMS samples are intersected by late-stage OM-bearing veins (Fig. S1), indicating distinct sources for silicate-bound and kerogen-bound N. Archean hydrothermal veins are commonly OM rich, e.g., the ca. 3.5 Ga Dresser Formation (Pilbara craton), and thought to be primarily microbial in origin and likely introduced (or extensively altered) by late-stage fluids (Duda et al., 2018). Thus, late-stage, ^{15}N-poor, OM-rich fluids in the Kidd Creek area could plausibly have been associated with the redistribution and sequestration of earlier hydrothermal biomass.

The elevated $\delta^{15}N_{bulk}$ values of the distal shales (relative to expected values for metamorphic alteration; Fig. 4A) also hint at active redox cycling of N in surface waters of the Abitibi greenstone belt. Moreover, these rocks exhibit higher TN contents relative to granitic country rocks (~ 20 µg/g; Jia and Kerrich, 2000) and very low $\delta^{13}C_{org}$ values ($\sim -40‰$). A major contribution of oxygenic photosynthesis to primary productivity is proposed to explain the mass-independent sulfur isotope record in the Abitibi greenstone belt (Kurzweil et al., 2013), which may have been stimulated by a large nutrient influx from local hydrothermal venting. Overall, this supports the emerging portrait of an established marine N cycle in the Neoarchean (Godfrey and Falkowski, 2009).

CONCLUSIONS

We show that high $\delta^{15}N$ values in meta-sediments from the Kidd Creek VMS area, Abitibi greenstone belt, are associated with hydrothermal alteration and Cu-Zn enrichments. However, unlike Jia and Kerrich (2004), we find that shales deposited distal to hydrothermal influences have much lower $\delta^{15}N$ values, which is not consistent with the hypothesis that the Archean atmosphere was unusually enriched in ^{15}N. Rather, the elevated $\delta^{15}N$ values can be explained by hydrothermal processes. We also find a large, unusual offset between $\delta^{15}N_{bulk}$ and $\delta^{15}N_{kerogen}$ in our samples that appears to be associated with late-stage OM-bearing veins and yields distinct sources for silicate-bound and organic-bound N. While secondary injection may account for part of the OM, the high $\delta^{15}N_{bulk}$ values likely reflect either microbial metabolisms utilizing a hydrothermal NH_4^+ reservoir or NH_4^+-NH_3 isotope exchange reactions under highly reducing conditions. Importantly, both scenarios imply

the presence of NH_4^+ in vent fluids that could have stimulated primary productivity in surface waters and suggest that hydrothermal vents may have constituted important nutrient sources for the Neoarchean biosphere.

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