# N2 in deep subsurface fracture fluids of the Canadian Shield: Source and possible recycling processes

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#### Abstract :

In addition to high concentrations of CH4 and H2, abundant dissolved N2 is found in subsurface fracture fluids in Precambrian cratons around the world. These fracture fluids have hydrogeological isolation times on order of thousands to millions and even billions of years. Assessing the sources and sinks of N2 and related (bio)geochemical processes that drive the nitrogen cycle in these long isolated systems can shed insights into the nitrogen cycles on early Earth with implications for other planets and moons. In this study, we collected dissolved gas samples from deep subsurface fracture fluids at seven sites (Kidd Creek, LaRonde, Nickel Rim, Fraser, Copper Cliff South, Thompson, and Birchtree) in the Canadian Shield. Multiple gas components (e.g., H2, O2 and Ar) were integrated with  $\delta$ 15NN2 values to characterize the N2 signatures. Results show that the dissolved N2 in deep subsurface fracture fluids from the Canadian Shield sites are more 15N-enriched than those from the Fennoscandian Shield and the Witwatersrand Basin in the Kaapvaal Craton. The nitrogen isotopic signatures of the Canadian Shield samples coupled with their hydrogeological framework indicate the N2 was sourced from fixed ammonium in silicate minerals in host rocks and was generated by metamorphic devolatilization. Modeling of nitrogen devolatilization from host rocks supports this interpretation, but also suggests that a second process, likely abiotic N2 reduction, is required to account for the observed 15N enrichment in the N2 samples from the Canadian Shield. A 10-year monitoring study for one of the boreholes, at 2.4 km of the Kidd Creek Observatory, shows a steady decrease in  $\delta 15NN2$  values with time, which coincides with the temporal isotopic evolution of some other gas components in this borehole. Although it cannot be confirmed at this time, this isotopic shift in N2 may be potentially attributed to microbial processes (e.g., anaerobic oxidation of ammonium). Nevertheless, the large 15N enrichments for the majority of the samples in this study suggest that the nitrogen cycle in the deep saline fracture fluids in the Canadian Shield is dominated by abiotic processes. This is in contrast to the nitrogen cycles in the subsurface fracture fluids in the Fennoscandian Shield and the Witwatersrand Basin, which have been shown to be strongly affected by extant microbial ecosystems discovered in those fracture waters.

# **Keywords** : Nitrogen cycle, Canadian Shield, deep subsurface, abiotic nitrogen reduction, microbial ammonium oxidation

### 1. Introduction

Precambrian cratons occupy the majority of the Earth's continental crust (> 70% by surface area; Goodwin, 1996). These remnants of early Earth's crust are dominated by (meta-)igneous rocks varying from ultramafic to felsic in composition (e.g., Hoffmann, 1989). Abundant fractures developed over the history of these igneous rocks host a large terrestrial subsurface water reservoir of up to 30% of the planet's total groundwater inventory (Warr et al., 2018). Geochemical signatures (e.g., salinity, major and trace elemental compositions, dissolved gas contents, redox condition,  $\delta^{18}$ O and  $\delta^{2}$ H) of these fluids i rate that they have been strongly influenced by water-rock reactions, and, in some cases, affected by mixing with varying amounts of secondary (paleo-)meteoric water (e.g., Ward et al., 2004; Onstott et al., 2006; Li et al., 2016; Heard et al., 2018; Warr et al., 2021a and references Cherein). Most of these deep subsurface fracture water systems have been hydrogeo, scally isolated over geological time scales, e.g., up to hundreds of million years to billions of pars in the Canadian Shield (Holland et al., 2013; Warr et al., 2018), up to tens to hu los vas of million years in the Fennoscandian Shield (Kietäväinen et al., 2014) and the Witwatersrand Basin in the Kaapvaal Craton, South Africa (Heard et al., 2018; Lippr nan.) et al., 2003). Closed-system water-rock interactions over these extended time periods has progressively produced chemicals (e.g., H<sub>2</sub>, hydrocarbons, sulfate) and highly reducing habitable environments favorable for chemo(litho)trophic microbes (Lin et al., 2005, 2006; Li et al., 2016; Magnabosco et al., 2018; Lollar et al., 2019).

Studies of the subsurface fracture fluids from the Kaapvaal Craton, the Canadian Shield and the Fennoscandian Shield have identified some general quasi-depth-controlled variations in geochemistry and microbial community attributed to the degree of penetration of (paleo-)meteoric water into the subsurface (Warr et al;., 2021a and references therein). Based on noble

gas studies, the shallower fracture fluids generally have shorter residence times, whereas the deeper, more saline fracture fluids have longer residence times (Lippmann et al., 2003; Lippmann-Pipke et al., 2011; Heard et al., 2018; Warr et al., 2018; 2021a). The shallow fracture fluids are mostly highly oxidizing fresh to brackish waters, and contain abundant biomass with diverse microbial communities; in contrast, the deep fracture fluids are mostly highly reducing saline to brine waters, and contain low-abundance biomass with less microbial diversity (e.g., Ward et al., 2004; Onstott et al., 2006; Lin et al., 2006; Magnabosco et al., 2015; Lollar et al., 2019).

These geochemical and microbiological differences an directly impact the isotopic signatures of the dissolved gaseous components in the fracture fluids. For example, different carbon recycling pathways have been clearly identified in these fracture fluids based on the carbon and hydrogen isotopic signatures c. CF.4 and other light n-alkanes (e.g., Sherwood Lollar et al., 1993a, b, 2002, 2006, 2008; Ward et al., 2004; Warr et al., 2021b) and clumped isotopic signatures of CH<sub>4</sub> and N<sub>2</sub> (Young et al., 2017; Labidi et al., 2020; Warr et al., 2021b). These studies have reported consistent abservations from both the Canadian Shield and the Kaapvaal Craton suggesting that CH, in the shallower fracture fluids is dominantly microbial, whereas CH<sub>4</sub> in the deeper, more come fracture fluids with longer residence times can show predominantly abiogenic signatures (Sherwood Lollar et al., 2006; 2008, 2021; Warr et al., 2021b;). More recently, formate and acetate in fluids at 2.4 to 3 km below surface (kmbs) at one of the key deep subsurface sites of the Canadian Shield, the Kidd Creek (KC) Observatory, have been demonstrated to be produced by abiotic organic synthesis (Sherwood Lollar et al., 2021). Multiple sulfur isotopic signatures of dissolved sulfate in fluids from 2.4 kmbs of the KC

Observatory also indicate that the dissolved sulfate in these fluids was derived from abiotic process by indirect radiolytic oxidation of sulfide minerals in host rocks (Li et al., 2016).

Despite numerous studies on the carbon and sulfur cycles in the subsurface fracture fluids in Precambrian cratons, to date, the cycle of another life-constituting element, nitrogen, has not been well examined, particularly in the Canadian Shield. N<sub>2</sub> is typically the second largest dissolved gas component by volume in subsurface fracture fluids in Precambrian cratons around the world. In an earlier study, Sherwood Lollar et al. (1993a) reported the  $\delta^{15}$ N values of N<sub>2</sub> collected from fracture fluids in the Fennoscandian Shield and the Canadian Shield. Thirteen N2 samples from the Fennoscandian Shield show a  $\delta^{15}$ N range 20m 0.2% to 5.1% (with one high value of 10.0‰), whereas four N<sub>2</sub> samples from the C2 iao. n Shield mostly show higher  $\delta^{15}N$ values (Thompson: 1.4‰; Matagami: 8.6‰; No ita. 11.8‰; Val d'Or: 9.1‰). Labidi et al. (2020) also reported two  $\delta^{15}N$  data from Su<sup>11</sup> ury (2.6‰ and 2.8‰) and two  $\delta^{15}N$  data from the KC Observatory (6.6‰ and 6.8‰). Disconved N<sub>2</sub> in subsurface fracture fluids from the Witwatersrand Basin in the Kaapv tat Craton was studied by Silver et al. (2012). After correction for air contamination using the N<sub>2</sub>/ $D_2$  ratio as an index, a  $\delta^{15}N_{N2}$  range from -1.3% to 5.8% was yielded and considered to result from complicated geochemical and, more importantly, biological recycling proce ses (Silver et al., 2012).

The relatively few  $\delta^{15}$ N data from the Canadian Shield make it difficult to compare with those from the Fennoscandian Shield and the Kaapvaal Craton for the understanding of nitrogen cycle in subsurface fracture fluids in Precambrian cratons. In this context, it is important to carry out a more comprehensive investigation of N<sub>2</sub> in deep fracture fluids in the Canadian Shield, particularly those from the KC Observatory. The KC Observatory located in Timmins (Ontario) is an iconic site for the study of subsurface fracture fluids, given the tremendous knowledge

about this site accumulated from studies over nearly three decades (e.g., Sherwood Lollar et al., 1993a, b, 2002, 2021; Doig et al. 1995; Holland et al., 2013; Li et al., 2016; Lollar et al., 2019). In particular, long-term monitoring has been possible at an observatory location 2.4 kmbs since 2007, commencing shortly after the exploratory boreholes were drilled. Noble gas studies indicate that the mean residence times of the fluids at KC were extremely long (e.g., 1.0 - 2.2 Ga at 2.9 kmbs; Warr et al., 2018), while hydrogeological draining of the fluids may result in some boreholes decreasing in age over time (e.g., at 2.4 kmbs, initially 1.1 – 1.7 Ga but has decreased to 0.2 - 0.6 Ga recently; Holland et al., 2013, Warr et al., 2019) is Jate, these fluids show the presence of chemolithotrophic organisms (sulfate-reducing vrganisms in particular) but with low biomass and low rates of activity (Li et al., 2016; Lollar et al., 2019; Sherwood Lollar et al., 2021; Warr et al., 2021b). The geochemical and isotop'c vigratures of these fluids (including dissolved components) may represent the closest abivitic end-members available in the terrestrial deep subsurface (e.g., Sherwood Lollar et al., 2021; Warr et al., 2021b). Such abiotically dominated sites provide a valuable opportunity to scess the long-term abiotic nitrogen recycling processes occurring in these highly reducing waters. This knowledge may further provide crucial insights into the geochemical processes that could have influenced the origin and early evolution of life on the early Earth, and inform models of possible habitability on other planets and moons (NASEM, 2019).

Here we report the gas concentrations and  $\delta^{15}N_{N2}$  values of 45 samples from 7 sites in the Canadian Shield (Fig. 1). In particular, 25 samples were collected from the KC Observatory from 2.1 to 2.9 kmbs, and at the 2.4 kmbs sampling location, over a temporal span of 10 years (2007-2017). This sample suite provides a high-density dataset to evaluate the spatial and temporal changes of the nitrogen cycle in these fracture water systems. Aiming to better constrain the

nitrogen source and recycling processes in the fracture fluids in the Canadian Shield, bulk-rock nitrogen concentrations and isotope compositions were also analyzed on 23 host rock samples from KC, Sudbury, and Thompson. For comparison, nitrogen isotope compositions were also measured on refractory carbon component in 6 graphite-bearing samples from KC.

#### 2. Geological background and samples

The samples in this study were collected from two sites in the Abitibi greenstone belt (i.e., KC and LaRonde), three sites in the Sudbury Basin (i.e., Copper Cuff South, Nickel Rim, and Fraser), and two neighboring sites (Birchtree and Thompson, in the Thompson nickel belt in the western Superior boundary zone, near Thompson, Maritour (Fig. 1).

The KC Observatory in Ontario is georegically located in the volcanic successions of the Kidd-Munro assemblage in the Abitibi. The host rocks at KC include 2.71 – 2.72 Ga ultramafic, mafic (gabbros and basalts) to felsic (maily rhyolites) rocks with graphite-bearing lenses formed in a rifting sub-proximal set floor setting (Bleeker and Parrish, 1996; Hannington et al., 1999; Prior et al., 1999). The rocks experienced regional metamorphism which started at 2.69 Ga, reached peak metamorphism of greenschist facies (~ 400 °C) at 2.64 Ga, and ended as late as 2.60 Ga locally (Barrie and Davis, 1990; Smith et al., 1993; Davis et al., 1994; Bleeker et al., 1999; Powell et al., 2011).

LaRonde (LR) in Quebec is geologically located in the Bousquet formation of the 2.7 Ga Blake River group in the Abitibi. The host rocks are composed of a continuous magmatic series of tholeiitic – transitional mafic to felsic rocks in the lower member, and transitional – calcalkaline intermediate to felsic rock in the upper member (Mercier-Langevin et al., 2007). The

rocks experienced a prograde metamorphism to upper greenschist – lower amphibolite facies and a subsequent greenschist-facies retrograde metamorphism (Dimroth et al., 1983).

Copper Cliff South (CCS), Nickel Rim (NR) and Fraser (FR) are all in the Sudbury impact basin (Ontario). The dominant rock assemblage in the region is the Sudbury Impact Complex (SIC) which was formed by meteoritic impact-induced melting of the Archean basement (Faggart et al., 1985) in ~1.85 Ga (Krogh et al., 1982; Davis, 2008). FR is in the middle of the North Range and NR is in the east of the South Range of the SIC. Both sites geologically lie in the footwall of the SIC that is dominated by 2.14 Ga granitic rocks (Meldrum et al., 1997) and Archean meta-volcanic and metasedimentary rocks that were metamorphosed to upper greenschist – lower amphibolite facies at 2.6° Ga with some reaching granulite facies at 2.65 Ga (Krogh et al., 1984). CCS is located in a radial offset quartz-diorite dyke in the South Range with brecciated country rocks and abu. <sup>1</sup>ant sulfide mineralization (Lightfoot and Farrow, 2002) related to the ~1.85 Ga bolide i nr. ct. Post-impact thermal influences by multiple orogenies, such as the Yavapai-M. zatzal (1.7-1.6 Ga), the Chieflakian-Pinwarian (1.5-1.4 Ga) and the Grenville (1.2-1.0 Ga), nove been found at various degrees across the Sudbury region, e.g., mid- to upper-green chis facies in the South Range (Fleet et al., 1987) and sub-greenschist facies (< 150 °C) in the North Range (Thompson et al., 1998).

The Thompson nickel belt (near Thompson, Manitoba) is a northeast-southwest trending belt formed in an early Proterozoic continental margin. It is constituted by reworked Archean basement and meta-supracrustal rocks (Hulbert et al., 2005). In the western part of the belt where BT and TH are located, the rocks are dominated by 2.2 - 2.0 Ga serpentinized ultramafic rocks, metagabbros, amphibolites, gneisses, schists, skarns, and quartzites (Hulbert et al., 2005;

Zwanzig et al., 2007). The rocks experienced a series of metamorphic events during 1850 – 1750 Ma (Couëslan et al., 2013) with peak metamorphic temperatures of ~ 700 °C in the Thompson area (Paktunç, 1984). Later (not yet dated) low-temperature (250 – 300 °C) alteration of rocks at Thompson by chloride-rich fluid is evidenced by the PGE-Au-As mineralization (Chen et al., 1993).

Gas samples were collected following the method describe 1 by Ward et al. (2004) and Holland et al. (2013). In brief, a packer was used to seal the bore note and funnel the water and gas flow from the borehole through a sterilized Tygon tube in to a bucket. After a period of flushing to ensure representative sampling, gases were intro-luced into an inverted beaker submerged into the fracture fluids collected in a bucket. The gases were then transferred through a 22-g syringe needle on a Luer attachment of the 'op of the beaker into 160 ml borosilicate vials with blue butyl stoppers which had been sternized, prefixed with 50 µL saturated HgCl<sub>2</sub> solution, and pre-evacuated.

Rocks samples were collected from exploration drill cores provided by the mines. A total of 23 samples were selected from representative lithologies of the host rocks from KC, Sudbury, and Thompson.

#### 3. Methods

Gas concentrations and nitrogen isotope compositions of  $N_2$  were analyzed at University of Toronto. Gas concentrations were generally measured within days after sample collection to avoid possible shifts in gas (e.g.,  $H_2$  and  $O_2$ ) concentrations due to diffusion and/or reaction, although the results of re-analyses in 2007 on a batch of samples collected in 2000 show no

significant difference in  $H_2$  and  $O_2$  concentrations in comparison with the results obtained in 2000. Gas concentrations were measured by a Varian gas chromatography equipped with Varian Molecular Sieve 5A PLOT fused silica column and a micro-thermal conductivity detector ( $\mu$ TCD) for H<sub>2</sub>, He, N<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, Ar and a flame ionization detector for alkanes following the published protocols (e.g., Ward et al., 2004). NH<sub>3</sub> is not specially examined here because it requires high pH condition to drive  $NH_3$  from fluids to gas phases (e.g., Deng et al., 2018), whereas the modeling based on the pH and temperature conditions of the studied fluid samples suggests that NH<sub>3</sub> mostly concentrates in fluids and barely occurs in the gas phases (Li et al., 2012). The  $2\sigma$  analytical error is < 5% of the absolute concentrations based on repeated analyses of lab standards and natural samples. The nitrogen isotopic ratio of N2 was measured by gas chromatography-isotope ratio mass spectrometry. An cliquot of a gas sample was taken by gastight syringe from a sample bottle and injecter into a Varian gas chromatography, in which a slow flow rate of 1.2 ml/min was used for the carrier gas (ultrahigh-purity helium) to ensure the separation of N<sub>2</sub> from other gas coraron cuts such as H<sub>2</sub> and O<sub>2</sub>. CO<sub>2</sub> and CO are not significant interferences in this analysis because their natural abundances in the gas samples are below the detection limit (< 0.01 vol%) is time window was set to allow N<sub>2</sub> but no other interference gases to be carried into a Finnig n 252 isotope ratio mass spectrometer for isotopic measurements. The isotopic ratios are reported using the  $\delta$  notation ( $\delta^{15}N = ({}^{15}N/{}^{14}N)_{sample}/({}^{15}N/{}^{14}N)_{standard} - 1$ ), in which "standard" is atmospheric N<sub>2</sub>. All samples were measured in duplicate. Repeat analyses of these samples and laboratory working standards cross-calibrated against international IAEA nitrogen reference materials gave  $2\sigma$  analytical errors better than 0.2%.

Nitrogen isotopic ratios of rocks were measured at University of Alberta following the method described by Li et al. (2021a). In brief, after removal of the surface by sawing, rock

chips from drill cores were ground into fine powders (< 200 mesh). For the graphite-bearing lens samples, nitrogen was measured on both bulk-rock samples and refractory reduced carbon residues following the extraction protocol of Eigenbrode and Freeman (2006). The powder samples were weighted and loaded into pre-cleaned one end-sealed quartz tube together with CuO reagents, pumped in a metal manifold, sealed under high vacuum, and combusted first at 1200 °C for 30 min to 60 min (depending on lithology; see details in Li et al., 2021a) and then at 900 °C overnight to completely release the fixed nitrogen in mineral. The sample tube was then cracked under high vacuum to release N<sub>2</sub>, which was further  $c_{12}\gamma_{5}z_{1}$  ically purified, quantified by a capacitance manometer, and carried by an ultrahigh-putity helium gas to a Thermo Finnigan MAT 253 for nitrogen isotopic measurements. The  $\delta^{15}N$  values are reported relative to the atmospheric N<sub>2</sub>. Repeat analyses of two standard's  $\sqrt{2}\sigma v$  Organic Content Soil and High Organic Content Soil) from Elemental Microanalys. Lad gave  $2\sigma$  analytical errors better than 0.2‰ (Li et al., 2021a).

# 4. Results

# 4.1. Gas concentrations and $\delta^{15}N_{N2}$ values

The major gas concentrations and  $\delta^{15}N$  values of N<sub>2</sub> are reported in Table 1. The results are briefly summarized below.

Twenty-five gas samples from KC are dominated by CH<sub>4</sub> (64 – 83 vol%) and other light n-alkanes (e.g., ethane, propane, butane; in total < 9 vol%). N<sub>2</sub> is the second most abundant gas component with concentrations varying from 4.5 vol% to 16.9 vol% and  $\delta^{15}$ N values from 3.2‰ to 8.0‰ (Table 1). These isotopic values fall in the  $\delta^{15}$ N range of 2.8‰ – 8.8‰ from a limited

set of KC samples in Montgomery (1994) and Labidi et al. (2020).  $H_2$  gas was detected in all KC samples except one, with variable concentrations from 0.3 vol% to 10.7 vol%.

Two gas samples from LR are also dominated by CH<sub>4</sub> (66 – 72 vol%) and N<sub>2</sub> (9 – 15 vol%) with  $\delta^{15}$ N values of 6.5‰ and 7.4‰, respectively. Both samples contain H<sub>2</sub> (1.8 vol% and 3.6 vol%, respectively). All these features are similar to those of the KC samples.

Six gas samples from CCS (on the south rim of the Sudbury Pasin) are characterized by extremely high H<sub>2</sub> concentrations (10-58 vol%). CH<sub>4</sub> is the *subset* major gas component in these samples (14 - 70 vol%). N<sub>2</sub> concentrations are generally low in the samples studied at this site (Table 1). The  $\delta^{15}N_{N2}$  values (0.6% to 4.2%) of these sumples are also much lower than those of the KC and LR samples. It is worth noting that var.  $b_2$  amounts of O<sub>2</sub> (0.4 – 5.5 vol%) are detected in these samples, which suggests significant air contamination (see Section 4.2). In a previous unpublished study by Montgome.v (1994), much higher N<sub>2</sub> concentrations of up to 65 vol% and  $\delta^{15}$ N values up to 17.5% wre reported from CCS. The other samples from the Sudbury Basin show significantly higher N<sub>2</sub> concentrations. The five NR gas samples are dominated by N<sub>2</sub> (47 – 5? vo.<sup>%</sup>), He (24 – 32 vol<sup>%</sup>) and CH<sub>4</sub> (15 – 24 vol<sup>%</sup>). H<sub>2</sub> occurs all samples in varying amoun s (0.01 – 2.7 vol%). The  $\delta^{15}N_{N2}$  values display a small range from 3.5‰ to 5.0‰. The only gas sample available from FR is also dominated by  $N_2$  (66 vol%), He (17 vol%) and CH<sub>4</sub> (20 vol%). It also contains much higher Ar concentration (5.2 vol%) than all the other studied gas samples from the Canadian Shield (< 2 vol%). The reason for this is not fully understood at this time. The FR sample has a  $\delta^{15}N_{N2}$  value of 5.0%, similar to those of the NR samples.

Three gas samples from BT and four gas samples from TH are all dominated by CH<sub>4</sub> and N<sub>2</sub>. The CH<sub>4</sub> concentrations (63 – 69 vol%) are higher than N<sub>2</sub> concentrations (29 – 31 vol%) in the BT samples, whereas the N<sub>2</sub> concentrations (46 – 66 vol%) are higher than the CH<sub>4</sub> concentrations (35 – 48 vol%) in the TH samples. Despite the difference in N<sub>2</sub> concentration, the  $\delta^{15}N_{N2}$  values are consistent between BT and TH, ranging from 7.4‰ to 8.7‰. All of the BT and TH gas samples except one contain detectable H<sub>2</sub>, generally at levels between 0.02 – 2.75 vol%.

### 4.2. Distinguishing sampling-related air contamination

A characteristic feature of the studied gas samples from the Canadian Shield is the ubiquitous occurrence of H<sub>2</sub> gas (Table 1). This indicates that highly reducing conditions have been established and maintained in the host fracture fluids of these gas samples, which is consistent with all past studies. These highly reduced fracture fluids should not contain any *insitu* O<sub>2</sub> gas (Holland et al., 2013; Warr et al., 2018, 2021a). Therefore, any O<sub>2</sub> detected in the gas samples should be indicative of recent air contamination, mostly likely during sampling.

To assess the air contamination in the studied samples,  $\delta^{15}N_{N2}$  values are compared with N<sub>2</sub>/O<sub>2</sub> and N<sub>2</sub>/Ar concentration ratios (Fig. 2). Fig. 2A illustrates a decreasing trend of  $\delta^{15}N_{N2}$  values following the decrease in N<sub>2</sub>/O<sub>2</sub> ratios toward the air end-member, particularly seen in some of the CCS and KC samples. The data comparison (Fig. 2A) shows that more consistent ranges of  $\delta^{15}N_{N2}$  values can be observed for samples with N<sub>2</sub>/O<sub>2</sub> ratios > 15 at each site. The  $\delta^{15}N_{N2}$  values of samples with N<sub>2</sub>/O<sub>2</sub> < 15 are more or less altered by air contamination.

Unlike  $O_2$ , which can be readily identified as a result of air contamination in these highly reducing fluids, <sup>40</sup>Ar (the dominant isotope of Ar) can be produced by subsurface processes and hence cannot be used to evaluate air contamination (Fig. 2B). <sup>40</sup>Ar, a product of the radioactive

decay of <sup>40</sup>K, can accumulate in the fracture waters over time and vary significantly depending on the lithology of local host rocks and isolation time of the fracture fluids (Warr et al., 2019). N<sub>2</sub> concentrations may also vary significantly, depending on the thermal history, nitrogen source, abiotic reactions, and biological activities (if any) in the fracture waters (Silver et al., 2012). These two factors can result in highly heterogeneous N<sub>2</sub>/Ar ratios in the deep subsurface of the Canadian Shield (Fig. 2B), which may be a result of *in-situ* processes and not necessarily reflect air contamination. The data compilation of less contaminated samples (i.e., N<sub>2</sub>/O<sub>2</sub> >15) on Fig. 2C illustrates that the N<sub>2</sub>/Ar ratios increase in order from LR, EP, NK, KC, to BT and TH. Therefore, without knowing the N<sub>2</sub>/Ar values of uncontaminated gases, N<sub>2</sub>/Ar ratios alone cannot be used to estimate the fractions of air components in gas amples from Precambrian cratons.

Accordingly, the discussion below on the  $\delta^{1^{\epsilon}}N_{\sqrt{2}}$  values of the Canadian Shield samples will focus only on those with  $N_2/O_2 > 15$ .

# 4.3. $\delta^{15}$ N values of rock samples

The nitrogen concentrations and  $\delta^{15}$ N values of rock samples are listed in Table 2. Six silicate host rock camples from KC, including three rhyolites, two silicified cherty breccia and one quartz feldspar porphyry, show a  $\delta^{15}$ N range from 6.0% to 10.4%. Six samples of the graphite-bearing lenses from KC give a  $\delta^{15}$ N range from 6.7% to 15.6% for bulk-rock nitrogen, but a lower  $\delta^{15}$ N range from 0.4% to 10.4% for extracted refractory reduced carbon residues.

Sudbury host rock samples comprise of two samples (a meta-gabbro and a breccia matrix) from the Creighton mine, which has similar wall rock to the CCS mine, and six samples from NR (two felsic gneisses, two felsic norites, one granodiorite, and one breccia). All the samples

give a small  $\delta^{15}$ N range from 1.3‰ to 3.4‰ except one felsic norite sample with a  $\delta^{15}$ N value of -5.6‰.

Three host rock samples from TH, inducing one gneiss, one schist, and one skarn, show relatively high  $\delta^{15}$ N values from 7.0% to 10.2%.

### 5. Discussion

# 5.1. $\delta^{15}N_{N2}$ variability across sites in the Canadian Shield

After discarding all the samples with N<sub>2</sub>/O<sub>2</sub> < 15, the  $\delta^{15}N_{N2}$  distribution (Fig. 2C) shows a general trend with the lowest values in NR and FR, ar a scadily increasing values from LR, KC, to BT and TH. However, this isotopic pattern is not confirmative at the moment given that only a small number of samples were collected it on a specific depth in each of the sites (except KC). A larger dataset from multiple depths at KC give much larger  $\delta^{15}N_{N2}$  variation than those of the other sites (Fig. 2C; see Section 5 + ver discussion). Two samples from different depths at CCS also show large  $\delta^{15}N_{N2}$  variation (Montgomery, 1994; Fig. 2A). Therefore, more data from each site are needed in future studies to examine the inter-site  $\delta^{15}N_{N2}$  variability and its controlling factors in the Canadian Shield.

#### 5.2. Comparison with the Fennoscandian Shield and the Kaapvaal Craton

The  $\delta^{15}$ N values of N<sub>2</sub> from subsurface fracture fluids have been reported from some sites on other Precambrian cratons, e.g., the Fennoscandian Shield (Sherwood Lollar et al., 1993a) and the Kaapvaal Craton (Silver et al., 2012). As mentioned above, the thirteen published gas samples from the Fennoscandian Shield (Sherwood Lollar et al., 1993a) have  $\delta^{15}N_{N2}$  values from 0.2‰ to 5.1‰ (except one high value of 10.0‰) with a peak at the bin of 0-1‰ (Fig. 3A). Silver

et al. (2012) reported the  $\delta^{15}N_{N2}$  values of eighteen gas samples from Beatrix (BE116, 325, 327), Driefontein (Dr938), Evander (EV219, 522, 818), Kloof (KL441, 739), Masimong (MM5), Merriespruit (MS151), Mponeng (MP104) in the Witwatersrand Basin in the Kaapvaal Craton. These fracture systems have mean residence times varying from 0.7 Ma (EV522) to 20 Ma (KL739 and MP104) with one sample (Dr938) having a <sup>14</sup>C-derived age of 1022 years (Lippmann et al., 2003; Lin et al., 2006; Silver et al., 2012 and reference therein). The hydrogen and oxygen isotope compositions of these fracture fluids spread fron. on (or close to) the global meteoric water line (GMWL) to above the GMWL (Lippman, et al., 2003; Ward et al., 2004; Lin et al., 2006; Onstott et al., 2006; Warr et al., 2021a). Their  $\delta^{15}N_{N2}$  values fall in the range of -1.3% to 5.8‰ (Fig. 3B). The  $\delta^{15}N_{N2}$  values do not correcte with either the residence times or the magnitude of isotopic deviation above the C MWL, indicating the major control on the  $\delta^{15}N_{N2}$ values of the samples in the Kaapvaal Crator may not be geological processes (e.g., fluid-rock interaction) but biological processes.

In contrast, the Canadian S iie.<sup>4</sup> samples show consistently higher  $\delta^{15}N_{N2}$  values (Fig. 3C). A total of thirty-five samples studied here cluster in a  $\delta^{15}N_{N2}$  range of 3.0‰ to 8.0‰ with a peak at the bin of 7–8‰ (Fig. 3C), while three historical samples from Montgomery (1994) and Sherwood Lollar (1993*e*) give more variable  $\delta^{15}N_{N2}$  values of 1.4‰, 1.5‰ and 17.5‰, respectively (Fig. 2A). The  $\delta^{15}N_{N2}$  discrepancy between the Canadian Shield samples and the samples from the Fennoscandian Shield and the Kaapvaal Craton could be attributed to the differences in nitrogen source and abiotic and biological processes among these deep subsurface fracture waters, which are discussed in detail below.

#### 5.3. Source of N<sub>2</sub> in the Canadian Shield

Several sources could potentially contribute to the  $N_2$  in the terrestrial subsurface fracture water systems, such as ancient atmospheric  $N_2$ , dissolved inorganic nitrogen species (nitrate, nitrite, ammonium) in pore water and/or fluid inclusions in host rocks, and fixed nitrogen in host rocks.

In the studied samples from the Canadian Shield, although noble gas studies imply that these fracture fluids contain a minor initial component of noble gas (e.g., Xe) derived from ancient air (Holland et al., 2013; Warr et al., 2018), a ballpark estimation based on the concentration data of gases and rocks in Li et al. (2016) and  $tv_{T}^{-1}c_{\alpha}$ .  $M_{2}$  concentration of seawater (Kipfer et al., 2002) suggests that the ancient air contributed at most 0.1 - 6% of the gas components. Therefore, ancient atmospheric  $N_{2}$  can be  $e_{N}$  (uded as the main source. In addition, a recent study discovered extreme  ${}^{15}N{}^{15}N$  enrichment  $N_{2}$  (Yeung et al., 2017). Assuming the ancient atmospheric  $N_{2}$  had for parable  ${}^{15}N{}^{15}N$  enrichment, and little re-ordering of the internal bonding of  $N_{2}$  molecules is these low-temperature fracture systems, a  ${}^{15}N{}^{15}N$ enrichment would be expected if signified at amount of ancient atmospheric  $N_{2}$  contributed to the fluids. However, Labidi et al. (2x<sup>2</sup>0) found no  ${}^{15}N{}^{15}N$  enrichment in the KC samples. This suggests that the amounts of accient  $N_{2}$  from both ancient air and modern air contamination, are relatively small in the 'total  $N_{2}$  of the samples.

Dissolved inorganic nitrogen species in pore water and fluid inclusions in host rock have been proposed to account for the abundant nitrate,  $N_2$  and ammonium in the subsurface fracture waters in the Witwatersrand Basin in the Kaapvaal Craton, South Africa (Silver et al., 2012). In this model, it requires (1) a high NH<sub>3</sub>-NH<sub>4</sub><sup>+</sup> pool in fluid inclusions in the first place, (2) efficient migration of nitrogen in fluid inclusions to fracture fluids, and (3) abiotic and biological recycling processes to convert NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> to other nitrogen species (e.g., N<sub>2</sub> in this case). These

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conditions are relatively difficult to reach in the Canadian Shield where the igneous-rock dominated host rocks contain small volumes of primary fluid inclusions. Furthermore, geochemical and hydrogeological analyses have shown that contribution of young surface fluids is little in these fracture systems (e.g., Warr et al., 2021a), ruling out later infiltration of dissolved inorganic nitrogen from surface.

Sedimentary rocks are a commonly considered source for  $N_2$  in basinal environments. However, in the Canadian Shield, host rocks are dominated by c yst. Inne rocks. At KC where host rock lithology has been well characterized from drill cores, graphite-bearing lenses occupy a very small volume in host rocks. The nitrogen concentrations of the graphite-bearing lenses (40-99 ppm; Table 2) are significantly smaller than those of typical deep-sea sediments and their metamorphosed equivalents (hundreds to through, 4s of ppm; e.g., Bebout and Fogel, 1992; Busigny et al., 2003; Sadofsky and Bebout, 2004; Li and Bebout, 2005). Therefore, the graphitebearing lenses can less likely account to the widely occurring gases in the highly confined and locally controlled fracture water compartments (Warr et al., 2018). This conclusion is further supported by the carbon and hydrogen isotopic signatures of n-alkanes in the gas samples. The  $\delta^{13}$ C and  $\delta^2$ H patterns of A-alkanes are very different to that of conventional thermogenic gases (Sherwood Lollar et al., 1993b, 2002, 2008; Warr et al., 2021b). Overall, both isotopic fingerprints and hydrogeological frameworks do not favor organics as the main source of the gases.

Significant amounts of nitrogen (in form of ammonium) can be assimilated into the crystal structures of secondary phyllosilicate minerals (e.g., clay and serpentine) formed during the alteration of igneous rocks by seawater and/or hydrothermal fluids (Busigny et al., 2005; Li

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et al., 2007). The nitrogen measurement on six representative silicate samples from KC give a nitrogen concentration range from 12 ppm to 34 ppm (average: ~ 24 ppm; Table 2) and a  $\delta^{15}$ N range from 6.0‰ to 10.3‰ (average: 8.0‰). Given the large volume of the silicate host rocks in Precambrian cratons, such high nitrogen concentrations of the igneous host rocks represent a huge nitrogen reservoir, with an inventory orders in magnitude higher than that in the small volume of fluids. Mobilization by devolatilization of a small proportion of this reservoir is able to account for the N<sub>2</sub> in the subsurface fracture waters.

To devolatilize the ammonium fixed in the igneous heat recks, it requires relatively high temperatures. In light of previous laboratory and field studies (e.g., Haendel et al., 1986; Bebout and Fogel, 1992), nitrogen devolatilization from mine rals and rocks could have easily taken place under the peak (and retrograde) metar ... phir conditions in the study sites, e.g., 400 °C at KC, 700 °C at TH, and variable temperatures , <sup>1</sup>epending on the distance to the crater; Abramov and Kring, 2004) during the impact e era et Sudbury. At crustal conditions, high temperatures facilitate N<sub>2</sub> as the devolatilization product (e.g., Bebout and Fogel, 1992; Li et al., 2009). The lower temperature limit for N<sub>2</sub> a volatilization from minerals and rocks is however unconstrained. Even t. kin 7 th 2 smectite-illite transition temperature of 60 °C (Freed and Peacor, 1989) as the lower limit,  $\therefore$  is still higher than the current temperatures of the studied fracture fluid systems. In particular, the Canadian Shield has been relatively stable and maintained a low thermal gradient since at least 2 Ga (Slack, 1974). Temperature estimation using the method of Li et al. (2016) suggests that the temperature at KC should have been < 60 °C since at latest 1.3 Ga for the 2.1 kmbs site and 0.9 Ga for the 2.9 kmbs site. Therefore, the observed N<sub>2</sub> was mostly likely produced during earlier time periods. N<sub>2</sub> production would have been most efficient during the peak metamorphism at each site, and diminish exponentially with the decrease in temperature with time. Given that the analyzed host rocks consistently show high nitrogen concentrations (Table 2), it only requires a very small (almost negligible) fraction of the total nitrogen in the rocks to account for the observed  $N_2$  in the fluids, which can be easily satisfied.

#### 5.4. Possible N recycling processes in subsurface fracture fluids

#### 5.4.1. Abiotic N<sub>2</sub> reduction

Based on above discussions, the N<sub>2</sub> in the deep subsurface fracture fluids in the Canadian Shield most likely originated by devolatilization of fixed ammor run, in their silicate host rocks. Nitrogen devolatilization from rocks is associated with an iso opil effect with preferential uptake of <sup>14</sup>N by N<sub>2</sub> and preferential retention of <sup>15</sup>N in host rock (e.g., Bebout and Fogel, 1992; Haendel et al., 1986; Li et al., 2021b, c). The magnitude of <sup>15</sup>N depletion in the N<sub>2</sub> product is dependent on two factors, i.e., the temperative accordent isotope fractionation factor and the fraction of ammonium in rock that is converte  $^{1}$  into N<sub>2</sub>. The nitrogen isotope fractionation factors between N<sub>2</sub> and clay minerals can be derived from Li et al. (2021b, c) to be -13.2% at 60 °C, -10.9‰ at 100 °C, -6.2‰ at 2 '0 °C, -4.1‰ at 400 °C, -2.3‰ at 700 °C and -1.5‰ at 1000 °C. Based on these fractionation <sup>c</sup>actors, the theoretical  $\delta^{15}$ N differences between N<sub>2</sub> product and remaining ammonium in vost rocks along the progress of metamorphic devolatilization are illustrated by a Rayleigh fractionation model in Fig. 4A-C for KC, Sudbury and Thompson, respectively. Comparison of average  $\delta^{15}N$  values between N<sub>2</sub> and host rocks yield  $\Delta^{15}N_{N2-rock}$ values of -0.3% for the 2.1 kmbs site, -1.1% for the 2.4 kmbs site, and -3.1% for the 2.9 kmbs site at KC, +2.5‰ at NR, +4.0‰ at FR, +0.3‰ at TH and -0.4‰ at BT. All these values are higher than the expected values for N<sub>2</sub> devolatilization at their peak metamorphic conditions (Fig. 4A-C). Any N<sub>2</sub> generated from retrograde metamorphism would make the isotope discrepancy ever larger. At CCS, although all the samples in this study have been severely contaminated by

air during sampling, their values are still higher than the predicted values (Fig. 4B), not even mention the extremely high  $\delta^{15}$ N values (up to 17.5‰) observed on less air-contaminated samples (Montgomery, 1994). These results indicate, while the magnitude and direction of isotope fractionation are indeed consistent with N<sub>2</sub> production via devolatilization of ammonium in host rocks, the extents of observed isotopic discrepancy between N<sub>2</sub> and host rocks require an additional process to explain the <sup>15</sup>N enrichments in N<sub>2</sub>.

Diffusive loss of N<sub>2</sub> and abiotic N<sub>2</sub> reduction are two known processes that can induce <sup>15</sup>N enrichments in remaining N<sub>2</sub>. Extensive studies of the notic gas concentrations (in the KC system in particular) have demonstrated that diffusion cannet be a major factor due to the concordance in the ages of the fluids derived from both light (helium and neon) and heavy (argon and xenon) noble gases. In systems where diffusion is a significant process, preferential loss of light noble gases would produce an artifac. of significantly younger apparent ages for helium and neon – which is notably not observed in any of the KC studies (Holland et al., 2013; Warr et al., 2018). Accordingly, diffusion process is likely to significantly impact the  $\delta^{15}N_{N2}$ . Rather than diffusion, abiotic N<sub>2</sub> reduction may play an important role. Following the cooling of the fluids, N<sub>2</sub> input from metrans rpinc devolatilization diminished to negligible level. Meanwhile, the nonstop interaction be ween water and  $Fe^{2+}$ -bearing minerals (e.g., olivine, pyroxene, biotite, pyrite) in host rocks can produce secondary minerals to seal the fracture system and subsequently establish and maintain a highly reducing environment enriched in  $H_2$  and dissolved  $Fe^{2+}$  (Li et al., 2016) inside the fracture system. These reducing agents in the fuids, as well as abundant  $Fe^{2+}$ bearing minerals in host rocks, would facilitate abiotic reduction reactions. This is supported by the observation that abiogenic products (e.g., alkanes, acetate, and formate) dominate the gaseous and/or dissolved organic compounds in the KC fracture fluids (Sherwood Lollar et al.,

2021) and also widely occur (if not dominate) in other sites in the Canadian Shield (Sherwood Lollar et al., 2006).

Abiotic  $N_2$  reduction in a geological setting generally refers to the mineral catalyzed reduction of  $N_2$  to produced  $NH_3$  or  $NH_4^+$  in fluids, via reactions such as equation (1):

$$N_2 + 6Fe^{2+} + 8H^+ \to 2NH_4^+ + 6Fe^{3+} \tag{1}$$

Laboratory experiments demonstrate that abiotic N2 reduction is most efficient at 500 °C (Brandes et al., 1998), but can also occur at temperatures as low as 2.° °C (Smirnov et al., 2008). Abiotic N<sub>2</sub> reduction generally produces a kinetic nitrogen isotopic offect due to the difficulty in breaking the strong N $\equiv$ N bond of N<sub>2</sub>. Based on the nitrogen sotopic measurements of altered igneous rocks, Li et al. (2007, 2014) yielded nitrogen is not sic enrichment factors of -15% to -11‰ for abiotic N<sub>2</sub> reduction at medium- to high- $\iota$  nr erature hydrothermal conditions (>300 °C). The magnitude of kinetic nitrogen isotopic eff.ct could be larger at lower temperatures (Li et al., 2009), but no data are available yet. Usin, the average value of -13‰ (Li et al., 2007, 2014) as the lower limit and a Rayleigh fractionation model (Fig. 4D-F), a ballpark estimate can be made for the fractions of  $N_2$  required to be reduced in order to match the observed  $\delta^{15}N$  value in the studied samples. The results suggest that the fractions of the initial N2 that has been abiotically reduced is 25 - 63% at 2.1 kmbs, 21 - 61% at 2.4 kmbs, and 7 - 54% at 2.9 kmbs, respectively (Fig. 4D). This decreasing trend along depth is self-consistent with the temperature and time framework that 2.1 kmbs has the shortest time for  $N_2$  production but longest time and lowest temperature for abiotic  $N_2$  reduction, whereas the 2.9 kmbs has the longest time for  $N_2$ production but shortest time and highest temperature for abiotic N<sub>2</sub> reduction. Similar extents of abiotic N<sub>2</sub> reduction are also obtained from NR (27 - 70%), FR (35 - 74%), TH (18 - 65%), and

BT (14 - 63%) (Fig. 4 E, F). Future examinations on concentrations and isotope compositions of ammonium in the fluids may help to test this possibility.

It is worth noting that, based on mass balance and isotopic comparison, Silver et al. (2012) also proposed that abiotic  $N_2$  reduction could have occurred in the subsurface fracture fluids in the Kaapvaal Craton. This implies that abiotic  $N_2$  reduction might occur widely in Precambrian cratons.

#### 5.4.2. The role of radiolysis?

Another process that is worth briefly discussing is r. diolysis. Energy released from the decay of radioactive isotopes of K, U, Th in host rocks halo been shown to play an important role in the long-term production of deep subsurface hydrogen (e.g., Lin et al., 2005; Sherwood Lollar et al., 2014), carbon (Sherwood Lollar et al., 2021), and sulfur (Lin et al., 2006; Li et al., 2016) in deep fracture fluids in the Precambrian cratons around the world. An intriguing question is how much this process may contribute on the nitrogen cycle in these deep saline fracture fluids.

Silver et al. (2012) carrie <sup>4</sup> ou laboratory experiments to irradiate  $NH_3/NH_4^+$  in anaerobic solutions and observed production of nitrite and nitrate. Consequently, radiolysis has been proposed to be part of the multiple abiotic and biotic mechanisms to drive the nitrogen cycle in the subsurface fluids in the Kaapvaal Craton (Silver et al., 2012). Radiolytic impact on fixed ammonium in minerals and rocks is poorly examined by far. It is unclear whether radiolysis in the Precambrian cratonic environments facilitate N<sub>2</sub> production. But laboratory experiments on the N<sub>2</sub>-H<sub>2</sub>-H<sub>2</sub>O system (e.g., Etoh et al., 1987; Karasawa et al., 1991) have demonstrated that N<sub>2</sub> can be consumed by radiolysis to form not only  $NH_4^+$  as the dominant product (Karasawa et al., 1991) but also  $NO_3^-$  (Etoh et al., 1987), via overall reactions described in equations (2)-(3).

$$\begin{cases} N_2 \xrightarrow{radiation} N^{\cdot} + N^{\cdot} \\ H_2 O \xrightarrow{radiation} H^{\cdot} + O^{\cdot} \\ \end{cases}$$

$$\begin{cases} N^{\cdot} + 3H^{\cdot} + H^+ \longrightarrow NH_4^+ \\ 2N^{\cdot} + 5O^{\cdot} + 2OH^- \longrightarrow 2NO_2^- + H_2O \end{cases}$$

$$(3)$$

This differs from the mineral catalyzed abiotic  $N_2$  reduction process in equation (1). However, the nitrogen isotope fractionation during radiolytic decomposition of  $N_2$  has not been constrained, although a kinetic isotopic effect likely occurs. Future studies integrating laboratory examination of nitrogen isotope fractionations during radiolysis of the  $N_2$ -H<sub>2</sub>· H<sub>2</sub>C system and the analyses of concentrations and isotope compositions of ammonium and n trate (if there is any) in fracture fluids are necessary to further assess these processes in he c'eep subsurface of Precambrian cratons.

## 5.4.3. Microbial nitrogen recycling?

The samples studied here contain, set of N<sub>2</sub> samples from one of the long-term monitoring boreholes (BH12299 a. 2.4 kmbs) at the KC Observatory collected over nearly 10 years since the completion of the borehole drilling in May 2007. Interestingly, the  $\delta^{15}N_{N2}$  values of this set of samples (Taule 1) display a trend of steady decrease (for >1‰) over time (Fig. 5). Since significant addition of an air component over time can be ruled out based on the <sup>15</sup>N<sup>15</sup>N results (Labidi et al., 2020), this trend suggests that another *in-situ* source of <sup>15</sup>N-depleted N<sub>2</sub> has been progressively added into the original N<sub>2</sub> reservoir in this borehole over the monitoring period. Although the N<sub>2</sub> in the deeper fracture fluids (e.g., 2.9 kmbs) at the KC Observatory is relatively <sup>15</sup>N depleted, it cannot be the source for the 2.4 kmbs fracture fluids because current evidence supports hydrogeologic isolation between these fracture systems (Warr et al., 2018, 2021b). One potential *in-situ* source for a <sup>15</sup>N-depleted N<sub>2</sub> source in the 2.4 kmbs fracture system

is dissolved ammonium. The temperature and pH conditions of the KC fluids favor the preservation of ammonium as the net product from abiotic  $N_2$  reduction (Li et al., 2012). This may therefore provide an ideal <sup>15</sup>N-depleted source for this secondary  $N_2$ .

The abiotic conversion of  $NH_4^+/NH_3$  to N<sub>2</sub> requires either oxic condition and/or relatively high temperature (>500 °C) without catalyst (Li et a., 2009). Even with efficient catalyst (e.g., Fe), the conversion rate is very slow at temperatures < 300 °C (Li et al., 2021d). In addition, no evidence to show an oxic environment in the studied fracture system. Thus, abiotic conversion of NH4<sup>+</sup>/NH3 at the low-temperature environment (24 °C at 2.4 http://www.s) may not contribute detectable N<sub>2</sub> to BH12299 fluid at a decadal time scale. Microbially-driven anaerobic oxidation of ammonium (e.g., Van De Graaf et al., 1995; Byrne et al., 2008) is a more efficient mechanism to convert ammonium to N<sub>2</sub>. Microbial recycling  $c^{c}$  ni<sup>t</sup>rogen has been suggested to occur in subsurface fracture fluids in the Kaapvaal 'ra' on (Silver et al., 2012; Lau et al 2016) and elsewhere in the Canadian Shield (Sheik vt al., 2021), but cannot be explored further for the KC samples due to the lack of biogeochem. A data and isotopic compositions of other nitrogen species (ammonium, nitrite or ni rate, if there is any) in these fracture fluids. It is worth highlighting though that recent cludies using cell counts and culture-based methods have identified low abundance of H<sub>2</sub>-utilizing, alkane-oxidizing sulfate-reducing bacteria in the KC fracture fluids (Lollar et al., 2019; Wilpiszeski et al., 2020). This directly supports the prevailing hypothesis that microbial activities could have been sustained over geological timescale in the long isolated KC fracture fluids based on sulfur isotopic studies (Li et al., 2016). Microbial activities related to methanogenesis and methanotrophy in the 2.4 kmbs KC fracture fluids have been further inferred from the isotopic signatures of CH<sub>4</sub> (Sherwood Lollar et al., 2002; Young et al., 2017, Warr et al., 2021b). In particular, a potential ongoing addition of biogenic  $CH_4$  to the

same fracture fluid system (BH12299) has been suggested based on a temporal decrease in the mass-18 isotopologues of  $CH_4$  over the last decade (Warr et al., 2021b). A speculation is that the KC fracture fluids could have been or is being influenced by microbial activities involving multiple metabolic pathways including  $H_2$  oxidation, sulfate reduction, methanogenesis, anaerobic oxidation of methane, and anaerobic oxidation of ammonium. This hypothesis will need to be tested by future microbial studies with detailed constraints on metabolic pathways and their geochemical fingerprints.

### 6. Conclusions

 $N_2$  in the highly reducing saline fracture waters of the Canadian Shield provides a novel opportunity to look into the (bio)geochemical ni rogen recycling processes in deep subsurface systems that have been long investigated in the context of the deep carbon cycle and subsurface life, but to date with very little characterization and quantification of the deep nitrogen cycle. Here we observed that the  $N_2$  in subsurface fracture waters with residence times from hundreds of million years to billions of years in the Canadian Shield were more enriched in <sup>15</sup>N than the  $N_2$ samples from fracture waters with residence times of hundreds of thousands to tens of millions of years in the Fennoscandian Shield and the Kaapvaal Craton. Detailed isotopic comparison between the Canadian Shield  $N_2$  samples and their potential sources excludes air, dissolved inorganic nitrogen, and organic compounds in host rocks as their sources. Instead, fixed ammonium in igneous host rocks is the most likely source. Modeling of nitrogen devolatilization of igneous rocks supports this interpretation, but also suggests that a second process is required to account for the observed <sup>15</sup>N enrichments in the  $N_2$  samples from the Canadian Shield. Longterm abiotic  $N_2$  reduction in the closed fracture water systems is the most likely process. The

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data in this study imply a common occurrence of abiotic  $N_2$  reduction in the long isolated, highly reducing fracture water systems in the Canadian Shield, and possibly in similar environments on the early Earth and other planets. The accumulation of the ammonium product can not only provide a critical reagent for abiotic synthesis of amino acid (an essential building block for life) toward the origin of life but also supply a necessary nutrient to support potential ammonium assimilating or anaerobic ammonium oxidizing microbes in these environments.

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		$H_2$	He	Ar	$O_2$	CH <sub>4</sub>	$N_2$			$\delta^{15}$
Loca-	Sample ID	(vol	(vol	(vol	(vol	(vol	(vol	N <sub>2</sub> /O <sub>2</sub>	N <sub>2</sub> /	$N_{N2}$
tion	<b>I</b>	(VOI %)	(VOI %)	(VOI %)	(VOI %)	(VOI %)	(VOI %)		Ar	(%_)
		/0)	70)	/0)	/0)	/0)	/0)			(200)
Kidd	10.1.2000-KCL6900-1F	0.33	n.d.	0.23	0.66	75.0	7.93	12.0	34.5	6.8
Creek	10-1-2000-KCL6900-2D	1.95	n.d.	0.29	0.60	73.6	9.32	15.5	32.1	8.0
	10-1-2000-KCL6900-3A	2.47	n.d.	0.34	0.66	72.4	11.3	17.1	33.3	7.7
	10-1-2000-KCL6900-4D	1.32	n.d.	0.35	0.88	70.4	12.6	14.4	36.3	7.0
	10-1-2000-KCL6900-5D	2.03	n.d.	0.39	0.69	70.7	14.0	20.3	35.9	7.3
	10-1-2000-KCL6900-6B	1.40	n.d.	0.33	0.95	75.0	11.9	12.5	36.1	6.4
	12.2.2008-KC7850-12261	3.16	2.45	0.39	0.20	72.1	13.8	69.2	35.5	6.8
	10.5.2007-KC7850-12262	8.37	2.91	0.35	0 48	9.1,	14.0	29.2	40.1	7.5
	22.10.2015-KC7850-12262	2.7	2.00	0.43	1.96	56.7	26.4	13.5	61.4	6.7
	27.8.2007-KC7850-12287A	10.6	2.47	0.34	1.5+	72.1	16.1	10.5	47.4	5.4
	20.6.2008-KC7850-12287A	3.61	2.45	0.55	J.24	70.1	14.4	60.2	40.1	7.4
	12.2.2008-KC7850-12299	6.52	2.15	L.15	0.40	71.9	16.8	42.2	37.5	7.4
	19.6.2008-KC7850-12299	3.32	2.42	<i>J</i> .42	0.14	67.7	15.3	109.6	36.5	7.2
	31.3.2009-KC7850-12299	4.82	2.87	9.40	0.19	64.3	14.8	77.9	37.0	7.4
	12.01.2010-KC7850-12299	4.62		0.40	0.12	71.4	14.9	124.5	37.4	7.5
	21.10.2010-KC7850-12299	3.91	2.02	n.d.	< 0.0	70.3	15.3	>		6.9
	29.2.2012-KC7850-12299	3.19	2.39	n.d.	< 0.0	71.9	14.6	>		7.1
	20.09.2013-KC7850-12299	5.58	2.69	0.21	0.11	70.9	13.5	122.7	64.3	6.4
	02.04.2014-KC7850-12299	. 52	1.60	0.28	0.32	74.6	9.88	30.9	35.3	5.1
	12.07.2016-KC7850-12299 <sup>*</sup>	2 60 °	2.41	0.35	< 0.0	71.3	13.3	>	38.2	6.5
	25.01.2017-KC7850-12299*	+.80	3.70	0.54	0.11	71.6	15.4	140.0	28.5	6.3
	08.2.2012-KC9500-13675	< 0.0	1.63	n.d.	< 0.0	78.7	4.53	>		3.2
	1.3.2012-KC9500-13684	5.30	2.10	n.d.	< 0.0	75.8	6.80	>		6.5
	29.11.2012-КС9500-Вы?	16.6	0.43	0.29	0.06	71.0	10.5	175.0	36.2	5.5
	13.07.2016-KC9500-L יhA	0.70	1.77	0.27	0.27	71.6	10.3	38.3	38.3	4.3
LaRon	24.03.2016-Lx 546 22900-LR-	1.83	5.09	1.33	0.63	66.1	15.2	24.2	11.5	7.4
	24.03.2016-LR64, 0-L2900-LR-	3.63	7.20	0.79	0.15	72.1	8.92	59.5	11.3	6.5
Cop-	CCSM-GH-11-7-2001-1E	54.0	3.46	0.07	0.40	33.1	2.87	7.2	41.0	2.3
Cliff	CCSM-GH-11-7-2001-2E	43.0	3.38	0.23	5.54	14.6	20.0	3.6	87.0	0.6
South	CCSM-GH-11-7-2001-3D	9.94	4.37	0.16	0.57	70.1	5.61	9.8	35.1	4.2
	CCSM-GH-11-7-2001-5E	57.5	2.62	0.07	0.49	23.9	2.74	5.6	39.1	1.6
	CCSM-GH-11-7-2001-6E	51.0	6.42	0.12	0.43	31.7	3.10	7.2	25.8	2.8
	CCSM-GH-11-7-2001-7E	19.7	2.52	0.28	0.49	57.9	5.41	11.0	19.3	2.7
Nickel	29.11.2013-	0.01	32.2	1.51	0.21	15.4	52.6	250.7	34.9	3.5
Rim	05.03.2014-	0.03	29.9	1.50	< 0.0	19.3	48.0	>	32.1	3.5
	05.03.2014-	1.64	27.7	1.51	< 0.0	n.a.	48.8	>	32.4	3.9
	05.03.2014-	2.67	26.1	1.91	< 0.0	24.2	47.3	>	24.8	4.0
	22.10.2014-	0.01	24.1	1.61	< 0.0	24.3	47.7	>	29.6	3.0

Table1. Major components<sup>§</sup> and  $\delta^{15}N_{N2}$  value of gas samples from deep subsurface fracture fluids in the Canadian Shield.

Loca- tion	Sample ID	H <sub>2</sub> (vol %)	He (vol %)	Ar (vol %)	O <sub>2</sub> (vol %)	CH <sub>4</sub> (vol %)	N2 (vol %)	N <sub>2</sub> /O <sub>2</sub>	N <sub>2</sub> / Ar	δ <sup>15</sup> N <sub>N2</sub> (‰)
Fraser	06.03.2014_FML4700_FR4777	< 0.0	16.6	5.24	< 0.0	19.8	65.7	>	12.5	5.0
Birch-	28.5.2007-BT3950L-gas stopper	0.02	1.35	0.22	0.34	62.9	29.2	86.1	133.	8.3
	6-11-2007-BT3900-9167N-BH	<0.0	1.38	0.23	0.35	68.7	30.9	88.3	134.	7.8
	27-3-2008-BT3900-9167N-BT1	0.08	1.33	0.24	0.16	62.9	30.5	190.9	127.	7.9
Thomp	1065750 13.06.06 (3-403-2)	2.75	2.40	0.51	1.92	34.7	46.2	24.1	90.7	8.3
	1065760 14.06.06 (1-401-2)	0.79	2.70	0.42	3.63	36.5	65.5	18.0	156.	7.4
	1163630 13.06.06 (7-399-5)	0.30	2.99	0.28	0.77	36.6	60.7	78.9	217.	8.6
	1065800 13.06.06 (4-405-3)	0.03	2.80	0.28	0.65	4 <sup>5</sup> 5	51.7	79.7	184.	8.7

<sup>§</sup> Major Gas contents of these samples have been reported by Sherwo d J ollar et al., 2006; Li et al. (2016); Telling et al. (2018); Warr et al. (2019). The contents of N<sub>2</sub>, Ar, and  $v_2$  reported here, if slightly different to those in the literature, were re-analyzed results on the same  $g < b v^{(1)}$  used for  $\delta^{15}N_{N2}$  analysis. <sup>\*</sup> Labidi et al. (2020) reported  $\delta^{15}N$  values of 6.6‰ for sample 1? 07.2016-KC7850-12299 and 6.7‰ for

<sup>\*</sup> Labidi et al. (2020) reported  $\delta^{15}$ N values of 6.6‰ for sample 1. 07.2016-KC7850-12299 and 6.7‰ for sample 25.01.2017-KC7850-12299.

5

Location Sample ID		Lithology	Bulk-	Bulk-	Reduced
	-		rock	rock	carbon
	BH12612A (465.30-465.62 m)	Graphite-bearing lens	68.9	7.0	7.0
	BH12612A (470.50-470.96 m)	Graphite-bearing lens	67.6	6.7	6.7
	BH12612A (392.80-393.15 m)	Graphite-bearing lens	98.6	9.3	
	BH12612A (413.38-413.75 m)	Graphite-bearing lens	40.5	8.7	1.3
	BH12299 (369.5 m)	Graphite-bearing lens	54.9	15.6	10.4
	BH12299 (472.4 m)	Graphite-bearing lens	89.8	10.2	0.4
Kidd Creek		70.1	9.6	5.2	
	BH12612A (232.10-232.26 m)	Rhyolite	30.9	7.8	
	BH12612A (243.30-243.07 m)	Rhyolite	2. 7	7.3	
	BH12612A (248.80-249.35 m)	Rhyolite	213	6.0	
	BH12612A (292.70-293.15 m)	Silicified cherty	23.0	10.3	
	BH12612A (353.20-353.38 m)	Silicified cherty	11.9	10.4	
	BH12612A (475.85-476.02 m)	Quartz feldspar	.9.3	6.3	
		Averag	23.7	8.0	
	Creighton Mine BH131106	Meta-gabbro	14.1	2.6	
	Creighton Mine BH131106	Breccia matrix	14.9	2.3	
		Average	14.5	2.4	
	Nickel Rim BH130075	Felsic r, nei ss	12.7	1.3	
Sudbury	Nickel Rim BH170143 (75.87-	Fei. ic norite	13.6	3.4	
	Nickel Rim BH170143	F elsic norite	49.3	-5.6	
	Nickel Rim BH170143	Granodiorite	9.7	2.2	
	Nickel Rim BH170143	Felsic gneiss	12.3	3.1	
	Nickel Rim BH170143	Breccia	10.0	1.8	
		Average	17.9	1.0	
	Thompson mine assorted con	Archean gneiss	30.2	7.0	
Thompson	Thompson mine assort durre	Thompson Formation	50.9	8.1	
1	Thompson mine assorted core	schist	50.2	10.2	
		Average	43.8	8.4	

# Table 2. $\delta^{15}N$ values of rock samples from Kidd Creek, Sudbury, and Thompson

## **Figure captions**

Fig. 1. Location map of sample sites for this study together with the sites with  $\delta^{15}N_{N2}$  values reported in Sherwood Lollar et al. (1993a). The general geology of the Canadian Shield is shown in the inserted panel (revised from Hoffmann, 1989; Li et al., 2016; Warr et al., 2019). BT = Birchtree; TH = Thompson; KC = Kidd Creek; FR = Fraser; NR = Nickel Rim; CCS = Copper Cliff South; LR = LaRonde; VDO = Val D'Or; NT = Norita

Fig. 2. Comparison of  $\delta^{15}$ N values of N<sub>2</sub> with N<sub>2</sub>/O<sub>2</sub> ratio (A) and N<sub>2</sub>/Ar ratio (B, C) for subsurface fracture waters from the Canadian Shield. Error bars are smaller than data \_ymbols. These highly reducing fracture waters produce H<sub>2</sub> and do not contain O<sub>2</sub>, thus the N<sub>2</sub>/O<sub>2</sub> atio can be used as a robust index for air contamination. The vertical line (N<sub>2</sub>/O<sub>2</sub> = 15) in pane. A d vides significantly contaminated samples to the left and less contaminated samples to the right. In contrast, the fracture waters contain various amounts of <sup>40</sup>Ar (and N<sub>2</sub>/Ar ratio) from the decay of  ${}^{0}$ K in host rocks. Thus N<sub>2</sub>/Ar ratios cannot be used to quantify the air component. All samples with known N<sub>2</sub>/Ar ratios  $\delta^{15}$ N values are compiled in Panel B. Whereas only samples with known N<sub>2</sub>/O<sub>2</sub> v duce of >15 are plotted in panel C. Historical samples marked by "(M)" are unpublished the is d ata from Montgomery (1994); samples marked by "(BSL)" are from Sherwood Lollar et al. (1993a). Poth are shown as filled grey symbols.

Fig. 3. Comparison of  $\delta^{15}$ N values of  $N_2$  in subsurface fracture waters from the Kaapvaal Craton (A), the Fennoscandian Shield (B), and the Caudian Shield (C). The Canadian Shield samples are consistently more <sup>15</sup>N enriched than those from the other two cratons. See text for discussion.

Fig. 4. Comparison of  $\Delta^{-N}_{N2-rock}$  between observed values and theoretical values of metamorphic devolatilization calculated  $^{L}$  y Rayleigh fractionation modeling (A-C), and increase in  $\delta^{15}N$  of  $N_2$  (expressed as  $\Delta^{15}N_{\text{Remianing N2-initial N2}}$ ) after abiotic nitrogen reduction (D-F). The f in both panels denote the fraction of remaining nitrogen in the reactant. See text for discussion.

Fig. 5. Diagram showing steady decrease in the  $\delta^{15}$ N value of N<sub>2</sub> from one single borehole at 2.4 km below surface of the Kidd Creek mine over a 10-year period.

#### **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:





Figure 2



Figure 3



 $\Delta^{15}\mathsf{N}_{\mathsf{N}_{2}\text{-rock}} (\%_{0})$ 



Figure 5