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

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Nitrogen cycle, Canadian Shield, deep subsurface, abiotic nitrogen reduction, microbial ammonium oxidation

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 $\delta^{15}\text{N}_{\text{N}_2}$ 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 $\delta^{15}\text{N}_{\text{N}_2}$ 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.

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, $\delta^{18}\text{O}$ and $\delta^2\text{H}$) of these fluids indicate 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 therein). Most of these deep subsurface fracture water systems have been hydrogeologically isolated over geological time scales, e.g., up to hundreds of million years to billions of years in the Canadian Shield (Holland et al., 2013; Warr et al., 2018), up to tens to hundreds 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; Lippmann et al., 2003). Closed-system water-rock interactions over these extended time periods has progressively produced chemicals (e.g., H_2 , 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 can 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 of CH₄ 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 CH₄ and N₂ (Young et al., 2017; Labidi et al., 2020; Warr et al., 2021b). These studies have reported consistent observations from both the Canadian Shield and the Kaapvaal Craton suggesting that CH₄ in the shallower fracture fluids is dominantly microbial, whereas CH₄ in the deeper, more saline 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_2 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_2 collected from fracture fluids in the Fennoscandian Shield and the Canadian Shield. Thirteen N_2 samples from the Fennoscandian Shield show a $\delta^{15}N$ range from 0.2‰ to 5.1‰ (with one high value of 10.0‰), whereas four N_2 samples from the Canadian Shield mostly show higher $\delta^{15}N$ values (Thompson: 1.4‰; Matagami: 8.6‰; Norita: 11.8‰; Val d'Or: 9.1‰). Labidi et al. (2020) also reported two $\delta^{15}N$ data from Sudbury (2.6‰ and 2.8‰) and two $\delta^{15}N$ data from the KC Observatory (6.6‰ and 6.8‰). Dissolved N_2 in subsurface fracture fluids from the Witwatersrand Basin in the Kaapvaal Craton was studied by Silver et al. (2012). After correction for air contamination using the N_2/O_2 ratio as an index, a $\delta^{15}N_{N_2}$ range from -1.3‰ to 5.8‰ was yielded and considered to result from complicated geochemical and, more importantly, biological recycling processes (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_2 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., 2018). To date, these fluids show the presence of chemolithotrophic organisms (sulfate-reducing organisms 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 isotopic signatures of these fluids (including dissolved components) may represent the closest abiotic 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 assess 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 $\delta^{15}\text{N}_{\text{N}_2}$ 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 Cliff 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, Manitoba (Fig. 1).

The KC Observatory in Ontario is geologically 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 (mainly rhyolites) rocks with graphite-bearing lenses formed in a rifting sub-proximal seafloor 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 – calc-alkaline 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 2.64 Ga granitic rocks (Meldrum et al., 1997) and Archean meta-volcanic and metasedimentary rocks that were metamorphosed to upper greenschist – lower amphibolite facies at 2.69 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 abundant sulfide mineralization (Lightfoot and Farrow, 2002) related to the ~1.85 Ga bolide impact. Post-impact thermal influences by multiple orogenies, such as the Yavapai-Mazatzal (1.7-1.6 Ga), the Chieflakian-Pinwarian (1.5-1.4 Ga) and the Grenville (1.2-1.0 Ga), have been found at various degrees across the Sudbury region, e.g., mid- to upper-greenschist 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 described by Ward et al. (2004) and Holland et al. (2013). In brief, a packer was used to seal the borehole and funnel the water and gas flow from the borehole through a sterilized Tygon tube into a bucket. After a period of flushing to ensure representative sampling, gases were introduced 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 at the top of the beaker into 160 ml borosilicate vials with blue butyl stoppers which had been sterilized, prefixed with 50 µL saturated HgCl₂ 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 N₂ were analyzed at University of Toronto. Gas concentrations were generally measured within days after sample collection to avoid possible shifts in gas (e.g., H₂ and O₂) 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 H₂ and O₂ 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 (μ TCD) for H₂, He, N₂, CO₂, O₂, Ar and a flame ionization detector for alkanes following the published protocols (e.g., Ward et al., 2004). NH₃ is not specially examined here because it requires high pH condition to drive NH₃ 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 NH₃ mostly concentrates in fluids and barely occurs in the gas phases (Li et al., 2012). The 2 σ 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 aliquot of a gas sample was taken by gas-tight syringe from a sample bottle and injected 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 N₂ from other gas components such as H₂ and O₂. CO₂ 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%). A time window was set to allow N₂ but no other interference gases to be carried into a Finnigan 252 isotope ratio mass spectrometer for isotopic measurements. The isotopic ratios are reported using the δ notation ($\delta^{15}\text{N} = (^{15}\text{N}/^{14}\text{N})_{\text{sample}}/(^{15}\text{N}/^{14}\text{N})_{\text{standard}} - 1$), in which “standard” is atmospheric N₂. 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 σ 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 minerals. The sample tube was then cracked under high vacuum to release N₂, which was further cryogenically purified, quantified by a capacitance manometer, and carried by an ultrahigh-purity helium gas to a Thermo Finnigan MAT 253 for nitrogen isotopic measurements. The $\delta^{15}\text{N}$ values are reported relative to the atmospheric N₂. Repeat analyses of two standards (Low Organic Content Soil and High Organic Content Soil) from Elemental Microanalysis Ltd gave 2 σ analytical errors better than 0.2‰ (Li et al., 2021a).

4. Results

4.1. Gas concentrations and $\delta^{15}\text{N}_{\text{N}_2}$ values

The major gas concentrations and $\delta^{15}\text{N}$ values of N₂ are reported in Table 1. The results are briefly summarized below.

Twenty-five gas samples from KC are dominated by CH₄ (64 – 83 vol%) and other light n-alkanes (e.g., ethane, propane, butane; in total < 9 vol%). N₂ is the second most abundant gas component with concentrations varying from 4.5 vol% to 16.9 vol% and $\delta^{15}\text{N}$ values from 3.2‰ to 8.0‰ (Table 1). These isotopic values fall in the $\delta^{15}\text{N}$ range of 2.8‰ – 8.8‰ from a limited

set of KC samples in Montgomery (1994) and Labidi et al. (2020). H₂ 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 CH₄ (66 – 72 vol%) and N₂ (9 – 15 vol%) with $\delta^{15}\text{N}$ values of 6.5‰ and 7.4‰, respectively. Both samples contain H₂ (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 Basin) are characterized by extremely high H₂ concentrations (10 – 58 vol%). CH₄ is the other major gas component in these samples (14 – 70 vol%). N₂ concentrations are generally low in the samples studied at this site (Table 1). The $\delta^{15}\text{N}_{\text{N}_2}$ values (0.6‰ to 4.2‰) of these samples are also much lower than those of the KC and LR samples. It is worth noting that variable amounts of O₂ (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 Montgomery (1994), much higher N₂ concentrations of up to 65 vol% and $\delta^{15}\text{N}$ values up to 17.5‰ were reported from CCS. The other samples from the Sudbury Basin show significantly higher N₂ concentrations. The five NR gas samples are dominated by N₂ (47 – 53 vol%), He (24 – 32 vol%) and CH₄ (15 – 24 vol%). H₂ occurs all samples in varying amounts (0.01 – 2.7 vol%). The $\delta^{15}\text{N}_{\text{N}_2}$ values display a small range from 3.5‰ to 5.0‰. The only gas sample available from FR is also dominated by N₂ (66 vol%), He (17 vol%) and CH₄ (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 $\delta^{15}\text{N}_{\text{N}_2}$ 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 CH₄ and N₂. The CH₄ concentrations (63 – 69 vol%) are higher than N₂ concentrations (29 – 31 vol%) in the BT samples, whereas the N₂ concentrations (46 – 66 vol%) are higher than the CH₄ concentrations (35 – 48 vol%) in the TH samples. Despite the difference in N₂ concentration, the $\delta^{15}\text{N}_{\text{N}_2}$ 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 H₂, 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 H₂ 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 *in-situ* O₂ gas (Holland et al., 2013; Warr et al., 2018, 2021a). Therefore, any O₂ 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, $\delta^{15}\text{N}_{\text{N}_2}$ values are compared with N₂/O₂ and N₂/Ar concentration ratios (Fig. 2). Fig. 2A illustrates a decreasing trend of $\delta^{15}\text{N}_{\text{N}_2}$ values following the decrease in N₂/O₂ 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 $\delta^{15}\text{N}_{\text{N}_2}$ values can be observed for samples with N₂/O₂ ratios > 15 at each site. The $\delta^{15}\text{N}_{\text{N}_2}$ values of samples with N₂/O₂ < 15 are more or less altered by air contamination.

Unlike O₂, which can be readily identified as a result of air contamination in these highly reducing fluids, ⁴⁰Ar (the dominant isotope of Ar) can be produced by subsurface processes and hence cannot be used to evaluate air contamination (Fig. 2B). ⁴⁰Ar, a product of the radioactive

decay of ^{40}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_2 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_2/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., $\text{N}_2/\text{O}_2 > 15$) on Fig. 2C illustrates that the N_2/Ar ratios increase in order from LR, FR, NR, KC, to BT and TH. Therefore, without knowing the N_2/Ar values of uncontaminated gases, N_2/Ar ratios alone cannot be used to estimate the fractions of air components in gas samples from Precambrian cratons.

Accordingly, the discussion below on the $\delta^{15}\text{N}_{\text{N}_2}$ values of the Canadian Shield samples will focus only on those with $\text{N}_2/\text{O}_2 > 15$.

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

The nitrogen concentrations and $\delta^{15}\text{N}$ values of rock samples are listed in Table 2.

Six silicate host rock samples from KC, including three rhyolites, two silicified cherty breccia and one quartz feldspar porphyry, show a $\delta^{15}\text{N}$ range from 6.0‰ to 10.4‰. Six samples of the graphite-bearing lenses from KC give a $\delta^{15}\text{N}$ range from 6.7‰ to 15.6‰ for bulk-rock nitrogen, but a lower $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ range from 1.3‰ to 3.4‰ except one felsic norite sample with a $\delta^{15}\text{N}$ value of -5.6‰.

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

5. Discussion

5.1. $\delta^{15}\text{N}_{\text{N}_2}$ variability across sites in the Canadian Shield

After discarding all the samples with $\text{N}_2/\text{O}_2 < 15$, the $\delta^{15}\text{N}_{\text{N}_2}$ distribution (Fig. 2C) shows a general trend with the lowest values in NR and FR, and steadily 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 from a specific depth in each of the sites (except KC). A larger dataset from multiple depths at KC give much larger $\delta^{15}\text{N}_{\text{N}_2}$ variation than those of the other sites (Fig. 2C; see Section 5.4 for discussion). Two samples from different depths at CCS also show large $\delta^{15}\text{N}_{\text{N}_2}$ variation (Montgomery, 1994; Fig. 2A). Therefore, more data from each site are needed in future studies to examine the inter-site $\delta^{15}\text{N}_{\text{N}_2}$ variability and its controlling factors in the Canadian Shield.

5.2. Comparison with the Fennoscandian Shield and the Kaapvaal Craton

The $\delta^{15}\text{N}$ values of N_2 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 $\delta^{15}\text{N}_{\text{N}_2}$ 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 $\delta^{15}\text{N}_{\text{N}_2}$ 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 ^{14}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 from on (or close to) the global meteoric water line (GMWL) to above the GMWL (Lippmann et al., 2003; Ward et al., 2004; Lin et al., 2006; Onstott et al., 2006; Warr et al., 2021a). Their $\delta^{15}\text{N}_{\text{N}_2}$ values fall in the range of -1.3‰ to 5.8‰ (Fig. 3B). The $\delta^{15}\text{N}_{\text{N}_2}$ values do not correlate with either the residence times or the magnitude of isotopic deviation above the GMWL, indicating the major control on the $\delta^{15}\text{N}_{\text{N}_2}$ values of the samples in the Kaapvaal Craton may not be geological processes (e.g., fluid-rock interaction) but biological processes.

In contrast, the Canadian Shield samples show consistently higher $\delta^{15}\text{N}_{\text{N}_2}$ values (Fig. 3C). A total of thirty-five samples studied here cluster in a $\delta^{15}\text{N}_{\text{N}_2}$ range of 3.0‰ to 8.0‰ with a peak at the bin of $7\text{--}8\text{‰}$ (Fig. 3C), while three historical samples from Montgomery (1994) and Sherwood Lollar (1993a) give more variable $\delta^{15}\text{N}_{\text{N}_2}$ values of 1.4‰ , 1.5‰ and 17.5‰ , respectively (Fig. 2A). The $\delta^{15}\text{N}_{\text{N}_2}$ 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_2 in the Canadian Shield

Several sources could potentially contribute to the N₂ in the terrestrial subsurface fracture water systems, such as ancient atmospheric N₂, 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 typical N₂ 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 N₂ can be excluded as the main source. In addition, a recent study discovered extreme ¹⁵N¹⁵N enrichment of atmospheric N₂ (Yeung et al., 2017). Assuming the ancient atmospheric N₂ had comparable ¹⁵N¹⁵N enrichment, and little re-ordering of the internal bonding of N₂ molecules in these low-temperature fracture systems, a ¹⁵N¹⁵N enrichment would be expected if significant amount of ancient atmospheric N₂ contributed to the fluids. However, Labidi et al. (2020) found no ¹⁵N¹⁵N enrichment in the KC samples. This suggests that the amounts of atmospheric N₂, from both ancient air and modern air contamination, are relatively small in the total N₂ 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, N₂ 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 NH₃-NH₄⁺ 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 NH₃/NH₄⁺ to other nitrogen species (e.g., N₂ in this case). These

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 N₂ in basinal environments. However, in the Canadian Shield, host rocks are dominated by crystalline 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 thousands of ppm; e.g., Bebout and Fogel, 1992; Busigny et al., 2003; Sadofsky and Bebout, 2004; Li and Bebout, 2005). Therefore, the graphite-bearing lenses can less likely account for 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 $\delta^{13}\text{C}$ and $\delta^2\text{H}$ patterns of n-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

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 $\delta^{15}\text{N}$ 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_2 in the subsurface fracture waters.

To devolatilize the ammonium fixed in the igneous host rocks, 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 minerals and rocks could have easily taken place under the peak (and retrograde) metamorphic conditions in the study sites, e.g., 400 °C at KC, 700 °C at TH, and variable temperatures (depending on the distance to the crater; Abramov and Kring, 2004) during the impact event at Sudbury. At crustal conditions, high temperatures facilitate N_2 as the devolatilization product (e.g., Bebout and Fogel, 1992; Li et al., 2009). The lower temperature limit for N_2 devolatilization from minerals and rocks is however unconstrained. Even taking the smectite-illite transition temperature of 60 °C (Freed and Peacor, 1989) as the lower limit, it 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_2 was mostly likely produced during earlier time periods. N_2 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 N₂ in the fluids, which can be easily satisfied.

5.4. Possible N recycling processes in subsurface fracture fluids

5.4.1. Abiotic N₂ reduction

Based on above discussions, the N₂ in the deep subsurface fracture fluids in the Canadian Shield most likely originated by devolatilization of fixed ammonium in their silicate host rocks. Nitrogen devolatilization from rocks is associated with an isotopic effect with preferential uptake of ¹⁴N by N₂ and preferential retention of ¹⁵N in host rock (e.g., Bebout and Fogel, 1992; Haendel et al., 1986; Li et al., 2021b, c). The magnitude of ¹⁵N depletion in the N₂ product is dependent on two factors, i.e., the temperature-dependent isotope fractionation factor and the fraction of ammonium in rock that is converted into N₂. The nitrogen isotope fractionation factors between N₂ 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 200 °C, −4.1‰ at 400 °C, −2.3‰ at 700 °C and −1.5‰ at 1000 °C. Based on these fractionation factors, the theoretical δ¹⁵N differences between N₂ product and remaining ammonium in host 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 δ¹⁵N values between N₂ and host rocks yield Δ¹⁵N_{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 N₂ devolatilization at their peak metamorphic conditions (Fig. 4A-C). Any N₂ 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 $\delta^{15}\text{N}$ 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_2 production via devolatilization of ammonium in host rocks, the extents of observed isotopic discrepancy between N_2 and host rocks require an additional process to explain the ^{15}N enrichments in N_2 .

Diffusive loss of N_2 and abiotic N_2 reduction are two known processes that can induce ^{15}N enrichments in remaining N_2 . Extensive studies of the noble gas concentrations (in the KC system in particular) have demonstrated that diffusion cannot 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 artifact 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 less likely to significantly impact the $\delta^{15}\text{N}_{\text{N}_2}$. Rather than diffusion, abiotic N_2 reduction may play an important role. Following the cooling of the fluids, N_2 input from metamorphic devolatilization diminished to negligible level. Meanwhile, the nonstop interaction between 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 fluids, 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 N₂ reduction in a geological setting generally refers to the mineral catalyzed reduction of N₂ to produced NH₃ or NH₄⁺ in fluids, via reactions such as equation (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 22 °C (Smirnov et al., 2008). Abiotic N₂ reduction generally produces a kinetic nitrogen isotopic effect due to the difficulty in breaking the strong N≡N bond of N₂. Based on the nitrogen isotopic measurements of altered igneous rocks, Li et al. (2007, 2014) yielded nitrogen isotopic enrichment factors of –15‰ to –11‰ for abiotic N₂ reduction at medium- to high-temperature hydrothermal conditions (>300 °C). The magnitude of kinetic nitrogen isotopic effect could be larger at lower temperatures (Li et al., 2009), but no data are available yet. Using 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 N₂ required to be reduced in order to match the observed δ¹⁵N 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 N₂ production but longest time and lowest temperature for abiotic N₂ reduction, whereas the 2.9 kmbs has the longest time for N₂ production but shortest time and highest temperature for abiotic N₂ reduction. Similar extents of abiotic N₂ 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 N₂ reduction could have occurred in the subsurface fracture fluids in the Kaapvaal Craton. This implies that abiotic N₂ reduction might occur widely in Precambrian cratons.

5.4.2. The role of radiolysis?

Another process that is worth briefly discussing is radiolysis. Energy released from the decay of radioactive isotopes of K, U, Th in host rocks has 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 to the nitrogen cycle in these deep saline fracture fluids.

Silver et al. (2012) carried out laboratory experiments to irradiate NH₃/NH₄⁺ 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 N₂ production. But laboratory experiments on the N₂-H₂-H₂O system (e.g., Etoh et al., 1987; Karasawa et al., 1991) have demonstrated that N₂ can be consumed by radiolysis to form not only NH₄⁺ as the dominant product (Karasawa et al., 1991) but also NO₃⁻ (Etoh et al., 1987), via overall reactions described in equations (2)-(3).

This differs from the mineral catalyzed abiotic N₂ reduction process in equation (1). However, the nitrogen isotope fractionation during radiolytic decomposition of N₂ has not been constrained, although a kinetic isotopic effect likely occurs. Future studies integrating laboratory examination of nitrogen isotope fractionations during radiolysis of the N₂-H₂-H₂O system and the analyses of concentrations and isotope compositions of ammonium and nitrate (if there is any) in fracture fluids are necessary to further assess these processes in the deep subsurface of Precambrian cratons.

5.4.3. Microbial nitrogen recycling?

The samples studied here contain a set of N₂ samples from one of the long-term monitoring boreholes (BH12299 at 2.4 kmbs) at the KC Observatory collected over nearly 10 years since the completion of the borehole drilling in May 2007. Interestingly, the δ¹⁵N_{N₂} values of this set of samples (Table 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 ¹⁵N/¹⁵N results (Labidi et al., 2020), this trend suggests that another *in-situ* source of ¹⁵N-depleted N₂ has been progressively added into the original N₂ reservoir in this borehole over the monitoring period. Although the N₂ in the deeper fracture fluids (e.g., 2.9 kmbs) at the KC Observatory is relatively ¹⁵N 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 ¹⁵N-depleted N₂ 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 ^{15}N -depleted source for this secondary N_2 .

The abiotic conversion of NH_4^+/NH_3 to N_2 requires either oxic condition and/or relatively high temperature ($>500^\circ C$) without catalyst (Li et al., 2009). Even with efficient catalyst (e.g., Fe), the conversion rate is very slow at temperatures $< 300^\circ C$ (Li et al., 2021d). In addition, no evidence to show an oxic environment in the studied fracture systems. Thus, abiotic conversion of NH_4^+/NH_3 at the low-temperature environment ($24^\circ C$ at 2.4 kmbs) may not contribute detectable N_2 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_2 . Microbial recycling of nitrogen has been suggested to occur in subsurface fracture fluids in the Kaapvaal Craton (Silver et al., 2012; Lau et al 2016) and elsewhere in the Canadian Shield (Sheik et al., 2021), but cannot be explored further for the KC samples due to the lack of biogeochemical data and isotopic compositions of other nitrogen species (ammonium, nitrite or nitrate, if there is any) in these fracture fluids. It is worth highlighting though that recent studies using cell counts and culture-based methods have identified low abundance of H_2 -utilizing, alkane-oxidizing sulfate-reducing bacteria in the KC fracture fluids (Lollar et al., 2019; Wilpiseski 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_4 (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 CH₄ 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 H₂ 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

N₂ in the highly reducing saline fracture waters of the Canadian Shield provides a novel opportunity to look into the (bio)geochemical nitrogen 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 N₂ in subsurface fracture waters with residence times from hundreds of million years to billions of years in the Canadian Shield were more enriched in ¹⁵N than the N₂ 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 N₂ 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 ¹⁵N enrichments in the N₂ samples from the Canadian Shield. Long-term abiotic N₂ reduction in the closed fracture water systems is the most likely process. The

data in this study imply a common occurrence of abiotic N₂ 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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Figure captions

Fig. 1. Location map of sample sites for this study together with the sites with $\delta^{15}\text{N}_{\text{N}_2}$ 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 $\delta^{15}\text{N}$ values of N_2 with N_2/O_2 ratio (A) and N_2/Ar ratio (B, C) for subsurface fracture waters from the Canadian Shield. Error bars are smaller than data symbols. These highly reducing fracture waters produce H_2 and do not contain O_2 , thus the N_2/O_2 ratio can be used as a robust index for air contamination. The vertical line ($\text{N}_2/\text{O}_2 = 15$) in panel A divides significantly contaminated samples to the left and less contaminated samples to the right. In contrast, the fracture waters contain various amounts of ^{40}Ar (and N_2/Ar ratio) from the decay of ^{40}K in host rocks. Thus N_2/Ar ratios cannot be used to quantify the air component. All samples with known N_2/Ar ratios $\delta^{15}\text{N}$ values are compiled in Panel B. Whereas only samples with known N_2/O_2 values of >15 are plotted in panel C. Historical samples marked by “(M)” are unpublished thesis data from Montgomery (1994); samples marked by “(BSL)” are from Sherwood Lollar et al. (1993a). Both are shown as filled grey symbols.

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

Fig. 4. Comparison of $\Delta^{15}\text{N}_{\text{N}_2\text{-rock}}$ between observed values and theoretical values of metamorphic devolatilization calculated by Rayleigh fractionation modeling (A-C), and increase in $\delta^{15}\text{N}$ of N_2 (expressed as $\Delta^{15}\text{N}_{\text{Remaining N}_2\text{-initial N}_2}$) 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 $\delta^{15}\text{N}$ value of N_2 from one single borehole at 2.4 km below surface of the Kidd Creek mine over a 10-year period.

Figure 1

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Figure 2

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Figure 3

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Figure 5

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Table1. Major components^s and $\delta^{15}\text{N}_{\text{N}_2}$ value of gas samples from deep subsurface fracture fluids in the Canadian Shield.

Location	Sample ID	H ₂ (vol%)	He (vol%)	Ar (vol%)	O ₂ (vol%)	CH ₄ (vol%)	N ₂ (vol%)	N ₂ /O ₂	N ₂ /Ar	$\delta^{15}\text{N}_{\text{N}_2}$ (‰)
Kidd Creek	10.1.2000-KCL6900-1F	0.33	n.d.	0.23	0.66	75.05	7.93	12.0	34.5	6.8
	10-1-2000-KCL6900-2D	1.95	n.d.	0.29	0.60	73.60	9.32	15.5	32.1	8.0
	10-1-2000-KCL6900-3A	2.47	n.d.	0.34	0.66	72.48	11.31	17.1	33.3	7.7
	10-1-2000-KCL6900-4D	1.32	n.d.	0.35	0.88	70.48	12.69	14.4	36.3	7.0
	10-1-2000-KCL6900-5D	2.03	n.d.	0.39	0.69	70.70	14.01	20.3	35.9	7.3
	10-1-2000-KCL6900-6B	1.40	n.d.	0.33	0.95	75.08	11.90	12.5	36.1	6.4
	12.2.2008-KC7850-12261	3.16	2.45	0.39	0.20	72.15	13.84	69.2	35.5	6.8
	10.5.2007-KC7850-12262	8.37	2.91	0.35	0.48	69.10	14.03	29.2	40.1	7.5
	22.10.2015-KC7850-12262	2.7	2.00	0.43	1.96	56.70	26.40	13.5	61.4	6.7
	27.8.2007-KC7850-12287A	10.67	2.47	0.34	1.54	72.17	16.10	10.5	47.4	5.4
	20.6.2008-KC7850-12287A	3.61	2.45	0.36	0.24	70.10	14.45	60.2	40.1	7.4
	12.2.2008-KC7850-12299	6.52	2.15	0.45	0.40	71.98	16.87	42.2	37.5	7.4
	19.6.2008-KC7850-12299	3.32	2.42	0.42	0.14	67.70	15.35	109.6	36.5	7.2
	31.3.2009-KC7850-12299	4.82	2.87	0.40	0.19	64.37	14.81	77.9	37.0	7.4
	12.01.2010-KC7850-12299	4.62	2.54	0.40	0.12	71.49	14.94	124.5	37.4	7.5
	21.10.2010-KC7850-12299	3.97	2.62	n.d.	<0.05	70.32	15.32	> 306.4		6.9
	29.2.2012-KC7850-12299	3.19	2.39	n.d.	<0.01	71.92	14.60	> 1460.0		7.1
	20.09.2013-KC7850-12299	5.58	2.69	0.21	0.11	70.98	13.50	122.7	64.3	6.4
	02.04.2014-KC7850-12299	2.52	1.60	0.28	0.32	74.6	9.88	30.9	35.3	5.1
	12.07.2016-KC7850-12299*	3.60	2.41	0.35	<0.01	71.3	13.36	> 1336.0	38.2	6.5
	25.01.2017-KC7850-12299*	4.80	3.70	0.54	0.11	71.6	15.40	140.0	28.5	6.3
	08.2.2012-KC9500-13675	<0.01	1.63	n.d.	<0.01	78.70	4.53	> 453.0		3.2
	1.3.2012-KC9500-13684	5.30	2.10	n.d.	<0.01	75.83	6.80	> 680.0		6.5
	29.11.2012-KC9500-BH2	16.6	0.43	0.29	0.06	71.0	10.50	175.0	36.2	5.5
	13.07.2016-KC9500-bubA	0.70	1.77	0.27	0.27	71.6	10.34	38.3	38.3	4.3
LaRonde	24.03.2016-LR6480-L2900-LR-290-	1.83	5.09	1.33	0.63	66.11	15.25	24.2	11.5	7.4
	24.03.2016-LR6480-L2900-LR-290-	3.63	7.20	0.79	0.15	72.10	8.92	59.5	11.3	6.5

Location	Sample ID	H ₂ (vol%)	He (vol%)	Ar (vol%)	O ₂ (vol%)	CH ₄ (vol%)	N ₂ (vol%)	N ₂ /O ₂	N ₂ /Ar	$\delta^{15}\text{N}_{\text{N}_2}$ (‰)
Copper Cliff South	CCSM-GH-11-7-2001-1E	54.00	3.46	0.07	0.40	33.15	2.87	7.2	41.0	2.3
	CCSM-GH-11-7-2001-2E	43.00	3.38	0.23	5.54	14.68	20.02	3.6	87.0	0.6
	CCSM-GH-11-7-2001-3D	9.94	4.37	0.16	0.57	70.19	5.61	9.8	35.1	4.2
	CCSM-GH-11-7-2001-5E	57.59	2.62	0.07	0.49	23.96	2.74	5.6	39.1	1.6
	CCSM-GH-11-7-2001-6E	51.00	6.42	0.12	0.43	31.79	3.10	7.2	25.8	2.8
	CCSM-GH-11-7-2001-7E	19.7	2.52	0.28	0.49	57.97	5.41	11.0	19.3	2.7
Nickel Rim	29.11.2013-NR1730m_NR170128	0.01	32.23	1.51	0.21	15.40	52.65	250.7	34.9	3.5
	05.03.2014-NR1730m_NR170128	0.03	29.90	1.50	<0.01	19.38	48.09	> 4809.0	32.1	3.5
	05.03.2014-NR1730m_NR170182	1.64	27.73	1.51	<0.01	n.a.	48.87	> 4887.0	32.4	3.9
	05.03.2014-NR1730m_NR170183	2.67	26.19	1.91	<0.01	24.29	47.35	> 4735.0	24.8	4.0
	22.10.2014-NR1730m_NR170128	0.01	24.12	1.61	<0.01	24.34	47.73	> 4773.0	29.6	3.0
Fraser	06.03.2014_FML4700_FR47774	<0.01	16.68	5.24	<0.01	19.82	65.76	> 6576.0	12.5	5.0
Birchtree	28.5.2007-BT3950L-gas stopper BH	0.02	1.35	0.22	0.34	62.9	29.26	86.1	133.0	8.3
	6-11-2007-BT3900-9167N-BH (Floor#2)	<0.005	1.38	0.23	0.35	68.7	30.92	88.3	134.4	7.8
	27-3-2008-BT3900-9167N-BT1	0.08	1.33	0.24	0.16	62.9	30.54	190.9	127.3	7.9
Thompson	1065750 13.06.06 (3-403-2)	2.75	2.40	0.51	1.92	34.7	46.26	24.1	90.7	8.3
	1065760 14.06.06 (1-401-2)	0.79	2.70	0.42	3.63	36.5	65.51	18.0	156.0	7.4
	1163630 13.06.06 (7-399-5)	0.30	2.99	0.28	0.77	36.6	60.77	78.9	217.0	8.6
	1065800 13.06.06 (4-405-3)	0.03	2.80	0.28	0.65	45.5	51.78	79.7	184.9	8.7

[§] Major Gas contents of these samples have been reported by Sherwood Lollar et al., 2006; Li et al. (2016); Telling et al. (2018); Warr et al. (2019). The contents of N₂, Ar, and O₂ reported here, if slightly different to those in the literature, were re-analyzed results on the same gas bottle used for $\delta^{15}\text{N}_{\text{N}_2}$ analysis.

* Labidi et al. (2020) reported $\delta^{15}\text{N}$ values of 6.6‰ for sample 12.07.2016-KC7850-12299 and 6.7‰ for sample 25.01.2017-KC7850-12299.

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

Location	Sample ID	Lithology	Bulk-rock N (ppm)	Bulk-rock $\delta^{15}\text{N}$ (‰)	Reduced carbon component $\delta^{15}\text{N}$ (‰)
Kidd Creek	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
	Average		70.1	9.6	5.2
	BH12612A (232.10-232.26 m)	Rhyolite	30.9	7.8	
	BH12612A (243.30-243.07 m)	Rhyolite	22.7	7.3	
	BH12612A (248.80-249.35 m)	Rhyolite	34.3	6.0	
	BH12612A (292.70-293.15 m)	Silicified cherty breccia	23.0	10.3	
	BH12612A (353.20-353.38 m)	Silicified cherty breccia	11.9	10.4	
	BH12612A (475.85-476.02 m)	Quartz feldspar porphyry	19.3	6.3	
	Average		23.7	8.0	
	Creighton Mine BH131106 (395.50-396.60 m)	Meta-gabbro	14.1	2.6	
Sudbury	Creighton Mine BH131106 (395.50-396.60 m)	Breccia matrix	14.9	2.3	
	Average		14.5	2.4	
	Nickel Rim BH130075 (319.96-320.14m)	Felsic gneiss	12.7	1.3	
	Nickel Rim BH170143 (75.87-76.07m)	Felsic norite	13.6	3.4	
	Nickel Rim BH170143 (109.98-110.16 m)	Felsic norite	49.3	-5.6	
	Nickel Rim BH170143 (178.00-178.20 m)	Granodiorite	9.7	2.2	
	Nickel Rim BH170143 (283.91-284.04 m)	Felsic gneiss	12.3	3.1	
	Nickel Rim BH170143 (349.90-364.11)	Breccia	10.0	1.8	
	Average		17.9	1.0	
	Thompson mine assorted core	Archean gneiss	30.2	7.0	
	Thompson mine assorted core	Thompson Formation skarn	50.9	8.1	
Thompson	Thompson mine assorted core	schist	50.2	10.2	
Average			43.8	8.4	