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Oliver Warr, Barbara Sherwood Lollar, Jonathan Fellowes, Chelsea N. Sutcliffe, Jill M. McDermott, Greg Holland, Jennifer C. Mabry, Christopher J. Ballentine

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**Tracing ancient hydrogeological fracture network age and compartmentalisation using
noble gases**

Authors: ^{1,2}Oliver Warr (*corresponding author*), ²Barbara Sherwood Lollar, ³Jonathan Fellowes,
²Chelsea N. Sutcliffe, ²Jill M. McDermott, ³Greg Holland, ¹Jennifer C. Mabry & ¹Christopher J.
Ballentine

¹ Department of Earth Sciences, University of Oxford, South Parks Road, Oxford, OX1 3AN,
United Kingdom. Email: oliver.warr@utoronto.ca, phone: +1 416 978 3022

² Department of Earth Sciences, University of Toronto, Toronto, Ontario, Canada.

³ School of Earth, Atmospheric and Environmental Sciences, Williamson Building,
University of Manchester, Manchester, M13 9PL, United Kingdom.

Abstract

We show that fluid volumes residing within the Precambrian crystalline basement account for ca 30 % of the total groundwater inventory of the Earth (> 30 million km^3). The residence times and scientific importance of this groundwater are only now receiving attention with ancient fracture fluids identified in Canada and South Africa showing: 1. microbial life which has existed in isolation for millions of years; 2. significant hydrogen and hydrocarbon production via water-rock reactions; and 3. preserving noble gas components from the early atmosphere. Noble gas (He, Ne, Ar, Kr, Xe) abundance and isotopic compositions provide the primary evidence for fluid mean residence time (MRT). Here we extend the noble gas data from the Kidd Creek Mine in Timmins Ontario Canada, a volcanogenic massive sulfide (VMS) deposit formed at 2.7 Ga, in which fracture fluids with MRTs of 1.1-1.7 Ga were identified at 2.4km depth (Holland et al., 2013); to fracture fluids at 2.9km depth. We compare here the Kidd Creek Mine study with noble gas compositions determined in fracture fluids taken from two mines (Mine 1 & Mine 2) at 1.7 and 1.4 km depth below surface in the Sudbury Basin formed by a meteorite impact at 1.849 Ga.

The 2.9 km samples at Kidd Creek Mine show the highest radiogenic isotopic ratios observed to date in free fluids (e.g. $^{21}\text{Ne}/^{22}\text{Ne} = 0.6$ and $^{40}\text{Ar}/^{36}\text{Ar} = 102,000$) and have MRTs of 1.0 to 2.2 Ga. In contrast, resampled 2.4 km fluids indicated a less ancient MRT (0.2-0.6 Ga) compared with the previous study (1.1-1.7 Ga). This is consistent with a change in the age distribution of fluids feeding the fractures as they drain, with a decreasing proportion of the most ancient end-member fluids. $^{129}\text{Xe}/^{136}\text{Xe}$ ratios for these fluids confirm that boreholes at 2.4 km versus 2.9 km are sourced from hydrogeologically distinct systems. In contrast, results for the Sudbury mines

have MRTs of 0.2-0.6 and 0.2-0.9 Ga for Mines 1 and 2 respectively. While still old compared to almost all groundwaters reported in the literature to date, these younger residence times compared to Kidd Creek Mine are consistent with significant fracturing created by the impact event, facilitating more hydrogeologic connection and mixing of fluids in the basin. In all samples from both Kidd Creek Mine and Sudbury, a $^{124-128}\text{Xe}$ excess is identified over modern air values. This is attributed to an early atmospheric xenon component, previously identified at Kidd Creek Mine but which has to date not been observed in fluids with a residence time as recent as 0.2-0.6 Ga. The temporal and spatial sampling at Kidd Creek Mine is also used to verify our proposed conceptual model which provides key constraints regarding distribution, volumes and residence times of fracture fluids on the smaller, regional, scale.

1 Introduction

Brines rich in helium, hydrogen, methane and nitrogen within Precambrian crustal rocks have been shown to provide habitable environments for subsurface microbial life (Chivian et al., 2008; Lin et al., 2006; Lau et al., 2016; Magnabosco et al., 2016). The global significance of such ancient rocks for sustaining subsurface life has recently been demonstrated through the identification of water-rock reactions producing electron donors (e.g. hydrogen; Sherwood Lollar et al., 2014) and electron acceptors (e.g. dissolved sulfate; Li et al., 2016). Recent studies have also shown there is significant methanogenesis in these fracture waters, via both microbial methanogenesis, and abiotic water-rock interactions such as Fischer-Tropsch synthesis (Sherwood Lollar et al., 2002; Sherwood Lollar et al., 2006; Kietäväinen and Purkamo, 2015). The significance of these Precambrian crustal systems in global hydrogen production and deep

carbon cycles has only recently been investigated (Sherwood Lollar and Ballentine, 2009; Etiope and Sherwood Lollar, 2013; Sherwood Lollar et al., 2014). Given the long residence times of some of these fracture fluids (> 1 Ga Holland et al., 2013; Lippmann-Pipke et al., 2011), and the discovery of ancient components of other elements (e.g. Archean atmospheric derived xenon Holland et al., 2013; mass independent sulfur isotope signatures; Li et al., 2016), it is reasonable to expect these types of system may have affected global cycles over geological and planetary timescales. The exploration for microbial life (Pedersen et al., 2005; Lin et al., 2006; Chivian et al., 2008), in these ancient terrestrial rocks focuses on developing an understanding of the distribution of biomass and biodiversity, which when coupled with a quantitative estimate of the mean residence times of the fluids within which life is found may provide insights into the evolution and distribution of microbial life over the course of the Earth's history (Sherwood Lollar and Ballentine, 2009; Onstott et al., 2010; Kietäväinen and Purkamo, 2015).

To advance this new area of research, the distribution of residence times of the fluids within different regions of the >70 % of the continental lithosphere that is Precambrian in age is required. This information will address the compartmentalization of the deep hydrogeosphere - the degree of hydrogeological connection between different fracture fluid systems, and/or their degree of isolation from each other and the surface hydrosphere. The unique properties of noble gases can be applied to constrain these variables (Holland et al., 2013; Lippmann-Pipke et al., 2011; Sherwood Lollar and Ballentine, 2009).

The Kidd Creek Mine deposit in the Superior Province of the Canadian Shield is the site where previous noble gas analysis of fluid samples rich in helium, hydrogen, methane and nitrogen collected at 2.4 km depth from a copper-zinc mine in Timmins, Ontario, identified the oldest isolated fracture fluids, with a mean residence time range of 1.1 – 1.7 Ga (Holland et al., 2013).

This age was based on a radiogenic excess of ^4He , ^{21}Ne , ^{40}Ar and ^{136}Xe , a preserved early atmospheric $^{124-128}\text{Xe}$ signal and a sedimentary-derived ^{129}Xe excess (assumed to be from a localised sedimentary source). This study documented fluids with the longest mean residence times ever observed in the crust to date, and showed that fracture fluids in these Precambrian systems could be isolated on planetary timescales. Since this study the Kidd Creek Mine has been expanded to an even deeper level (2.9 km). The three main objectives of this study were 1. to resample the fracture fluids identified by Holland et al. (2013) in order to test the hypothesis that in the 44 months since the previous study the mean residence time would decrease due to draining of fractures (See Section 5.2 & Figure 7); 2. to sample the new deeper levels of the Kidd Creek Mine site to understand the distribution of ancient fluids; and 3. to compare and contrast the fluids from Kidd Creek Mine to those of two new sites in the Sudbury Basin. The two Sudbury mines are situated in 2.6-2.7 Ga Archean bedrock underlying the Sudbury Igneous Complex, a 1.849 Ga formation produced by a bolide impact (Krogh et al., 1984; Card, 1994; Davis, 2008). The impact produced major fracturing of the bedrock and hence likely opened significantly more lines of structural weakness along which fluid movement and mixing could occur compared to the relatively less disturbed geologic setting at Kidd Creek Mine.

2 Geological Background

2.1 Geology of the Superior Province of the Canadian Shield - Kidd Creek Mine, near Timmins, Ontario, Canada

Kidd Creek Mine, Timmins, Ontario (Figure 1) is situated 24 km north of the town of Timmins, within a stratiform Volcanogenic Massive Sulphide (VMS) deposit of 2.7 Ga age (Thurstun et al., 2008). This deposit lies within the Kidd-Munro assemblage of the Southern Volcanic Zone of the Abitibi greenstone belt of the Superior Province of the Canadian Shield (Bleeker and Parrish, 1996). The Kidd-Munro assemblage itself consists of a series of steeply dipping interlayered felsic, mafic, ultramafic and metasedimentary deposits. One of the primary economic resources, the stringer ore, is predominantly associated with the upper felsic region and formed as a result of silica and metal-rich hydrothermal fluid circulation below the seafloor. Above the stringer ore deposits lie banded and massive sulphide ores. These are considered to have been initially deposited as inorganic precipitates formed where hydrothermal solutions rich in metals entered the seawater. Intermittent argillite to chert carbonaceous horizons within the assemblage represent periods of volcanic quiescence during which proximal seafloor sediments accumulated. Following deposition of the Kidd-Munro assemblage, the entire formation was metamorphosed to greenschist facies during the last major regional metamorphic event at 2.67-2.69 Ga. The last known episode of metasomatism occurred at 2.64 Ga (Davis et al., 1994; Bleeker and Parrish, 1996; Thurstun et al., 2008; Berger et al., 2011).

Kidd Creek Mine was opened in 1964 as an open pit. Since then it has been developed vertically to a depth of 2.9 km. In this facility, mining involves lateral coring via multiple boreholes at each level as described in detail in Li et al. (2016). Exploration boreholes frequently intersect pockets of fracture fluids trapped within the host rock. Once pierced, fluids from these pockets have been observed to flow over prolonged time periods, in some cases > 7 years since first discovered by

our team. Gas samples taken from these fracture fluids were analyzed for their noble gas content, following the methods of Ward et al. (2004) and Holland et al. (2013).

2.2 Geology of the Sudbury Basin and underlying Archean basement, near Sudbury, Ontario, Canada

The Sudbury Basin is located approximately 300 km south-east of Kidd Creek Mine (Figure 1). The Sudbury Impact Complex (SIC) formed at 1.849 Ga by an estimated 10-15 km diameter meteorite impacting the Archean basement (consisting of carbonaceous shale, metavolcanic and metasedimentary rocks, gneisses & related intrusive rocks, primarily 2.6-2.7 Ga in age, Card, 1994; Meldrum et al., 1997; Davis, 2008). The resulting impact-induced melting and differentiation formed noritic to gabbroic cumulates overlain by residual granophyres (Pattison, 2009). Magmatic sulphide deposits at the base of the SIC contact, along with associated dykes and breccia in the footwall together, form one of the world's largest nickel, copper, platinum, and palladium economic resources exploited by multiple mining operations (Long, 2009). The region has been deformed by three main major orogenic events: the Penokean (1.89-1.830 Ga); the Mazatzal (1.7-1.6 Ga) and the Grenville (1.4-1.0 Ga). Most recently the North-Eastern section of the Sudbury structure was deformed by yet another impactor forming Lake Wanapitei (37 Ma). The basin and underlying Archean basement rocks have been heavily faulted and folded and metamorphosed up to granulite facies between 2.6-2.7 Ga and more recently amphibolite facies at 1.9-1.8 Ga (James and Golightly, 2009 and references therein).

Both Sudbury mines sampled in this study are located in the footwall of the basin, hosted in 2.6-2.7 Ga Levack Gneiss Archean basement. The first mine (Mine 1) is at 1.7 km depth and the

second mine (Mine 2) is at 1.4 km depth. Both Mine 1 and Mine 2 are nickel-copper mines and are located in the northeast and northwest region of the Sudbury Impact Complex, approximately 25 & 33 km from the City of Sudbury respectively. Mine 1 has been in operation since 2006 and Mine 2 since 1984. As with Kidd Creek Mine, isolated pockets of fracture fluids within the host rock were accessed via lateral boreholes.

2.3 Sample Collection

All samples were collected at the borehole collars from which fluids (and dissolved gases) were naturally flowing (Table 1) (see Holland et al., 2013 and Li et al., 2016 for detailed description). Briefly, as in previous studies, an inflatable packer was inserted into the borehole opening to prevent any atmospheric contamination (e.g. Holland et al., 2013; Sherwood Lollar et al., 2002; Ward et al., 2004). Fluids from each borehole were allowed to separate into gas and water phases by flowing through a gas stripper. Gas samples from fracture fluids were collected in refrigeration-grade, internally polished, 3/8" diameter copper tubes used routinely in noble gas studies. Prior to sample collection, any air contamination was flushed out of the sampling apparatus and copper tubes by flowing borehole fluids through the equipment for a minimum of 20 minutes (as a function of the flowrates and volume of the sampling apparatus). Once flushing to remove air contamination was complete and a representative sample of the fracture fluids established, the copper tubes were cold-welded shut using a hydraulic crimping device. Samples were collected from Kidd Creek Mine at 2.4 km and 2.9 km depth and from Sudbury Mines 1 and 2 at 1.7 and 1.4 km depth respectively. As noted, the sample at 2.4 km were samples from

the same boreholes reported by Holland et al. (2013). For the samples at 2.9 km, due to mine operations, no water samples could be collected (standing water only in the boreholes with no artesian flow in this case), but gas samples were collected using the same methodology as above.

3 Sample Analysis

Samples were analyzed using a combined dual mass spectrometer and purification system in the Noble Laboratory at the Department of Earth Sciences, University of Oxford (Barry et al., 2016). Samples were mounted on to the purification system by clamping the copper tubes adjacent to the cold weld using standard clamping procedures, removing the cold weld, and connecting to the line using a stainless-steel tube fitting to form a metal on metal seal. Ultra-High Vacuum (UHV) was reached using a combination of roughing and turbo pumps. Prior to sample analysis the integrity of the metal seal for each mounted sample was verified via standard helium leak testing (e.g. Warr et al., 2015).

3.1 Separation of noble gases

Given the extremely radiogenic nature of these samples, efficient separation of helium from neon and argon from krypton and xenon was essential. This was achieved through a process of repeat cycling of the respective traps, and static or dynamic pumping for He/Ne and Ar/Kr and Ar/Xe respectively. In all cases separation with no loss or fractionation was verified using procedural air calibrations which were analyzed using the same protocols. Removal of helium was confirmed via the Helix SFT prior to neon release, and argon separation was verified via measurement post-Kr and Xe analysis. In both cases, residual helium and argon analyzed during

the neon and the krypton/xenon analyses respectively were estimated to be < 0.005 % of their original intensities and have no pressure effect on the neon or krypton/xenon measurements.

3.2 Analytical procedure

Initially samples and procedural standards were expanded to a known volume fitted with a 1000 Torr Baratron, and the pressure and temperature of the sample was recorded. Next the sample was exposed to approximately 30 g of activated titanium sponge held at 1223 K (950 °C) to chemically remove the majority of the active gases. After 30 minutes the sponge was allowed to cool for a further 30 minutes to allow removal of H_2 (Stout and Gibbons, 1955). The sample was further purified for an additional 15 minutes using a combination of a hot (SAES GP-50) and cold (SAES NP-10) getters. The cleaned gas was then passed through a series of helium-cooled calibrated cryogenic traps to 1. remove water vapour (stainless steel, 180 K) 2. trap argon, krypton and xenon (stainless steel, 33 K) and 3. trap helium and neon (charcoal, 15 K). Each trapping stage lasted 15 minutes (Barry et al., 2016).

For helium analysis, the charcoal trap was heated to 31 K for 15 minutes, split using known volume expansions and then measured using a HELIX SFT. Peak centres were defined manually and 3He and 4He were measured simultaneously on an electron multiplier and on a Faraday respectively.

In order to measure neon, it was necessary to first remove any residual helium from the system. This was efficiently achieved by developing a technique for these highly radiogenic samples which cycled the charcoal trap to 50 K for 15 minutes then back down to 31 K for a further 15

minutes. This allowed any potential trace helium ($\ll 1\%$) still adsorbed to the charcoal as well as residual helium in the headspace, to be released while trapping all neon. The gas was then expanded to the manifold and pumped, during which the charcoal trap was isolated. This non-dynamic heating, cooling and pumping process was repeated two further times.

Next, following the methods of Barry et al. (2016), the charcoal trap was heated to 90 K for 15 minutes to release all neon and a known volume was inlet into the ARGUS VI for measurement. Each analysis consisted of peak-jumping in which ^{20}Ne and ^{22}Ne were measured on Faraday cups and ^{21}Ne was measured on a multiplier. Additionally, during each cycle, ^{40}Ar and CO_2 were measured to allow correction for $^{40}\text{Ar}^{++}$ and CO_2^{++} interference peaks. Following the measurement, the charcoal trap was heated to 300 K, opened to the vacuum pump to remove any remaining sample, and then isolated from the line.

For argon measurements, the stainless-steel trap was heated to 200 K for 15 minutes to release all noble gases; from which a small aliquot is taken. Once this aliquot was taken the trap was cooled back down to 52 K to re-trap the heavy noble gases. The aliquot was expanded and diluted using calibrated volumes to reduce the ^{40}Ar to measurable levels. The gas was then inlet to the ARGUS VI which measured ^{36}Ar and ^{38}Ar on an electron multiplier and ^{40}Ar on a Faraday cup via peak-jumping.

In order to measure krypton and xenon it was necessary to isolate and remove the residual argon. This was accomplished through a series of trap cycling and pumping steps specifically developed for these highly radiogenic samples. Here the stainless-steel trap was cycled from 52 K to 70 K, to release Ar, then back down to 52 K, waiting 15 minutes to allow full re-trapping of Kr and Xe then 5 minutes dynamic pumping to remove the argon. After 5 cycles the stainless-steel trap was

heated to 200 K to ensure release of all noble gases. The sample was then inlet into the ARGUS where all krypton and xenon isotopes were measured in one analysis using peak jumping. During this measurement ^{78}Kr , ^{124}Xe and ^{126}Xe were measured on the electron multiplier and the remaining isotopes were measured using Faraday cups.

3.3 Standards and line blanks

At the beginning of the sample suite a full procedural air standard was run from an air cylinder which was collected 24.11.14 in University Parks, Oxford, UK. This standard was collected under known environmental conditions (5 °C, 89 % humidity and 1027 mBar pressure) as per standard procedures for noble gas analysis (Warr et al., 2015; Barry et al., 2016)). For comparison between sample and standard the pressure was measured using the 1000 Torr Baratron over the same volume used for sample inlet. Analysis of the air standard followed the same procedure as the samples. Additionally, a full procedural system blank using the sample protocol was also run mid-way through the sample suite to provide a measure of background for subtraction. To factor in any day-to day changes in mass spectrometer sensitivity, and confirm reproducibility, a separate and fully automated standard was analysed, usually overnight, in between samples, procedural blanks and procedural air standards.

All analytical errors were propagated using the standard addition in quadrature method (e.g. Warr et al., 2015). Where averages are used (e.g. for each mine level Tables 2-5) the error is taken as the standard deviation of individual data points, which is always comparable to, or greater than, analytical uncertainty for the individual data points.

4 Results

All ratios and concentrations of representative isotopes are presented respectively in Tables 2-6.

4.1 Concentrations of noble gases

In geological systems where water-rock reactions have been shown to produce significant concentrations of reactive gases such as H_2 , methane, and other hydrocarbon gases (Sherwood Lollar et al., 2002; Sherwood Lollar et al., 2014), absolute concentrations of conservative noble gases per cm^3 of gas (Table 2) are of limited utility. This is because noble gas concentrations within the gas phase may have been affected by both *in situ* H_2 and CH_4 production and addition, and loss of reactive gases through other sinks in the subsurface (e.g. water rock interactions, or microbial uptake). As a result of these processes noble gas concentrations within the gas phase can become passively enriched or diluted. However, initial concentrations within the fracture fluids can be reconstructed using non-radiogenic isotopes coupled with measured isotopic ratios after the method of Holland et al., 2013. This method assumes that the ^{36}Ar in the sampled gas is entirely derived from water that equilibrated with the atmosphere. Here we take seawater at 10 °C as our initial ^{36}Ar composition (Kipfer et al., 2002) following the arguments of Holland et al (2013). The ^{36}Ar concentration measured in the gas phase then allows calculation of the volume of water required to completely degas to provide that amount of ^{36}Ar (e.g. Ballentine et al., 1991; Ballentine et al., 2002), thereby allowing calculation of the total gas/water ratio for the concentration of each individual species within this nominal associated water mass. Selected radiogenic and non-radiogenic noble gas isotopes are given as concentrations within the nominal associated water mass and presented as concentrations in cm^3 per cm^3 of fracture fluid at STP

conditions (Table 3, 4). Values for all isotopes are additionally provided in Appendix A. These are the concentrations which are discussed in the remainder of this section.

4.2 Concentrations of air-saturated components

Through normalising non-radiogenic isotopes (Table 3) to a single isotope (^{36}Ar) it is possible to compare elemental ratios in samples with elemental ratios in air-saturated seawater at 10 °C, in order to identify any elemental fractionation within each system and assess how reasonable the inferred starting composition is. This is presented in Figure 2.

Partial degassing of fluids with an initial ASW concentration via open Rayleigh degassing would result in a gas composition enriched in ^{20}Ne and depleted in ^{84}Kr and ^{130}Xe relative to ^{36}Ar . This observation does not match observed ratios for the resampled boreholes from 2.4 km at Kidd Creek Mine, nor samples from Mines 1 & 2. Hence no major fractionation related to degassing is inferred for ^{20}Ne , ^{84}Kr or ^{130}Xe for these samples. This lack of observable solubility-dependent loss/gain outside of uncertainty suggests that near complete degassing of the original fluid phase has occurred. Hence the data for these samples do not require any post-processing to account for only partial degassing of the fracture fluid. Small deviations from expected elemental ratios are likely due to the large current uncertainty in initial temperature and salinity from the assumed starting conditions (seawater at 10 °C), both of which can have an effect on noble gas solubility (Crovetto et al., 1982; Smith, 1985; Smith and Kennedy, 1983).

In contrast, in the case of Kidd Creek Mine samples from 2.9 km depth, there is evidence for Rayleigh fractionation on a localised borehole scale (Appendix C) which has created an enrichment of ^{20}Ne coupled with a deficit of ^{84}Kr and ^{130}Xe relative to ^{36}Ar . With ^{36}Ar values

depleted by 17 % from the assumed starting conditions. A correction for this has been applied to each noble gas (30.6 %, 29.6 %, 17.0 %, 11.4 %, & 8.4 % for helium – xenon respectively) based on their respective solubilities and the recalculated radiogenic excesses for each noble gas are presented in Table 7. These are the values referred to when discussing radiogenic concentrations and the residence time calculations in Section 4.10. A comprehensive discussion and quantification of the degassing is provided in Appendix C.

4.3 Helium

In all samples in this study, the $^3\text{He}/^4\text{He}$ ratios are consistent with typical crustal radiogenic production rates estimated for crystalline rock globally (Ballentine and Burnard, 2002). Consistent with previous work in these tectonically quiescent environments, no mantle component is observed (Sherwood Lollar et al., 1993; Lippmann-Pipke et al., 2011; Holland et al., 2013). The $^3\text{He}/^4\text{He}$ ratios for all samples are given in Table 5. As per convention these ratios are given in R_A where 1 R_A is the atmospheric ratio (1.4×10^{-6}). All helium ratios are highly radiogenic ($< 0.026 R_A$). This is reinforced by the absolute average concentrations of ^4He per cm^3 of fracture fluid which in Kidd Creek Mine range between 0.08 (at 2.4 km) and 0.36 cm^3 ^4He per cm^3 of fracture fluid (at 2.9 km) and 0.06 and 0.03 cm^3 ^4He per cm^3 of fracture fluid in Mine 1 (at 1.7 km) and Mine 2 (at 1.4 km) respectively for the Sudbury system. These concentrations are at least six orders of magnitude greater than the initial ASW concentration (Kipfer et al., 2002). Consequently, any air-derived component present is negligible and no corrections need to be applied.

4.4 Neon

For all samples, isotopic ratios of $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ are greater than ASW due to a resolvable excess of radiogenic ^{21}Ne and ^{22}Ne . In the resampled fracture fluids from 2.4 km at Kidd Creek Mine, average ^{21}Ne excesses are $3.2 \times 10^{-9} \text{ cm}^3 \text{ }^{21}\text{Ne}$ per cm^3 of fracture fluid. Greater average excesses over an ASW starting composition are observed in the deeper 2.9 km level samples ($1.6 \times 10^{-8} \text{ cm}^3 \text{ }^{21}\text{Ne}$ per cm^3 of fracture fluid) which, like helium, indicates the deeper level contains a larger radiogenic excess. In the Sudbury samples, average radiogenic neon excesses are smaller overall, with Mines 1 and 2 having a ^{21}Ne excess of 1.8×10^{-9} and $1.2 \times 10^{-9} \text{ cm}^3 \text{ }^{21}\text{Ne}$ per cm^3 of fracture fluid respectively.

The measured isotopes of neon from Table 4 are presented graphically in Figure 3.

As seen in Figure 3, samples from Kidd Creek Mine at the deeper level (2.9 km) are even more displaced from initial air ratios (ASW) relative to their 2.4 km counterparts. Indeed, the $^{21}\text{Ne}/^{22}\text{Ne}$ ratios for the 2.9 km samples are the highest ever measured in crustal samples, free fluids or otherwise (Lippmann-Pipke et al., 2011). As was seen in Holland et al. (2013), the data from this study indicate that fracture fluids in these Precambrian crystalline systems are characterised by a radiogenic $^{20}\text{Ne}/^{22}\text{Ne}$ end-member that is significantly elevated (red line) compared to what had previously been expected for crystalline rock (black line, Kennedy et al., 1990; Ballentine and Burnard, 2002). The new samples from 2.4 km depth at Kidd Creek Mine (black squares) similarly preserve an elevated crustal production of neon, however, they have somewhat lower $^{21}\text{Ne}/^{20}\text{Ne}$ and $^{22}\text{Ne}/^{20}\text{Ne}$ ratios compared to the 2013 study (blue squares) when they were first sampled > 7 years ago. Only the data for Mine 2 from Sudbury lie close to the traditional ASW-crustal mixing line (black line), as did one sample from the Holland et al.

(2013) study. The implications of this data for neon production rate are discussed in Section 5.55.

4.5 Argon

Concentrations of ^{40}Ar are also elevated in all fluid systems due to radiogenic decay of ^{40}K , with concentrations as high as $0.10 \text{ cm}^3 \text{ }^{40}\text{Ar}$ per cm^3 of fracture fluid in the case of the samples from Kidd Creek Mine 2.9 km. Concentrations of ^{40}Ar for the samples from 2.4 km (0.01), and in both Sudbury Mines (0.004 and $0.02 \text{ cm}^3 \text{ }^{40}\text{Ar}$ per cm^3 of fracture fluid respectively) are lower than this, but in all cases the radiogenic component accounts for an extraordinary over 93 % of all ^{40}Ar present.

The 2013 samples reported for 2.4 km had $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of up to ~44,000, which at the time were the highest crustal values ever measured in a free fluid. In this paper, $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for samples from the deeper level of Kidd Creek Mine (2.9 km) reach in excess of 125,000 (102,000 average). The resampling of the fluids at 2.4 km depth revealed a lower $^{40}\text{Ar}/^{36}\text{Ar}$ ratio than in the 2013 study, with an average value of 15,100, compared with the previous average of 31,100. Radiogenic ages based on He, Ne and Ar measurements are discussed in Section 4.10.

While the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio for the two Sudbury mines are much lower than those in Kidd Creek Mine, an identifiable radiogenic excess from atmospheric ratio (295.5, Ozima and Podosek, 2002) is nonetheless observed. This ratio increases from 4353 in Mine 1 to 17589 in Mine 2. As noted with the ^{40}Ar excess, these high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios all indicate fluids with a high radiogenic excess relative to the assumed starting composition.

4.6 Krypton

All krypton abundances and ratios are given in Appendix A. As ^{80}Kr has no known production pathways within the crust (Ballentine and Burnard, 2002, and references therein) this is typically the isotope chosen for normalisation (in a method analogous to ^{36}Ar normalization discussed above). In this dataset, there are small deviations in $^{78}\text{Kr}/^{80}\text{Kr}$ and $^{86}\text{Kr}/^{80}\text{Kr}$ from atmosphere (Table A6), but no correlation with age or mass fractionation trends are observed.

4.7 Xenon

As per the standard approach in noble gas geochemistry, all Xe isotope data are normalised to ^{130}Xe , the Xe isotope with no major radiogenic production pathways (Table 5). Compositions are expressed as in Figure 4 then as deviations relative to ^{130}Xe , and elevated $^{131-136}\text{Xe}/^{130}\text{Xe}$ ratios are typical within the crust due to radioactive decay of uranium and plutonium. It is possible to determine the source of radiogenic xenon through comparison with the well-defined fission spectra for each parent radionuclide (Ballentine and Burnard, 2002 and references therein). By anchoring the ^{238}U fission spectra to ^{136}Xe a good agreement is observed between the predicted and observed $^{131-134}\text{Xe}$ excess in the samples (Figure 4). This indicates that the radiogenic xenon excess (Xe^*) in all locations can be explained via ^{238}U fission and accumulation of radiogenic Xe over time.

$^{136}\text{Xe}^*$ is greatest in Kidd Creek Mine samples from 2.9 km ($9.9 \times 10^{-10} \text{ cm}^3$ ^{136}Xe per cm^3 of fracture fluid) and is an order of magnitude greater than $^{136}\text{Xe}^*$ resampled from 2.4 km fluids

($7.1 \times 10^{-10} \text{ cm}^3 \text{ }^{136}\text{Xe}$ per cm^3 of fracture fluid). In Sudbury samples, $^{136}\text{Xe}^*$ show a smaller range (5.1×10^{-11} and $2.3 \times 10^{-10} \text{ cm}^3 \text{ }^{136}\text{Xe}$ per cm^3 of fracture fluid in Mines 1 and 2 respectively), consistent with a lower radiogenic excess in the fluids Mine 2 versus Mine 1 in the Sudbury Basin compared to Kidd Creek Mine fluids.

In addition to radiogenic xenon, a small excess over ASW is observed in the ‘shielded’ ($^{124-128}\text{Xe}$) isotopes which have no significant production within crustal environments (Ballentine and Burnard, 2002). These are given as percentages in Table 8.

By dividing the percentage deviation by the relative mass difference of the light isotope relative to ^{130}Xe the enrichment in shielded isotopes per amu is calculated. The average enrichment is observed to be the greatest in Kidd Creek Mine samples from 2.9 km (6.7 ‰) followed by Mine 2 (3.0 ‰), Kidd Creek Mine samples from 2.4 km (2.6 ‰) and lastly samples from Mine 1 (2.5 ‰). As was previously observed in Holland et al. (2013) the light Xe isotopes at both levels of Kidd Creek Mine also show an additional ^{129}Xe excess far beyond that which may be linked by mass fractionation to the $^{124-128}\text{Xe}$ excess (Table 8, Figure 5). A ^{129}Xe excess was also observed in 2013 (Holland et al., 2013). The interpretation and implication of this is presented in Section 5.33.

4.8 Radiogenic noble gases

At Kidd Creek Mine, resampling of previous boreholes from Holland et al. (2013) at 2.4 km depth indicate a reduction in all radiogenically-derived noble gas concentrations expressed as per

cm³ of fracture fluid since initial sampling 44 months prior. In contrast, in the recently completed boreholes sampled immediately after drilling at 2.9 km, the concentrations of noble gases within the fluids are the highest ever reported in the literature. The exception to this is xenon, which shows a similar radiogenic concentration to the samples collected in 2013 from 2.4 km. In both Sudbury mines, a lower excess of radiogenic noble gases is observed per cm³ of fracture fluid (Table 4).

4.9 Radiogenic residence time calculations

The approach for deriving residence times for fracture fluids is as follows: 1. initial composition of the pore fluids is assumed to be approximately that of seawater at 10 °C with corresponding noble gas content; 2. gas phases are quantitatively recovered from the fluids during sampling; 3. reasonable estimates of combined matrix and fracture porosity (termed bulk porosity here) are applied; 4. noble gases behave conservatively; and 5. all radiogenic noble gases are produced *in situ* in a closed system within the crystalline rock formations.

In the case of the first assumption, given that the host rock was originally formed within a proximal marine environment (Thurston et al., 2008), it is reasonable to assume the initial pore fluids would be seawater with the corresponding noble gas content. Given the rate at which gas exsolved from the water phase (Table 1), coupled with the known strong affinity of noble gases for a gaseous phase (Crovetto et al., 1982; Ballentine et al., 2002; Warr et al., 2015), total degassing of the water phase can reasonably be ensured during sampling. In addition, degassing processes prior to sampling that affected noble gas concentrations for the samples from Kidd Creek Mine 2.9 km (Figure 2) can be corrected for as seen in Section 4.2. Bulk porosity estimates for crystalline rock of the Canadian Shield vary in a narrow range of ~1 % +/- 0.45 %

with bulk porosity principally existing as fractures within the crystalline rock, decreasing as a function of depth as per Equation 3 (Sherwood Lollar et al., 2014 and references therein). Any gas phase not in solution is expected to occupy negligible volume within these fractures due to the hydrostatic-or-greater pressure of the system (Holland et al., 2013). In contrast, the assumption that all noble gases efficiently migrate into the fluid phase is a simplification at relatively low temperatures, even over up to Ga timescales, but within the closed system assumption means that the derived ages are minimum estimates. Release of the noble gases from the minerals in which they are produced will depend on the mineral size distribution, and both temporal and thermal history (Fulda and Lippolt, 2000; Lippmann et al., 2003; Baxter, 2010; Tolstikhin et al., 2014).

The final assumption is that of a closed system on a connected fracture fluid scale. For the systems presented here we use two lines of evidence to support this assumption. First, the ASW-derived noble gases (^{20}Ne , ^{84}Kr & ^{130}Xe) show reasonable agreement with the assumed starting composition based on ^{36}Ar concentrations (Figure 2). Any noble gas loss/gain through diffusive or bulk gas phase migration in or out of the fracture network would likely result in major elemental fractionation, with neon being the most affected and xenon the least based on their respective diffusivities and differences in the relative partitioning between different phases. As discussed, this trend is not observed in any of the samples in this study (Figure 2). Additionally, any external exchange of noble gases would likely result in variable excesses in the radiogenic noble gases which would be reflected in poorly correlated radiogenic ages between the different noble gas systems ($^4\text{He}^*$, $^{21}\text{Ne}^*$, $^{40}\text{Ar}^*$, $^{136}\text{Xe}^*$). Crucially this is not observed (Table 9). All residence time estimates are in agreement with one another within error (Table 9), with the exception of some variation outside uncertainty for the estimates derived from $^{21}\text{Ne}^*$ that is

discussed in the following section. These two lines of evidence support that any exchange with external systems is negligible. Therefore, as in the 2013 study (Holland et al., 2013) all systems presented here are assumed to reflect closed systems on a regional/deposit scale.

4.10 Radiogenic Ages

Residence time estimates for fracture fluids are based on resolved radiogenic $^4\text{He}^*$, $^{21}\text{Ne}^*$, $^{40}\text{Ar}^*$ and $^{136}\text{Xe}^*$ that accumulate in subsurface fluids due to radioactive decay of uranium, thorium and potassium over geologic timescales (Ballentine and Burnard, 2002). If these are assumed to have been produced *in situ*, an estimate of the time since isolation can be calculated.

The noble gas content per cm^3 of host rock is calculated by multiplying the radiogenic noble gases concentrations per cm^3 of fluid by an estimate of bulk porosity calculated using Equation 3 (Sherwood Lollar et al., 2014). This is converted into *in situ* radiogenic noble gas concentration per gram of host rock by dividing this number by typical density of crystalline rock ($\sim 2.7 \text{ g/cm}^3$). Using this approach the noble gas content per gram of host rock is obtained. In order to derive residence times, the concentrations of the parent elements for each noble gas were taken from the literature. For Kidd Creek Mine the same Kidd Munro concentrations were used as from Holland et al., 2013 ($\text{Th} = 9 \pm 0.2 \text{ ppm}$, $\text{U} = 2 \pm 0.1 \text{ ppm}$ and $\text{K} = 2 \% \pm 0.05$, based on values taken from Moulton et al., 2011) and for the Sudbury Mines the average tonalite gneiss from the Levack Gneiss Complex was used ($\text{Th} = 8 \pm 0.1 \text{ ppm}$, $\text{U} = 1 \pm 0.2 \text{ ppm}$ and $\text{K} = 1.86 \pm 0.05 \%$, Meldrum et al., 1997). These were combined with the respective decay constants and the total production per decay to estimate production as a function of time. The equations for $^4\text{He}^*$ and $^{40}\text{Ar}^*$ production are as follows:

$${}^4\text{He}^* = 8 \times [{}^{238}\text{U}] \times (e^{\lambda_{238}t} - 1) + 7 \times [{}^{235}\text{U}] \times (e^{\lambda_{235}t} - 1) + 6 \times [{}^{232}\text{Th}] \times (e^{\lambda_{232}t} - 1) \quad (1)$$

$${}^{40}\text{Ar}^* = 0.105 \times [{}^{40}\text{K}] \times (e^{\lambda_{40}t} - 1) \quad (2)$$

where $[{}^{238}\text{U}]$, $[{}^{235}\text{U}]$, $[{}^{232}\text{Th}]$ and $[{}^{40}\text{K}]$ are elemental concentrations in ppm in the host rock, λ_{238} , λ_{235} , λ_{232} and λ_{40} are the decay constants (year^{-1}) 8, 7, 6 are the total atoms of ${}^4\text{He}$ produced from the complete decay chain of each parent radionuclide, 0.105 is the ${}^{40}\text{K}$ fraction which decays to ${}^{40}\text{Ar}$ and t is time in years (Ballentine and Burnard, 2002; Holland et al., 2013).

As in the previous study (Holland et al., 2013), residence times for both ${}^{21}\text{Ne}^*$ and ${}^{136}\text{Xe}^*$ were derived using the relationship between ${}^4\text{He}^*$, ${}^{21}\text{Ne}^*$ and ${}^{136}\text{Xe}^*$ (9.96×10^6 and 3.033×10^8 for ${}^4\text{He}^*/{}^{21}\text{Ne}^*$ and ${}^4\text{He}^*/{}^{136}\text{Xe}^*$ respectively, Ballentine and Burnard, 2002). We assign error bars based on the maximum possible uncertainty associated with this calculation, which is the uncertainty in the bulk porosity estimate (1 % +/- 0.45 % adjusted for depth; Equation 3, after Sherwood Lollar et al., 2014 and references therein) combined in quadrature with the calculated analytical uncertainty and the published analytical uncertainty in the radioelement concentration. These ages and their corresponding 1 σ uncertainty are presented in Table 9 and Figure 6.

From Table 9 it is observed that all fracture fluids residence times agree with one another within uncertainty for boreholes within a given level at Kidd Creek Mine, with no discernible time series. This suggests that, as hypothesized in the conceptual model which we propose in Section 5.2, boreholes from the same level of the mine are intersecting and draining fracture fluids with similar residence times. This is both supported by the similar noble gas isotopic compositions and fluid $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data (Tables 2-8, 10). Accordingly, the method of averaging fluid data

for all boreholes for a given mine level, as done in the 2013 study, remains valid for the data in the present study.

Based on the averages, the mean residence times of the fluids have decreased for the samples at 2.4 km depth at Kidd Creek Mine (0.2 to 0.6 Ga, 0.4 Ga average) since the initial 2013 study (1.1 to 1.7 Ga, 1.2 Ga average). This behaviour is consistent with the hydrogeological conceptual model of draining fracture fluids as which was discussed in more detail in Section 5.2.

At the deeper (2.9 km) level of Kidd Creek Mine, fluid mean residence times are the oldest yet reported (1.7 Ga average mean residence time). While $^{21}\text{Ne}^*$ gives the youngest estimate (1.0 Ga), $^4\text{He}^*$, $^{40}\text{Ar}^*$ and $^{136}\text{Xe}^*$ estimates are all consistent, with estimates ranging between 1.7 to 2.2 Ga. In the case of neon, the average age, calculated using the $^4\text{He}^*/^{21}\text{Ne}^*$ production rate in modern crust, is much lower than its radiogenic counterparts. This is discussed further in Section 5.5.

While the fluids in both Sudbury mines have significantly younger mean residence times, they are still indicative of systems which have been hydrogeologically isolated over significant periods of time. With estimated mean residence times ranging from 0.2 – 0.6 Ga (Mine 1) and 0.2 – 0.9 Ga (Mine 2) these are still older than any previously published systems except for Kidd Creek Mine. Although Mine 1 helium and neon ages are greater than Mine 2, the opposite is observed for argon and krypton. This results in overall average residence times of 0.3 and 0.5 Ga respectively. All ages are presented graphically in Figure 6.

5 Discussion

Despite their potential significance in global hydrogen production and deep carbon cycles the volume and distribution of these deep crustal fluids remain poorly constrained. Here the first global estimates of deep crustal reservoirs are calculated as a crucial first step to address this (Section 5.1). A newly-developed conceptual model is also presented in tandem which models distribution, volumes and residence times of fracture fluids within a vertical profile (Section 5.2). This model is expected to provide a much enhanced understanding of fracture fluids on a regional scale. This model is evaluated using both the data generated for this study and previously published data by Holland et al. (2013).

In the previously mentioned Holland et al. (2013) study three novel noble gas characteristics were observed: 1. a ^{129}Xe excess attributed to local sediments; 2. a $^{124-128}\text{Xe}$ excess was identified and attributed to an early atmospheric component; and 3. an elevated $^{21}\text{Ne}/^{22}\text{Ne}$ end-member well above typical crustal values (Holland et al., 2013). In this study three new localities have been identified which clearly preserve fluids on similarly ancient timescales and allow evaluation of the original interpretation of these geochemical features and assess the common elements within other systems. Additionally, the original boreholes at 2.4 km depth at Kidd Mine have been resampled. The geochemical characteristics of each of these are used as the basis to validate key aspects of the proposed conceptual model.

5.1 Global estimates of deep crustal reservoirs

To assess the impact such deep old fracture fluids can have on global cycles it is also essential to have estimates of both their total volume and distribution within the crust. In a recent study Gleeson et al. (2016) used ^3H data to estimate the depth penetration of young (< 50-100-year-

old) groundwater in the first 2 km of the continental crust, and two-dimensional models of bulk porosity-depth relationships for different crustal rocks integrated with cross-sectional steady-state models of groundwater flow to estimate the global volume of modern groundwater. The analysis yielded the important insight that the volume of modern groundwater (350,000 km³ to 630,000 km³ for 50 year and 100-year-old water, respectively) is by far the largest component of the planet's active hydrologic cycle (with the exception of the oceans at ~ 1 billion km³). Given the central role of groundwater in sustaining the Earth's agricultural, social, economic activities, climate and ecosystems, this work generated widespread attention. The even more fundamental corollary of their findings, however, went unnoticed. Specifically, that the $\leq 630,000$ km³ of groundwater that they estimated for modern groundwater (<50-100 years) represents only 1.5 - 2.8 % of the total groundwater inventory to 2 km depth (~ 22.6 million km³; Gleeson et al., 2016). The result is that 97.2 - 98.5 % of groundwater is much older, and we know almost nothing about the age or distribution of that immense "hidden hydrogeosphere" which is not actively interacting with the short-term hydrologic cycle. Similarly, the implications of this deep hydrogeosphere for the habitability of the Earth's crust and for subsurface ecosystems are also poorly constrained.

As Gleeson et al. (2016) noted, empirical databases for groundwater, even to 2 km depth, are rare – necessitating a modelling approach to derive even first order estimates of groundwater inventory. No estimate has yet been done on the volume of groundwater beyond this arbitrary 2 km cut-off, but a first order estimate can be made here. Below 2 km depth, the bulk of the terrestrial crust is crystalline basement (> 80 % estimated in Gleeson et al. 2016). This estimate is consistent with surface area estimates for the Precambrian crust which indicate crystalline rocks of the Precambrian constitute > 30 % of the exposed continental area at surface and > 72 %

of the bedrock surface area in total for the planet (Goodwin, 1996). Hence, for depths deeper than 2 km in the continental crust we can consider the Precambrian crust as a basis for a representative, but conservative, estimate for determining the groundwater inventory at depth. Including younger Paleozoic crystalline rocks would only increase this estimate and therefore can be neglected for this first order analysis.

Given the total surface area of the continents is $1.48 \times 10^8 \text{ km}^2$ and knowing that 72 % of that crust is Precambrian crystalline rock ($1.06 \times 10^8 \text{ km}^2$; Goodwin, 1996), we can calculate the volume of groundwater in the crust to depth by incorporating bulk porosity estimates. Measured values of bulk porosity within fractures for crystalline basement rocks range from 0.1 to 2.3 % (Aquilina et al., 2004; Stober, 1997; Stober and Bucher, 2007) with a mean of $1 \% \pm 0.45 \%$ (2σ) (Bucher and Stober, 2010). Due to the limited number of such empirical measurements, Sherwood Lollar et al. (2014) took a modelling approach and estimate bulk porosity that exponentially declines with depth after the models of Bethke (1985). The equation is given as:

$$\Phi = (1.6e^{-z/4.8})/100 \quad (3)$$

where ϕ is bulk porosity (%) and z is depth (km). To 10 km depth, this approach predicts an average bulk porosity of 0.96 %, consistent with the above measurements from the literature and the value used by Gleeson et al. (2016) for crystalline rocks of the upper crust.

The depth of water-filled fractures in the crust is more uncertain. At $> 15 \text{ km}$ depth, temperatures are likely too warm for brittle faulting and ductile creep persists (Sleep and Zoback, 2007). To at least 10 km however, brittle crust faults should contain water, likely under hydrostatic pressure (Townend and Zoback, 2000 and references therein). Using the surface area of Precambrian crystalline rock, an average bulk porosity of 1 %, to a depth of 10 km then, suggests another 8.5

million km³ should be added to the groundwater inventory in addition to the 22.6 million km³ estimated for the top 2 km (Gleeson et al., 2016). This indicates that fluids residing in Precambrian crystalline basement may account for somewhere in the region of 30 % of the total groundwater inventory of the earth. The residence times of this total groundwater inventory of > 30 million km³ is, to date, almost completely unknown. This study represents an important first step in addressing this gap through defining an approach for estimating the mean residence times of such fluids and expanding beyond the earlier study at Kidd Creek Mine to demonstrate that such ancient fluids (Ma to Ga) are a characteristic feature of the Precambrian deep crust.

5.2 Conceptual model

Based on this study and previous investigations of saline fracture fluids in the deep Precambrian cratons (Sherwood Lollar et al., 2007; Lippman-Pipke et al., 2011; Holland et al., 2013), the following conceptual model has been developed to better constrain distribution, volumes and residence times of fracture fluids within a vertical profile (Figure 7). Fracture fluids in deep crystalline rock decrease in frequency and are increasingly hydrogeologically isolated one from another with increasing depth in the crust (Sleep and Zoback, 2007; Golders Associates 2010). Based on the results of Holland et al (2013), it is reasonable to assume that the deeper, more hydrogeologically isolated fractures contain fluids with the oldest residence times, and as a corollary, that less deep fractures will contain a larger volume of fluids with relatively less ancient residence time distributions.

Within the host rocks investigated in this study, the discrete fracture systems contain highly saline fluids and dissolved gases under pressure. The distribution of these fractures are the dominant control on bulk porosity and associated permeability. The fractures are highly variable

in terms of geometry, spacing and structure which results in high variations in bulk porosity, permeability and fluid volume locally. While a few studies exist in Precambrian rock where the actual fracture distribution have been mapped (Manzi et al., 2012); such information is not typically available and does not exist for the sites investigated in this study. Conceptually however, it is clear that individual boreholes drilled into the crystalline rock intersect one or more these fracture networks, providing a means for the host fluids to migrate out of the host rock and any given borehole will intersect multiple fractures (Figure 7). Accordingly, the fluids sampled from each borehole are the sum total of all fluids being discharged from each contributing fracture. With each fracture containing fluids of possibly different geological residence times, the resulting noble gas-derived mean residence time for the samples collected at the borehole collar thus represents the mean residence time of all fluids contributing to the fracture flow. The borehole-specific mean residence times are dependent on the isolation age, the volumes and the fluid discharge rates for each contributing fracture. Where boreholes intersect the same fracture networks, this will result in similar geochemistry and residence times. This model for fractured rock is analogous to those applied to unconsolidated porous media in the sense that any groundwater is a composite reservoir contributed to from multiple flowlines with a certain degree of heterogeneity in provenance and age as a function of the hydrogeological setting (Bethke and Johnson, 2008; Goode, 1996). This “mixed reservoir” aspect of any hydrogeologic system is amplified for fractured rock systems due to the high degree of heterogeneity inherent to fractured rock (Golders Associates 2010). Over time, stress regimes within the host rock change, and in the tectonically quiescent rocks of the Precambrian Shields this is primarily caused by large scale, regional stress variations (Sleep and Zoback, 2007). Stress changes on a regional scale may result in both reactivation of pre-existing planes of weakness

and the development of new, localised fractures. Localised changes to the stress regime may additionally be produced due to mining activity. Through all of these processes new, fluid-bearing fractures are expected to contribute to the sampling boreholes over time. Since the preservation potential of these fracture networks is expected to be lower as a function of increasing age, statistically these fluids are likely to be representative of younger residence times.

As a result mean residence times may also change, as some fractures drain out and contribute less to the overall volume discharging from the boreholes while new ones become connected. Based on these considerations the new investigation at Kidd Creek Mine allows assessment of two hypotheses: a. that resampling of the Holland et al 2013 boreholes would show less ancient mean residence times as the contribution from the more older, isolated fractures decreased over time; and b. the new deeper boreholes at 2.9 km would provide fluid mean residence times comparable to or even older than those of the Holland et al. 2013 study (Sleep and Zoback, 2007; Townend and Zoback, 2000). Where applicable we evaluate these hypotheses in the remainder of the discussion section using the geochemical data presented in this study.

One final point to consider within the conceptual model is the potential for natural bias within the sampled fluids which may too have a bearing on the calculated residence times. In this kind of environment fluids are principally considered to exist within fractures, rather than at grain boundaries or as fluid inclusions. The mean residence times of the fluids are therefore net combination of all fractures sampled. However, it is reasonable to consider that the larger fractures are more likely to be intersected by an exploratory borehole than their smaller-scale

counterparts. Given that a relationship between fluid volume and residence time may exist (as hypothesised here) there may be a biasing towards boreholes sampling younger, rather than older fluids at any given level. Accordingly the mean residence times presented here would remain conservative estimates, even if there is a natural bias present in the fluids being sampled.

5.3 ^{129}Xe anomaly

In the 2013 study a ^{129}Xe excess far in excess of any early atmosphere component or possible mantle component was identified in the fractures waters at Kidd Creek Mine. This was attributed to a radiogenic ^{129}Xe excess produced from ^{129}I likely sorbed to the carbon-rich formations of the Kidd Creek Mine deposit during deposition in a proximal seafloor environment. Preservation of the ^{129}Xe results from decay of ^{129}I was attributed to rapid periods of intense volcanism that quickly capped the sedimentary layers – creating a closed system in which ^{129}I (and resulting ^{129}Xe) were sequestered (Holland et al., 2013). In this study an even greater $^{129}\text{Xe}/^{130}\text{Xe}$ excess is identified in the fluids from 2.9 km at Kidd Creek Mine. The increase in $^{129}\text{Xe}/^{130}\text{Xe}$ ratios however is small compared to the $^{136}\text{Xe}/^{130}\text{Xe}$ ratio. In contrast, a very large $^{136}\text{Xe}/^{130}\text{Xe}$ deviation is observed from 21 % to 87 % (i.e. 4.1 ± 0.5 times higher in the 2.9 km samples versus those from 2.4 km). The $^{129}\text{Xe}/^{130}\text{Xe}$ only increases from 1.2 % to 3.8 % (3.3 ± 0.6 times higher. Though these values lie within uncertainty of one another, based on standard deviation, when standard error is calculated (which can be used in this case to evaluate the accuracy of the mean value) these values lie outside of uncertainty of one another (4.1 ± 0.2 & 3.3 ± 0.3) indicating the average increases are distinct for these two isotopes.

This lack of proportional co-variation between the radiogenic ^{136}Xe , and sedimentary-derived ^{129}Xe , is not consistent with a single homogenised ancient fluid of uniform age (containing the ^{129}Xe excess) mixing variably with a single modern fluid component to produce the observed excesses. Instead, this supports the interpretation that boreholes at 2.4 km and 2.9 km sample different fracture systems, consistent with the proposed conceptual model of hydrogeologically isolated fracture networks preserving fluids of different provenance and age. As a result, different ^{129}Xe and ^{136}Xe excesses in the fluids could result from variances in the ^{129}Xe excess (due to different degrees of water-rock interaction), coupled with an isolation age-dependent $^{136}\text{Xe}^*$ component.

In contrast to the Kidd Creek Mine fluids, no ^{129}Xe excess is observed in either of the two Sudbury mines. Given that the Sudbury Basin system was the loci of a major bolide impact at 1.8 Ga, massively fracturing the terrain on a regional scale over hundreds of km, the absence of the ^{129}Xe excess observed at the well-preserved Kidd Creek Mine deposit was expected. This highlights the ability of noble gases to discern between the distribution of fracture fluids of different age and provenance as a function of different geologic settings.

5.4 Ancient atmospheric signal

A fractionated excess in the shielded xenon isotopes ($^{124-128}\text{Xe}$) relative to modern air values is present in ancient fracture fluids and may also be present in the $^{131-136}\text{Xe}$ isotopes (Appendix C). These cannot be explained using any known xenon production pathways or *in situ* mass fractionation processes (which would affect all xenon isotopes) and have previously been

attributed to atmospheric Xe loss over geological time by ionisation of xenon in the early atmosphere (Pujol et al., 2009; Pujol et al., 2011, Avice 2014). This has been used as basis for resolving the ‘xenon paradox’; the observation that Earth has ~90 % lower Xe abundance than predicted by meteorite and Solar abundance patterns (Anders and Owen, 1977; Podosek and Ozima, 2000; Pepin and Porcelli, 2002). The atmosphere Xe loss model has been used to derive an atmospheric isotopic evolution curve for xenon, from an initial Xe-U/solar composition evolving to modern values (Pujol et al., 2011; Holland et al., 2013; Avice and Marty, 2014). The exact mechanisms and rates involved in this isotopic fractionation and loss are presently poorly constrained (Avice and Marty, 2014; Hébrard and Marty, 2014). Current models are exclusively based on xenon data from fluid inclusions (e.g. Pujol et al., 2011; Avice and Marty, 2014), the majority of which are greater than 2 Ga (Hébrard and Marty, 2014). To date, data covering the 2 Ga – present day timescale is sparse. Expanding the dataset to cover this range will allow for better constraints on the rates and timing of the xenon isotopic evolution of the Earth’s atmosphere over planetary timescales; and identification of the mechanism that may control any such process (Hébrard and Marty, 2014). To investigate this aspect of atmospheric Xe in the light of the samples in this study, Figure 5 (and Table 8) show the data for all the light excesses of Xe relative to modern atmosphere.

An average $^{124-128}\text{Xe}$ excess is observed for all samples (Figure 5). Once again samples from 2.9 km depth show the largest excesses, while the resampled fracture fluids at 2.4 km show a smaller excess compared to the initial 2013 observation. This trend is in agreement with a hydrogeologic conceptual model which predicts that due to fractures draining over time a younger mean residence time will be observed in these boreholes, as well as either a lower (or even no) $^{124-128}\text{Xe}$ excess. This model is summarised in Section 5.2. This is because exact $^{124-128}\text{Xe}$ excess

present within a fracture fluid is dependent on three key factors; 1. the rates, evolution and termination of the process driving this fractionation, 2. The point at which the fracture fluid became isolated from the early atmosphere and, 3 the relative proportion of each fracture fluid component within the fracture network.

The presence of a resolvable $^{124-128}\text{Xe}$ excess in the Sudbury system fluids is of particular interest. These are the fluids with the youngest mean residence times (0.3-0.5 Ga) in which such a signal has been identified and indicates that at both locations one or more of the oldest fracture fluid components (which combined yield the mean residence times) contain an early atmospheric Xe signal. In addition we argue that the concept of such shallow (<2 km) fractures preserving fluids from before the SIC-forming impact event is unrealistic. This is due to the magnitude and scope of the event which is the second largest impact identified globally and caused ejecta to spread over at least a 650 km radius (Grieve and Therriault, 2000; Jirsa et al., 2011). Any fluid components in either Sudbury mine are therefore likely younger than the impact event at 1.85 Ga. The implication of this is that the fractionation mechanisms proposed to create the $^{124-128}\text{Xe}$ anomalies noted in previous literature must in fact have continued beyond 2 Ga and has been preserved in one or more fluid components. These fluid components, likely combined with younger fluids, have subsequently resulted in the calculated mean residence times 0.3 & 0.5 Ga for the two Sudbury mines. The identification of an early atmospheric Xe component in fluids younger than 1.85 Ga is more consistent with models which indicate ionisation of the atmospheric Xe continuing until more recently (Pujol et al., 2011; Hébrard and Marty, 2014) rather than those which suggest it ended earlier than 2 Ga (Avice and Marty, 2014). Further investigation of this novel type of sample containing early atmospheric Xe components in

addition to the traditional reliance on fluid inclusions, will allow better evaluation of alternative Xe loss mechanisms such as hydro-dynamic escape (Pepin, 2000).

5.5 Ancient neon signal

Nucleogenic neon in Precambrian systems have recently been shown to have a distinct $^{21}\text{Ne}/^{22}\text{Ne}$ end-member ($^{21}\text{Ne}/^{22}\text{Ne} = 3.1 - 3.5$ at the $^{20}\text{Ne}/^{22}\text{Ne}$ intercept) compared to the canonical values previously observed for the crust (Kendrick et al., 2011; Lippmann-Pipke et al., 2011; Holland et al., 2013). Typically nucleogenic $^{21}\text{Ne}/^{22}\text{Ne}$ end-members have values of 0.47 - 0.79 at the $^{20}\text{Ne}/^{22}\text{Ne}$ intercept for modern crustal production (Kennedy et al., 1990; Ballentine and Burnard, 2002). Given that nucleogenic neon is produced via $^{17,18}\text{O}(\alpha, n)^{20,21}\text{Ne}$, $^{19}\text{F}(\alpha, n)^{22}\text{Na}(\beta^+)^{22}\text{Ne}$ and $^{19}\text{F}(\alpha, p)^{22}\text{Ne}$ (Wetherill, 1954), the dominant control on $^{21}\text{Ne}/^{22}\text{Ne}$ production is the ratio of oxygen to fluorine (O/F) in the proximity of U and Th-derived α particles ($\sim 40 \mu\text{m}$ Wetherill, 1954; Kennedy et al., 1990; Ballentine 1997; Ballentine and Burnard, 2002). In modern crust, $^{21}\text{Ne}/^{22}\text{Ne}$ production rates are lower by a factor of ~ 8 based on that predicted by average O/F ratios (Kennedy et al., 1990; Ballentine 1997; Ballentine and Burnard, 2002; Lippmann-Pipke et al., 2011). This has been interpreted as a relative localised enrichment of F within Th and U-bearing minerals resulting in a greater ^{22}Ne production than expected based on the bulk ratios (Kennedy et al., 1990). In Precambrian rocks, however, depletion in F has been observed resulting in bulk O/F ratios being elevated by roughly an order of magnitude (Lippmann-Pipke et al., 2011). This relative F deficit, resulting in reduced ^{22}Ne production, has been suggested as the potential cause for the elevated $^{21}\text{Ne}/^{22}\text{Ne}$ $^{21}\text{Ne}/^{22}\text{Ne}$ end-member values > 3 observed for the first time in the fracture waters of the South African gold mines (Lippmann-Pipke et al., 2011).

In this study, with the exception of Mine 2, all fluid samples also show elevated $^{21}\text{Ne}/^{22}\text{Ne}$ relative to $^{20}\text{Ne}/^{22}\text{Ne}$ (Figure 3). Lippmann-Pipke et al. (2011) attributed this to release of Ne-rich fluid inclusions from an earlier Precambrian source into the sampled younger fracture fluids (Lippmann-Pipke et al., 2011). However, in the case of Kidd Creek Mine, a similar explanation (fluid inclusion leakage) would require significant volumes of fluid addition from inclusion given the large volumes of water produced from these fracture fluid networks (Holland et al., 2013; Table 1). The simplest explanation is that the nucleogenic $^{21}\text{Ne}/^{22}\text{Ne}$ is a component of the original fracture fluids and has been produced based on the average O/F ratios within $\sim 40\ \mu\text{m}$ of any α emitters (U & Th) within the host rock. This average O/F ratio within would need to be greater than that of the modern crust by a factor of 4.9. This is lower than that observed by Lippmann-Pipke et al. (11.9) in rocks aged between 2.7 – 3.1 Ga. Although a speculative relationship between age and evolving $^{21}\text{Ne}/^{22}\text{Ne}$ crustal production ratios might be inferred, this difference may also simply reflect the specific formation histories and mineralogy of each locality and warrants further investigation.

5.6 Temporal evolution in the context of a hydrogeologic conceptual model for fracture networks

This study provides the longest temporal record of deep fracture fluids published to date. The resampling of 2.4 km depth after 44 months provides insight into the temporal evolution of this system. All radiogenic excesses per cm^3 of fluid decreased and radiogenic/non-radiogenic ratios evolved towards ASW ratios. In the case of ^4He , average abundances per cm^3 of fluid decreased by a factor of 1.85. At the same time the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio and the $^{136}\text{Xe}/^{130}\text{Xe}$ % deviation

decreased by factors of 2.07 and 1.86 respectively. In the case of neon a vector-based approach is applied. For this, the shift of each average $^{20}\text{Ne}/^{22}\text{Ne}$ & $^{21}\text{Ne}/^{22}\text{Ne}$ from the starting (ASW) composition was calculated and combined using the formula $a^2 + b^2 = c^2$. By dividing the combined value from the original study by the resampled combined value from the data presented here the relative decrease in radiogenic isotopes is quantified. This reveals a radiogenic reduction by a factor of 1.95 which is in line with that of the other isotope systems.

This consistent reduction of all noble gas excesses indicates a bulk (i.e. unfractionated) change in the mixing ratio between the initial ancient end-member composition as documented in Holland et al. (2013) and a less ancient component resulting in reduction in mean residence times. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values continue to rule out any modern meteoric fluid component impacting these samples (Table 10, Figure 8). Hence this secondary fluid must represent younger, but still old fluids discharging from the fracture network and contributing to the overall fluid discharging at the borehole collar (point of sampling). Such fluid evolution is consistent with the proposed conceptual model (Section 5.2).

6 Summary/conclusions

This work highlights that the isolated ancient fluid system discovered at 2.4 km depth in 2013 is not unique. We have expanded from this initial discovery to include three additional isolated fluid systems with average mean residence times spanning from 0.3 to 1.7 Ga.

The deeper level at Kidd Mine reveal the oldest mean fluid residence times ever encountered in free fluids (1.7 Ga). The resampled 2.4 km meanwhile indicates the addition of younger, yet still old fracture fluids, consistent with the conceptual model for these types of system. As the distance between the two levels is sufficient for the fluids to be isotopically distinct from one another, isolation between the two levels can be inferred. This gives additional constraints over the maximum size of the fluid reservoirs contributing to each system. The isolation occurred earlier for the deeper level based on radiogenic and early atmospheric ages which also fits with the proposed conceptual model. Outside of Kidd Mine the two new mines in the Sudbury system both indicate younger mean fluid residence times (0.3 Ga and 0.5 Ga for Mine 1 & 2 respectively) revealing the presence of ‘meso-age’ systems as well as the truly ancient. In all localities, a shielded xenon anomaly is present which has typically been attributed to an early atmosphere component. Given the timing of the Sudbury impact, which puts a maximum age on the oldest fluid component within these two mine systems (1.849 Ga), this work therefore reveals the process which fractionated xenon was still in operation beyond 2 Ga.

The discovery of each additional system suggests that ancient fluids may be far more pervasive within the deep crust than originally thought. Consequently, their occurrence needs to be more extensively documented, and quantitatively estimated. Future noble gas studies can identify additional ancient fluid systems, assess the volumes involved and determine the degree of hydrogeologic connection or isolation, from surface systems. Crucially though, the noble gases provide a temporal timeframe which can be combined with additional noble gas, stable isotope and biological investigation to glean insight into the geochemical and biological evolution of our planet.

7 Acknowledgements

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Figures

Figure 1. Location map of Kidd Creek Mine in Timmins and Mines 1 & 2 in the Sudbury Basin.

Latitude & Longitude of each mine are as follows; Kidd Creek Mine: 48° 41' 24" North, 81° 22'

0" West, Mine 1: 46° 39' 25" North, 80° 47' 34" West, Mine 2: 46° 39' 46" North, 81° 20' 34" West.

Figure 2. Average isotopic ratios from each locality relative to ^{36}Ar . The dashed line at 1 is the isotopic ratio for Air Saturated Water (ASW). ASW ratios given here are derived from seawater at 10 °C (Kipfer et al., 2002).

Figure 3. Comparison of neon isotopic ratios for samples from this and previous study. Data presented are 2.4 km samples from this work (black squares) and the 2013 study (blue squares), 2.9 km (red circles), Sudbury Mine 1 (green diamonds) and Mine 2 (gold star). Also given is the Air Saturated Water (ASW) value (orange cross), the mantle (solar) composition (blue cross, Graham, 2002). The two mixing lines shown for mixing between ASW and typical crustal radiogenic $^{21}\text{Ne}/^{22}\text{Ne}$ end-members for the crust (black line - from Ballentine & Burnard, 2002) and for mixing between ASW and an elevated $^{21}\text{Ne}/^{22}\text{Ne}$ end-member first defined by the fracture fluid and fluid inclusion data from the Archean-aged Witwatersrand Basin (red line - Lippman-Pipke et al., 2011).

Figure 4. Xenon excesses over modern air (normalised to ^{130}Xe). For each ^{136}Xe excess the relative fission spectra for uranium is plotted (dotted lines) which reaches good agreement with measured excesses for ^{134}Xe , ^{132}Xe and ^{131}Xe . Fission values taken from Ballentine and Burnard, (2002) and references therein. Fissiogenic excesses were calculated by anchoring the ^{238}U fission spectra to ^{136}Xe and calculating the expected corresponding $^{131-134}\text{Xe}$ excess.

Figure 5. Percentage deviations of $^{124-129}\text{Xe}/^{130}\text{Xe}$ in samples compared to modern atmospheric ratios. Values plotted are averages for each isotope per sampling level at each mine (Table 8).

The average percentage fractionation line for the $^{124-128}\text{Xe}$ excesses (dashed lines) was calculated as follows: 1. All individual percentage excesses for $^{124-128}\text{Xe}$ for each sample were divided by their respective mass difference from ^{130}Xe and an average excess per amu was calculated for each sample. 2. An average excess per amu was calculated for each sample. Lastly 3. Each average excess was multiplied by the mass difference from ^{130}Xe and plotted for each isotope. At Kidd Creek Mine, an additional ^{129}Xe excess is observed as described in Section 5.3, but not seen in the Sudbury Basin samples.

Figure 6. Mean residence time estimates based on radiogenic noble gas accumulation, presented graphically for all samples and compared to results from Holland et al. (2013). For context the last known major metasomatic event at Kidd Creek Mine, and the timing of the Sudbury bolide impact are also provided in the figure (Bleeker and Parrish, 1996; Davis, 2008). Analytical uncertainties for noble gas analysis are small. The large uncertainties for the error bars in this figure reflect minimum and maximum estimates in mean residence time estimates based on uncertainty in bulk porosity estimates for crystalline rock (see text) and are used to provide the most conservative possible sense of the mean residence time ranges derived from the data. Where analytical uncertainty exceeds known geological age, the upper limits of uncertainty have been restricted accordingly.

Figure 7. Schematic diagram outlining conceptual model for fractures within crystalline basement rock.

Figure 8. $\delta^{18}\text{O}$ & $\delta^2\text{H}$ values for fracture fluids at 2.4 km for ¹the original study and ²resampled fluids (this work). Values are given in Table 10. All values remain significantly elevated above the Global Meteoric Water Line with no isotopic evolution over time. This indicates the less old fluid present in the later samples has undergone a comparable extensive water-rock interaction

and therefore rules out the presence of recent meteoric water. Faded symbols for Kidd Creek Mine 2.9 km & Sudbury are supplementary values from additional sample suites (Frape et al., 1984; Li et al., 2016) which highlight the consistency of the noble gas-associated values with the rest of the ^2H & ^{18}O data (with no evidence of their movement towards the GMWL).

Tables

Borehole	Date	Fluid flow (ml/min)	Gas flow (cm ³ /min)
Kidd Creek Mine (2.4 km)			
12287	20.09.13	N.M.	variable
12299	03.04.14	180	300
Kidd Creek Mine (2.9 km)			
13684	01.03.12	*	1760
13684	14.06.12	*	1200
BH2	29.11.12	N.M.	3600
BH2	16.01.13	N.M.	1000
Sudbury Mine 1 (1.7 km)			
170128	29.11.13	2390	2000
170128	05.03.14	2140	410-1200
170128	22.10.14	2060	170-420
Sudbury Mine 2 (1.4 km)			
47774	06.03.14	2830	1130

Table 1. Locations, dates and flow rates of samples collected from each locality. Dates are presented in DD/MM/YY format. Flowrates given in ml/min and cm³/min for water and gas respectively. N.M. indicates not measured. * indicates standing water only, no artesian flow. Depth of level below land surface is also provided.

Sample	²⁰ Ne	error	³⁶ Ar	error	⁸⁴ Kr	error	¹³⁰ Xe	error
Air	1.65E-05		3.14E-05		6.50E-07		3.54E-09	
Kidd Mine								
(2.4 km)								
12287	1.71E-08	0.01E-08	2.22E-07	0.02E-07	5.79E-09	0.07E-09	6.46E-11	0.10E-11
12299	5.40E-08	0.05E-08	3.23E-07	0.03E-07	9.00E-09	0.11E-09	8.85E-11	0.14E-11
Average	3.55E-08	2.61E-08	2.73E-07	0.71E-07	7.4E-09	2.27E-09	7.66E-11	1.69E-11
Kidd Mine								
(2.9 km)								
13684	6.74E-09	0.06E-09	2.65E-08	0.05E-08	7.09E-10	0.08E-10	8.17E-12	0.12E-12
13684	9.02E-09	0.08E-09	2.28E-08	0.05E-08	7.99E-10	0.10E-10	9.09E-12	0.13E-12
BH2	8.42E-09	0.09E-09	2.66E-08	0.07E-08	8.76E-10	0.11E-10	1.11E-11	0.02E-11
BH2	1.03E-08	0.01E-08	3.07E-08	0.13E-08	9.26E-10	0.11E-10	1.17E-11	0.02E-11
Average	8.62E-09	1.49E-09	2.67E-08	0.32E-08	8.28E-10	0.94E-10	1.00E-11	0.17E-11
Sudbury Mine 1								
(1.7 km)								
170128	7.93E-07	0.08E-07	4.89E-06	0.05E-06	1.41E-07	0.02E-07	1.09E-09	0.02E-09
170128	6.15E-07	0.05E-07	4.12E-06	0.04E-06	1.26E-07	0.02E-07	1.02E-09	0.02E-09
170128	6.59E-07	0.07E-07	6.92E-06	0.07E-06	2.15E-07	0.03E-07	1.75E-09	0.03E-09
Average	6.89E-07	0.93E-07	5.31E-06	1.45E-06	1.61E-07	0.48E-08	1.29E-09	0.40E-09
Sudbury Mine 2								
(1.4 km)								
47774	3.31E-07	0.03E-07	3.72E-06	0.04E-06	1.11E-07	0.01E-07	1.01E-09	0.02E-09
Average	3.31E-07	0.03E-07	3.72E-06	0.04E-06	1.11E-07	0.01E-07	1.01E-09	0.02E-09

Table 2. Concentrations of non-radiogenic noble gas isotopes in gas samples. Values given in cm³ per cm³ of gas under STP conditions to three significant figures. Isotopes presented here represent non-radiogenic noble gas isotopes which are present in the geological system, that is, atmospheric-derived noble gas naturally occurring in the groundwaters due to water which had equilibrated with atmospheric noble gases at the time of recharge. For each level both individual samples and an average concentration are presented. For each average value the error

incorporates the standard deviation (1σ) of each individual measurement. Air values (compiled by (Ozima and Podosek, 2002) have been given for reference.

Sample	^{20}Ne	error	^{36}Ar	error	^{84}Kr	error	^{130}Xe	error
ASW	1.48E-07		1.01E-06		4.00E-08		5.21E-10	
Kidd Mine								
(2.4 km)								
12287	7.74E-08	0.06E-08	1.01E-06	0.01E-06	2.63E-08	0.03E-08	2.93E-10	0.05E-10
12299	1.69E-07	0.02E-07	1.01E-06	0.01E-06	2.81E-08	0.03E-08	2.76E-10	0.04E-10
Average	1.23E-07	0.65E-07	1.01E-06	0.00E+00	2.72E-08	0.13E-08	2.85E-10	0.12E-10
Kidd Mine								
(2.9 km)								
13684	2.57E-07	0.02E-07	1.01E-06	0.02E-08	2.70E-08	0.03E-08	3.11E-10	0.05E-10
13684	3.99E-07	0.03E-07	1.01E-06	0.02E-08	3.54E-08	0.04E-08	4.03E-10	0.06E-10
BH2	3.19E-07	0.04E-07	1.01E-06	0.02E-08	3.32E-08	0.04E-08	4.19E-10	0.06E-10
BH2	3.39E-07	0.03E-07	1.01E-06	0.04E-08	3.04E-08	0.04E-08	3.85E-10	0.06E-10
Average	3.29E-07	0.59E-07	1.01E-06	0.00E+00	3.15E-08	0.36E-08	3.79E-10	0.48E-10
Sudbury Mine 1								
(1.7 km)								
170128	1.64E-07	0.02E-07	1.01E-06	0.01E-06	2.92E-08	0.04E-08	2.26E-10	0.04E-10
170128	1.51E-07	0.01E-07	1.01E-06	0.01E-06	3.08E-08	0.04E-08	2.49E-10	0.04E-10
170128	9.61E-08	0.10E-08	1.01E-06	0.01E-06	3.13E-08	0.04E-08	2.55E-10	0.04E-10
Average	1.37E-07	0.39E-07	1.01E-06	0.00E+00	3.04E-08	0.11E-08	2.43E-10	0.15E-10
Sudbury Mine 2								
(1.4 km)								
47774	8.98E-08	0.08E-08	1.01E-06	0.01E-06	3.00E-08	0.04E-08	2.75E-10	0.04E-10
Average	8.98E-08	0.08E-08	1.01E-06	0.00E+00	3.00E-08	0.04E-08	2.75E-10	0.04E-10

Table 3. Concentrations of non-radiogenic noble gas isotopes expressed per cm^3 of fracture fluid to three significant figures. Concentrations are calculated by dividing the concentration per cm^3 of gas by the total amount of water which has been degassed. Degassed water volume is derived

assuming a ^{36}Ar content of $1.01 \times 10^{-6} \text{ cm}^3/\text{cm}^3$ of water based on concentrations in seawater at 10°C after the methods of (Kipfer et al., 2002). For each level both individual samples and an average concentration is presented. The error on the average value incorporates the standard deviation (1σ). Air Saturated seawater at 10°C are provided for reference (Kipfer et al., 2002).

Sample	$^3\text{He}/^4\text{He}$ (R/R _A)	error	$^{20}\text{Ne}/^{22}\text{Ne}$ error	$^{21}\text{Ne}/^{22}\text{Ne}$ error	$^{40}\text{Ar}/^{36}\text{Ar}$ error	$^{38}\text{Ar}/^{36}\text{Ar}$ error				
Air/ASW	1.0000		9.80		0.029		295.5		1.880E-01	
Kidd Mine (2.4 km)										
12287	2.30E-02	0.07E-02	8.64	0.02	2.861E-01	0.002 E-01	16300	100	1.94E-01	0.02
12299	2.14E-02	0.05E-02	8.770	0.004	2.397E-01	0.001 E-01	13800	100	1.93E-01	0.02
Average	2.22E-02	0.11E-02	8.71	0.09	2.63E-01	0.33 E-01	15100	1780	1.94E-01	0.01
Kidd Mine (2.9 km)										
13684	2.56E-02	0.06E-02	5.06	0.01	5.935E-01	0.002E-01	77500	1270	2.25E-01	0.05E-01
13684	2.47E-02	0.06E-02	5.27	0.02	5.722E-01	0.003E-01	91000	1990	1.99E-01	0.09E-01
BH2	2.59E-02	0.05E-02	5.324	0.004	6.189E-01	0.002E-01	116000	2680	2.28E-01	0.07E-01
BH2	2.61E-02	0.05E-02	5.44	0.01	6.056E-01	0.005E-01	125000	5230	1.83E-01	0.12E-01
Average	2.56E-02	0.06E-02	5.27	0.16	5.98E-01	0.20E-01	102000	22000	2.09E-01	0.22E-01
Sudbury Mine 1 (1.7 km)										
170128	1.96E-02	0.04E-02	8.728	0.004	1.38E-01	0.001E-01	4330	5	1.912E-01	0.005E-01
170128	1.95E-02	0.04E-02	8.772	0.004	1.39E-01	0.001E-01	4430	6	1.954E-01	0.004E-01
170128	1.95E-02	0.04E-02	8.88	0.01	1.37E-01	0.001E-01	4310	4	1.918E-01	0.005E-01
Average	1.95E-02	0.01E-02	8.79	0.08	1.38E-01	0.01E-01	4350	63	1.93E-01	0.02E-01
Sudbury Mine 2 (1.4 km)										
47774	2.30E-02	0.0005	7.960	0.002	1.324E-01	0.001E-01	17600	82	1.97E-01	0.01E-01
Average	2.30E-2	0.001	7.960	0.002	1.324E-01	0.001E-01	17600	82	1.97E-01	0.01E-01

Table 4. Noble gas isotope ratios for the sample suite given to three significant figures. Where the uncertainty is lower than the third significant figure an additional significant figure is given. For each level both individual samples and an average concentration is presented. The error on the average value is taken as the standard deviation (1σ). Helium $^3\text{He}/^4\text{He}$ ratios are given in R/R_A where $R_{A(\text{air})} = 1$. Absolute $^3\text{He}/^4\text{He}_{(\text{air})} = 1.399 \times 10^{-6}$ (Mamyrin et al., 1970). Air/ASW values (compiled by (Ozima and Podosek, 2002) have been given for reference.

Sample	$^{124}\text{Xe}/^{130}\text{Xe}$	error	$^{126}\text{Xe}/^{130}\text{Xe}$	error	$^{128}\text{Xe}/^{130}\text{Xe}$	error	$^{129}\text{Xe}/^{130}\text{Xe}$	error
Air/ASW	2.34E-02		2.18E-02		4.72E-01		6.496	
Kidd Mine (2.4 km)								
12287	2.37E-02	0.01E-02	2.18 E-02	0.01E-02	4.79E-01	0.02E-01	6.56	0.03
12299	2.37E-02	0.02E-02	2.18 E-02	0.02E-02	4.74E-01	0.04E-01	6.61	0.04
Average	2.370E-02	0.003E-02	2.183 E-02	0.001E-02	4.76E-01	0.03E-01	6.58	0.03
Kidd Mine (2.9 km)								
13684	2.40E-02	0.01E-02	2.19 E-02	0.01E-02	4.82E-01	0.02E-01	6.72	0.02
13684	2.39E-02	0.01E-02	2.20 E-02	0.01E-02	4.78E-01	0.02E-01	6.71	0.01
BH2	2.42E-02	0.02E-02	2.23 E-02	0.01E-02	4.86E-01	0.02E-01	6.80	0.02
BH2	2.41E-02	0.01E-02	2.23 E-02	0.01E-02	4.83E-01	0.02E-01	6.75	0.01
Average	2.41E-02	0.01E-02	2.21 E-02	0.02E-02	4.82E-01	0.03E-01	6.75	0.04
Sudbury Mine 1 (1.7 km)								
170128	2.37E-02	0.01E-02	2.19 E-02	0.01E-02	4.74E-01	0.02E-01	6.52	0.03
170128	2.37E-02	0.01E-02	2.19 E-02	0.01E-02	4.75E-01	0.02E-01	6.53	0.03
170128	2.35E-02	0.01E-02	2.21 E-02	0.01E-02	4.76E-01	0.02E-01	6.51	0.03
Average	2.36E-02	0.01E-02	2.20 E-02	0.01E-02	4.75E-01	0.01E-01	6.52	0.01
Sudbury Mine 2 (1.4 km)								
47774	2.34E-02	0.01E-02	2.21 E-02	0.01E-02	4.77E-01	0.03E-01	6.55	0.03
Average	2.34E-02	0.01E-02	2.21 E-02	0.01E-02	4.77E-01	0.03E-01	6.55	0.03
Sample	$^{131}\text{Xe}/^{130}\text{Xe}$	error	$^{132}\text{Xe}/^{130}\text{Xe}$	error	$^{134}\text{Xe}/^{130}\text{Xe}$	error	$^{136}\text{Xe}/^{130}\text{Xe}$	error
Air/ASW	5.213		6.607		2.563		2.176	
Kidd Mine (2.4 km)								
12287	5.22	0.03	6.72	0.03	2.77	0.01	2.41	0.01
12299	5.45	0.03	6.78	0.04	2.80	0.02	2.44	0.01
Average	5.33	0.16	6.75	0.04	2.79	0.02	2.42	0.02
Kidd Mine (2.9 km)								
13684	5.33	0.01	7.60	0.02	4.16	0.02	4.11	0.02
13684	5.94	0.02	7.51	0.02	4.03	0.01	3.94	0.01
BH2	5.35	0.01	7.66	0.02	4.24	0.01	4.21	0.02
BH2	5.31	0.01	7.53	0.02	4.09	0.01	4.01	0.01
Average	5.48	0.30	7.58	0.07	4.13	0.09	4.07	0.12
Sudbury Mine 1 (1.7 km)								
170128	5.22	0.02	6.72	0.03	2.75	0.01	2.39	0.01
170128	5.23	0.02	6.74	0.03	2.76	0.01	2.40	0.01
170128	5.21	0.02	6.71	0.03	2.74	0.01	2.37	0.01
Average	5.22	0.01	6.72	0.02	2.75	0.01	2.39	0.01
Sudbury Mine 2 (1.4 km)								
47774	5.27	0.03	7.08	0.04	3.27	0.02	3.00	0.02
Average	5.27	0.03	7.08	0.04	3.27	0.02	3.00	0.02

Table 5. Xenon noble gas isotope ratios for the sample suite given to three significant figures. Where the uncertainty is lower than the third significant figure an additional significant figure is given. For each level both individual samples and an average concentration is presented. The error on the average value incorporates the standard deviation (1σ). Air values (compiled by (Ozima and Podosek, 2002) have been given for reference.

Sample	$^4\text{He}^*$	error	$^{21}\text{Ne}^*$	error	$^{40}\text{Ar}^*$	error	$^{136}\text{Xe}^*$	error
Kidd Mine								
(2.4 km)								
12287	6.88E-02	0.10E-02	2.33E-09	0.03E-09	1.62E-02	0.02E-02	6.87E-11	0.15E-11
12299	9.49E-02	0.13E-02	4.11E-09	0.05E-09	1.36E-02	0.02E-02	7.27E-11	0.17E-11
Average	8.19E-02	1.85E-02	3.22E-09	1.26E-09	1.49E-02	0.18E-02	7.07E-11	0.28E-11
Kidd Mine								
(2.9 km)								
13684	6.69E-01	0.09E-01	2.93E-08	0.04E-08	7.79E-02	0.16E-02	6.02E-10	0.13E-10
13684	8.65E-01	0.12E-01	4.22E-08	0.05E-08	9.15E-02	0.22E-02	7.11E-10	0.15E-10
BH2	9.09E-01	0.13E-01	3.61E-08	0.06E-08	1.17E-01	0.03E-01	8.51E-10	0.18E-10
BH2	7.47E-01	0.11E-01	3.67E-08	0.04E-08	1.26E-01	0.05E-01	7.06E-10	0.15E-10
Average	7.97E-01	1.10E-01	3.61E-08	5.29E-09	1.03E-01	2.22E-02	7.17E-10	1.03E-10
Sudbury Mine 1								
(1.7 km)								
170128	6.96E-02	0.10E-02	2.11E-09	0.03E-09	4.07E-03	0.05E-03	4.81E-11	0.11E-11
170128	5.88E-02	0.09E-02	1.93E-09	0.02E-09	4.17E-03	0.05E-03	5.48E-11	0.12E-11
170128	3.95E-02	0.06E-02	1.20E-09	0.02E-09	4.05E-03	0.06E-03	5.07E-11	0.12E-11
Average	5.60E-02	1.53E-02	1.75E-09	0.48E-09	4.09E-03	0.06E-03	5.12E-11	0.34E-11
Sudbury Mine 2								
(1.4 km)								
47774	2.79E-02	0.04E-02	1.23E-09	0.02E-11	1.75E-02	0.02E-02	2.27E-10	0.05E-10
Average	2.79E-02	0.04E-02	1.23E-09	0.02E-11	1.75E-02	0.02E-02	2.27E-10	0.05E-10

Table 6. Concentrations of excess radiogenic noble gas isotopes expressed per cm^3 of fracture fluid given to three significant figures. The method for deriving concentrations within the fracture fluid is outlined in the main text. Isotopes presented here represent radiogenic noble gas isotopes which have accumulated within the system over time due to naturally occurring radioactive decay of parent isotopes. *In situ* radiogenic noble gas concentrations are derived by multiplying the measured ratios (Tables 5 & 6) by non-radiogenic concentrations (Table 3) and subtracting this from total concentrations of the radiogenic isotopes. For each level both individual samples and an average concentration is presented. The error on the average value incorporates the standard deviation (1σ).

Sample	$^4\text{He}^*$	error	$^{21}\text{Ne}^*$	error	$^{40}\text{Ar}^*$	error	$^{136}\text{Xe}^*$	error
Kidd Mine								
(2.9 km)								
13684	3.84E-01	0.05E-01	1.69E-08	0.02E-08	7.79E-02	0.16E-02	1.01E-09	0.02E-09
13684	3.19E-01	0.05E-01	1.56E-08	0.02E-08	9.15E-02	0.23E-02	9.20E-10	0.19E-10
BH2	4.21E-01	0.06E-01	1.67E-08	0.03E-08	1.17E-01	0.30E-02	1.06E-09	0.02E-09
BH2	3.25E-01	0.05E-01	1.60E-08	0.02E-08	1.26E-01	0.55E-02	9.55E-10	0.20E-10
Average	3.58E-01	0.49E-01	1.62E-08	0.237E-08	1.03E-01	0.22E-01	9.85E-10	1.41E-10

Table 7. Corrected concentrations of excess radiogenic noble gas isotopes per cm^3 of fracture fluid for Kidd Creek Mine at 2.9 km depth given to three significant figures. Excesses corrected for effect of Rayleigh degassing using ASW-derived component (see text).

Sample	^{124}Xe (%)	error	^{126}Xe (%)	error	^{128}Xe (%)	error	^{129}Xe (%)	error
Kidd Mine								
(2.4 km)								
12287	1.51	0.01	0.165	0.001	1.50	0.01	0.96	0.01
12299	1.30	0.01	0.115	0.001	0.535	0.004	1.72	0.01
Average	1.40	0.14	0.140	0.036	1.02	0.68	1.34	0.54
Kidd Mine								
(2.9 km)								
13684	2.73	0.02	0.616	0.003	2.23	0.01	3.48	0.01
13684	2.39	0.01	1.05	0.01	1.33	0.01	3.36	0.01
BH2	3.39	0.02	2.12	0.01	2.97	0.02	4.64	0.01
BH2	3.30	0.02	2.39	0.01	2.44	0.01	3.91	0.01
Average	2.95	0.48	1.54	0.85	2.24	0.68	3.85	0.58
Sudbury Mine								
1 (1.7 km)								
170128	1.62	0.01	0.563	0.003	0.613	0.003	0.315	0.001
170128	1.34	0.01	0.536	0.003	0.626	0.002	0.537	0.002
170128	0.51	0.003	1.22	0.01	0.887	0.004	0.204	0.001
Average	1.16	0.57	0.772	0.386	0.709	0.154	0.352	0.170
Sudbury Mine								
2 (1.4 km)								
47774	0.036	0.0002	1.45	0.01	1.09	0.01	0.768	0.004

Table 8. Percentage deviations of $^{124-129}\text{Xe}/^{130}\text{Xe}$ in samples over modern atmospheric ratios given to three significant figures. Where the uncertainty is lower than the third significant figure an additional significant figure is given. Average values and the standard deviation are also provided.

Sample location	^4He Age	$\pm$	^{21}Ne Age	$\pm$	^{40}Ar Age	$\pm$	^{136}Xe Age	$\pm$	Ave	$\pm$
12261	850	386	1340	609	971	439	1509	686	1168	309
12299-1	1493	678	1527	697	1396	632	1666	757	1521	112
12299-2	951	432	1594	728	999	453	1321	601	1216	301
12299-3	1142	515	1570	720	1095	496	1613	731	1355	274
12287-2	666	303	1174	538	884	400	919	418	911	208
Kidd Mine (2.4 km)¹	1026	577	1443	683	1078	559	1411	719	1240	218
12287	482	219	166	75	638	288	149	68	359	241
12299	658	298	290	132	552	249	157	71	414	231
Kidd Mine (2.4 km)²	570	289	228	136	595	278	153	70	387	229
13684	2149	975	1024	464	1884	850	1763	800	1705	482
13684	1834	832	951	431	2078	938	1627	738	1622	484
BH2	2316	1050	1015	460	2387	1077	1842	836	1890	632
BH2	1860	844	973	441	2493	1129	1683	764	1752	625
Kidd Mine (2.9 km)	2023	959	986	470	2226	1112	1729	822	1741	543
170128	790	389	245	121	224	101	171	84	357	290
170128	671	331	225	111	229	103	194	96	330	228
170128	456	225	140	69	222	100	180	89	250	142
Sudbury Mine 1 (1.7 km)	640	360	204	115	225	101	182	90	313	219
47774	344	170	153	75	850	383	828	408	544	350
Sudbury Mine 2 (1.4 km)	344	170	153	75	850	383	828	408	544	350

Table 9. Individual borehole and overall average ages for each sampling locality for each radiogenic isotope based on radiogenic excesses. Ages given in Ma. ¹Represents the age of Kidd Mine at 2.4 km depth recalculated from Holland et al. (2013) using new estimates of bulk porosity as a function of depth and renormalizing to ³⁶Ar (Sherwood Lollar et al., 2014). ²Represents ages derived from samples taken from the same boreholes as the Holland et al. (2013) study 44 months later. Residence times are calculated from the average radiogenic excess per sample location (Tables 4 and 7). The observed uncertainty is primarily a result of poor constraints on the bulk porosity ($\pm 45\%$) rather than analytical uncertainty (1-2 %).

Sample location	$\delta^{18}\text{O}$	error	$\delta^2\text{H}$	error
12261	-12.8	0.2	-32.0	0.8
12299-1	-12.8	0.2	-38.6	0.8
12299-2	-13.3	0.2	-35.8	0.8
12299-3	-13.5	0.2	-36.7	0.8
12287-2	-13.0	0.2	-40.5	0.8
Kidd Mine (2.4 km)¹	-13.1	0.3	-36.7	3.2
12287	-13.1	0.2	-35.3	0.8
12299	-12.9	0.2	-33.1	0.8
Kidd Mine (2.4 km)²	-13.0	0.2	-34.2	1.6

Table 10. $\delta^{18}\text{O}$ & $\delta^2\text{H}$ values for fracture fluids at 2.4 km for ¹the original study and ²resampled fluids (this work). Values are expressed as per mil (‰) variations from Vienna Standard Mean Ocean Water (VSMOW). Errors for individual measurements are ± 0.2 and ± 0.8 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ respectively. Analytical techniques are outlined in Appendix B.