86Kr excess and other noble gases identify a billion-year-old radiogenically-enriched groundwater system

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Deep within the Precambrian basement rocks of the Earth, groundwaters can sustain subsurface microbial communities, and are targets of investigation both for geologic storage of carbon and/or nuclear waste, and for new reservoirs of rapidly depleting resources of helium. Noble gas-derived residence times have revealed deep hydrological settings where groundwaters are preserved on millions to billion-year timescales. Here we report groundwaters enriched in the highest concentrations of radiogenic products yet discovered in fluids, with an associated 86Kr excess in the free fluid, and residence times >1 billion years. This brine, from a South African gold mine 3 km below surface, demonstrates that ancient groundwaters preserved in the deep continental crust on billion-year geologic timescales may be more widespread than previously understood. The findings have implications beyond Earth, where on rocky planets such as Mars, subsurface water may persist on long timescales despite surface conditions that no longer provide a habitable zone.
The Precambrian crystalline basement represents approximately 72% of the continental crust by surface area and is estimated to host up to 30% of the total groundwater inventory of the Earth. Annual H2 production in these environments via water-rock reactions has recently been shown to be comparable to that of the oceanic crust. In these deep crustal environments, long-term radiogenic and other processes of water-rock reactions including serpentinization produce complex fluids characterized by Ca-Na-Cl salinity and products of abiotic organic synthesis such as acetate and formate as well as CH4 and higher hydrocarbons via Fischer-Tropsch-type reactions. These processes are capable of sustaining chemolithotrophic deep subsurface microbial communities. Typically disconnected from the modern surface hydrologic cycle, these fracture fluids accumulate radiogenic noble gases produced as by-products of radioelement (U, Th, K) decay over geologic time, with mean residence times ranging over ka-Ga timescales and have distinctive isotopic and elemental fluid compositions and high concentrations of reduced gases (e.g. H2, CH4) from long-term, low-K serpentinite-water-rock interaction. Subsurface microbial communities have been identified in these fracture networks and investigations of their genomic lineage is providing insight into the evolutionary history of the deep biosphere and the transport, and timing of isolation of deep life within the planetary crust. Due to the long timescales involved, conventional short-lived tracers such as 3He, or 14C cannot be applied, and instead geochronology of the fluids depends on measuring and interpreting the accumulation of radiogenic 4He, 21Ne, 40Ar, and 136Xe, produced through the decay of U, Th, and K in the host rocks. At Kidd Creek Observatory on the Canadian Precambrian Shield, concordant noble gas-derived residence time estimates from four independent noble gas tracers identified fluids with residence times of up to 1.7 Ga, the oldest free-flowing fluids on record. The concordance of the noble gas systems, and other multiple lines of evidence (e.g. δ18O, δ3H, sulfur isotopes) demonstrated the Kidd Creek fracture network was an example of extended hydrogeologic isolation of fluids. On the other end of the open-closed spectrum, some deep crustal environments are impacted by the penetration of surface-derived paleometeoric water with residence times in the ka-Ma range to depths of more than 1 km.

Moab Khotson Mine (26.9792°S, 26.7815°E) is a gold and uranium mine located in the Witwatersrand Basin, within the Kaapvaal Craton, South Africa. Geologically, the craton formed approximately 3.7–2.6 Ga and consists of granites-greenstones, tonalite-trondhjemite-granodiorite gneisses, mafic-ultramafic rocks and sedimentary rocks. The Witwatersrand Basin formed due to tectono-magmatic activity between 3.074 and 2.642 Ga. The Witwatersrand Supergroup is subdivided into the Central Rand Group, consisting primarily of terrigenous quartzites with minor conglomerates and shales, and overlying the West Rand Group, which consists of transitional marine-to-continentals shelves and quartzites. Deposition of Witwatersrand Supergroup terminated at 2.714 Ga when the overlying Ventersdorp Supergroup lavas were deposited. The principal economic target at Moab Khotson is the U-Au-rich Vaal Reef conglomerate, which is stratigraphically located in the middle of the Central Rand Group.

Here we report noble gas concentrations and isotopic data from a borehole drilled at the mine into the uppermost West Rand Group at an average inclination of 47° starting at 2.896 km below land surface (kmbs), and extending 810 m to a depth of 3.491 kmbs. This borehole intersects fractures including a major mineralized fracture zone at a depth of 3.213 kmbs in a subhorizontal mafic intrusion located 50 m above the 2.914 ± 8 Ga Crown Lava. The fracture system releases a Ca-Na-Cl brine in situ pressure = 102 bars and temperature = 54 °C with high concentrations of reduced gases such as H2, CH4, C2H6, δ3H and δ3H isotope values for the fluids plot well above the Global Meteoric Water Line (GMWL), confirming that this fracture fluid system is isolated from the surface hydrologic cycle (Supplementary Tables 1, 4). The noble gas data presented here reveal these fluids have a residence time of >1 billion years, confirm the unambiguous presence of a preserved 86Kr excess observed in a free fluid, and reveal that preservation of fluids on billion-year geologic timescales are a feature of the deep continental crust on a global scale. Distinctive patterns in the light versus heavy noble gas signatures here quantify processes controlling hydrogeologic isolation in these deep fracture systems. This is critical to advancing our understanding of the timing and degree to which deep subsurface groundwater systems are open versus closed to the surface hydrosphere, and provide insight into the processes controlling accumulation versus diffusive loss.

Results

In the subsurface, noble gases have three potential sources; Air-Saturated Water (ASW), the mantle, and in situ radiogenic production in the crust through radioactive decay of U, Th, and K producing noble gases such as 4He, 21Ne, 40Ar, and 131-136Xe. There is no evidence of a significant mantle input at Moab Khotson, consistent with previous studies. The Moab Khotson noble gas samples show highly radiogenic ratios with a He/Ra of 0.02 (where Ra represents the air 4He/Ra ratio of 1.4 × 10^-6), 40Ar/Ra ratios of up to 49,000, and the distinctive elevated radiogenic Ne/22Ne ratios found to date only in hydrogeologically isolated fluids in the Precambrian crusted such as the Kidd Creek billion-year-old fluids.

86Kr – an emerging tracer. Remarkable deviations from ASW like those observed in Ne (Fig. 1) and Xe isotopes (Fig. 2) are also apparent in the 86Kr/80Kr ratio. Excess Kr (meaning 86Kr added in the crust due to radiogenic processes) is calculated as Eq. (1):

\[ 86Kr^* = \frac{86Kr_{FF} - 86Kr_{ASW} \times 80Kr_{ASW}}{80Kr_{ASW}} \]
the 238U fission origin for observed 131–136Xe∗ (Fig. 2), and the agreement of 86Kr*/136Xe* with in situ production ratios, all identify an environment in which the heavy noble gas signatures are dominated by radiogenic processes to an extent never previously identified.

Billion-year fluid residence times. The highly radiogenic-environment at Moab Khotson demonstrated by the 86Kr* and 131–136Xe* excess has important implications for estimating fluid residence times. Starting with the simple assumption of average host rock U, Th, and K concentrations for the region of 2.33 ppm, 10.9 ppm, and 1.91%, respectively, and total noble gas release from the host matrix, the apparent residence times calculated for 4He*, 21Ne*, 40Ar*, and 136Xe* for the Moab Khotson fluids vary significantly. Estimates range from 1.03 Ga (4He*), 1.36 Ga (21Ne*), 1.20 Ga (40Ar*) to 4.11 Ga (136Xe*), with the apparent Xe-derived residence time unrealistically far in excess of the geologic setting (Supplementary Table 5). Such discordant residence times derived from the different noble gases indicate that simple assumptions of average regional crustal U, Th, and K concentrations are insufficient to describe the system, in particular the high 136Xe* excess. The high concentrations of U within this gold-uranium mine setting would have had a major impact on the accumulation of 4He*, 21Ne*, 86Kr*, and 136Xe*, but do not affect residence time estimates based on 40Ar*, as the production of 40Ar is exclusively derived from decay of 40K. Thus, although apparent ages are shown for completeness for all four noble gas systems (Supplementary Table 5), and alternative frameworks are considered (see Methods), the most reasonable and conservative estimate of residence times at Moab Khotson must be the estimate of 1.2 Ga based on 40Ar* (see Methods). The dependence and sensitivity of this residence time on the key parameters of radionuclide concentration, noble gas release, porosity, and rock density are fully evaluated in the Methods. The U concentrations that can reconcile the difference between the conservative 40Ar* estimate of 1.2 Ga and 136Xe* estimates can be calculated, and the 40Ar* and 136Xe* estimates reconcile for a local U concentration of 19.8 ppm. Such an enhancement above the average values observed elsewhere in the Central Rand Group is consistent with the elevated uranium concentrations in the mining area in general26,36,37, and even higher local U values of 309–2847 ppm29 reported for the proximal U-rich Vaal Reef conglomerate being extracted at the mine.

To date, deep fracture waters with more than a billion-year residence time had only been identified at Kidd Creek on the Canadian Shield2,14. The 1.2 Ga estimate calculated here for Moab Khotson confirms that the Kidd Creek system is not unique, and most importantly demonstrates that on a global scale the deep crystalline rocks of the Earth’s Precambrian cratons can preserve settings wherein ancient fracture fluids rich in products of water-rock reactions (including both serpentinization and radiolysis)6,11,12,19 can be sustained on a geologic timescale. The noble gas residence times and their fidelity to in situ production ratios allow a search strategy for identifying ancient fracture water systems around the world where additional research on the deep subsurface hydrosphere should be focused.
Diffusive loss of the lighter elements. In addition to critical constraints on fracture water residence times from the heavier noble gases, the light noble gases in particular provide process-level information on transport within the deep fracture networks. Although the residence time estimates from \(^{4}\text{He}\)* and \(^{21}\text{Ne}\)* at first glance apparently agree within uncertainty with the value of 1.2 Ga derived from \(^{40}\text{Ar}\)* (Supplementary Table 5), the abundant evidence of high radiogenic input in this environment attested to by the \(^{86}\text{Kr}\)* and \(^{136}\text{Xe}\)* (Supplementary Table 5), the abundant evidence of high radiogenic input in this environment attested to by the \(^{86}\text{Kr}\)* and \(^{136}\text{Xe}\)* (Supplementary Table 5). The consistency between the observed \(^{131}\text{Xe}\)* and expected fissionogenic production ratios from Fig. 2, coupled with the \(^{86}\text{Kr}\)* and \(^{136}\text{Xe}\)* production matching predicted production ratios from Fig. 3, confirm negligible diffusive loss of both \(\text{Kr}\) and \(\text{Xe}\). For simplicity, this model considers slow, long-term progressive diffusion over long geologic time. However, regional tectonic events, as discussed in the following section, may have resulted in periods of enhanced rate of loss of these light elements. Overall, the noble gas data reveals that while Moab Khotsong is, like Kidd Creek, preserving ancient fluids on unprecedented geologic timescales and hydrogeologically closed to mixing with younger fluids derived from the surface photosphere, the system is open to diffusive loss of the lighter components. This therefore highlights the wealth of process information on fluid residence time and transport available from the suite of light to heavy noble gases.

**Discussion**

Crystalline rock-hosted fracture fluids in Precambrian cratons globally create settings where products of water-rock reaction, including radiolysis and serpentinization, can accumulate and preserve habitable environments on timescales much longer than the <200-million-year-old oceanic crust. Most studies to date have focused on fracture systems still in connection with the surface on timescales of up to tens of millions of years. Considerable attention too has focused on an example of extended hydrogeologic isolation at Kidd Creek in Canada where concordant residence times indicate isolation on a 1–2-billion-year timescale. Understanding the processes controlling isolation versus connection of deep fracture networks, and the implications for the nature and distribution of microbial life hosted within these environments, requires targeted investigation of sites along the spectrum from open to closed. To date, the Witwatersrand Basin has provided the largest and most diverse spectrum of continental sites, ranging from those with meteoric groundwaters less than a decade to few thousand years old, to sites dominated by paleoceanic water that recharged from surface to ~3 km depth up to 100 Ma years ago. Data
from the basement crust is commonly considered for overlying light molecules produced in the basement 3,4,6,11,46 are less the oceanic crust 3,4,30, long-term event at 2.02 Ga 42. At another major impact crater, the Sudbury Moab Khotsong are among the most elevated above the GMWL may exist in long-term isolation 11,19,47. With respect to noble gas budgets, the global production of noble gases in these deep crustal fluids that signifi- cant volumes at depths of 1.4 to 1.7 km were attributed to the regional effects of fracturing related to the impact that enabled greater penetration of younger fluids into the crust than observed at Kidd Creek 5. The spectrum of paleo- meteoric waters penetrating to great depth at many sites in the Witwatersrand Basin may similarly have been facilitated by the impact, and late-stage intrusive processes, and augmented by late-stage plateau elevation 17,18,21,36,41.

The data from the newly investigated site at Moab Khotsong in this study extends the spectrum of sites in South Africa by demonstrating the presence of an ancient billion-year-old brine end-member. Previously published δ18O and δD data for Moab Khotsong are among the most elevated above the GMWL ever reported 5 (Supplementary Table 1). This paper quantitatively establishes the Ga-residence times and confirms the 85Kr* and noble gas signatures that demonstrate the unprecedented radiogenic content of the Moab Khotsong fracture fluids. Importantly, the data demonstrate that while no hydrogeologic mixing with younger fluids is occurring, diffusive transport is an important process controlling loss of He and Ne relative to the heavy noble gases (Ar, Kr, Xe). This study provides critical insight into the degree to which deep fracture networks represent virtual time capsules in the crust, as at Kidd Creek, or whether, as at Moab Khotsong, the system may be hydrogeologically closed to penetration and mixing with surface-derived fluids, but still open to diffusive loss of light elements on long geologic timescales. Specifically, Moab Khotsong confirms that significant loss of more mobile fluid components (e.g. He, Ne, and potentially H2) can occur even where fluids have Ga residence times. Though He flux from the basement crust is commonly considered for overlying geologic systems 30,39,43–45, outward fluxes of H2, CH4, and other light molecules produced in the basement 4,5,6,11,46 are less common 44. Given that deep crustic systems are estimated globally to produce H2 and He on the same order of magnitude as the oceanic crust 3,4,30, long-term flux from ‘more open’ systems such as Moab Khotsong into overlying lithologies may additionally provide a deep flux of H2 too within significant volumes of the crust over planetary timescales. Conversely, where diffusive fluxes are minimal (e.g. Kidd Creek), these deep fracture fluids may exist in long-term isolation 11,19,47. With respect to noble gas budgets, the global production of noble gases in these deep crustal settings has been recently revealed to be comparable to production from the oceanic crust and mid-ocean ridges 4. This paper demonstrates, through a process-based investigation applying the full suite of noble gases, that deep continental settings have the capacity to accumulate gases and fluids on up to billion-year timescales. Distinguishing between diffusive flux out of the subsurface, and/or geologic accumulation of these components, is critical to evaluating the significance of potential sites for geologic storage 36,39,45,48 and in the context of formation of economic-grade noble gas reservoirs in a world rapidly running short of helium 49.

This study demonstrates how, in these radiogenically-dominated environments, even conservative noble gas signatures can be substantially different compared to average crust, and underscores the necessity to re-evaluate our understanding of radiogenic processes and end-members, both for conservative noble gases, and for reactive molecules such as H2, SO2 or acetate produced by radiolysis in addition to other water-rock reactions such as serpentinitization 3,11,19. Such radiogenically enriched-environments will inevitably also impact assumptions about the in situ production processes, rates and background levels for radiogenic-linked groundwater dating tracers such as 3H, 14C, 3Cl, and 3Kr, in addition to radiogenic noble gases. The findings of this study underscore the need to expand understanding of key radiogenic processes in the crust, both continental and marine, to validate quantitative models of fluid age and transport critical to understanding the degree of isolation, or degree of connection, of the subsurface to surface processes. Constraining radiogenic processes and their associated fluxes will provide refined habitability models of the subsurface, both for the Earth and on other solar system bodies, where habitability driven by radiolysis is a major driver of current investigation 2,14,30–32.

Methods
Sample collection. Two noble gas samples were collected in 2019 from a borehole located at 2.9 kmbs in Moab Khotsong Mine, South Africa, following methods described in previous studies 14,17. Briefly, gas tight Tygon tubing was connected to a sampling valve on an Inconel U-tube/packer device. This device had been installed into the borehole to collect fluids entering the borehole from intersecting fracture fluid networks. A downhole pressure/temperature sensor (GEO PSI, Cal- gary, AB T2E 8Z9, Canada) indicated that the in situ fluid pressure was 10.2 MPa and temperature was 54 °C. The sampling valve was then opened and the pressurized fluids flowed through a gas stripper to separate the gas and water phases. Gas samples were collected in triplicate per standard sampling techniques in refrigeration-grade, internally polished, 3/8” diameter copper tubes. Prior to sample collection, gas flow rates were measured and, based on this, the sampling apparatus was flushed a minimum of 6 times the internal volume to ensure the collected gas samples were representative of the fracture network. Once flushing was complete, the copper tubes were cold-welded shut in sequence using a hydraulic crimping device.

For gas compositional analysis, samples were collected in pre-evacuated 160 ml borosilicate glass serum vials containing 100 μg of saturated HgCl2 using a gas-tight syringe with a 22-g syringe needle following established methods developed for sampling these gases 64,65.

Noble gas analysis. The noble gas samples were extracted, purified, and measured at the Noble Laboratory, University of Oxford using existing protocols 55 previously modified for analyzing highly radiogenic gas samples 56,17. These published protocols are outlined here and were used for samples, procedural standards and blanks. First, samples were expanded to a calibrated volume containing a 1000 Torr Bar- col and high vacuum, and this sample was then brought to the hot and temperature of ~300 °C. The sample was introduced to activated titanium sponge (~30 g) held at 1223 K (950 °C) for 15 min to chemically remove the majority of the active gases (e.g., N2, CH4, C2H6). The titanium sponge was then allowed to cool while still exposed to the sample for a further 30 min to allow removal of H2. An additional purification step was then applied to the sample using a combination of a hot (SAES GP-50) and cold (SAES NP-10) getters for a further 15 min to remove any residual active gases remaining in the sample. Next, the purified sample was passed through a series of calibrated, liquid-helium-cooled cryogenic traps of decreasing temperature to first isolate and remove any water vapour (stainless steel trap held at 180 K), then trap the argon, krypton and xenon components (stainless steel trap held at 33 K) and lastly trap helium and neon (charcoal trap held at 15 K). Each of these three trapping stages lasted 15 min 2,17,57.

For the helium analysis, the gas was first released by heating the charcoal trap to 31 K for 15 min. The released helium was then split using calibrated volume expansions and an aliquot was introduced and measured using a ThermoFisher Scientific HELIX SFT. Peak centres were defined manually and the two isotopes of helium, 3He and 4He, were measured simultaneously on an electron multiplier and on a Faraday respectively.

Prior to measuring neon, the residual helium first needed removal from the cryogenic trap. This was efficiently achieved following the published method of Warren et al. 52 by cycling the charcoal trap to 50 K for 15 min then back down to 31 K for a further 15 min. The gas was then expanded to the manifold and pumped, during which the charcoal trap was isolated. This cycle of heating, cooling and static pumping was repeated two additional times and ensured any residual helium in the trapping volume was efficiently removed without affecting the neon. With the residual helium removed the neon component was then released from the charcoal trap by heating to 90 K for 15 min. After this, a calibrated volume was inlet into a ThermoFisher Scientific ARGUS VI for measurement. During each analytical cycle 20Ne and 22Ne were measured on Faraday cups and 3He was measured on a multiplier. 40Ar and CO2 were additionally measured during this analysis in order to correct for any minor 38Ar+ interference peaks 55. Once neon analysis was complete the charcoal trap was opened to the vacuum pump and heated to 300 K to release and remove any remaining sample.
For argon, the stainless-steel trap was initially heated to 200 K for 15 min to release all trapped noble gases (Ar-Kr-Xe) and a small aliquot of this gas was taken. The trap was then cooled back down to 22 K to allow re-trapping of the heavy noble gases. While this re-trapping was taking place, the argon aliquot was expanded and diluted using calibrated volumes and then inlet to the ThermoFisher Scientific ARGUS VI which measured 40Ar on a Faraday cup and 36Ar and 38Ar on an electron multiplier via peak-jumping.

Prior to krypton and xenon, the residual argon also required removal from the cryogenic trap. As with the helium removal, this was achieved following published methods of heating, re-cooling and pumping specifically developed for analyzing highly radiogenic samples. First, for this, the stainless-steel trap was heated for 5 min from 52 K to 70 K and then cooled back down to 52 K, to allow argon release and full re-trapping of krypton and xenon followed by 2 min dynamic pumping to remove the argon. After 10 cycles the stainless-steel trap was heated to 200 K to ensure full release of all krypton and xenon. The sample was then inlet into the ThermoFisher Scientific ARGUS VI where all krypton and xenon isotopes were measured in one analysis using peak jumping with 135Xe and 133Xe measured on the electron multiplier and all other isotopes were measured using Faraday cups. Per standard procedures for noble gas analyses, samples were blank-corrected and normalized using full procedural air standards and blanks which were purified and analyzed using the same protocols as the samples outlined here to allow for direct comparison. All blanks for He, Ne, Ar and 40Ar+ corrections were <1% on the measured noble gas isotopes. The standard was collected in University Parks, Oxford, UK, under known environmental conditions (15.7 °C, 28% humidity and 1032 mBar pressure). All measured noble gas concentrations and ratios are provided in Supplementary Tables 1 and 2 respectively.

Calculating fluid residence times. The noble gas-derived fracture fluid residence times were calculated based on a closed system with radiogenic ingrowth model in line with previous widely published methods and are summarized as follows. First, the radiogenic excesses of 40Ne, 40Ar and 136Xe per cm3 of fracture fluids were multiplied by the porosity to calculate the radiogenic excess concentration per cm3 of rock. A porosity of 0.9% (±0.4%) was taken for this lithology based on depth porosity models and in line with previously published values for the Witwatersrand Basins. This was then multiplied by the density (2.85 g/cm3) to derive the radiogenic excess per gram of rock. For He and Ar this was incorporated into Eqs. (3) and (4):
is consistent with the published range of 0.1–2% reported for typical crystalline rocks in the Witwatersrand Basin4,5. This range is also consistent with modeling approaches for porosity changes as a function of depth in the crust which estimate an average porosity of 0.96% for the upper 10 km of the crust1,6,7. The porosity value applied here of 0.9% is derived from this depth-dependent approach and is within the published ranges for these settings. Additionally, for this study an uncertainty of ±0.4% is applied, following previous approaches1,14,17, to reflect variability in this key parameter. Finally, the variability that may exist on regional-global scales.

This therefore provides a spectrum of residence times which reasonably incorporates natural variation in these types of setting. Lastly, although negligible diffuse loss of 40Ar* is considered here in contrast to 4He* and 21Ne*, given the difference in diffusion coefficients (main text)3,11, any modest loss would slow slightly increase the 40Ar* subsurface residence times presented here, again, highlighting the conservative nature of this age estimate. Consequently, the residence time of 1.20 ± 0.54 Ga presented here also represents the most robust estimate for 40Ar*. As is typically the case for radiogenic noble gas-derived residence time estimates2,3,4,14,17 the variability in porosity estimates represents the dominant source of uncertainty.

**Uranium-rich Ne production.** While 4He*, 8Kr*, and 131–136Xe are all directly produced via uranium decay, 21Ne and 22Ne are produced in the subsurface principally through the interaction of radon and krypton in the host rock through the following two reactions: 182O(a,n)18Ne and 19F(n,n)18Ne. Consequently mineralogy (specifically the localized O/F ratio in the vicinity of U-bearing minerals) can significantly affect subsurface Ne production1,8,9. At Moab Khotson, the U-rich Vaal Reef is the primary U-bearing lithology mined10. Studies of the Vaal Reef mineralogy have indicated that uranium in the Vaal Reef is principally concentrated in three minerals: uraninite, coffinite, and brannerite11. In such minerals, the measured production of 4He*/21Ne* is considerably higher compared to production ratios of 1.0–2.2 × 10^7 previously applied to other deep subsurface sites in South Africa, Canada and Finland2,12,13,14,15, which all have U concentrations closer to global average concentrations in the crustal rock. Using the 4He*/21Ne* production ratios of 3.5 × 10^7 and 4.6 × 10^7 for uraniumite and coffinite, respectively16, along with their proportional abundances, a more representative 4He*/21Ne* production ratio of 3.95 × 10^7 is applied here to reflect 21Ne production in a U-rich environment at Moab Khotson. This 4He*/21Ne* production ratio is 2.3 × greater than the average crustal production rate and reflects the notably lower 1–22 Ga residence time calculated for the Vaal Reef. This is inferred here to be due to a lower interaction between radon and krypton in the host rock as indicated by decreased neutron fluxes generated from a light element interaction per alpha particle generation for U-rich mineralologies10,16.

**Other Kr isotope production.** Although 8Kr* produced via spontaneous fission of 238U additionally produces both 4Kr* and 8Kr*, the production rates with respect to 4Kr* are considerably lower and are 0.13–0.22 and 0.03–0.08, respectively17. With 4Kr* in ASH, naturally 5.3x more abundant than 8Kr*, and with the 4Kr* production rate being so low, any radogenic addition to either isotope falls well within analytical uncertainty for these samples. Likewise, although the highly radioactive environment makes Moab Khotson a prime candidate for 4Kr* and 8Kr* analysis, neither could be measured using conventional noble gas analytical techniques, given their low concentrations and production rates18.

**Sensitivity assessment of model outcomes.** Although the majority of noble gas studies for these deep subsurface environments typically incorporate in situ long-term production and accumulation2,9,14,18,19,36,37, alternative models to incorporating mixing, or addition from ancient metamorphic fluids have also been applied to interpret noble gas data from the Witwatersrand Basin12,21,23. This alternative model was additionally considered here for the robustness of our findings. In this scenario, instead of calculating the mean residence time through long-term 40Ar* release and accumulation, release is exclusively modelled in the context of high temperature hydrothermal activity when temperatures and pressures were sufficiently high (350 ± 50 °C and 1.5–3 kbar)23 to facilitate efficient and rapid noble gas release from the host mineralogy25. Under such parameters the oldest theoretical fluid component in the Witwatersrand could correspond to the last recorded period of regional metamorphism at 2.1–2.0 Ga 25,67 and subsequent low temperature release would be considered negligible for 40Ar*, in line with previously reported 40Ar* mineral ages for the region which approach the last regional metamorphism17,28,29. Low temperature release of He, (and potential Ne) would remain plausible due to their greater mobility and a more energetic production route for He (α-recoil)30. Likewise, Xe (and Kr) may also be potentially released at low temperature due to recoil loss30.

Importantly, even interpreting the noble gas data presented here under this alternative framework, results in only relatively minor overall differences from those described in the main text (only a slight increase in the maximum 40Ar* age 1.74 Ga (based on 1.20 ± 0.54 Ga (main text), to 2.1–2.0 Ga 25,67, and hence no change in the major conclusions of this paper. Likewise, the observed differences between the light and heavy noble gases (and the associated low ratios – Fig. 3) continue to support long-term light diffuse loss as a major process affecting the Moab Khotson system. Given that 4He* (and 21Ne*) are expected to be released at a comparable or greater rate than 4Kr* and 131Xe, the estimates of 82 and 75% total loss for He* and of the 21Ne*, would, in this alternative framework, instead represent minimum loss over total production. Lastly, with regards to a local U concentration, assuming a fluid age of 2 Ga and a starting 136Xe concentration of zero (i.e. all derived from in situ radiogenic production), a minimum U value of 9.8 ppm is calculated, not substantially different from the value of 19.8 ppm. This concentration decreases proportionally as the relative percent of 136Xe* associated with hydrothermal release is increased from 0%. None of these relatively minor differences though meaningfully affect the fundamental conclusions as described in the main text and hence provide additional support for the robustness of the study’s major conclusions and implications.

Although this model is presented here to provide a sensitivity assessment of the overall findings, it is worth noting within the geologic setting of the Witwatersrand Basin, previously published data from a variety of different sites support the assumption of 100% release for the light noble gases. Specifically, modelled 4He* and 40Ar* residence times (which consider 100% release for both noble gases and closed system accumulation) are highly consistent over Ka-Ma timescales17,18. This concordance is difficult to reconcile within a regional model involving variable mixing between a 40Ar*-rich hydrothermal fluid and more modern counterparts, such as is involved in this alternative framework. Further, the alternative framework considers only thermal release of 40Ar*. However, K-Ar mineralogical analyses indicate that the fluids associated with this hydrothermal activity likely had initial 40Ar*/36Ar ratios between 274–4169 which is consistent with the proposed initial seawater ratio of 295.5 applied here as the starting fluid. Crucially this initial range falls two orders of magnitude below the ratio of 48,617 measured in these fluids (Supplementary Table 2). Thus, a post-hydrothermal (and therefore low temperature) source of 40Ar* still is required. Release of noble gases over geologic timescales can additionally occur at low temperatures both through secondary mineralization and associated water-rock reactions28,30 and diffusion into, and along grain boundaries20. Related to this, Sleep and Zoback17 specifically reported that fracture opening occurs, even in quiescent cratons (such as the setting for this study), on a kilometre scale on a periodicity of 1 to several millions year. Even in hydrogeologically isolated, tectonically quiescent settings such as this, over the > 2-billion-year age of this geologic setting, fracture opening and the potential for fracture intersection and fluid mixing, and release of noble gases, is an ongoing process. Consequently, localized, effective progressive degassing of 40Ar* (and other noble gases) can occur from lithological units in the proximity of fracture networks into the fluids where they accumulate, while more distal mineralogies may retain higher proportions their noble gases. To elaborate and clarify a little further, in all geologic settings, the specific mechanisms of release from the host lithology into the fluids are never instantaneous (in the absolute sense), be it diffusion, mineral alteration, or through (micro)fractures and so on. However, as long as the rate of release (Ma) is relatively rapid to the overall fluid residence time, (here hundreds of Ma to Ga), this can be reasonably approximated as progressive, on-going release of noble gases from the host rock into the fracture fluid networks, as we apply here. It should be noted though that in fractured rock settings where fluid residence times are considerably lower than these ~Ma release timescales these noble gas-based approach can potentially underestimate calculated residence times. In such scenarios, additional, independent, short-lived radioelement tracers (e.g., 3H, 14C, 36Cl, 39Ar) may also therefore be applied to evaluate the release of noble gases into the fluids over these shorter timescales e.g.17,36,37. These, or comparable approaches, will provide the basis for essential calibration of existing models and allow for accurate constraints on the shortest residence times that noble gases can determine in these settings. Critical, any of these additional concepts do not significantly affect the principal findings of this study, and the alternative model discussed above instead provides an additional residence time of 2.1–2.0 Ga that robustly defines residence times for the accumulation of the same range of billion-year-old residence times as the main text. Here though, where fluids have hundreds of Ma to Ga residence times, considering 100% release in this context (and zero retention) therefore results in the most conservative estimates of radiogenic noble gas concentrations in the system being considered which correspond to conservative residence time estimates. Due to these above points, the accumulation model with 100% release (as outlined in the main text) is considered the best fit to the noble gas data presented here with 1.2 Ga remaining the most conservative estimate of fluid residence times.

**Data availability**

The data generated in this study are provided in the Supplementary Information file.

Received: 21 September 2021; Accepted: 15 June 2022; Published online: 30 June 2022

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Acknowledgements

This study was financially supported by the Natural Sciences and Engineering Research Council of Canada Discovery and Accelerator grants (B.S.L.) and Nuclear Waste Management Organization of Canada grants (B.S.L. and C.J.B.) with additional funding by CIFAR to Earth 4D Fellows B.S.L. and C.J.B., and University of Oxford internal funds (C.J.B.). Sampling infrastructure and operations funded via NSF grants EAR1917682 and EAR2026853 (T.L.K. and T.C.O.). ICDP grant to H. Ogasawra of Ritsumeikan University, Japan and the DSeis international team supported the cost of drilling the borehole at Moab Khotson Mine. NSF grant EAR1739151 to T.C.O. supported the construction and installation of the U-tube in the borehole. We thank B. Liebenberg and the staff of Lesedi Drilling & Mining (Pty) Ltd and Van Heerden Esterhuizen and Brenda Freese of Moab Khotson Mine and the management of Harmony Gold Mining Company Ltd. for their logistical support. Finally, we thank Dr. B. Freifeld of Class VI Solutions, Inc., Z. Garvin of Princeton University, Drs. E. Cason and J-G Vermeulen of the University of the Free State and Prof. E. van Heerden and C. van Vuuren of iWater for the design, construction and deployment of the U-tube and shipping of samples in accordance with relevant permits and local laws.

Author contributions

O.W., B.S.L., C.J.B. and T.C.O. designed the noble gas study. O.W., T.C.O., T.L.K., D.M.N. collected samples from Moab Khotson Mine. O.W., D.I.H. and C.J.B. measured noble gases in the NOBLE Laboratory, Oxford, UK. O.W. and B.S.L. measured compositional and water isotopic data in Toronto, Canada. O.W., B.S.L. and C.J.B. interpreted the data and wrote the manuscript with contributions from all co-authors.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-022-31412-2.

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Peer review information Nature Communications thanks Shaun Frag, Riiïka Kietävainen and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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