Fracturing-induced release of radiogenic $^4$He and $^{234}$U into groundwater during the last deglaciation: An alternative source to crustal helium fluxes in periglacial aquifers

Pauline Méjean1,2, Daniele L. Pinti1, Bassam Ghaleb1, and Marie Larocque1

1GEOTOP and Département des sciences de la Terre et de l’atmosphère, Université du Québec à Montréal, Montreal, Quebec, Canada, 2Now at Laboratoire de développement Analytique Nucléaire Isotopique et Élémentaire, CEA, Saclay, France

Abstract External $^4$He sources have been invoked to explain $^4$He concentrations in groundwater greater than those expected from in situ U and Th production. In a fractured aquifer of Ordovician age located in the St. Lawrence Lowlands (Quebec, Canada), $^4$He concentrations of up to $4.48 \times 10^{-5}$ cm$^3$ STP g$^{-1}$ were measured. Such concentrations are $\sim$1000 times higher than would be expected from in situ production. A concomitant increase in $^4$He concentration and $^{234}$U/$^{238}$U activity ratio is shown, suggesting a common release process in groundwater for $^{234}$U and $^4$He. This process has tentatively been identified as glaciation-induced rock fracturing following the Laurentide Ice Sheet retreat. The resulting increase in exposed grain surface facilitates $^{234}$U release by $\alpha$-recoil and that of radiogenic $^4$He by diffusion. Using a model of helium diffusion from a spherical grain, it is shown that rock fracturing facilitated the release of accumulated $^4$He at rates ranging from $4.2 \times 10^{-10}$ to $1.06 \times 10^{-8}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$. These release rates are between 1000 and 30,000 times higher than the local U and Th steady state production rate, of $3.5 \pm 1.4 \times 10^{-13}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$. Integration of $^4$He release rates over time yields a radiogenic $^4$He concentration of between $3.85 \times 10^{-6}$ and $7.12 \times 10^{-5}$ cm$^3$ STP g$^{-1}$ in the range of concentrations measured in the St. Lawrence Lowlands fractured aquifers. Results support the occurrence of a local radiogenic helium source to explain the excesses measured in groundwater without requiring a significant external He crustal flux.

1. Introduction

Groundwater is the largest reservoir of freshwater available for human use. Of the 22.6 Mkm$^3$ of groundwater contained within the first 2 km of the upper crust, less than 6% is modern groundwater (i.e., is less than 50 years in age) [Gleeson et al., 2016]. The rest ranges from a few thousand [Aggarwal et al., 2015] to potentially hundreds of millions of years in age [Bottomley et al., 1984; Lippmann-Pipke et al., 2011; Pinti et al., 2011; Holland et al., 2013]. Precisely constraining the age of the remaining volume of old groundwater is essential to evaluate these groundwater reservoirs, which will be increasingly solicited by the growing world population as modern groundwater becomes increasingly endangered by global change stresses.

Younger groundwater (less than 50 years old) can be precisely dated using $^3$H/$^3$He [e.g., Tolstikhin and Kamensky, 1969]. Dating older groundwater is a challenge, because water-rock interaction alters the initial concentration of radionuclides [e.g., Phillips and Castro, 2003]. An example is $^{14}$C (half-life = 5730 years), which is primarily introduced into groundwater in the soil zone through biological processes. Along the flow path, $^{14}$C activity decreases according to radioactive decay [Plummer and Glynn, 2013]. However, exchange with carbonates [Fontes, 1992] and the addition of $^{14}$C from old organic matter or CH$_4$ [Aravena et al., 1995] can significantly alter the original $^{14}$C activity, resulting in older apparent ages.

Radiogenic $^4$He is the decay product of $^{238}$U, $^{235}$U, and $^{232}$Th contained in rocks. The produced $^4$He is transferred from rocks into groundwater mainly by diffusion and $\alpha$-recoil [e.g., Torgersen, 1980]. Because of the inert nature of helium as a noble gas, and the long half-lives of the parent nuclides, the U-Th/$^4$He dating method can potentially be used to estimate groundwater ages ranging from a few hundred years to hundreds of millions of years [Marine, 1979; Andrews and Kay, 1983; Torgersen, 1980; Solomon et al., 1996; Pinti et al., 2011]. However, numerous studies [see e.g., Pinti and Marty, 1998; Phillips and Castro, 2003; Kulongoski and Hilton, 2011 for a review] report U-Th/$^4$He ages consistently older than the hydrogeological ages. This
difference, the so-called $^4$He excess [e.g., Torgersen and Clarke, 1985], is interpreted as resulting from an additional source of radiogenic helium, external to the aquifer.

Torgersen and Clarke [1985] found that the $^4$He excess in groundwater of the Great Artesian Basin of Australia was equivalent to the total crustal production of radiogenic $^4$He beneath the basin. A basal flux of radiogenic helium entering the aquifers was found to be able to balance the total helium budget in groundwater. Mazor [1995], Tolstikhin et al. [1996], and Lehmann et al. [2003] contested this model, suggesting instead that aquifers have heterogeneous hydraulic conductivities, and that connate (stagnant) water might exist [Pinti et al., 1997], accumulating large amounts of radiogenic helium. Freshwater mixed with stagnant water [Tolstikhin et al., 1996] or pore water from low-permeability shales [Tolstikhin et al., 2005] might cause the $^4$He excesses.

In numerous glaciated granular aquifers, it was observed that $^4$He was released into water at high rates, on the order of 300–600 times greater than those expected from local U and Th production [Solomon et al., 1996]. These authors developed a model to demonstrate that only a portion of the $^4$He produced (i.e., the portion located close to the surface of the aquifer grains) can be released at steady state by diffusion and/or $\alpha$-recoil. During rock fracturing, the increased surface area of the grain exposed to water induces the rapid release of $^4$He produced and accumulated in the rock, creating helium excess in groundwater.

Vautour et al. [2015] measured $^4$He excesses of up to $4.48 \times 10^{-3}$ cm$^3$ STP g$^{-1}$ in groundwater circulating in the Ordovician-age-fractured aquifer of the Becancour watershed in the St. Lawrence Lowlands of Quebec (Canada). Measured helium content is about 1000 times higher than that expected from local production in rocks. Vautour et al. [2015] interpreted the helium excesses in groundwater as deriving from a crustal flux entering the bottom of the aquifer. Helium flux was estimated to be $0.1-2 \times 10^{-7}$ cm$^3$ STP cm$^{-2}$ yr$^{-1}$ (i.e., tens to hundreds of times lower than the average continental crust flux of $3.3 \times 10^{-6}$ cm$^3$ STP cm$^{-2}$ yr$^{-1}$) [O’Nions and Oxburgh, 1983].

Méjean et al. [2016] measured the $^{234}$U/$^{238}$U activity ratios ($^{234}$U/$^{238}$U$^{\text{act}}$ hereafter) in the groundwater of the same aquifer as Vautour et al. [2015]. Observed relationships between the $^{234}$U/$^{238}$U$^{\text{act}}$, the lithology of the aquifers, and the alkalinity and the chemistry of water clearly indicated that U was sourced from the aquifer and $^{234}$U/$^{238}$U fractionation (i.e., $^{234}$U/$^{238}$U$^{\text{act}}$ $\ll 1$) was controlled locally by the ejection of $^{234}$U into the water by $\alpha$-recoil, while its parent element, $^{238}$U, was firmly trapped in the solid phase. Méjean et al. [2016] found an inverse relationship between the $^{234}$U/$^{238}$U$^{\text{act}}$ and the $^{3}$He/$^4$He ratios: freshwater, devoid of radiogenic helium, shows an $^{234}$U/$^{238}$U$^{\text{act}}$ of close to unity (i.e., at secular equilibrium); older groundwater is progressively enriched in radiogenic helium (i.e., the $^3$He/$^4$He ratio decreases) and the $^{234}$U/$^{238}$U$^{\text{act}}$ increases to as much as 6. This relationship calls for a local enrichment mechanism for both $^{234}$U and $^4$He, within the aquifer rather than an external source of helium as suggested by Vautour et al. [2015]. Méjean et al. [2016] suggested that the opening of new fractures might provide additional surfaces from which $^{234}$U migrates by $\alpha$-recoil and $^4$He migrates by diffusion into water at high rates but did not quantify these processes.

Here the potential of the U-He relationship to identify radiogenic $^4$He sources within aquifers is shown. These sources can resolve the radiogenic $^4$He excess found in groundwater without requiring significant crustal fluxes. It is shown that in periglacial aquifers, glaciation-induced fracturing results in high helium release rates, providing a dominant $^4$He input in the aquifer. Helium and uranium data from Méjean et al. [2016] and Vautour et al. [2015] are revisited and integrated in a coupled model of $^{234}$U-$^{238}$U fractionation and radiogenic $^4$He release into groundwater by glaciation-induced fracturing, using equations developed by Andrews et al. [1982] and Solomon et al. [1996].

2. Hydrogeology and Water Chemistry

The hydrogeological setting of the Becancour River watershed (2859 km$^2$; Figure 1) in the St. Lawrence Lowlands is briefly described here to highlight the context of this work. Details can be found in Larocque et al. [2013], Vautour et al. [2015], and Méjean et al. [2016]. The regional aquifer of the Becancour River watershed is mainly composed of fractured Ordovician carbonate-shale deposits belonging to the St. Lawrence Platform [Larocque et al., 2013]. Recharge to this aquifer occurs in the Appalachian Mountains, where Cambrian to Devonian sicolastic and metasedimentary rocks (shales and schists) outcrop [Larocque et al., 2013]. Unconsolidated Quaternary fluvioglacial, deltaic, and lacustrine sands (Lobtinière and Villes Fortes sands) are found in the middle and downstream portions of the Becancour River watershed [Godbout, 2013]. These deposits create granular aquifers of limited extent and thickness, partially buried under deposits of marine
clay. These clay deposits are the result of marine transgression-regression cycles caused by the marine Champlain Sea invasion, dated at 9750 B.P. [Occhietti et al., 2001].

Groundwater flows regionally from the main recharge area in the Appalachian Mountains to the St. Lawrence River (Figure 1) [Larocque et al., 2013]. Groundwater mainly discharges as base flows in the Becancour watershed.
River and its tributaries. Local recharge occurs in the lower part of the watershed, where Champlain Sea clays are discontinuous [Larocque et al., 2013], complicating the groundwater flow path. The hydraulic conductivities of the Ordovician fractured bedrock aquifer are low to moderate (\(\sim 10^{-9}\) to \(\sim 10^{-6}\) m s\(^{-1}\)), while those of the Quaternary aquifer are moderate (\(\sim 10^{-6}\) to \(\sim 10^{-5}\) m s\(^{-1}\)). Porosities are 1–5% and 10–20%, respectively, for the Ordovician fractured aquifer and for the Quaternary granular aquifer [Tran Ngoc et al., 2014; Benoît et al., 2011]. Groundwater has a low salinity, of between 0.06 and 0.78 g L\(^{-1}\). Groundwater types are as follows [Meyzonnat et al., 2016]: (1) Ca-HCO\(_3\) and Ca-HCO\(_3\)-SO\(_4\) in freshwater near the Appalachian Foothills main recharge; (2) Na-HCO\(_3\) and Na-HCO\(_3\)-SO\(_4\) evolved water, with Ca\(_{\text{dissolved}}\) exchanged with Na\(_{\text{mineral}}\) in the middle portion of the watershed; and (3) slightly mineralized waters (Ca-HCO\(_3\)-Cl, Na and Na-HCO\(_3\)-Cl types) close to the St. Lawrence River, where chlorine is derived from marine-glacial pore water originating from the Champlain Sea marine transgression.

Groundwater ages calculated with radionuclide-based methods are variable. Freshwater containing tritium has been dated at less than 60 years using the \(^{3}H/^{3}He\) method [Vautour et al., 2015]. More evolved waters have uncorrected \(^{14}C\) up to 15 kyr, while NETHPATH \(^{14}C\)-adjusted equivalent ages are up to 6.7 kyr [Vautour et al., 2015]. These values are in the range of those obtained by other authors in neighboring watersheds of the St. Lawrence Lowlands, ranging from 17–6 kyr [Nicolet-St. François watershed] [Saby et al., 2016] to 14–4 kyr (Monteriege Est watershed) [Beaudry, 2013].

3. Methods

3.1. Sampling and Analytical Procedures

Groundwater from the Ordovician aquifer was sampled from 20 municipal, domestic, and instrumented wells, with depths ranging between 15 and 65 m. Wells drilled into the fractured aquifer are equipped with a casing through the sections crossing the unconsolidated Quaternary deposits. They are open boreholes when they reach the Ordovician-age-fractured aquifer. Three domestic wells were sampled from the Quaternary aquifer, at depths ranging from 6 to 15 m (BEC105, BEC117, and BEC118), and all were equipped with a casing and a bottom screen. A Waterra\textsuperscript{\textregistered} Inertial Pump System was used to collect water from domestic and instrumented wells. Water was collected at the wellhead in municipal pumping stations. Groundwater was collected for helium analyses using a copper tube (9.5 cm of diameter), sealed with clamps to avoid atmospheric contamination [e.g., Vautour et al., 2015]. Water for uranium isotopic analyses was collected in 1 L Nalgene\textsuperscript{\textregistered} bottles, filtered (0.7 \(\mu\)m Millipore), and acidified to a pH of \(\sim 2\). Helium was measured with a MAP-215 mass spectrometer at the University of Michigan. Please refer to Castro et al. [2009] and Vautour et al. [2015] for details on the analytical procedures, uncertainties, and reproducibility of helium isotopic analyses. Uranium was extracted using a method modified from Edwards et al. [1987] and analyzed with a VG-SECTOR Thermo-Ionization Mass Spectrometer equipped with an ion counter at the radioisotope laboratory of GEOTOP in Montréal. Analytical uncertainties on U concentrations were less than 1%. Uncertainties on the \((^{234}\text{U}/^{238}\text{U})_{\text{act}}\) vary from 0.4 to 5%, with an average error of \(\sim 1.3\%\) (\(2\sigma\)). Please refer to Méjean et al. [2016] for details on U isotopic analyses.

3.2. Modeling \(^{234}\text{U}\) Release Into Groundwater

To quantify the release of both radiogenic \(^{4}\text{He}\) and \(^{234}\text{U}\) isotopes into groundwater, a coupled model of \(^{234}\text{U}/^{238}\text{U}\) fractionation and \(^{4}\text{He}\) enhanced accumulation rate was developed using relevant equations from Andrews et al. [1982] and Solomon et al. [1996].

The ejection and accumulation rates of \(^{234}\text{U}\) in groundwater were simulated using the relationship between stress-induced fracturing of the aquifer matrix and the formation of new exchange surfaces where \(x\)-recoil can preferentially take place, facilitating the release of \(^{234}\text{U}\) [Andrews et al., 1982]. This model assumes that groundwater acquires U by partial dissolution of rock at the recharge site and may undergo evolution in its uranium concentration by water-rock interaction, or after U deposition by ejection of \(^{234}\text{U}\) caused by \(^{234}\text{Th}\) recoil.

For groundwater in a reducing environment with an initial \((^{234}\text{U}/^{238}\text{U})_{\text{initial},\text{act}}\) entering the \(x\)-recoil zone (i.e., an aquifer under reducing conditions where \(x\)-recoil dominated over dissolution), the evolution of the activity ratio with the age of the groundwater \((^{234}\text{U}/^{238}\text{U})_{\text{act},\text{final}}\) can be estimated using the following relationship of Andrews et al. [1982]:
\[
\frac{^{234}\text{U}}{^{238}\text{U}}_{\text{act,final}} = 1 + \left[ \frac{^{234}\text{U}}{^{238}\text{U}}_{\text{act,initial}} - 1 \right] \times e^{-\lambda t} + 0.235 \times \rho \times S \times R \times \left[ 1 - e^{-\lambda t} \right] \times \frac{U_{\text{rock}}}{U_{\text{water}}} \quad (1)
\]

In equation (1), the first term accounts for the decay of the \(^{234}\text{U}\) excess accumulated in groundwater during recharge (i.e., in the unconfined part of the aquifer). The second term accounts for the \(\alpha\)-recoil effect on the \(^{234}\text{U}/^{238}\text{U}\) ratio when groundwater reaches the confined part of the aquifer (i.e., under reducing conditions) \([\text{Andrews et al., 1982}]\). The variable \(S\) is the specific surface area (i.e., the surface area of rock in contact with water (in \(\text{cm}^2 \text{cm}^{-3}\)); \(\rho\) is the density of the aquifer rock (2.72 \(\text{g cm}^{-3}\) for the carbonate-dominated lithologies found in the Becancour aquifers); 0.235 is the probability that \(^{234}\text{Th}\) atoms actually escape from the rock surface into the water \([\text{Bonotto and Andrews, 1993}]; \^{234}\text{U} \text{decay constant (2.826 } \times 10^{-10} \text{ yr}^{-1})\]
\([\text{Cheng et al., 2000}]\); \([U]_{\text{rock}}\) and \([U]_{\text{water}}\) are the \(U\) content in the aquifer rock and in the water, respectively; and \(R\) is the distance of \(\alpha\)-recoil for \(^{234}\text{Th}\), which is estimated to be \(3 \times 10^{-6} \text{ cm}\) in \([\text{Andrews and Kay, 1983}]\).

The boundary conditions for the model are (1) \(^{234}\text{U}/^{238}\text{U}\) ratio recorded in the water when entering the \(\alpha\)-recoil-dominated zone, which corresponds to the shallowest groundwater sampled in the study area (BEC118: \([^{234}\text{U}/^{238}\text{U}]_{\text{act}} = 1.14\)); \([^{234}\text{U}/^{238}\text{U}]_{\text{act}} = 6.07\) in the BEC101 6.7 kyr-old groundwater was calculated, extrapolating it from equation (1) as follows:

\[
S = \frac{^{234}\text{U}}{^{238}\text{U}}_{\text{act,final}} - \left[ \frac{^{234}\text{U}}{^{238}\text{U}}_{\text{act,initial}} - 1 \right] \times e^{-\lambda t} - 0.235 \times \rho \times S \times R \times \left[ 1 - e^{-\lambda t} \right] \times \frac{U_{\text{rock}}}{U_{\text{water}}} \quad (2)
\]

From \(S\), and assuming an aquifer matrix composed of grains produced by stress-induced fracturing, the grain size, \(r\) (cm), is deduced from the relationship of \([\text{Bonotto and Andrews, 1993}]: r = \frac{3}{\phi} \times S \quad (3)\]

In equation (3), the term \(\phi\) is the mean matrix porosity, which is assumed to be 3% for the Becancour fractured aquifer \([\text{Vautour et al., 2015}].\)

### 3.3. Modeling \(^4\text{He}\) Release Into Groundwater

The \(^4\text{He}\) release model of \([\text{Solomon et al., 1996}]\) assumes helium diffusion out of a spherical grain. The diffusive flux of radiogenic \(^4\text{He}\) from a single grain is calculated using Fick’s first law of diffusion. The equation that governs the release of helium per unit of weight of solids, \(N\) (\(\text{cm}^3 \text{ STP g}^{-1}\)), is \([\text{Solomon et al., 1996}]\)

\[
N = 6 \times \dot{\lambda} \times (C_0 - C_wK_{\text{part}}) \times \Sigma e^{-\lambda N \tau} \quad (4)
\]

where \(\dot{\lambda}\) (\(\text{s}^{-1}\)) is the leakage coefficient that determines the rate at which previously accumulated \(\text{He}\) diffuses from the aquifer solids into groundwater; \(n\) is the number of sequences generated using the iterative method; \(C_0\) is the initial concentration in the grain; \(C_w\) is the \(^4\text{He}\) concentration measured in the groundwater; and \(K_{\text{part}}\) is the partition coefficient for \(\text{He}\) in a water-solid system, assumed to be 1 \([\text{Solomon et al., 1996}]\).

The leakage coefficient, \(\dot{\lambda}\), depends in turn on the grain size of the aquifer matrix, through the relationship:

\[
\dot{\lambda} = \frac{D_s}{r^2} \quad (5)
\]

where \(D_s\) is the solid-state diffusion coefficient (i.e., diffusion initiated in the solid phase by the occurrence of surface defects, which include grain boundaries; \(\text{cm}^2 \text{ s}^{-1}\)), and \(r\) is the geometric mean grain size (cm).

### 4. Results and Discussion

#### 4.1. U-Th Isotope Systematics in Groundwater of the Becancour Aquifer

The measured uranium concentrations in the Becancour fractured aquifer of Ordovician age are very low and display a high degree of variability, with values ranging from 0.003 ± 0.00002 to 2.939 ± 0.012 ppb.
Water (ASW; 4.6 $\times$ $10^{-8}$ cm$^3$ STP g$_{H_2O}$ at 10°C) [Smith and Kennedy, 1983]. The ($^{234}$U/$^{238}$U)$_{act}$ should be close to unity (i.e., at secular equilibrium). Indeed, freshwater in the area is of Ca-HCO$_3$ type and derives from the dissolution of carbonates in the unconfined part of the aquifer. Dissolution of the rock is a zero-order rate process that results in the transfer of U into groundwater with the same ($^{234}$U/$^{238}$U)$_{act}$ as the bulk rock, which is closer to the secular equilibrium [Méjean et al., 2016]. Freshwater of well BEC118 best represents this end-member, with $^4$He = 6.04 $\times$ $10^{-8}$ cm$^3$ STP g$_{H_2O}^{-1}$ and ($^{234}$U/$^{238}$U)$_{act}$ = 1.14 [Méjean et al., 2016]. The $^3$H/$^4$He calculated age for this sample is 2.7 ± 0.1 years [Vautour et al., 2015]. The second component is older groundwater, having accumulated large amounts of radiogenic $^4$He (1.2–4.5 $\times$ $10^{-5}$ cm$^3$ STP g$_{H_2O}^{-1}$) and showing the most fractionated ($^{234}$U/$^{238}$U)$_{act}$ value, of up to 6 (end member 2; black star; Figure 2). This evolved water was identified with that collected at well BEC101. Interestingly, this groundwater has a Na-HCO$_3$ chemistry, indicating longer water-rock interaction by ionic exchange [Meyzonnat et al., 2016]. This groundwater was sampled in the confined part of the fractured bedrock, where dissolution processes are negligible, and where $^{234}$U-$^{238}$U fractionation is dominated by $\alpha$-recoil processes [Méjean et al., 2016]. The uncorrected $^{14}$C age of BEC101 groundwater is 15.4 kyr and the NETPATH $^{14}$C-adjusted age is 6.7 kyr.

Most of the samples plot on a mixing line connecting end-members 1 and 2 (Figure 2). To explain the scattered points that do not lie on the mixing curve between end-members 1 and 2, a third end-member is required. Two samples (BEC105 and BEC107) plot on a mixing line between end-member 1 and a third end-member containing large amounts of radiogenic $^4$He (1.2–4.5 $\times$ $10^{-5}$ cm$^3$ STP g$_{H_2O}^{-1}$), but only slightly fractionated, with ($^{234}$U/$^{238}$U)$_{act}$ of up to 1.6. Groundwater sampled from well BEC126 derives from the mixing of end-members 3 and 2 (Figure 2). BEC126 is an important, yet intriguing sample. The well is located upgradient, closer to the recharge area. Groundwater, of Ca-HCO$_3$ type, is the least saline in the Becancour River watershed, with a Total Dissolved Solids (TDS) concentration of 0.22 g L$^{-1}$ [Vautour et al., 2015]. Even if the highest $^4$He content in the watershed was measured in BEC126 (4.5 $\times$ $10^{-5}$ cm$^3$ STP g$_{H_2O}^{-1}$) [Vautour et al., 2015], the water chemistry and the occurrence of a notable amount of tritium (4.4 TU) clearly indicates that freshwater dominates. To resolve this apparent contradiction (i.e., freshwater containing large excesses of radiogenic $^4$He), it must be assumed that this sample represents the situation where rock dissolution liberates the $^4$He that was produced, partially retained and accumulated in the aquifer matrix for a long, geological time. The occurrence of the third end-member, enriched in radiogenic helium, would support the model of Solomon et al. [1996], which suggests that aquifer grains partially retain radiogenic $^4$He for long, geological periods. Dissolution of the rock and the release of the accumulated radiogenic helium would create the observed $^4$He excess in groundwater, together with a ($^{234}$U/$^{238}$U)$_{act}$ of close to unity (Figure 2).
4.2. Causes of Enhanced $^{234}$U and $^4$He Release Into Groundwater

The cause of $^4$He and $^{234}$U release and accumulation in groundwater is assumed here to be rock fracturing. Radiogenic $^4$He is released from the rock and accumulated into groundwater through diffusion and $\alpha$-recoil \cite{Torgersen, 1980; Torgersen and O'Donnell, 1991}. If the grain size is larger than the $\alpha$-recoil distance (30–100 nm for $^{234}$Th; 30–100 $\mu$m for $^4$He) \cite{Harvey, 1962} or its diffusion length ($\sqrt{D \cdot t}$), only a fraction of the radiogenic $^4$He accumulated in the rock will be released into the groundwater \cite{Solomon et al., 1996}. Part of the produced radiogenic helium will instead be retained in the rock until rock fracturing either increases the grain surface area, facilitating helium release by diffusion, and/or reduces the grain size, facilitating helium ejection by $\alpha$-recoil \cite{Solomon et al., 1996}.

The main mechanism of $^{234}$U release into groundwater is also $\alpha$-recoil but is a more complex, multistep process than for helium. When $^{238}$U contained in the rock decays, $\alpha$-particles transmit the kinetic energy to $^{234}$Th, the $^{238}$U daughter nuclide. A portion of the $^{234}$Th is ejected from the grain into the water. The insoluble $^{234}$Th is adsorbed onto the grain surface and then decays to $^{234}$U. The $^{234}$U located in damaged lattice
sites or on the surface of the grain will escape into the water, while $^{238}$U will mainly be retained in the crystal lattice [Kigoshi, 1971]. As is the case for helium, the larger the surface area that is exposed to water increases the probability that $^{234}$U is near the grain surface, facilitating its release into pore water.

Continental ice sheets played an important role in the Quaternary hydrogeology of North America [McIntosh and Walter, 2005, 2006; Neuzil, 2012; McIntosh et al., 2011; Person et al., 2012]. The Laurentide Ice Sheet retreat, initiated around 12,200 years ago, could be the main cause of stress-induced changes and associated mechanical fracturing of the Becancour bedrock aquifer (Figure 3). Loading and unloading caused by the Laurentide Ice Sheet migration might have induced large-scale near-surface tectonic stresses, inducing subvertical tensile fractures used by groundwater as flow paths [Lemieux et al., 2008].

As the Laurentide Ice Sheet started to retreat, large amounts of subglacial water flowed in the aquifer, promoting the partial dissolution of the aquifer rocks. This process is expected to have released U with little $^{234}$U-$^{238}$U isotopic fractionation ($^{234}$U/$^{238}$U$_{act}$ ≈ 1) (Figure 3a). Bedrock dissolution also caused the rapid release of large amounts of $^4$He accumulated over time in the bedrock into the water (Figure 3a). This situation might reflect the U-He isotopic composition of end-member 3 in Figure 2. If sample BEC126 contains this meltwater (Figure 2), then it should be imprinted in its isotopic signature. The stable isotopic composition of BEC126 groundwater shows a δ$^{18}$O value of −11.7‰, which is heavier than the expected δ$^{18}$O value of −16.5‰ for glacial meltwater in the area [Cloutier et al., 2010; Montcoudiol et al., 2015]. However, the noble gas calculated paleotemperature (NGT) [Stute and Schlosser, 1993] for BEC126 is −0.26 ± 3°C, significantly colder (3–7°C) than the other water samples in the region [Vautour et al., 2015].

Between 12.2 and 6.7 kyr before present, the near-surface stress induced by the ice sheet retreat increased fracture density as isostatic rebound and unbending of the crust progressed [Grollimund and Zoback, 2000; Lamarche et al., 2007] (Figure 3b). Over the past 6.7 kyr, the hydrogeological system of the St. Lawrence Platform reached the present-day configuration (Figure 3b). The invasion of subglacial water ended, and newly recharged water started to flow into a more highly fractured aquifer and to accumulate $^{234}$U and $^4$He released through the newly formed surfaces in the reduced and confined part of the aquifer. This situation is illustrated by fractionated ($^{234}$U/$^{238}$U$_{act}$) ratios of up to 6.07, accompanied by large amounts of radiogenic $^4$He, as observed in the 6.7 kyr-old BEC101 groundwater (end-member 2 in Figure 2).

4.3. Modeling the Release of $^{234}$U and $^4$He Into Groundwater

Once groundwater reaches reducing conditions in the aquifer, and the chemical leaching of $^{234}$U ceases, ($^{234}$U/$^{238}$U$_{act}$) may evolve over time to a balance between the $^{234}$U physical leaching and its decay. The ($^{234}$U/$^{238}$U$_{act}$) evolution can be seen in Figure 4, where ($^{234}$U/$^{238}$U$_{act}$) is plotted against groundwater residence time. The simulation is done using equation (1), and was calculated using an initial ($^{234}$U/$^{238}$U)$_{act}$ of 1.14 (BEC118; representing the activity ratio recorded in the water before entering the confined part of the aquifer) and a final ($^{234}$U/$^{238}$U)$_{act}$ value of 6.07 (BEC101; the maximum value measured in groundwater from the deeper Ordovician aquifer), after a contact time of 6.7 kyr, the $^{14}$C-adjusted age for BEC101 groundwater [Vautour et al., 2015]. Using the relationship described above and equation (2), an $S$ of 5379 cm$^2$ cm$^{-3}$ is calculated. This specific surface represents the extent of rock surface in contact with pore water.

The relationship between specific surface and grain size (equation (3)) is used to calculate a grain radius of 18 μm. The calculated grain size is even lower than the recoil path length of an alpha particle [Torgersen and Stute, 2013]. This means that the produced radiogenic $^4$He will not be retained in
the grain and should be released by \( z \)-recoil and diffusion from the grain, and thus provided a local \(^{4}\text{He} \) input into the aquifer.

Using only one \( S \) value for the entire regional aquifer is a major limitation of our model. It is known that there is older groundwater in the region, with corrected \(^{14}\text{C} \) ages of higher than 10 kyr [Saby et al., 2016], but the \((^{234}\text{U}/^{238}\text{U})_{\text{act}} \) was not measured. If we assume that the maximum \((^{234}\text{U}/^{238}\text{U})_{\text{act}} \) value in the region is 6.07, then the maximum grain size associated with, e.g., 12.2 kyr-old groundwater (equivalent to the time since deglaciation began) will be 33 \( \mu \text{m} \). Further U isotope measurements in old groundwater samples are needed to obtain a reasonable average value for the surface area and thus for the aquifer grain size.

The calculated grain size radius of 18 \( \mu \text{m} \) is used to estimate the release of helium per unit weight of solids, \( N \) (in \( \text{cm}^3 \text{ STP g}^{-1} \text{ rock yr}^{-1} \)), since the start of the last deglaciation (\( t_0 = 12.2 \text{ ka} \)), using equation (4) [Solomon et al., 1996]. Results of the simulation are reported in Figure 5. In equation (4), \( C_0 \), the amount of radiogenic \(^{4}\text{He} \) (in \( \text{cm}^3 \text{ STP g}^{-1} \text{ rock} \)) produced and retained in the grain since its deposition and \( D_s \), the helium diffusion coefficient (in \( \text{cm}^2 \text{ s}^{-1} \)), are the most difficult parameters to constrain but are essential.

Assuming an average \(^{4}\text{He} \) production rate of \( 3.5 \pm 1.4 \times 10^{-13} \text{ cm}^3 \text{ STP g}^{-1} \text{ yr}^{-1} \), calculated using U and Th contents measured in the aquifer rocks by [Vautour et al., 2015], and an average formation age of 445 Ma, the total amount of \(^{4}\text{He} \) produced is \( 1.6 \pm 0.9 \times 10^{-4} \text{ cm}^3 \text{ STP g}^{-1} \text{ rock} \). This amount cannot be taken directly as \( C_0 \), because helium is continuously diffused out the aquifer grains, also at ambient temperature [e.g., Mamygin and Tolstikhin, 1984]. To calculate the remaining amount of helium preserved in the aquifer grain, the steady state release factor of helium, \( \Lambda_{^{4}\text{He}} \) \((^{4}\text{He}_{\text{released}}/^{4}\text{He}_{\text{produced}}) \) [e.g., Torgersen, 1980; Torgersen and Stute, 2013] also needs to be calculated. This can theoretically be calculated using equations based on \( z \)-recoil, rapid or slow diffusion, or weathering, which are the three main helium release mechanisms suggested by Torgersen [1980]. However, an accurate estimate of \( \Lambda_{^{4}\text{He}} \) requires precise knowledge of the grain size, prior to glacial-induced fracturing, which is not the case for the current study. There is an alternative approach to estimate the \( \Lambda_{^{4}\text{He}} \). Vautour et al. [2015] noted that the calculated U-Th/\(^{4}\text{He} \) ages for samples BEC112, 137, 138, 147, and 148 were much lower (250–1808 years) than the \(^{14}\text{C} \) ages (3288–7342

![Figure 5](image-url)
years). To explain this discrepancy, it is either assumed that the radiogenic He production rate is much lower than the average value of $3.5 \pm 1.4 \times 10^{-13}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$ or that radiogenic helium is partially retained in the rock, with a calculated $\lambda_{\text{He}}$ ranging from 0.07 to 0.27. Assuming that the calculated $\lambda_{\text{He}}$ are typical steady state release factors of the studied aquifers and that they did not substantially change over time, $C_0$ in equation (4) can be calculated to be $1.04 \pm 0.7 \times 10^{-4}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$, corresponding to a helium loss of 27% of the total accumulated amount ($C_0$-$27% = C_0$). This value can be considered to be a very conservative upper limit. The lower limit can reasonably be assumed to be 10% of the total produced radiogenic helium. The calculated lower initial concentration is $1.6 \pm 0.9 \times 10^{-5}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$ ($C_0$-$90% = C_0$).

The second parameter to estimate is the diffusion coefficient of He, which can vary greatly pending the mineral phase and lithology of where it resides. In the present work, two values of the diffusion coefficient, $D_s$, are assumed for the carbonate-rich shale dominant lithology of the regional fractured aquifer: $D_{s1} = 1.0 \times 10^{-18}$ cm$^2$ s$^{-1}$ and $D_{s2} = 1.0 \times 10^{-19}$ cm$^2$ s$^{-1}$. These values encompass the range of diffusion coefficients obtained for carbonate [Copeland et al., 2007; Pinti et al., 2012] and silicate rocks [Solomon et al., 1996]. It is worth noting that laboratory experiments are needed in the near future to measure the helium diffusion coefficient in the aquifer matrix, as done previously in similar studies [Solomon et al., 1996; Carey et al., 2004].

Figure 5 reports the results of the simulated radiogenic helium release rate since the last deglaciation, assuming a $C_0 = 1.04 \pm 0.7 \times 10^{-4}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$ (Figure 5a) and a $C_0 = 1.6 \pm 0.9 \times 10^{-5}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$ (Figure 5b) respectively. In each diagram, the two curves have been calculated for the two diffusion coefficients $D_{s1}$ and $D_{s2}$, respectively. In these simulations, it can be observed that between 100,000 years (using $C_01$; Figure 5a) and 90,000 years (using $C_02$, Figure 5b) are required before the high helium release rate induced by fracturing reached the total amount of helium accumulated in groundwater will range from $3.89 \times 10^{10}$ to $0.36 \times 10^{10}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$.

Assuming that radiogenic He measured in groundwater is mainly produced locally by U and Th decay, the production rate by U and Th decay (cm$^3$ STP g$^{-1}$ yr$^{-1}$) can be calculated using the lower concentration of 6.7 kyr, and the slowest diffusion coefficient, $D_{s2}$, all other simulated helium concentrations are within the range of concentrations previously measured in St. Lawrence Lowlands groundwater, from $1.16 \times 10^{-5}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$ to $7.75 \times 10^{-5}$ cm$^3$ STP g$^{-1}$ yr$^{-1}$ [Pinti et al., 2013; Vautour et al., 2015; Saby et al., 2016]. An important implication of the spherical diffusion model is that the fractured aquifer will release He at a higher rate over thousands of years than will the steady state U-Th He production. It can be assumed that He released since deglaciation could explain radiogenic He currently measured in the aquifer if He loss through the top of the aquifer is limited.

### 4.4 Implications for Calculating (U-Th)/He Groundwater Ages

Assuming that radiogenic He measured in groundwater is mainly produced locally by U and Th decay, (U-Th)/He groundwater residence times can be estimated following the relationship:

$$t = \frac{[^{4}\text{He}_{\text{ter}}]}{P_{4\text{He}} \times \lambda_{4\text{He}} \times (1-e^{-\frac{t}{\rho}})}$$

$[^{4}\text{He}_{\text{ter}}]$ is the amount of radiogenic He measured in groundwater (cm$^3$ STP g$^{-1}$ water); $P_{4\text{He}}$ is the radiogenic He production rate by U and Th decay (cm$^3$ STP g$^{-1}$ yr$^{-1}$); $\lambda_{4\text{He}}$ is the He retention factor.
In the present work, the sources of radiogenic \(^4\)He in groundwater from the fractured regional aquifer of the St. Lawrence Lowlands were reevaluated. The relationship between U fractionation and radiogenic \(^4\)He excesses suggests a process within the aquifer to explain the \(^{234}\)U and \(^4\)He excesses, providing a complementary approach to the hypothesis previously suggested by Vautour et al. [2015] of external sources of helium. Using a coupled model of \(^{234}\)U and \(^4\)He release from aquifer grains following glacial-induced rock fracturing, it has been shown that the instantaneous release of accumulated helium from the host rock could be between \(4.2 \times 10^{-10}\) and \(1.06 \times 10^{-8}\) cm\(^3\) STP g\(^{-1}\) yr\(^{-1}\) (i.e., 2–46 times those calculated in Sturgeon Falls by Solomon et al. [1996]). The resulting \(\Lambda_{4He}\) is in the range of \(10^3\) to \(10^4\). The difference between \(\Lambda_{4He}\) calculated by Solomon et al. [1996] and those from this study might be related to the choice of the helium diffusion coefficients used, which are unknown for the carbonate-rich shale lithology of the St. Lawrence Lowlands aquifers. Helium release rates and diffusion coefficients must therefore be determined through laboratory experiments in order to correctly estimate the He retention factor, and thus (U-Th)/\(^4\)He groundwater ages.

4. Conclusions

The results of this work do not preclude the existence of an external \(^4\)He flux resulting from He production within the crystalline basement beneath the studied sedimentary basin and entering the bottom of the aquifers. However, as noted by Torgersen and Stute [2013], glacial-produced fracturing and the related enhanced release of \(^4\)He (\(\Lambda_{4He} > 1\)) may be common at high latitudes and may provide a dominant \(^4\)He input within periglacial aquifer systems. The next step would be to investigate whether similar relationships between \(^{234}\)U-\(^{238}\)U fractionation and helium isotopes exist in other hydrological systems and in different climates, suggesting either internal sources of helium in groundwater generally or that enhanced \(^{234}\)U and \(^4\)He release is restricted to high-latitude aquifers.

References


Harvey, B. G. (1962), Introduction to Nuclear Physics and Chemistry, 382 pp., Prentice Hall, N. J.


MÉJEAN ET AL.

NEW ESTIMATION OF IN SITU 4He PRODUCTION

5688


Tran Ngoc, T., R. Lefebvre, E. Konstantinovskaya, and M. Malo (2014), Characterization of deep saline aquifers in the Bécancour area, St. Lawrence Lowlands, Québec, Canada: Implications for CO2 geological storage, Environ. Geol., 72(1), 119–146.