GENERAL OVERVIEW

Objective: This project seeks to improve the application of noble gas isotope studies to multiphase fluid processes in the Earth’s crust by (1) identifying the important noble gas carrier phases in sediments to address the processes that have led to the observed enrichment and depletion patterns in sedimentary rocks and fluids, (2) examine the mechanisms by which such noble gas patterns are acquired, trapped and subsequently released to mobile crustal fluids, and (3) evaluate the time and length scales for the transport of noble gas components, such as radiogenic $^4\text{He}$, through the continental crust.

Project Description: Sedimentary rocks and oil field gases typically are enriched in heavy noble gases: Xe/Ar ratios of ~10-10,000 times the ratio in air have been observed that cannot be explained by adsorption hypotheses. Laboratory experiments designed to isolate sedimentary phases for noble gas analysis are conducted to identify the carrier phase(s). It has been observed that radiogenic $^4\text{He}$ accumulates in confined aquifer waters at rates that exceed the rate of local production and approaching the whole crustal production rate. A literature evaluation of $^4\text{He}$, $^3\text{He}$ crustal fluxes is being conducted to evaluate crustal scale mass transport in terms of the rate, mechanisms, temporal and spatial variability and the role played by tectonic processes.

Results: The laboratory study has concentrated on noble gas abundances in a variety of sedimentary silica samples. We have found that, in general, samples of inorganic silica have noble gas abundances that are consistent with occlusion of air-saturated water in fluid inclusions and lack requisite enrichment/depletion factors needed to explain the noble gas inventory in oil field fluids. However, numerous replicate analyses of noble gases extracted from silica spicules from live sponges (Calyxnaeensis) show significantly enriched Ar, Kr, and Xe concentrations ($[\text{Ng}]_{\text{sample}}/[\text{Ng}]_{\text{asw}} > 1$), but with very little if any mass dependence in the acquisition and trapping of Ar, Kr and Xe. Noble gases in silica samples from the
(diatomaceous) Monterey Formation (Elk Hills oil field, CA) and an Atlantic box core were found to be somewhat depleted with respect to the sponge spicule, fractionated in a fashion favoring the heavy noble gases, and approach the compositions that have been observed in bulk deep sea sediments. We suspect that the differences in noble gas absolute and relative abundances between the sponge spicule samples and the more evolved diatomaceous samples are related to either (1) fundamental differences in the biologically controlled mineralization or (2) post-depositional effects related to the progressive crystallization of amorphous silica (e.g. opal-A) to more ordered structures. Laboratory cultured diatoms and box core sea sediment samples collected as a function of depth within the sediment column have been processed for analysis of the silica phases to address these questions.

Through a statistical evaluation using a global data base covering many geologic environments, we have determined that the log normal mean of the radiogenic $^4$He flux across the Earth’s continental crust is $4.18 \times 10^{10}$ $^4$He atoms m$^2$ s$^{-1}$. Furthermore, it was found that the range of the continental $^4$He degassing flux increases with decreasing time and space scales. The statistics can be interpreted as reflecting natural variability and suggest that the mechanisms transporting the crustal helium degassing flux contain a high degree of both spatial and temporal variability. This estimate of the log normal mean of the continental degassing flux of $^4$He is approximately equivalent to the radiogenic production rate for $^4$He in the whole crust. Large scale vertical mass transport in continental crust is estimated as scaled values of the order $10^5$ cm$^2$s$^{-1}$ for helium (over 2Byr and 40km vertically) vs. $10^2$ cm$^2$s$^{-1}$ for heat. This rate of mass transport requires not only release of He from the solid phase via diffusion, fracturing or comminution; but also an enhanced rate of mass transport facilitated by some degree of fluid advection. This further implies a separation of heat and mass during transport.

**FUTURE PLANS**

As detailed below, the project continues without the University of Connecticut but with the involvement of Thomas Torgersen through his independent research and development (IRD) activities within his new position as Program Officer with the National Science Foundation. In this capacity, Torgersen will continue to be intellectually involved in the analysis of ongoing and planned experiments albeit within an unofficial capacity.

As part of the ongoing productivity of this effort, I attach copies of published manuscripts:


As well as copies of three chapter prepared for an IAEA publication on "Dating Old Groundwater"

To: Dr. Nick Woodward, nick.woodward@science.doe.gov
Geosciences Research Program
Office of Basic Energy Science
Department of Energy

From: Thomas Torgersen (on leave from University of Connecticut)
Program Officer Hydrologic Sciences
National Science Foundation

Date: 15 March 2010

RE: DE-FG02-95ER14528 (Air-derived noble gases in sediments: sites and mechanisms for trapped components)

Permission to Transfer remaining/incoming funds to LBNL collaborator, B.M. Kennedy

I have recently taken a position as Program Officer (Hydrologic Sciences) at the National Science Foundation. As a consequence, 100% of my salary as well as accommodation of my individual research program are covered by policy and funds of the NSF (NSF allows me 20% time and IR/D (individual research and development) support to continue my participation and intellectual involvement in the above named project). This NSF appointment thus makes it impossible to devote the UConn funds allotted to this project to be appropriately invested in this research.

I therefore request permission to transfer all present UConn allocations for DE-FG02-95ER14528 (approximately $74,000) to my collaborator, B.M. Kennedy at LBNL. It is my understanding that increments of the continuing grant for 15 May 2010 to 14 May 2011 as well as 15 May 2011 to 14 May 2012 will be transferred by OBES/Geosciences on a to-be-determined-and-appropriate basis directly to my collaborator B.M. Kennedy, LBNL. This transfer will enable the research funds to be optimally used in support of my component of this research program which will continue these noble gas research projects currently funded by the DOE’s Office of Science, Geoscience. This research will focus on: (1) high precision noble gas abundance measurements in natural fluid samples; (2) siting and trapping of noble gases in sediments, with an emphasis on biogenic silica and carbon-rich phases; (3) the role of fluids in fault weakening and the role of faults as deep fluid conduits; and (4) development of quaternary dating technique using U-Th-4He and cosmogenic 3He systematics in U and Th-poor volcanic minerals, such as olivine. The transfer of funds will be supervised by Dr. B. Mack Kennedy, Staff Scientist and CIG Group Leader.

The work will be conducted by a post doctoral fellow (to be named) and a research scientist (Evan Kha). The research will be supervised by Dr. B. Mack Kennedy, Staff Scientist and CIG Group Leader.

It is my understanding that the grant will remain open at UConn with a zero balance and that all necessary annual reports will be delivered as expected.
Helium measurements of pore fluids obtained from the San Andreas Fault Observatory at Depth (SAFOD, USA) drill cores

S. Ali · M. Stute · T. Torgersen · G. Winckler · B. M. Kennedy

Abstract $^4$He accumulated in fluids is a well established geochemical tracer used to study crustal fluid dynamics. Direct fluid samples are not always collectable; therefore, a method to extract rare gases from matrix fluids of whole rocks by diffusion has been adapted. Helium was measured on matrix fluids extracted from sandstones and mudstones recovered during the San Andreas Fault Observatory at Depth (SAFOD) drilling in California, USA. Samples were typically collected as subcores or from drillcore fragments. Helium concentration and isotope ratios were measured 4–6 times on each sample, and indicate a bulk $^4$He diffusion coefficient of $3.5 \pm 1.3 \times 10^{-8}$ cm$^2$s$^{-1}$ at 21°C, compared to previously published diffusion coefficients of $1.2 \times 10^{-18}$ cm$^2$s$^{-1}$ (21°C) to $3.0 \times 10^{-15}$ cm$^2$s$^{-1}$ (150°C) in the sands and clays. Correcting the diffusion coefficient of $^4$He$_{\text{water}}$ for matrix porosity (~3%) and tortuosity (~6–13) produces effective diffusion coefficients of $1 \times 10^{-8}$ cm$^2$s$^{-1}$ (21°C) and $1 \times 10^{-7}$ (120°C), effectively isolating pore fluid $^4$He from the $^4$He contained in the rock matrix. Model calculations indicate that <6% of helium initially dissolved in pore fluids was lost during the sampling process. Complete and quantitative extraction of the pore fluids provide minimum in situ porosity values for sandstones 2.8±0.4% (SD, n=4) and mudstones 3.1±0.8% (SD, n=4).

Keywords Stable isotopes · Pore fluids · Porosity · Tortuosity · USA

Introduction

The mechanisms and rates of fluid transport in rock are important controls on (1) basic fluid transport in the Earth’s crust (Fyfe 1978; Torgersen 1989), (2) radioactive waste disposal (i.e. Olanrewaju 2009) or carbon dioxide storage in deep geological formations (e.g. Orr 2009 and references therein), and (3) understanding fluid processes in fault zones (Sano et al. 1986; Kulougoski et al. 2003, 2005; Kennedy and van Soest 2007; Suer et al. 2008). Below melting temperatures, fluid flow represents the most common form of chemical transport in the crust (Fyfe 1978; NRC 1990), thus pore-fluid chemistry and geochemical tracers are essential in constraining sources, sinks and timescales for fluid flow. These processes can be evaluated in situ only on short time and space scales. Long timescale quantification of fluid flow typically requires geochemical tracer techniques and collection of in situ fluids. Traditionally, geochemical measurements are performed on fluid-only samples collected from wells or bailers in boreholes. However, direct fluid samples are not always available, may be of poor quality because of contamination, or do not provide adequate spatial resolution.

The San Andreas Fault Observatory at Depth (SAFOD) drilling project (California, USA) was undertaken to investigate the physical, chemical and hydrologic processes controlling faulting and earthquake generation within a seismically active, major plate-bounding fault (Zoback 2006). Geophysical logs from the SAFOD drill hole show several sharp transitions in resistivity across the damage zone (3,200–3,400 m-measured depth (MD) in

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the drill hole) (Hickman et al. 2007), which could be a result of weak and highly fractured rocks and/or changes in pore-fluid pressure (Mishina 2009). To trace the origin and transport of fluids within the San Andreas Fault (SAF), the low natural abundance, chemical inertness, and distinct isotopic signature of noble gases are exploited to provide insight into source and timescales of fluids in the different crustal environments that comprise the SAF. For the SAFOD drilling project, the drilling plan did not (generally) expect enough fluid inflow throughout scheduled drilling phases to enable fluid-only sampling. Furthermore, slow flow and drilling costs suggested that devoting time to allow the drill hole to infill with fluids might have been prohibitively expensive. Within these constraints, whole rock samples were used to collect matrix pore-fluid samples from SAFOD solid phase drill cores, adapting a methodology pioneered by the Institute for Environmental Physics at the University of Heidelberg, Germany. Upon recovery and suitable containment, the relaxation of the rock (released from, e.g. 2 km of lithostatic pressure) allowed the matrix pore fluids to be extracted. This paper demonstrates an effective method to extract matrix pore fluids and helium from drill core samples and represents the first attempt to extract pore fluids from altered sedimentary rocks from an actively creeping fault zone undergoing repeated or continuous fluid–rock interaction at 120°C in situ temperature.

**Geological setting: the SAFOD drill site**

The SAFOD drill site is located near Parkfield, California. Here, the fault separates the North American Plate in the northeast from the Pacific Plate in the southwest. SAFOD phases 1 and 2 (conducted in 2004 and 2005, respectively) included drilling the main hole to a vertical depth of ~1.7 km followed by an angled descent intersecting the trace of the SAF at ~2.7 km vertical depth, or ~4 km measured depth (MD) along the borehole. The SAFOD main hole was drilled in 2004 to a depth of 3,051 m-MD (phase 1) and deepened to 3,987 m in 2005 (phase 2). Spot cores were obtained from 1,462–1,469 and 3,056–3,067 m-MD during phase 1, and from 3,990–3,993 m-MD during phase 2. Phase 3 recovered cores from 3,141–3,153, 3,186–3,198, 3,294–3,313 m-MD in 2007. Figure 1 highlights the drill-hole lithology as well as the sample depths in the context of geophysical log data. The bulk mineralogy of the SAFOD drill cuttings show an arkosic rock sequence from 1,920–2,550 m-MD, separated by a clay-rich zone at 2,550–2,680 m-MD and a fine-grained sequence at 2,680–3,150 m-MD. A lithologic change occurs at ~3,150 m-MD, where arenites are replaced by fine-grained siltstone and shale fragments. The section at 3,150–3,550 m-MD is characterized by a fine-grained quartz-feldspar rich mudrock (siltstone and shales) with interbedded sandstones (Bradbury et al. 2007). The relative locations of depths corresponding to the Pacific Plate, SAF damage zone, and the North American Plate are based on geophysical logs from Zoback et al. (2010).

Other studies have been performed on fluids collected in the study area (Kennedy et al. 1997). Fluid samples from springs, seeps and wells associated with the SAF have been analyzed to investigate whether fluid movements play a role in the SAF dynamics (Kennedy et al. 1997). SAFOD drilling hiatuses in 2004 and 2005 allowed...
some direct fluid sampling but the inflow zones (depths) were not well constrained and the number of samples obtained does not allow adequate examination of SAF fluid processes (Thordsen et al. 2005).

Erzinger et al. (2004) and Wiersberg and Erzinger (2007) applied real-time mud-gas analyses during drilling, a well-known monitoring technique from oil and gas drilling, to gain information on crustal fluids and gases encountered in the SAFOD hole. The mud-logging method takes advantage of gas release via mechanical crushing of rocks during drilling and provides initial qualitative information about the gas content of the drilled section. However, it does not provide a high-resolution quantitative measure of fluid composition (e.g. concentration of dissolved gases; Erzinger et al. 2004).

To fill this gap in knowledge about the fluid composition in the SAFOD fault zone, this project collected 2.54-cm subcore rock samples from the primary project drill core’s recovered and extracted matrix pore fluids contained within the subcore samples. In this manner, it was possible to collect a suite of samples across the seismogenic zone, measure noble gases, and define fault zone processes with gradients in helium isotope concentration. Described here in detail is the methodology for this sampling and extraction procedure and use of the method to detail the tortuosity of the rocks sampled as controls on pore fluid transport.

Methods

Onsite sampling

A methodology pioneered by the Institute for Environmental Physics at the University of Heidelberg (Osenbrück 1996; Lippmann et al. 1997, 2002; Osenbrück et al. 1998; Rübel et al. 1999; Rübel et al. 2002) was adapted. SAFOD scientific drill cores (~10 cm diameter) in aluminum (Al) liners were recovered to the surface as soon as possible after coring. The ends of the core segments were then subcored using a 2.54-cm-hollow-stem rock drill with de-ionized water (DI) as drilling fluid. This procedure avoids sampling material on the outside of the core that may have degassed already (see Figs. 2.9 and 2.10 of Osenbrück 1996) or has been contaminated with drilling fluids during recovery of the core in the borehole. On other occasions, similarly-sized loose rock fragments were obtained from inside the core barrel where sub coring was not possible due to the brittle nature of rock type (i.e. in siltstone or shale). See Fig. 1 for sample depths. The subcore sample was immediately dried with a paper towel and placed into a stainless-steel high vacuum container and sealed (Fig. 2a).

The air inside the container was pumped out with a rotary pump for 30 s and the container was then filled with research grade nitrogen (N2) to a pressure of about 100 mbar. The container was again evacuated for 30 s and filled with N2 to 100 mbars. Finally the subcore sample container was evacuated for 45 s before it was closed off. The drill core samples analyzed for this study are marked in Fig. 1 and summarized in Table 1.

Tests of field sampling procedure

In order to quantify the amount of fluid lost during the drying, pumping and purging processes in the field (discussed in section Onsite sampling), the field procedure on resaturated shaley siltstone and sandstone samples was replicated in the laboratory. Each rock sample was dried in an oven at 120°C to constant weight, and was submerged in carbon dioxide gas (pCO2 ∼1,000 mbar) for 2 days to replace air within the sample pore spaces and fractures. Then the sample was placed in degassed DI water for 2 days to resaturate all accessible pore spaces and fractures before it underwent the same evacuation process as in the field procedure. The sample weight was measured before and after the evacuation process to determine the amount of pore fluid lost during the sampling process in the field. H2O loss results based on differential weighing are listed in Table 2. Then the sample was dried again at 120°C to constant weight in the oven. The mass of DI water taken up during resaturation

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Fig. 2 Field sampling apparatus. a Stainless steel vacuum sample container next to a subcore sample. b Field set-up diagram for evacuating and flushing sample with research grade N2 before sample is sealed.
resaturated, wet weight–dry weight) allows one to calculate the porosity (porosity2, listed in Table 2) of the sample at low pressure (i.e. 1 bar compared to lithospheric pressure at depths).

Noble gas isotopic analyses
Subcore samples were secured in specially designed soft plastic storage boxes and transported as checked luggage by airplane to Lamont Doherty Earth Observatory (LDEO), New York (USA). Upon arrival at LDEO, two different storage schemes for the samples were used. One set of sample containers were held at room temperature (21°C) for 985 days and were analyzed for noble gases six or seven times until the matrix pore fluids were completely degassed. The second set of sample containers were first stored at room temperature (21°C) for 224 days and then stored in an oven at 120°C (Williams et al. 2004) for 775 days; this transition to a higher temperature oven was done after the first or second isotope analyses to speed the gas release from the matrix pore fluids.

The full suite of noble gas isotopes (\(^{3}\)He, \(^{4}\)He, \(^{20}\)Ne, \(^{21}\)Ne, \(^{22}\)Ne, \(^{36}\)Ar, \(^{38}\)Ar, \(^{40}\)Ar, \(^{84},^{86}\)Kr, and \(^{129},^{131},^{132},^{134},^{136}\)Xe) were determined by mass spectrometry using the LDEO facilities and standard procedures (e.g. Stute et al. 1995). Gases were extracted from the sample container after the rock had relaxed over various time periods. The gas from the sample container was transferred for 30 min through a capillary tube and a stainless steel trap at ethanol-dry-ice temperature and a 3-Å molecular sieve trap at room temperature and pressure. STP standard temperature and pressure. NA not applicable; SD standard deviation

Table 1 | Helium and neon abundance and helium isotope ratios (normalized to air) of pore fluids obtained from diffusion (source 1: this study), mud-gas samples (source 2: Wiersberg and Erzinger 2007) released during drilling, and well fluid samples (source 3: measured at Lawrence Berkeley National Laboratory (LBNL), this study), all obtained from SAFOD drill holes. m-MD sample recovery depth (measured depth along borehole). Well fluid samples were collected in between drilling phases, which allowed for fluid accumulation in the well for several months. R/Ra values measured at LBNL and (He) calculated based on F(\(^{4}\)He) and F(\(^{40}\)Ar) values and Ar concentrations (Thordsen et al. 2005).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample depth (m-MD)</th>
<th>(^{4})He (×10(^{-5}) ccSTP g(^{-1}))</th>
<th>SD (1σ)</th>
<th>R/Ra</th>
<th>SD (1σ)</th>
<th>Air 4(^{\text{He}}) contribution (%)</th>
<th>(^{20})Ne (×10(^{-7}) ccSTP g(^{-1}))</th>
<th>SD (1σ)</th>
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<td>0.00</td>
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<td>0.59(^{a})</td>
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\(^{a}\) Some degassing may have occurred in these samples

Table 2 | Density and porosity values of drill subcore samples used in this study compared to geophysical data from the same depths (m-MD). Porosity1 (minimum porosity) is based on the mass of water extracted during noble gas measurements and subsequent sample drying at 120°C. Porosity2 is based on mass of water used to resaturate hand samples after complete extraction of noble gases and drying. H2O loss (%) refers to the amount of water lost during experimental pumping and flushing with high purity N2 after each individual sample was resaturated with degassed DI water. Neutron density and neutron porosity data are from geophysical logs (available from SAFOD 2008a, b, c).

<table>
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<tr>
<th>Sample ID</th>
<th>Sample depth (m-MD)</th>
<th>Rock sample Density (g ml(^{-1}))</th>
<th>Porosity2 (%)</th>
<th>H(_{2})O loss (%)</th>
<th>Porosity1 (%)</th>
<th>Neutron density (g ml(^{-1}))</th>
<th>Neutron porosity(^{a}) (%)</th>
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\(^{a}\) Field normalized compensated neutron porosity
NA not applicable

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temperature into an expansion volume (1,000 cc) by using water vapor from the sample as a carrier gas. A known fraction of dry gas was split off and chemically active gases were removed in a Ti/Zr getter at 800°C. The remaining noble gases were then transferred onto a trap filled with activated charcoal at 13 Kelvin. After quantitative adsorption, the individual gases were desorbed from the charcoal by stepwise heating and (after exposure to additional getters) transferred into a static sector field mass spectrometer with extended geometry (MAP 215-50, Mass Analyzer Products, Manchester). $^3$He was measured by pulse counting on an electron multiplier; all the other isotopes were analyzed on a Faraday cup. The overall procedure was calibrated by measuring known quantities of atmospheric air. The precision of isotope ratio determinations are ~2% for $^3$He/$^4$He ratios. The reproducibility of abundance measurements was estimated from air standard measurements to be 2% for He and Ne.

**Modeling methods**

Diffusion coefficients were determined by fitting the cumulative $^4$He concentrations with simple analytical and numerical solutions of the diffusion equation for spherical or cylindrical shapes (Crank 1975). Samples that experience two different storage-temperature regimes over time require a numerical solution. For numerical solutions of the diffusion equation, the rock sample’s actual surface geometry was used as the diffusion boundary. The sample geometry was determined by a three-dimensional (3D) scan via a portable Minolta VIVID 910 laser surface scanner (courtesy of W. Harcourt-Smith, American Museum of Natural History, New York State). As in the analytical solutions, the initial concentration was assumed to be a uniform value and the boundary concentration to be zero. The sample geometry was discretized with a 3D (three-dimensional) finite difference grid with a typical grid box size of 42 mm$^3$ grid over a 25 mm diameter rock sample. The diffusion equation was solved with a simple forward finite difference numerical scheme (Bear and Verruijt 1987).

**Porosity determination**

During each noble gas analysis, the sample water released by the relaxed rock was used as a carrier of gases contained in the container headspace and collected in a dry-ice-cooled trap. After completion of each extraction (30 min), the condensed water vapor was transferred into a removable water trap cooled to liquid-nitrogen temperature and quantified by differential weighing. Following the final extraction, the sample container was vented and each rock subcore sample was weighed immediately before being baked again at 120°C in an oven. Each sample’s weight was monitored over 3 days until the weight stayed constant indicating that all mobile water had been removed from the rock sample. The cumulative water content for each sample was determined by adding (1) the amount of transferred water vapor from the sum of extractions for isotopic analyses and (2) the remaining water removed during the bake-out in the oven, as determined by differential weighing of the sample before and after baking. The total water content is representative of the volume of void space in the rock sample. The bulk volume of sample was determined by measuring the displacement of DI water of the samples wrapped in a thin layer of adhesive plastic to avoid filling pore spaces with DI-water. The combination of measurements allows for the determination of bulk density and water content (porosity,$\phi$) of the samples (see Table 2). The total water content of each sample determined by this process is also used to calculate total helium concentration in the total fluid (i.e. cubic centimeters of helium at standard temperature and pressure per gram of water, ccSTP He g$^{-1}$ water).

**Results**

**Sampling procedure**

There are two potential sources of helium contamination that can alter the helium isotope ratios. First, the sampling process in the field required research grade (RG) nitrogen gas to flush out atmospheric gases from the sample container headspace. The helium ‘blank’ contribution from the RG nitrogen gas used in the field was less than 0.01%. The second potential source of helium contamination is residuals of air in the containers during sampling which was estimated from other noble gases and air-like ratios. Most of the air contamination is based on Ar, Kr and Xe values, all of which are also likely naturally present in the pore fluids and, thus, this estimate suggests a maximum helium contribution of less than 3% from air during the sampling process. Most samples have less than 1% air contribution to helium as shown in Table 1. Sample # TW4 is the only sample with a considerably higher air contribution (2.91%). $^{20}$Ne concentrations were used to check for possible degassing of the pore fluids during the sampling process. Pore fluid $^{20}$Ne concentrations ($2.6 \times 10^{-7} \pm 1.7 \times 10^{-7}$ (SD, $n=8$) ccSTP g$^{-1}$) are consistent with average air saturated Ne values in freshwater and seawater—$1.4 \times 10^{-7} - 2.2 \times 10^{-7}$ ccSTP g$^{-1}$ as suggested by Kipfer et al. (2002)—suggesting that pore fluids extracted from samples with 2.54 cm radius or similar thickness have not degassed during the sampling procedure.

**Isotope analysis**

The reconstructed total helium isotope ratios in matrix pore fluids recovered are 0.373Ra=0.006 (SD, $n=4$) from the Pacific Plate and 0.945Ra=0.007 (SD, $n=4$) from the North American Plate (Ra=1.384 × 10$^{-6}$), see Table 1. Figures 3 and 4 show the cumulative $^4$He concentration as a function of time, using the total extractable water content and cumulative $^4$He removed over time. The sample always held at room temperature (SAF 4; Fig. 3)
isotope ratios observed for the corresponding measurements (marked by ‘X’ in Fig. 4) are due to atmospheric helium accumulation in the sample container through tiny leaks, corresponding to less than 3% of individual measurements and less than 0.01% of the cumulative helium concentration.

**Helium diffusion coefficients**

Cumulative $^4$He concentrations as a function of time are used to determine the effective helium diffusion coefficient in the pore fluid matrix within the rock sample. Figure 5 represents normalized cumulative helium concentration as a function of time in days for samples held at room temperature only for 985 days. The following solutions (Crank 1975) are used to determine analytical solutions of the diffusion coefficients. The solution assumes a uniform initial concentrations of He in the rock sample and a $C=0$ boundary condition for a spherical (Eq. 1) and infinite cylindrical geometry (Eq. 2) of the samples.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-Dn^2\pi^2t}{r^2}\right)$$  \hspace{1cm} (1)

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{r^2\alpha_n^2} \exp\left(-D\alpha_n^2t\right)$$  \hspace{1cm} (2)

Fig. 3 Helium isotope data for sample SAF 4 (arkosic sandstone, 3059.3 m-MD) held at 21°C over six measurements and 985 days. Blue circles represent cumulative helium concentration in extracted matrix pore water over time, while red squares correspond to $^3$He/$^4$He isotope ratio (R are normalized to air, $Ra = 1.384 \times 10^{-10}$) plotted on the right axis. $1\sigma$ error bars for helium concentrations are smaller than the size of the blue symbols.

Fig. 4 Helium isotope data for SAF 6 (arkosic sandstone, 3064.2 m-MD) held at 21°C over two measurements totaling 224 days and then held at 120°C for four measurements totaling 775 days. Blue circles represent cumulative helium concentration in extracted pore water over time, while red squares correspond to $^3$He/$^4$He isotope ratio corresponding to $R/Ra$ axis on the right axis. The last three data points show negligible contribution to the cumulative helium concentration; however, the $^3$He/$^4$He has increased to above 1Ra, which corresponds to less than 3% blank contribution from tiny leaks in the container to individual analyses. The last three measurements combined have ~0.3% of the total cumulative helium concentration. (The absolute amount of gas in the last three measurements combined is less than $3 \times 10^{-8}$ ccSTP g$^{-1}$). $1\sigma$ error bars are smaller than the size of the symbols.

Fig. 5 Cumulative helium concentrations normalized to total helium concentration of each sample. Blue markers correspond to SAF 4 (arkosic sandstone, 3059.3 m-MD) and SAF 5 (arkosic sandstone, 3056.3 m-MD) where both samples were kept at 21°C over six measurements (985 days). $1\sigma$ error bars are smaller than the size of the symbols. Green dotted line represents the analytical solution bounded by cylindrical geometry with a diffusion coefficient of $D_{cylinder}=1.5 \times 10^{-8}$ cm$^2$ s$^{-1}$. Red dashed line represents the analytical solution bounded by spherical geometry corresponding to diffusion coefficient of $D_{sphere}=3.5 \times 10^{-8}$ cm$^2$ s$^{-1}$ ($\pm1.3 \times 10^{-8}$ cm$^2$ s$^{-1}$, grey shaded region). Numerical fits for $D_3=3.0 \times 10^{-8}$ cm$^2$ s$^{-1}$ (solid orange curve, $\pm1.0 \times 10^{-8}$ cm$^2$ s$^{-1}$) and $D_4=6.0 \times 10^{-8}$ cm$^2$ s$^{-1}$ (solid red curve, $\pm2.0 \times 10^{-8}$ cm$^2$ s$^{-1}$) superimposed on data and analytical solutions as described in Fig. 5. Black dashed line corresponds to theoretical diffusion with $D_t=1 \times 10^{-15}$ cm$^2$ s$^{-1}$ (Solomon et al. 1996) corresponding to diffusion of helium from solid rock matrix.
where $M_l$ is the summed quantity of diffusing substance which has left the object at time $t$, $M_\infty$ is the total quantity of substance diffused out of the body after infinite time, $D$ is the bulk diffusion coefficient, $r$ is the sample radius, and $\alpha_n$ are the roots of Bessel function of the first kind of order zero.

The solutions to Eqs. 1 and 2 are also plotted in Fig. 5. The dashed red and the dotted green lines represent the solutions to equations 1 (spherical boundary, $D_1$(sphere)$=3.5\pm1.3 \times 10^{-8}$ cm$^2$ s$^{-1}$) and Eqs. 2 (cylindrical boundary, $D_2$(cylinder)$=1.5\pm1.3 \times 10^{-8}$ cm$^2$ s$^{-1}$), respectively. The gray region represents the uncertainty in diffusion coefficients in Eq. 1 based on the data fit.

Numerical results represented by solid lines in Fig. 5 correspond to diffusion coefficients of $D_4$=$6.0\times10^{-8}\pm2.0\times10^{-8}$ cm$^2$ s$^{-1}$ (upper limit) and $D_3$=$3.0\times10^{-8}\pm1.0\times10^{-8}$ cm$^2$ s$^{-1}$ (best fit).

For samples held at room temperature for 224 days and then held at 120°C for over 700 days, the normalized cumulative helium concentration versus time is shown in Fig. 6. Due to the change in storage temperature, which one cannot take into account in the analytical solution, one needs to rely on the numerical solutions to determine diffusion rates. As shown in Fig. 6, the numerical solutions indicate a diffusion coefficient of $1.5 \times 10^{-7}$ cm$^2$ s$^{-1}$ at 120°C, a five-to-ten-fold increase compared to diffusion rates at room temperature.

**Porosity and density determinations**

Table 2 lists density and porosity data for all samples of this study. The method allows quantitative determination of the pore-fluid mass present in the samples at various depths; thus, enabling calculation of the minimum porosity (listed as porosity$_1$ in Table 2) of each individual sample because some void space could be unsaturated and some water could be lost by towel drying and pumping of the drill core subsample. Based on the resaturation experiments in the laboratory (summarized in Table 2), towel drying of each sample followed by the evacuation and flushing process in individual sample vacuum containers led to water loss of up to 4.6% in sandstone (Pacific Plate; SAF 4, SAF5, SAF6, SAF8) samples and up to 9% in siltstone (North American Plate; TW1, TW3, TW4, TW5) samples.

Average minimum porosity$_1$, (based on mass of pore water at depth) values of $2.8\pm0.4\%$ (SD, $n=4$) and average bulk density values of $2.1\pm0.3$ g ml$^{-1}$ (SD, $n=4$) are observed in the samples from the Pacific Plate. The North American Plate samples have similar average porosity$_1$ values of $3.1\pm0.8\%$ (SD, $n=4$) and average bulk density of $2.1\pm0.2$ g ml$^{-1}$ (SD, $n=4$). One shale sample from -3,400 m-MD has a porosity$_1$ of 6.1%, but this sample was obtained from the core catcher and shows obvious drilling marks. The original sample depth and the amount of time it was exposed in the borehole is uncertain and thus is not discussed further.

The resaturation experiment also provides a measure of the porosity of each sample under ambient pressure of 1 bar, which is also listed in Table 2 as porosity$_2$ (for definition, see section Helium diffusion coefficients). Porosity$_2$ values (6.6±1.6% (1 SD) for sandstones from the Pacific Plate, and 5.8±2.8% (1 SD) for North American siltstones) are also indistinguishable within error for samples from the North American and Pacific Plates, but they are consistently higher than porosity$_1$ values due to newly formed fractures during drilling and retrieval of the drill core to much lower pressures.

**Discussion**

**Sampling procedure**

This procedure was pioneered in Heidelberg by Osenbrück (1996). That study used larger sample size and 70 s of pumping (compared to 30-45 s of pumping and purging with N$_2$ used in this study) to evacuate each sample container before sealing the sample. Osenbrück (1996) observed complete degassing of noble gases within 1 month, which translated into 20–30% loss of noble gases during the sampling procedure. Given the calculated diffusion coefficients described previously (see section Helium diffusion coefficients), and assuming He loss due to diffusion at room temperature, a 4–6% loss of helium during sampling was estimated (this study) compared to 20–30% loss reported by Osenbrück (1996).

Laboratory tests showed that repeated pumping and purging with research grade N$_2$ (this study) is effective in removing >99.99% of the air (based on Ar, Kr and Xe analysis of each extraction) within the container (replaced with high purity N$_2$ at low pressure). 0.01% air contamination would affect the helium isotope ratio (R/Ra) by less than 1%, which is within the analytical uncertainty.

Hydrogeology Journal

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and, therefore, has no impact on the helium isotope data interpretation of these samples.

**Helium isotope concentrations and ratios**

Table 1 gives helium isotope ratios and helium abundance data derived by three different methods applied to samples from similar depths in the SAFOD drill hole. The pore-fluid diffusion method is described in this study. The mud-gas (Wiersberg and Erzinger 2007) samples are released from mechanical crushing of rocks during drilling and have relatively larger error bars due to atmospheric contamination. Lawrence Berkeley National Laboratory (LBNL) data (Table 1) are derived from fluid samples collected 4–6 months after drilling and during drilling hiatuses. The borehole walls were cased with cement to a depth of 3,050 m-MD before fluid was allowed to collect in the depth interval between 3,050 and 3,065 m-MD and subsequently sampled in 2005 (samples CA05WPT1, CA05WPT2, and 05SAF206 retrieved from 3,051–3,064 m-MD). After the borehole was deepened and cased to a measured depth of 3,990 m, fluids accumulated for several months before further fluid sampling in 2006 (samples SAF205 and SAF202 retrieved from 3,261 and 3,726 m-MD, see Table 1). Under these conditions, the fluid is expected to fill the borehole from the bottom (uncased section).

Matrix pore fluid helium concentrations are constant on both plates—Pacific Plate: $1.9 \pm 0.5 \times 10^{-5} \text{ ccSTP g}^{-1}$ (SD, $n=4$), North American Plate: $1.4 \pm 0.1 \times 10^{-5} \text{ ccSTP g}^{-1}$ (SD, $n=4$). The helium concentrations of fluid samples collected from open intervals of the borehole was calculated from $F(\text{He})$ and $F(\text{Ar})$ data (measured at LBNL; $F(\text{Ng})=[N_{\text{g}}]/[36\text{Ar}]$; $N_{\text{g}}$ describes a noble gas isotope) and Ar concentration data obtained from individual fluid sample splits (listed in Table 1). The direct fluid sample concentrations also yield similar average helium concentrations on both plates—Pacific Plate: $5 \pm 2 \times 10^{-5} \text{ ccSTP g}^{-1}$ (1 SD, $n=3$), North American Plate: $6 \pm 3 \times 10^{-5} \text{ ccSTP g}^{-1}$ (1 SD, $n=2$) although they are at least two times larger than the matrix pore fluid helium content (see Fig. 7a). If the $20\text{Ne}$ concentration data are a good indicator of the robustness of this (pore fluid extraction) method, then the higher $4\text{He}$ abundance in well fluids could likely be due to fracture fluids tapping into a different (older) reservoir compared to local fluids contained in matrix pore fluids. However, the consistent $3\text{He}/4\text{He}$ ratios observed in well fluids and pore fluids would suggest that the fluids contained in fractures and pore spaces are in equilibrium. However, there is not have enough information to further evaluate this possibility.

In general, gas abundances in well fluids are measured from the sample container head space on a gas chromatograph (GC). The helium concentrations in the well fluid samples recovered during the SAFOD drilling project were very small (very close to the GC detection limit). The well fluid [He] data listed in Table 1 are calculated based on $40\text{Ar}$ abundance data from the sample container head space measured on a GC (at US Geological Survey, Menlo Park, California) and $3\text{He}, 36\text{Ar}$ and $40\text{Ar}, 36\text{Ar}$ ratios from split fluid samples measured on a mass spectrometer (at Lawrence Berkeley National Laboratory, Berkeley, California; Thordsen et al. 2005). Thus, there is complete confidence in the well fluid helium abundance data presented in Table 1.

However, the pore fluid helium isotope ratios (Fig. 7b) suggest two distinct sources of fluids in the Pacific Plate—$R/\text{Ra}=0.373 \pm 0.006$ (1 SD, $n=4$) and the North American Plate—$R/\text{Ra}=0.945 \pm 0.007$ ($n=4$). These ratios are remarkably consistent with direct fluid data (LBNL data, Table 1) as well as mud-gas data (Wiersberg and Erzinger 2007), suggesting isotopic equilibrium on each side of the SAF. However, the pore fluid data are three times more precise as indicated by the error bars in Fig. 7b compared to mud-gas samples associated with the SAF (samples labeled as source 2 (Wiersberg and Erzinger 2007) in Table 1).
**Helium diffusivity**

Helium diffusion coefficients calculated with cylindrical and spherical boundary conditions are the same within one sigma error. As seen in Fig. 5, the numerical model (for $D_s=3 \times 10^{-8} \pm 1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $D_f=6 \times 10^{-8} \pm 2.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) mimics the analytical solutions, $D_1$ (sphere) and $D_2$ (cylinder), closely and provides the same diffusion coefficients (within error) for samples held at room temperature. $D_f$ in Fig. 5 is probably higher due to newly formed fractures in each sample under low pressure, which provide a connected path for fluid flow out of the rock matrix. It is observed that an approximate five-to-ten-fold increase in the diffusion coefficient of helium at 120°C relative to 21°C ($1.1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 21°C and $1.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 120°C) allows for faster sample degassing. Helium diffusion coefficients measured in the solid phase of sands and clays are $1.2 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ at 21°C and $3.0 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at 150°C (Solomon et al. 1996). Diffusion coefficients calculated in this study are several orders of magnitude larger and characterize helium derived from matrix pore fluids. Figure 5 also shows the theoretical cumulative helium concentration over 985 days for an estimate of a solid phase diffusivity of $D_s=1.0 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ in comparison to SAF 4 and SAF 5 data, as well as analytical and numerical diffusion curves. The stark contrast between this study’s data and the solid phase scenario (Solomon et al. 1996) illustrates that noble gases collected in this fashion represent matrix-pore-fluid noble gases and not solid-phase noble gases.

**Porosity and density**

In order to constrain helium concentrations, this method relies on accurate determination of matrix pore-water mass, which is accomplished by quantitative extraction of matrix pore fluids from each rock sample. The extracted water vapor is released from connected pore spaces filled with fluid and thus corresponds to the minimum porosity of each sample. Porosity and density data of each sample are compared to geophysical logs obtained from the same depth in Table 2. Density results of individual rock samples—Pacific Plate: $2.1 \pm 0.3 \text{ g ml}^{-1}$ (SD, $n=4$), North American Plate: $2.1 \pm 0.2 \text{ g ml}^{-1}$ (SD, $n=4$) are consistent with neutron density logs—Pacific Plate: $1.9 \pm 0.4 \text{ g ml}^{-1}$ (SD, $n=4$). The minimum in situ porosity ($\text{porosity}_1$) values—Pacific Plate: $2.8 \pm 0.4\%$ (SD, $n=4$) and North American Plate: $3.1 \pm 0.8\%$ (SD, $n=4$) obtained in this study are lower than the field normalized compensated neutron porosity log (SAFOD main hole downhole logging data phase 2 (2005): 2,812–3,043 m-MD (SAFOD 2008a); 2,975–3,387 m-MD (SAFOD 2008b); 3,387–3,799 m-MD (SAFOD 2008c) by at least a factor of two. Porosity values listed in Table 2 and derived from the resaturated weight in individual rock samples with DI water are much closer to the geophysical logging porosity values. However, the higher values in porosity are due to a combination of complete saturation of void spaces within the rock matrix with DI water and newly formed fractures due to lower pressure, which enhance the void space in the rock matrix allowing more water to be absorbed by each rock. Thus far, the porosity values (porosity in Table 2) obtained from this study are a minimum representation of porosity at depth. Based on the density and porosity data found in this study, individual sandstone and siltstone samples are indistinguishable from each other (see Table 2 and Fig. 1).

**Tortuosity**

Rocks in an active fault zone (e.g. the SAF) are altered by multiple fracture formation and fluid–rock interaction events that result in continuous evolution of connected pore spaces and fractures thereby affecting tortuosity in the rock matrix. A comprehensive list of theoretically derived tortuosity values, for a variety of unconsolidated sediments with porosities ranging from 30 to 100%, is summarized by Boudreau (1997). Tortuosity in low porosity, consolidated rocks is not well constrained. Diffusion coefficients of helium in pure water are $D_h=6.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 21°C (Jahne et al. 1987) and $17.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 150°C (Solomon et al. 1996). However, the observed diffusion coefficients of gases in pore fluids are also influenced by the porosity and tortuosity. Since this method provides porosity ($p$) and effective diffusivity ($D_e$) ($1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ to $6 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$), and the diffusion coefficient of helium ($D_h$) in water is known, the relationship described in Eq. 3 can be used (Van Brakel et al. 1975) to determine tortuosity ($\tau$) for samples with low porosity values of $\sim 3\%$.

$$D_e = \frac{D_h}{\tau^2} p$$

Using this method, tortuosity values of 6–13 are obtained, which are consistent with studies on shales (Katsube et al. 1991) and clay-enriched sandstones and siltstones (Salem 2000).

**Conclusions**

The method presented in this paper is effective in completely extracting pore-fluid content of sedimentary rocks. It provides a viable measure of dissolved gases in matrix pore fluids consistent with established mud-gas and direct-sampling fluid methods and allows for both noble gas abundance and isotope analyses. The field procedure minimizes noble gas loss by limiting sampling time to 2–5 h after core recovery. This procedure, however, requires quick onsite decision-making about sampling requirements and sampling frequency, which may not be desirable or possible at all times. Because the entire pore-fluid helium content and the complete pore-fluid mass were determined, additional properties such as in situ porosity ($\sim 3\%$) and tortuosity (6–13), were also calculated.
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Continental degassing flux of $^4$He and its variability

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[1] The existing measures of the $^4$He flux from the Earth’s continental solid surface have been evaluated collectively. The lognormal mean of continental crustal flux measurements ($n = 33$) globally covering many geological environments is $4.18 \times 10^{10}$ $^4$He atoms m$^{-2}$ s$^{-1}$ with an estimated one sigma variance of $*/45X$ based on an assumption of symmetric error bars (lognormal distribution provides a standard deviation with a multiplication or division factor (*/) by which the mean may statistically vary). The range of the continental $^4$He degassing flux (95th percentile) increases with decreasing time scales (to $*\sim10^6X$ at 0.5 year) and decreasing space scales (to $*\sim10^6X$ at 1 km). The statistics can be interpreted as reflecting natural variability and suggest that the mechanisms transporting the crustal helium degassing flux contain a high degree of both spatial and temporal variability. This lognormal mean of the continental degassing flux of $^4$He as well as the ($n = 271$) estimate of degassing from Precambrian Shield lakes are both approximately equivalent to the radiogenic production rate for $^4$He in the whole crust. Large-scale vertical mass transport in continental crust is estimated as scaled values of the order $10^{-5}$ cm$^2$ s$^{-1}$ for helium (over 2 Gyr and 40 km vertically) versus $10^{-2}$ cm$^2$ s$^{-1}$ for heat. This rate of mass transport requires not only release of He from the solid phase via diffusion, fracturing, or comminution but also an enhanced rate of mass transport facilitated by some degree of fluid advection. This further implies a separation of heat and mass during transport which will significantly influence the interpretations of heat and $^3$He/$^4$He relations.

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1. Introduction

[2] There have been many consistent estimates [e.g., Mamyrin and Tolstikhin, 1984, Table 10.1; Torgersen and Clarke, 1985] of the flux of helium from the continental crust based on calculations of in situ production and steady state release to the atmosphere assuming (1) U and Th content, (2) crustal thickness, and (3) 100% release of helium. These calculations yield a crustal degassing flux of the order $3 \times 10^{10}$ atoms $^4$He m$^{-2}$ s$^{-1}$ [e.g., Tolstikhin, 1975; Mamyrin and Tolstikhin, 1984, Table 10.1; Torgersen, 1989]. These “theory”
values are currently discussed over a factor of order 2X in variability. On the other hand, there have been many “direct measures” of the helium degassing flux based on the capture of the degassing flux (1) beneath a thermocline or pycnocline within a lake or sea, where the age of the deep water is used to calculate a flux, or (2) within a dated groundwater flow system to calculate a flux. Table 1 summarizes these “measurements” (hereafter the quotation marks are deleted, and it is accepted that measurements and theory denote the method by which a degassing flux is determined) of the degassing flux of 4He from continental crust, which range from not discernable (Lakes Huron, Erie, and Ontario; see text below) to 30,000 × 10^{10} atoms 4He m^{-2}s^{-1} (Lake Nyos). While each measurement of the degassing flux in Table 1 has an error (likely order of 3X) associated with the calculations and assumptions, it is clear that variability in the measurements of the 4He degassing flux from the continental crust is large. An understanding of the natural variability in the continental degassing flux of 4He is important to multiple questions in the Earth sciences.

[1] Metamorphic geology [e.g., Etheridge et al., 1983, 1984; Hu et al., 2009] and drill hole measurements [Torgersen and Clarke, 1992] suggest that large-scale vertical transport of fluids in the continental crust is likely advective and episodic. Is the variability of the measured degassing flux a reflection of this episodic and advective transport? What is the average bulk rate of helium transport in the crust, and how does it compare to the bulk rate of heat transport?

[2] 4He has long been investigated as a potential groundwater dating tool [e.g., Davis and DeWeist, 1966; Marine, 1979; Torgersen, 1980; Stute et al., 1992; Kulangoski et al., 2005; Zhou and Ballentine, 2006] utilizing both in situ production and an external flux. The use of 4He has also been extended to calibration of models [e.g., Castro et al., 1998a, 1998b; Castro et al., 2000; Betheke et al., 1999] and/or calibrating 4He accumulation with 4He to 36Cl correlations [Kulangoski et al., 2005; Maharal et al., 2009], all of which assume a steady state, spatially uniform external flux of He. How does the variability (in time and space) of the crustal degassing flux impact the interpretation of groundwater dating by 3He? Kulangoski et al. [2005] show the estimated 4He flux into the groundwaters of specific wells in California to vary by a factor of 300X over a distance of 12 km due to fault controls. How do hydrologic and faulting processes impact the rates of transport in the crust and the spatial variability of the degassing flux from the crust?

[3] Helium isotope ratios have been applied to the evaluation of tectons and magmatism in geologic provinces [e.g., Polyak and Tolstikhin, 1985; Oxburgh et al., 1986; Oxburgh and O’Nions, 1987; O’Nions and Oxburgh, 1988; see also Newell et al., 2005], and the analysis suggests broad generalizations. Oxburgh et al. [1986] suggest that (1) loading basins are dominated by 3He/4He ratios consistent with in situ production in the continental crust and (2) extensional terrains commonly reveal a strong but variable mantle 3He/4He component in addition to a continental crust signal. Additionally, many authors [e.g., Mamyrin and Tolstikhin, 1984, Figure 8.16; Polyak and Tolstikhin, 1985; Polyak et al., 2000, and references therein] have noted correlations between heat flow and 3He/4He, and recent work indicates that such applications can also be examined for the geologic past utilizing helium isotopes preserved in specific ore deposit fluid inclusions [e.g., Hu et al., 2009]. However, 3He/4He ratios are the result of mixing between mantle-sourced 3He-rich fluxes and crustal-sourced 4He-rich fluxes. Transport separation of heat and helium and temporal variations in these fluxes will result in a transport-controlled variability of 3He/4He versus heat relationships. How are the crustal degassing flux of 4He, the transport of mantle 3He through the crust, and heat flow related in space and time? Torgersen [1993] (following Lachenbruch and Sass [1978]) considered that extensional terrains might initiate an enhanced crustal 4He signature via fracturing [Torgersen and O’Donnell, 1991] and comminution [Solomon et al., 1996] as well as a high 3He signature as a result of (1) magma intrusion (which introduces heat and He as defined by the magma at the depth of magma intrusion) and (2) stretching or underplating (which solidifies mantle material to the base of the crust and can produce a separation of heat and He by large-scale transport across the entire crustal thickness). Can the variability in heat/helium relation be adequately partitioned among the different processes responsible for the introduction of mantle He? On another front, recent work by Kennedy and van Soest [2007] identified a relation between 3He/4He and tectonic strain rates across the Basin and Range Province (western United States), where high rates of strain are associated with higher helium isotope ratios. This research opens the possibility that mantle helium can...
<table>
<thead>
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<th>Region</th>
<th>$^4$He Flux, Reported (atoms m$^{-2}$ s$^{-1}$ × 10$^{-10}$)</th>
<th>Method</th>
<th>$^4$He Flux, Plotted Flux (atoms m$^{-2}$ s$^{-1}$ × 10$^{-10}$)</th>
<th>Time Scale</th>
<th>Space Scale (km)</th>
<th>Mantle $^4$He Flux, Reported (atoms m$^{-2}$ s$^{-1}$ × 10$^{-8}$)</th>
<th>$^3$He/$^4$He, &quot;Added Component&quot; Calculated This Study</th>
<th>Fraction Crustal</th>
<th>Crustal $^4$He Flux, Plotted (atoms m$^{-2}$ s$^{-1}$ × 10$^{-10}$)</th>
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<th>(^4\text{He Flux, Plotted Flux (atoms m}^{-2}\text{s}^{-1} \times \times_{10}^{10})) Time Scale</th>
<th>Space Scale (km)</th>
<th>Mantle (^4\text{He, &quot;Added Component&quot; Calculated, This Study} \times \times_{10}^{10}) Fraction</th>
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\(^a\)References are as follows: 1, O’Nions and Oxburgh [1988]; 2, Torgersen and Clarke [1985]; 3, Torgersen and Ivey [1985]; 4, Heaton [1984]; 5, State et al. [1992]; 6, Martel et al. [1989]; 7, Andrews et al. [1985]; 8, Marty et al. [1993]; 9, Pinti and Marty [1995]; 10, Pinti et al. [1997]; 11, Castro et al. [1998a, 1998b]; 12, S. Dewonck et al. (as cited by Ballentine et al. [2002]); 13, Torgersen et al. [1981]; 14, Campbell and Torgersen [1980]; 15, Torgersen and Clarke [1978]; 16, Torgersen [1983]; 17, Torgersen et al. [1977]; 18, Clarke et al. [1977], Clarke et al. [1983], and Top and Clarke [1981]; 19, Kijfer et al. [2002]; 20, Castro et al. [2000]; 21, State et al. [1995]; 22, Well et al. [2001] (in the work by Schlosser and Winckler [2002]); 23, Top and Clarke [1981]; 24, Torgersen [1989]; 25, this study.

\(^b\)The flux is \(<10^9\) \(^4\text{He atoms m}^{-2}\text{s}^{-1}\); the flux is chosen to best estimate symmetric log normal error bounds.
be introduced into the continental crust without mantle-sourced magma.

[6] In this paper, the measurements of the continental $^4\text{He}$ degassing flux (Table 1) are evaluated in terms of an appropriate mean as well as a spatial and temporal variability. By quantifying these basic characteristics, it is hoped that $^3\text{He}/^4\text{He}$ and $^4\text{He}$ flux measures can better evaluate (1) $^4\text{He}$ as a method of groundwater dating; (2) the role of tectonics and magmatism in enhancing crustal-scale mass transport and the fluxes of heat, $^4\text{He}$, and $^3\text{He}$; and (3) defining the rates, mechanisms, and variability of crustal-scale mass transport.

2. Results: Data Sources and Calculations

[7] Table 1 shows the measures of the continental $^4\text{He}$ degassing flux from various regions worldwide including lakes and groundwater basins. (The author is aware of several other estimates of the continental degassing flux [e.g., Sano et al., 1986; Kulangoski et al., 2005]; yet these can only poorly be associated with a characteristic time and/or space scale that is critical to the following analysis.) The primary flux data were compiled by Ballentine et al. [2002] for groundwater basins and Kipfer et al. [2002] for lakes from various sources as noted in the footnotes to Table 1. In addition to these quantifications, the method of Kipfer et al. [2002] (utilizing a plot of excess $^4\text{He}$ versus $^3\text{H}/^3\text{He}$ age of the water) was applied to Green Lake [Torgersen et al., 1981], Teggau Lake [Torgersen and Clarke, 1978], Lake 120 [Campbell and Torgersen, 1980], and Lake Taupo [Torgersen, 1983] and generally yielded defined fluxes. However, the data for Lakes Huron, Erie, and Ontario [Torgersen et al., 1977] resulted in slopes that were not well defined and can be approximated by fluxes from $<10^{10}$ atoms $^4\text{He}$ m$^{-2}$ s$^{-1}$ to indistinguishable from zero. Whether this represents an analytical limit of these early measures of helium isotopes or a true lower bound is not known.

[8] For each quantification of the continental $^4\text{He}$ degassing flux (Table 1), an appropriate time scale over which the degassing flux accumulated was estimated based on the groundwater flow time and/or the $^3\text{He}/^4\text{He}$ age of the lake bottom water. In addition, each measure of Table 1 has an estimated length scale based on the square root of the area over which the degassing flux accumulated or the length of the groundwater flow path. The flux data of Table 1 and as depicted in Figure 1 form the base data for this evaluation of the variability of the continental $^4\text{He}$ degassing flux.

[9] The data of Table 1 represent an interpretation of helium data collected by multiple investigators,
and there exist differences of opinion with regard to the interpretation of these data. For instance, Lehmann et al. [2003] conclude that excess He added to the flowing groundwaters of the Great Artesian Basin is the result of fluxes from the confining shales based on similarities between the observed helium (chlorine) isotope ratios and the calculated in situ production helium (chlorine) isotopes ratios. However, this does not negate the conclusion that the GAB contains $^{4}$He that has a source external to the aquifer. That the in situ $^{3}$He/$^{4}$He production ratio of the confining shales is not distinguishable from upper crustal $^{3}$He/$^{4}$He production ratios (given the error in effective production ratio that can be estimated from Ballentine and Burnard [2002, Table 4] and the analysis by Martel et al. [1990]) may not prove or disprove either conclusion. The quantifications of Table 1 (as initially deduced by Ballentine et al. [2002] and Kipfer et al. [2002]) are taken as the best available estimates of the degassing fluxes.

In addition to the $^{4}$He degassing fluxes identified above and included in Table 1, a suite of data is available from multiple Precambrian shield lakes studied by Clarke et al. [1977], Top and Clarke [1981], and Clarke et al. [1983]. Based on single samples measured for helium concentration, helium isotope ratio, and tritium below the thermocline of a lake, the method estimates the excess $^{4}$He accumulated in the lake over the time period determined by the $^{3}$H-$^{3}$He age of the water. O’Nions and Oxburgh [1988] show these single samples from lakes can provide an estimate of the $^{4}$He crustal degassing flux:

$$J_4 = \frac{\Delta \text{He} \times S \times Z}{100 \tau}$$

(1)

where $J_4$ is the flux of $^{4}$He, $\Delta$He is the helium solubility anomaly (in %), $S$ is the equilibrium solubility, $\tau$ is the $^{3}$H-$^{3}$He age of the water, and $Z$ is the sample depth. The major assumption required is that the sample depth is an approximation of the mean lake depth; this may not be a bad assumption in the case of the many small lakes utilized by Clarke and his coworkers. However, the bias in this flux estimate is most likely in the direction of an underestimate because $Z$ can be increased but not decreased. As $\Delta$He is the percent excess $^{4}$He calculated relative to equilibrium solubility, a solubility of $4.5 \times 10^{-8}$ ccSTP $^{4}$He g$^{-1}$ ($\sim$15C) has been assumed for this suite of 271 samples based on temperatures reported by Clarke and coworkers.

Clarke et al. [1983] included ~96 lakes in Saskatchewan for which 13 samples were taken from Dawn Lake below the thermocline. For Dawn Lake, each sample was taken to be an individual measure and was processed as per the equation cited above. Clarke et al. [1977] report similar measures from 10 lakes in Labrador, and Top and Clarke [1981] report lake measures from an additional 160 lakes in Labrador. Table 1 also includes
Figure 3. The continental degassing flux ordered by the space scale of the measurement (Table 1). The evolution of the lognormal mean is shown together with the $s^*(68.3\%)$ and $s^{*2}(95.5\%)$ lognormal standard deviations. The values for the Great Lakes fluxes have been chosen to be $10^7$ $^4$He atoms m$^{-2}$ s$^{-1}$ as per discussion in section 3.2. The resulting variance appears to encompass the measurements well on the high side on short space scales. It is conceded that the statistical variability shown in Figure 3 reflects the subjective choice of the values for the Great Lakes but that the general guidance on the variability of the continental $^4$He degassing flux as a function of time and space scale is reasonably represented.

Figure 4. The continental degassing fluxes ordered by the time scale of the measurement (Table 1). The evolution of the lognormal mean is shown together with the $s^*(68.3\%)$ and $s^{*2}(95.5\%)$ lognormal standard deviations. The values for the Great Lakes fluxes have been chosen to be $10^7$ $^4$He atoms m$^{-2}$ s$^{-1}$ as per discussion in section 3.2. Also shown are two sensitivity levels for measurement of an excess $^4$He contribution based on a 10 m deep lake and a 3000 m deep ocean. It is unlikely that a degassing flux could be observed below these lines. It is conceded that the statistical variability shown in Figure 4 reflects the subjective choice of the values for the Great Lakes but that the general guidance on the variability of the continental $^4$He degassing flux as a function of time and space scale is reasonably represented.
(1) the flux of mantle \(^4\)He as reported by the authors
or (2) the \(^3\)He/\(^4\)He of the added component as
deduced using the method of Weise [1986; see also
Weise and Moser, 1987; Stute et al., 1992; Castro
et al., 2000] on data given in the original publica-
tion or from plots of \(^3\)He/\(^4\)He versus Ne/\(^4\)He taking
into account estimates of tritiogenic \(^3\)He and initial
air-saturated water.

3. Discussion

Figures 1 and 2 show the lognormal mean and variance for the
"Clarke Lakes" suite (n = 271) of data [Clarke et al., 1977; Top and Clarke,
1981; Clarke et al., 1983] as well as (Figure 2) the Saskatchewan (n = 101) and Labrador lakes (n = 170) separately. The lognormal mean (variance) of the degassing measurements indicates the continental helium degassing flux to be \(4.57 \times 10^{10}\) \(^4\)He atoms m\(^{-2}\) s\(^{-1}\) (shown in Figure 1). This quantification is consistent with the theory value for the continental \(^4\)He degassing flux [e.g., Mamyrin and Tolstikhin, 1984, Table 10.1; Torgersen, 1989] and provides a variance that is meaningful in terms of process. However, this area \times time-weighted mean (standard deviation) is of less
interpretive value as an estimate of any locally
applicable small time- or space-scale degassing
flux.

3.1. Estimating the Degassing Flux: Clarke
(Precambrian Shield) Lakes

Figures 1 and 2 show the lognormal mean and variance for the “Clarke Lakes” suite (n = 271) of data [Clarke et al., 1977; Top and Clarke, 1981; Clarke et al., 1983] as well as (Figure 2) the Saskatchewan (n = 101) and Labrador lakes (n = 170) separately. The lognormal mean (variance) of the degassing measurements indicates the continental helium degassing flux to be \(4.57 \times 10^{10}\) \(^4\)He atoms m\(^{-2}\) s\(^{-1}\) (*/3.93X; lognormal mean provides a standard
deviation that describes the multiplication or division factor (/) by which the mean may statistically vary [see Limpert et al., 2001]). (Varying the assumed solubility between $4.3 \times 10^{-8}$ and $4.7 \times 10^{-8}$ ccSTP $^4\text{He g}^{-1}$ changes the lognormal mean from $4.3 \times 10^{10}$ $^4\text{He atoms m}^{-2} s^{-1}$ to $4.8 \times 10^{10}$ $^4\text{He atoms m}^{-2} s^{-1}$ with minimal impact on the lognormal variance.) Both the Saskatchewan and Labrador lakes yield lognormal means that are statistically equivalent. As the underlying cratons in both provinces represent terrains with an age of the order 2 Gyr, and with the exception of minor tectonic events and Plio-Pleistocene glaciation, it is assumed that statistical quantification of the continental $^4\text{He}$ degassing flux from the Precambrian Shield may represent a best estimate of a steady state condition. As this best estimate steady state condition is consistent with theory estimates of $^4\text{He}$ production from the underlying continental crust, it could be reasonably inferred that whole crustal production is the source term for a locally (Precambrian Shield) observed continental $^4\text{He}$ degassing flux.

### 3.2. Degassing Flux and Its Variance

[15] The fluxes of Table 1 (Figure 1) yield a lognormal mean of $4.18 \times 10^{10}$ atoms $^4\text{He m}^{-2} s^{-1}$ with a lognormal standard deviation of $\ast/45X$, comparable to the Clarke lakes values (see specifics of the chosen values for the Great Lakes fluxes discussed below). Thus, the variance of the measured continental $^4\text{He}$ degassing fluxes (Table 1) is order 10X the variance of the “uniform” Precambrian Shield craton. However, the specific values of this mean and the variance are dependent upon the values chosen to represent the Great Lakes [Torgersen et al., 1977], which can be explained by any degassing flux less than order $10^{9}^4\text{He atoms m}^{-2} s^{-1}$.

[16] Figures 3–5 show the individually plotted $^4\text{He}$ fluxes of Table 1 as a function of the space, time, and (area × time) scale of the measurements. The plots indicate the range and variability in the measured continental $^4\text{He}$ degassing fluxes increases as the space, time, or (area × time) scale of the measurements decreases. Yet it is clear that Figure 4 cannot adequately represent the range or statistics of pos-
possible $^4$He degassing flux measures because analytical precision cannot detect extremely low fluxes. Using a reasonable estimate of the (historic, not current) precision of $^4$He concentration measures ($2\%$ excess $^4$He), it is apparent that even significant fluxes at short time scales simply are not measurable. This suggests that even if the 1975 measurement technology of $^4$He in the Great Lakes [Torgersen et al., 1977] were vastly improved (or resampled), it remains a distinct possibility that the continental degassing flux of $^4$He into each Great Lake would remain unquantifiable simply because the time scale of the lake process is too short and the excess $^4$He signal is too small. It can also be seen that the estimate of $^4$He degassing flux from the oceanic crust into the world’s ocean is also near the limit of detection.

Three conditions were explored with regard to the specific value chosen to represent the three Great Lakes flux measures: (1) No values were used for the three Great Lakes; $n = 30$. (2) Three Great Lakes fluxes were chosen to be $1 \times 10^4$ $^4$He atoms m$^{-2}$ s$^{-1}$; $n = 33$. (3) Three Great Lakes fluxes were chosen to be $1 \times 10^2$ $^4$He atoms m$^{-2}$ s$^{-1}$; $n = 33$ as given in Table 1 and shown in Figures 3–5.

Using no values for the Great Lakes fluxes, the calculated lognormal mean ($n = 30$; $9.6 \times 10^{10}$ $^4$He atoms m$^{-2}$ s$^{-1}$) appears to be skewed toward a higher value than the (area × time)-weighted arithmetic mean ($n = 33$; $3.3 \pm 0.5 \times 10^{10}$ $^4$He atoms m$^{-2}$ s$^{-1}$). Using a minimum estimate of the Great Lakes degassing flux ($10^4$ $^4$He atoms m$^{-2}$ s$^{-1}$) yields a lognormal mean of $1.03 \times 10^{10}$ $^4$He atoms m$^{-2}$ s$^{-1}$, which is significantly less than the weighted arithmetic mean and results in a 95.5% confidence interval that grossly overestimates the distribution of the observed values at the high-flux side of the measurements. Therefore, the high-flux side of the data suite was used to guide the estimate of the whole crustal degassing flux and its variance. Using a chosen value of $10^3$ $^4$He atoms m$^{-2}$ s$^{-1}$ for each Great Lake and calculating the evolving lognormal variance as a function of decreasing space, time, or area × time, a 95.5% confidence interval can be obtained that encompasses most of the observed fluxes (Figures 3–5). While one could fine-tune the values chosen for each Great Lake to specifically include, e.g., the Lake Nyos value within the 95% limit of the variance, it is clear from the above discussion that the inability to quantify significant continental $^4$He degassing fluxes on the short time scale renders any calculation of the variance somewhat subjective. It is conceded that the statistical variance shown in Figures 3–5 reflects the subjective choice of the specific values for the Great Lakes but that the general guidance on the variance of the continental $^4$He degassing flux as a function of time and space scale is reasonably represented by Figures 3–5.

3.3. Interpretation of Continental $^4$He Degassing Fluxes

The lognormal mean of the continental degassing flux measurements ($n = 33$; lognormal mean $= 4.18 \times 10^{10}$ $^4$He atoms m$^{-2}$ s$^{-1}$; $s^* = **/45X$) is consistent with the time- and space-weighted arithmetic mean (std dev), the Clarke lakes (Precambrian Shield) mean, and the “theory” value based on in situ production of $^4$He from U and Th series decay and steady state degassing from the upper and lower continental crust (see Table 1). The statistical variance of the continental $^4$He degassing flux over multiple time and space scales (Figures 3–5) may be attributable to variability in the (1) unsteady state (episodic) mass transport rates in continental crust possibly driven by tectonics; (2) tectonic control of solid phase release of $^4$He due to, e.g., fracturing or comminution; (3) the addition of mantle helium via magma intrusion into the continental crust and/or high rates of tectonic strain at the base of the continental crust [Kennedy and van Soest, 2007]; or (4) magma intrusion control of solid phase $^4$He release and subsequent transport. Most importantly, Figures 3–5 can be interpreted as reflecting the natural variability in the continental degassing flux. At the space scale of 1 km (Figure 3), a time scale of 1 year (Figure 4), or a space-time scale of 1 km$^2$ yr$^{-1}$ (Figure 5) which approaches that of small lakes, the degassing flux shows a range for the 95.5% confidence interval of $>10^9$X which is significantly larger than the variability (95.5% variability of ~15X) exhibited by the Clarke lakes (Figure 1). The variability increases significantly when the space scale is less than about 300 km (Figure 3), the time scale is less than about 30 years (Figure 4), and the area × time product is less than about $10^5$ km$^2$ yr$^{-1}$ (Figure 6).

3.4. Limits on the Rates of Crustal Mass Transport

Assuming the Clarke lakes represent the best estimate for the pseudo-steady state degassing flux (2 Gyr craton), the calculation of the zeroth-order vertical mass transport rate in continental crust can be reevaluated. As illustrated by Torgersen [1989, Figure 3], this implies an effective vertical...
diffusivity (order $5 \times 10^{-5}$ cm$^2$ s$^{-1}$) that is far in excess of expected diffusion-controlled transport (order $10^{-8}$ cm$^2$ s$^{-1}$ based on the molecular diffusivity of He in water and porosity/tortuosity considerations). Thus, it is safe to conclude that mass transport of $^4$He through the continental crust is significantly aided by mechanisms of advective flow of fluids in the crust where the advecting fluid may be one of any number of carrier fluids (H$_2$O, CO$_2$, N$_2$, CH$_4$, etc.; e.g., the discussion by Ballentine and Sherwood Lollar [2002]). Furthermore, because effective rates of transport in the crust have been measured to be as low as $10^{-8}$ cm$^2$ s$^{-1}$, there is every likelihood that advective crustal-scale He transport is episodic in nature [e.g., Torgersen and Clarke, 1992]. Thus, there are short time intervals over which rapid, advective transport occurs and longer intervals over which transport occurs predominately at diffusion-controlled rates (order $10^{-8}$ cm$^2$ s$^{-1}$).

[21] This long-time-scale effective vertical rate of helium mass transport (order $5 \times 10^{-5}$ cm$^2$ s$^{-1}$) and/or the effective rate of diffusion of He in the bulk crust (order $10^{-8}$ cm$^2$ s$^{-1}$) can be compared to the thermal diffusivity of the crust (order $10^{-2}$ cm$^2$ s$^{-1}$ [Carslaw and Jaeger, 1957]). Helium transport in a simple crust is significantly (>10$^3$X) faster than one might predict from first principles yet remains significantly slower than the (conductive) rate of heat transport in the continental crust. This difference in transport rates during the nonadvective time period of episodic transport can effectively and significantly separate heat and $^4$He with regard to tectonic or magmatic intrusive events for considerable lengths of time [Torgersen, 1993, Figure 6]. Using the Clarke lakes estimate of the variance ($s^* = 3.9X$) as a stable shield against which to compare the variance observed in multiple terrains and tectonic environments worldwide (Table 1, $s^* = 45X$), one could conclude that episodic advective mass transport and tectonic/episodic controls on crustal-scale mass transport create conditions conducive to larger variability. This observation is underscored by the difference in the lognormal variance of the $^4$He degassing flux ($s^*/45X$) as compared to the lognormal variance of the continental heat flow. Using 14,203 measures of heat flow from continental regimes compiled by International Heat Flow Commission global heat flow database (http://www.heatflow.und.edu/index.html; accessed 30 January 2009), the lognormal mean heat flow is 62.2 mW m$^{-2}$ ($s^*/1.8X$; for comparison, an arithmetic mean of 65 ± 1.6 Wm$^{-2}$ was calculated by Pollack et al. [1993]). A simplistic interpretation would suggest that the variability in $^4$He flux as a result of transport and release is 10–25X greater than the variance in the heat flux as a result of reduced heat flow and thermal conductivity.

3.5. Continental $^3$He/$^4$He Mapping as a Tectonic Indicator

[22] Polyak and Tolstikhin [1985], Oxburgh et al. [1986], Kennedy and van Soest [2007], and many others have identified a mantle $^3$He signature in tectonic, extensional regimes. This might be simply stated as deep groundwater in loading basins appears to be dominated by crustally produced $^4$He whereas deep groundwater in extensional basins contains an obvious mantle $^3$He component [Ballentine et al., 2002]. Newell et al. [2005] have repeated the generality. This mantle $^3$He signature may be associated with either intrusive magmas at midlevels of the continental crust, magmatic underplating [Torgersen, 1993], or high rates of crustal strain [Kennedy and van Soest, 2007] occurring at the base of the crust. Each of these input controls would be associated with a different vertical distance through the crust, and both distance and transport rates (order $10^{-3}$ cm$^2$ s$^{-1}$ for helium and $10^{-2}$ cm$^2$ s$^{-1}$ for heat) would provide controls for separation of the $^3$He, $^4$He, and heat fluxes [see Torgersen, 1993, Figure 6]. Broad generalizations of processes in extensional or volcanic terrains must be addressed in more detail than simple or corrected $^3$He/$^4$He ratios. The (corrected) $^3$He/$^4$He ratio at any specific location is a function of the mantle-sourced $^4$He flux and how it interacts and mixes with the crust-sourced $^4$He flux and the possible temporal separation of these two sources that contribute to the local continental degassing flux and its variability in time. Thus, the mantle-sourced $^4$He ($^3$He) flux will be a function of (1) the flux of $^4$He ($^3$He) across the mantle-crust boundary [Kennedy and van Soest, 2007], the crustal thickness, and the vertical transport rate for He within the crust or (2) the magma-sourced $^4$He ($^3$He) flux that will be a function of the degassing flux from underplated magma, the depth of the process, and the transport rate within the crust. On the other hand, the crustal contribution to the $^4$He continental degassing flux is dependent upon the in situ $^4$He production from U and Th series isotopes and local release of $^4$He from the solid phase [e.g., Torgersen, 1980], as well as the fracturing release (via fracturing that is variable with depth [Torgersen and O’Donnell, 1991]) of $^4$He accumulated in the solid phase over (unknown) time and the rate of vertical mass transport, strain [Kennedy and van
In the crustal degassing. The lognormal and area Figure 6 shows the observed continental atoms Kulongoski et al. "Measures of the continental 10.1029/2009GC002930 G [1986] that contain a mantle degassing component with a variance of */3.9X. This small 2005] that exhibit high the mantle component of the continental degassing flux also increases with an increase in the crust-sourced degassing flux but is offset (by a factor of approximately 1000X in both axes) toward lower values of a mantle contribution. It is suggested therefore that any observed 3He/4He in crustal fluids may be indicative of two separate conditions corresponding to two separate mechanisms (volcanic versus tectonic strain) for the addition of helium with a mantle signature. It is possible that these two fields could be further separated by the heat flux since tectonic and volcanic provinces are likely to occupy differing positions in 3He/4He versus 4He crust versus heat flow space. However, the dynamics of transport that can separate 4He and heat suggests that such approaches will of necessity include temporal models of 3He, 4He and heat in the crust.

4. Conclusions

[25] Measures of the continental 4He degassing flux from the Earth’s surface reported in the literature have been evaluated. The time- and area-weighted arithmetic mean (standard deviation) 4He degassing flux is 3.32(±0.45) × 10^10 4He atoms m^{-2} s^{-1}. The 271 available measures of the crustal degassing flux into Precambrian shield lakes of Canada indicate a lognormal mean flux of 4.57 × 10^10 atoms 4He m^{-2} s^{-1} with a variance of */3.9X. This small degree of variance in what might be considered a “uniform, stable” Precambrian Shield terrain suggests that it may represent an approximation of „steady state” crustal degassing. The lognormal mean of measurements worldwide (n = 33; see details regarding Great Lakes values) of the crustal degassing flux is 4.18 × 10^10 4He atoms m^{-2} s^{-1} with a best estimate one sigma lognormal variance of */45X based on an assumption of symmetric error bars. This degree of variance can be interpreted as natural variability. The variance of the continental 4He degassing flux increases significantly with decreasing time scales and decreasing space scales, suggesting that the mechanisms of helium transport in the crust contain a high degree of spatial and temporal variability and episodic mechanisms of transport. Furthermore, a separation of the continental degassing flux into theoretical end-member contributions from mantle-sourced He and crust-sourced He suggests that high mantle-
sourced fluxes of helium can be attributed to either volcanic or tectonic strain mechanisms separated by a factor of approximately 1000X in the contributing fluxes. This observation indicates that simple interpretation of $^3$He/$^4$He in terms of magnitude of the crust versus mantle component contributions does not yield a unique description.

A mechanistic evaluation of helium isotope constraints on tectonics/magmatism might best be approached by modeling the vertical variation of the temporal evolution of heat flow, mantle helium fluxes, and the enhanced fluxes of crustal helium as a result of fracturing and comminution.

[26] The best estimate of the mean and variance in the degassing flux of $^4$He from continents is equivalent to the rate of production of $^4$He in the whole crust and underscores the necessity for large-scale mass transport in continental crust that may be estimated as order $10^{-3}$ cm$^2$ s$^{-1}$ for helium versus $10^{-2}$ cm$^2$ s$^{-1}$ for heat. Such rates of mass transport require not only release of He from the solid phase via diffusion, fracturing [Torgersen and O’Donnell, 1991], or comminution [Solomon et al., 1996] but also an enhanced rate of mass transport facilitated by some degree of fluid advection. In spite of this enhanced vertical mass transport, separation of heat and mass during crustal–scale transport remains an important question to resolve in the mechanisms of crustal extension.

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Dating old Groundwater: A Guidebook

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Chapter 1. Introduction .................................................................................................................. 9

Chapter 2: Characterization and Conceptualization of Groundwater-Flow Systems ............... 13
  2.1 Introduction .......................................................................................................................... 13
  2.2 The Groundwater-Flow System ......................................................................................... 13
    2.2.1 Hydrologic Cycle .......................................................................................................... 14
  2.3 Characterization of Groundwater-Flow Systems .............................................................. 17
    2.3.1 Geologic Framework ................................................................................................. 17
    2.3.2 Hydrologic Framework ............................................................................................. 18
    2.3.3 Hydrochemical Framework ....................................................................................... 21
  2.4 Development of a Numerical Groundwater-Flow Model .................................................. 25
  2.5 Summary Guidelines for the Characterization of Groundwater Systems and their Water-Age Distributions ...................................................................................................................... 26

3 Defining Groundwater Age ........................................................................................................ 31
  3.1 Introduction: Why do we need to date groundwater?......................................................... 31
  3.2 What does “Groundwater Age” mean? ............................................................................... 31
    3.2.1 Examples of Groundwater Age Distributions .............................................................. 35
  3.3 Characteristics of Ideal Tracers .......................................................................................... 36
  3.4 Additional Limitations on Tracer Model Ages ................................................................. 37
  3.5 Tracers in this book ............................................................................................................. 38

Chapter 4 Radiocarbon dating in groundwater systems .............................................................. 48
  4.1 Introduction ......................................................................................................................... 48
  4.2 Interpretation of Radiocarbon Age of Dissolved Inorganic Carbon in Groundwater ......... 51
    4.2.1 Determination of the Initial $^{14}$C Activity in Recharge Water, $A_0$ ......................... 51
  4.3 Summary of predominant geochemical reactions in groundwater systems affecting interpretation of radiocarbon age ...................................................................................................................... 64
  4.4 Generalized geochemical-adjustment models ..................................................................... 66
  4.5 Total dissolved carbon ....................................................................................................... 68
  4.6 Geochemical Mass-Transfer Models .................................................................................. 69
    4.6.1 Some practical precautions and special cases in geochemical mass-balance modeling ............................................................................................................................................... 71
  4.7 Examples using NETPATH ................................................................................................ 72
    4.7.1 Alliston aquifer, Ontario, Canada ................................................................................. 73
    4.7.2 Floridan aquifer, Florida, USA .................................................................................... 75
  4.8 Radiocarbon Dating of DOC ............................................................................................. 78
  4.9 Hydrodynamic and aquifer matrix effects on radiocarbon ages ......................................... 80
    4.9.1 Mixing Processes ......................................................................................................... 80
    4.9.2 Subsurface Production ............................................................................................... 81
    4.9.3 Diffusive Exchange with Confining Layers ............................................................... 81
    4.9.4 Transport Models ...................................................................................................... 82
    4.9.5 Analytical Solutions .................................................................................................. 82
    4.9.6 Matrix Diffusion in Unsaturated Zones ...................................................................... 85
    4.9.7 General Conclusions Regarding Effects of Hydrodynamics and Heterogeneity on Groundwater Radiocarbon Ages ...................................................................................................................... 86
4.10 Guidelines for Radiocarbon Dating of Dissolved Carbon in Groundwater Systems...... 87

Appendices..............................................................................................................................107
A1. Radiocarbon Reporting Units..........................................................................................107
A2. Isotopic fractionation in carbonate waters .....................................................................113
A3. Radiocarbon Calibration .................................................................................................120
A4. Field collection procedures .........................................................................................122
A5. Geochemical modeling software ..................................................................................124
A6. Selected AMS facilities for radiocarbon analysis .........................................................124

Chapter 5 $^{81}$Kr dating of old groundwater........................................................................126
5.1 Introduction.......................................................................................................................126
5.1.1 Krypton in the environment .......................................................................................126
5.1.2 Krypton in Hydrology ...............................................................................................127
5.2 Large-volume gas sampling techniques ........................................................................134
5.2.1 Sampling requirements ..............................................................................................134
5.2.2 Physical principles of gas extraction ..........................................................................135
5.2.3 Designs of gas extraction systems ............................................................................136
5.2.4 Specific parameters, remarks and extraction efficiencies ........................................138
5.2.5 Optimal design of gas extraction units .....................................................................140
5.3 Gas preparation and purification ....................................................................................140
5.3.1 Introduction ................................................................................................................140
5.3.2 Purification system at University of Bern .................................................................142
5.3.3 Combination distillation-GC ...................................................................................145
5.4 Detection methods for noble gas radio-nuclides ............................................................145
5.4.1 Low-level counting (LLC) .......................................................................................146
5.4.2 Accelerator Mass Spectrometry (AMS) .....................................................................147
5.4.3 Atom-Trap Trace Analysis (ATTA) ........................................................................149
5.4.4 Resonance Ionisation Mass Spectrometry (RIS) .....................................................151
5.5 First attempts of $^{81}$Kr dating: The multi tracer comparison in the Southwestern Great
Artesian Basin (GAB)...........................................................................................................152
5.5.1 Introduction ................................................................................................................152
5.5.2 Study area ..................................................................................................................153
5.5.3 $^{81}$Kr ages..................................................................................................................154
5.5.4 Comparison with helium data ..................................................................................155
5.5.5 Comparison with $^{36}$Cl data .....................................................................................156
5.5.6 Additional evidence for the correctness of $^{81}$Kr ages .............................................161
5.5.7 Summary ....................................................................................................................163
5.6 Addendum: Signal attenuation due to hydrodynamic dispersion ....................................165

6 Chlorine-36 Dating of Old Groundwater ......................................................................167
6.1 Basic Principles of $^{36}$Cl................................................................................................167
6.2 Chlorine-36 in the Hydrological Cycle .......................................................................167
6.2.1 Historical Summary ..................................................................................................167
6.2.2 Sampling Techniques for $^{36}$Cl ..............................................................................167
6.2.3 Chlorine-36 Sample Preparation and Measurement ................................................167
6.2.4 Chlorine-36 Research Groups and Laboratories ......................................................167
6.3 Specifics of the $^{36}$Cl Method .......................................................................................167
6.3.1 Meteoric Sources of $^{36}$Cl ......................................................................................167
6.3.2 Secular Variation in the Atmospheric Deposition of $^{36}$Cl ......................... 167
6.3.3 Processes affecting $^{36}$Cl during recharge ......................................................... 167
6.4 Subsurface processes influencing $^{36}$Cl concentrations and $^{36}$Cl/$^{35}$Cl ................ 168
6.4.1 Hypogene production of $^{36}$Cl ............................................................................. 168
6.4.2 Subsurface systematics of $^{36}$Cl........................................................................... 168
6.4.3 Use of other environmental tracers to interpret chloride systematics .................. 168
6.4.4 Comparison of $^{36}$Cl With Other Methods of Dating ........................................... 168
6.4.5 Summary ............................................................................................................. 168

7 Dating of old groundwater using uranium isotopes – Principles and applications ... 169
7.1 Introduction .............................................................................................................. 169
7.1.2 Scope and Objective ............................................................................................ 169
7.2 Natural abundance of uranium isotopes ................................................................. 169
7.3 Uranium geochemistry ............................................................................................ 169
7.4 Uranium isotope measurements .............................................................................. 169
7.5 Groundwater dating using uranium isotopes ......................................................... 169
7.5.1 A conceptual model incorporating water rock interaction .................................. 169
7.5.2 Identification of model parameters ...................................................................... 169
7.6 Case studies ........................................................................................................... 170
7.6.1 Carrizo sandstone aquifer, South Texas, USA ....................................................... 170
7.6.2 Milk River Aquifer, Canada ................................................................................ 170
7.6.3 Continental Intercalaire aquifer, north-west Sahara ........................................... 170

8 Helium (and other Noble Gases) as a Tool for Understanding Long Time-Scale Groundwater
Transport .................................................................................................................... 171
8.1 Introduction .............................................................................................................. 171
8.2 The Geochemical Construct for Apparent $^4$He Tracer Ages .................................. 171
8.3 Sampling and Analysis ............................................................................................ 171
8.3.1 Sampling Methods .............................................................................................. 171
8.3.2 Laboratory Processing Methods ........................................................................... 171
8.3.3 Mass Spectrometry .............................................................................................. 171
8.4 Identifying Multiple $^4$He Components from Measurements ................................... 171
8.4.1 Equilibrium with Air, $^{4}$He$_{eq}$ ............................................................................ 171
8.4.2 Excess “Air” Components, $^{4}$He$_{exc}$ ................................................................. 171
8.4.3 Radiogenic Production, $^{4}$He$_{rad}$ ...................................................................... 172
8.4.4 Summary ............................................................................................................. 173
8.5 Case Studies ........................................................................................................... 173
8.5.1 Setting the Stage ................................................................................................. 173
8.5.2 Simple Open System Aquifer Models .................................................................. 173
8.5.3 $^4$He as a component in Groundwater flow Models Evolves ................................ 173
8.5.4 Summary ............................................................................................................. 173
8.6 Conceptual $^4$He Tracer Ages as a Constraint on Groundwater “Age” .................. 173
8.6.1 $^4$He fluxes determined by vertical borehole variation in $^3$He/$^3$He .................... 173
8.6.2 Cajon Pass ............................................................................................................ 173
8.6.3 South African Ultra-deep Mine Waters ............................................................ 174
8.6.4 Deep Borehole Sampling .................................................................................... 174
8.6.5 Summary ............................................................................................................. 174
Chapter 9  System Analysis using Multi-Tracer Approaches ................................. 175
  9.1 Vertical profiles ........................................................................................................ 176
      9.1.1 Unconfined Homogeneous Aquifer .................................................................. 176
      9.1.2 Homogeneous Aquifer with different recharge and discharge zones .............. 186
      9.1.3 Aquifer systems, confined or partly confined .................................................... 192
      9.1.4 Summary .......................................................................................................... 194
  9.2 Horizontal Transects ............................................................................................... 195
      9.2.1 Transect along an assumed flow line .................................................................. 195
      9.2.2 Horizontal transects intersecting different flow lines ....................................... 197
      9.2.3 Summary .......................................................................................................... 199
  9.3 Important patterns of tracer versus tracer ............................................................. 200
      9.3.1 Combination of Tracers for different time scales .............................................. 200
      9.3.2 Combination of tracers with similar decay timescales ..................................... 204
      9.3.3 Linear accumulating tracer versus exponential decay tracer ........................... 205
      9.3.4 Noble Gas Patterns ........................................................................................... 208
Chapter 10: Numerical Flow Models and their Calibration using Tracer Based Ages ........ 212
  10.1 Introduction ............................................................................................................ 212
  10.2 Equations and numerical methods ........................................................................ 213
  10.3 Aquifer Geometry and Grid Design ...................................................................... 214
  10.4 Boundary Conditions ............................................................................................ 215
  10.5 Transient Simulations ............................................................................................ 216
  10.6 Model Calibration ................................................................................................. 216
  10.7 Calculation of Flow Model Ages .......................................................................... 218
  10.8 Simulation of Dispersion and Tracer Model Ages .................................................. 219
  10.9 Flow Model Calibration using Tracer Based Ages ................................................. 221
11 Case Study: Milk River Aquifer, Alberta, Canada ...................................................... 238
  11.1 Introduction ............................................................................................................ 238
  11.2 Geological, hydrological and geochemical background ....................................... 238
  11.3 Isotopic studies of the Milk River aquifer ............................................................. 238
      11.3.1 Radiocarbon, stable isotopes and dissolved constituents .................................. 238
      11.3.2 Dissolved gases ............................................................................................... 238
      11.3.3 Chlorine-36 and chloride ............................................................................... 238
      11.3.4 Iodine-129 ..................................................................................................... 238
      11.3.4 Uranium isotopes ......................................................................................... 238
  11.4 General discussion ............................................................................................... 238
  11.5 Conclusions .......................................................................................................... 238
Chapter 12 Case Study: Middle Rio Grande Basin, New Mexico, USA ............................ 239
  12.1 Introduction ............................................................................................................ 239
  12.2 Background: Hydrogeologic Setting .................................................................... 239
  12.3 The USGS Middle Rio Grande Basin Study .......................................................... 241
  12.4 Stable Isotopes, Helium-4, Radiocarbon Ages, and Hydrochemical Zones ........ 242
      12.4.1 Stable Isotopes ............................................................................................... 242
      12.4.2 Radiocarbon Age ........................................................................................... 244
      12.4.3 Helium-4 ....................................................................................................... 247
      12.4.4 Hydrochemical zones .................................................................................... 249
      12.4.5 Pre-development water levels ........................................................................ 250
12.4.6 Radiocarbon Age with Depth ................................................................. 252
12.4.6 Stable Isotopes, Deuterium Excess, and Radiocarbon Age .................. 252
12.4.7 Radiocarbon age profiles and recharge rates ........................................ 255
12.5 Summary of chemical- and environmental-tracer constraints on the flow system ... 256
12.6 Groundwater Model Development ............................................................ 257
12.7 Refining Conceptualization of Groundwater Flow in the Basin .................. 261
12.8 Paleorecharge Rates .................................................................................. 262
12.9 Concluding Remarks .................................................................................. 263

Chapter 13: Methods for Dating Very Old Groundwater: Eastern and Central Great Artesian Basin Case Study ................................................................. 267
13.1 Introduction .................................................................................................. 267
13.2 Deposition, Structure and Hydrogeology of the Eastern GAB .................... 268
13.3 Setting the Stage ......................................................................................... 269
13.4 Stable Isotope and $^{14}$C Measurements .................................................... 269
13.5 The 1982 Field Work: Stannum-to-Innamincka and Bonna Vista-to-Thargomindah .... 269
13.6 The 1985 Field Work: Fairlight Trust-to-Clayton, Athol-to-Mutti Mutti and Mt. Crispe-to-Curdimurka ................................................................. 271
13.7 Modelling $^{36}$Cl and $^4$He ........................................................................ 272
13.7 Geochemical Modelling of Groundwater Reaction Paths ......................... 272
13.9 The 2000 Benchmark and Synthesis ........................................................... 273
13.10 Continuing Work in the GAB ..................................................................... 275

Chapter 14: $^{81}$Kr Case study: The Nubian Aquifer (Egypt) ............................... 302
14.1 Nubian Aquifer .......................................................................................... 302
14.2 Methods ...................................................................................................... 302
14.3 $^{81}$Kr data .................................................................................................. 302
14.4 $^{36}$Cl data ................................................................................................... 304
14.5 Correlation of $^{36}$Cl and $^{81}$Kr data ............................................................ 305
14.6 $^4$He data .................................................................................................. 306
14.7 $^{14}$C data ................................................................................................... 307
14.8 Hydrogeologic and paleoclimatic implications of groundwater age data ......... 307

Literature ............................................................................................................ 309
DEFINING GROUNDWATER AGE

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INTRODUCTION: WHY DO WE NEED TO DATE GROUNDWATER?

Groundwater is an important resource in regard to both its quality and quantity. In all climate regimes, but particularly in arid regions, groundwater is a critically important source of water for human needs, and it is often important to determine whether water within specific aquifers represents a renewable or nonrenewable resource. Knowing the groundwater “age” within a specific aquifer could be useful in estimating the rate of groundwater renewal or a sustainable rate of water extraction. In many urban, industrial and agricultural sites, groundwater may be contaminated, and it becomes important to quantify the timescale of processes that transport contaminants. Groundwater may also be a key transport consideration for nuclear waste disposal or CO₂ sequestration sites. Knowing the “ages”, velocities and mixing rates of the groundwater can be used to evaluate the effectiveness of these sites. Furthermore, groundwater is an integral component of Earth/environmental systems that facilitates the transport of dissolved substances, and it has a direct effect on surface-water hydrology, soil formation, landform development, crustal weathering, deep metamorphism and the mechanical properties of the crust. It makes possible the existence of life forms, sometimes under extreme climatic, geochemical or physical conditions. Thus, the understanding of processes and timescales by which groundwater is transported and mixed remains of paramount importance to understanding the controls on its quantity and quality. In this context, temporal information about groundwater systems is needed and hence the subject of “groundwater dating” constitutes an important area of research and application.

This book investigates applications of selected chemical and isotopic substances that can be used to recognize and interpret age information pertaining to "old" groundwater (defined as water that was recharged on a timescale from approximately 1,000 to more than 1,000,000 years). But, as discussed below, only estimates of the “age” of water extracted from wells can be inferred. These groundwater age estimates are interpreted from measured concentrations of chemical and isotopic substances in the groundwater, and even then, there are many complicating factors, as discussed in this book. In spite of these limitations, much can be learned of the physics of groundwater flow and of the temporal aspects of groundwater systems from age interpretations of measured concentrations of environmental tracers in groundwater systems. This chapter places context around the concept of "age", its meaning and its interpretation and attempts to provide a unifying usage for the rest of the book.

WHAT DOES “GROUNDWATER AGE” MEAN?

The concept of an “idealized groundwater age” (Δt) implies an elapsed time between (a) when the water left the unsaturated zone (when it entered the groundwater) and (b) when the water was sampled in a specific position (x,y,z) presumably a specific distance (Δs) downstream in the groundwater system (Fig. 3.1A). The idea of radiometric “dating” of groundwater was proposed as an extension of radiocarbon
dating as applied to solid materials that contain carbon (e.g., wood, shells, charcoal, travertine) (Münnich, 1957). Radiocarbon dating of solids is usually applied to materials with a (presumably) well-defined initiation time (e.g., the year a tree ring was laid down or a band of travertine precipitated). The difference between this initiation time and the current time is the age of the sample. The atoms of carbon within the object are presumed to have remained fixed in place, with no new carbon added or old carbon lost, until the sample is analyzed for its radiocarbon content. The object is then “dated” by applying the radioactive decay equation using the current measured radiocarbon content and an assumed initial radiocarbon content. The interval of time calculated in this fashion is called the “C-14 model age”. Provided that the basic assumptions (the initial radiocarbon content and that atoms of carbon have been neither gained nor lost) are correct, the “C-14 model age” should equal the actual age. However, in many cases, the basic assumptions are not valid and the C-14 model age of the solid may significantly differ from its "true" age.

The groundwater literature has not always adequately distinguished the fundamental conceptual differences between the age of solid material and the age of groundwater that result from the mobile and mixable nature of water. As a result, much of the groundwater dating literature refers to an idealized concept of groundwater age (see above) which has a conceptual origin in what has been referred to as a “hydraulic age” (e.g., Davis and Bentley, 1982). From Darcy’s Law, it is known that given the permeability of a porous medium and the hydraulic gradient across it, one can calculate the specific discharge, and if the effective porosity is also known, the average interstitial velocity of the water can be calculated. By extrapolation, if the exact permeability distribution within an entire groundwater system and its distribution of hydraulic gradients are known, one can calculate the velocity distributions and a travel time from the water table to any given point within the system. The physics of groundwater movement thus dictates that any groundwater has travelled to its current location under a given set of physical conditions in a time frame determined by those conditions. This simple concept of groundwater movement has often been referred to as “piston” flow. The difficulty of adequately characterizing the permeability distribution of subsurface materials has led to the measurement of environmental tracers as a means to estimate this “idealized groundwater age”. However, because solutes and tracers disperse (mix) in groundwater and because piston flow neglects many aspects of this dispersion and mixing, the information hypothetically contained within an estimate of such an “idealized groundwater age” would still need to be interpreted within a process context. Consider, for example, the flow system depicted in Fig. 3.1 where the direction s is along the flow path and s⊥1 and s⊥2 represent orthogonal directions to s. We pose the following questions:

- What if the groundwater arrived at position (x,y,z) mostly by flow in the s-direction but was additionally under the influence of specific dispersive mixing parallel to the flow direction (Ds) as well as perpendicular to the flow direction (Ds⊥1, Ds⊥2)? How does simple flow and simple mixing influence the interpretation of an “idealized groundwater age”?
- What if the groundwater arrived at position (x,y,z) by flow from two (or more) similar but not identical entryway sources(Fig. 3.1B, Fig. 3.2)?
• How does multi-component mixing from distinctly different source regions under convergent flow impact the meaning and interpretation of an “idealized groundwater age” (Fig. 3.1E)?
• What if the groundwater system has not operated at a steady state, e.g. \( v_s = f(t) \)? How does (would) the observed “idealized groundwater age” at position \( x,y,z \) vary as a function of time (\( \Delta t = f(x,y,z,t) \))? For the case where hydraulic heads may have varied significantly over the timescale of the groundwater age, what if the groundwater arrived at position \( x,y,z \) by flow in a direction that is not equivalent to the currently defined flow direction? Within the concept of this “idealized groundwater age”, a calculation of groundwater velocity in the \( s \)-direction (\( v_s \)) is possible but not meaningful in this context.

These examples illustrate that even within the simple definition of an “idealized groundwater age”, its interpretation in terms of the processes that control the “idealized groundwater age” remains complex. Additionally, this illustrates an important concept:

• It is the net impact of all processes by which groundwater reaches the position \((x,y,z,t,\)) that determine the groundwater age.

The corollary is:

• The understanding of groundwater age at a specific location \((x,y,z,t,\)) requires knowledge of all processes by which groundwater flows to that specific location.

These considerations demonstrate that a more physically-based definition of groundwater age is needed.

GROUNDWATER AGE DISTRIBUTION

The “idealized age” of a single molecule of water has been defined above as the elapsed time since the molecule left the unsaturated zone. However, samples of groundwater are finite in volume and contain very large numbers of molecules. In a bulk fashion, groundwater moves in response to spatial gradients in fluid potential. In addition to this, inasmuch as water is a fluid and the relative positions of the molecules are not fixed, those molecules move in random paths as well as by bulk flow (Fig. 3.2). These potential-driven and entropy-driven transport processes interact in a complex fashion to produce transport processes variously described as “advection”, “diffusion”, “hydrodynamic dispersion”, and so on (see Phillips and Castro, 2003, for a discussion of the influence of the various transport processes on groundwater age tracers). One implication of groundwater transport is that the transport path of any individual molecule of water may (and almost certainly does) differ from the mean path obtained by averaging many molecules (Figure 3.1). The result is that any finite-sized sample of groundwater contains water molecules that have resided in the system for differing periods of time. This being the case, a groundwater sample at a specific location cannot be adequately characterized by any single-value of “age”; rather, it is characterized by a frequency distribution of ages (Fig. 3.1B, etc.).

The concept of fluid age defined by a frequency distribution of ages was
introduced by Danckwerts (1953). Since then, it has been widely applied in fluid
dynamics, chemical engineering, atmospheric science, oceanography, and hydrology
(see Hooper, 2003, Loaiciga, 2004, and McGuire and McDonnell, 2006, for reviews of
applications to hydrology). In the chemical-engineering literature, the concept is
generally referred to as the “residence-time distribution function”. The residence-time
distribution is a mathematically rigorous and practically useful function (see references
above for examples).

In this book, we will generally use “frequency distribution of age ” rather than
“residence-time distribution”. This is simply to avoid confusion since “residence-time
distribution” has been traditionally used in the chemical-engineering literature to refer to
the distribution in the discharge of a system whereas we generally are referring to the
distribution in a finite sample from within the system. The mathematics of these two
cases differ. Maloszewski and Zuber (1982) have provided mathematical formulations
applicable to age distributions in groundwater systems and Maloszewski et al. (1983)
give examples of their application. McGuire and McDonnell (2006) review analogous
mathematical approaches for the outputs of drainage basins. Goode (1996) pioneered
a flexible numerical approach to simulating age distributions in complex groundwater
systems and Varni and Carrera (1998) estimate the frequency distribution of age at a
single point.

An extreme example of a frequency distribution for groundwater age would arise
from an extensive, hydraulically uniform aquifer with a high recharge rate that is
spatially localized (e.g., at a small area of outcrop of the formation). This system will be
advection-dominated because the spatially-uniform aquifer minimizes the effects of
dispersive mixing relative to advective transport and the high recharge rate produces
small gradients of groundwater age with flow distance. In the absence of convergent
flow lines, the distribution of groundwater ages within a small sample of the
groundwater in this case will have a prominent mode with a relatively narrow distribution
around that mode. As the ratio of dispersion to advection increases, the frequency
distribution of ages (spread around the mode) increases.

Although it is tempting to characterize the “age” of a water sample by calculating
some central tendency, unless the system is strongly advection-dominated, this can
yield quite misleading results. For example, imagine a small, rapidly recharged aquifer
that is bounded by thick shale of extremely low permeability. The shale is still diffusing
connate water (that was present when the shale was deposited in the Cretaceous) into
the aquifer. If 99.9% of the water discharged from the aquifer was recharged 5 years
ago and 0.1% is water from the shale, the average age of the discharge is 65,000
years. This number conveys no useful information about the system and is in fact quite
misleading if taken at face value. However, in the case that the system is strongly
advection-dominated, an estimate of the mode of the frequency distribution of
groundwater age can provide useful information.

To summarize, the “age” of a sample of groundwater is a function of the
frequency distribution of the elapsed times of transit since each of the individual water
molecules crossed the water table (Fig. 3.1B,C,D). Unfortunately, this frequency
distribution is difficult (to impossible) to determine for groundwater systems even in a
course sense. For estimating groundwater ages, we must rely on either inferences from
the concentration of chemical or isotopic tracers measured in a water sample; or on
calculations based on the physics of fluid mass transport. If the age estimate is obtained from a chemical tracer measurement, then a conceptual/mathematical model must be employed to convert tracer concentrations into an age; the single age value that results is called the “tracer-based model age”. For example, a groundwater age obtained using $^{14}$C-tracer data and the radioactive decay equation would be called a “tracer-based model age” or more specifically “$^{14}$C-based model age”. This terminology reinforces the principle that the calculated age is inseparable from the conceptual/mathematical model employed and the assumptions that model includes. It is therefore a useful measure of the age only to the extent that the model corresponds to the characteristics of the system. Following a not uncommon practice, we will simplify the expression as (specific case) "$^{14}$C-model age" or (general case) "tracer-model age".

In the majority of cases, the mathematical models and the assumptions employed to interpret tracer data do not include mixing processes and yield single-values of the tracer-model ages (errors cited are typically associated with tracer measurement error and do not contain information about the frequency distribution of the age). These single values of the tracer-model ages may correspond to the mean ages of the age distributions, but in most cases probably do not. Multiple tracers, combined with knowledge of the hydrogeology, often can help to understand (at least in a qualitative fashion) the relation between a single-value of a tracer-model age at a location and the frequency distribution of groundwater ages at that location.

**EXAMPLES OF GROUNDWATER AGE DISTRIBUTIONS**

The examples given above illustrate possible forms of the frequency distribution of groundwater age in some simple hypothetical groundwater systems. Several examples of the frequency distributions in more realistic systems have been provided by numerical modeling.

As mentioned above, if the age estimate is obtained from application of the physics of fluid mass transport, it is called here the “hydraulic age” which represents one type of "flow-model age". In many cases such calculations include only advective transport, in which case a single value for the hydraulic age is obtained. In more complete models additional processes may be included and in this case a “hydraulic age distribution” may be calculated. An excellent example of this approach is provided by Goode (1996), who illustrated the role of dispersion with a simple numerical groundwater flow model for a layered system (0-30m, hydraulic conductivity is $10^{-5}$ m s$^{-1}$; 30-70m, hydraulic conductivity is $10^{-6}$ m s$^{-1}$). Fig. 3.3a shows the hydraulic head contours (0.2m contours) of a simple flow system which determines the streamlines shown in Fig. 3.3b. For the case with advection-only and no dispersion (Fig. 3.3c) the groundwater age structure (10 year intervals) is noticeably different than for the case of advection with dispersion (Fig. 3.3d; $D_m=1.16 \times 10^{-8}$ m$^2$s$^{-1}$; $\alpha_L=6$m, $\alpha_T=0.6$m) especially at the boundary of the slow flow region in the zone of upflowing streamlines. The younger ages in the upflowing streamline region under the advection with dispersion case (Fig. 3.3d) are the result of dispersive mixing between slow moving streamlines and fast moving streamlines. The no-dispersion case (Fig. 3.3c) results in a more isolated pocket of flow and older groundwater ages.

Goode (1996) and Bethke and Johnson (2008) generalized these dispersion-mixing and convergent-mixing issues that impact the transport and mixing processes in
groundwater flow systems and that influence the groundwater age distribution. For 1D groundwater flow without dispersion (piston flow; Fig. 3.1A), groundwater at a specific location should result in a single idealized groundwater age. However, for groundwater flow with even 1D longitudinal dispersion (e.g. in the same direction as the flow velocity) the multiple micro-scale pathways (Fig. 3.2) produce a frequency distribution of groundwater ages. When 2D and 3D flow are included, transverse dispersion may mix (a) pathways of different lengths (possibly different recharge entryways) with the same velocity; or (b) pathways with identical path lengths but with different velocities. The net impact of 2D and 3D transverse dispersion is then to create mixtures and increase the width of the groundwater age distribution (Fig. 3.1C).

For the longest timescale of flow, molecular diffusion may ultimately mix aquitard groundwater with the aquifer groundwater (Fig. 3.1D). Because aquitard groundwater usually is characterized by distinctly older ages, the mixing of aquitard water with aquifer water (noting the Cretaceous shale example above) will induce a long asymmetric tail on the old-side of the frequency distribution of age (Fig. 3.1D). The frequency distribution of groundwater age is thus dependent upon how much aquitard water was incorporated and the frequency distribution of ages within the aquitard groundwater.

In addition to simple dispersion-induced mixing, groundwater flow paths may also converge to cause mixing; or aquifer structure may induce mixing of groundwaters from layered aquifer systems. As illustrated in Fig. 3.1E, the process of convergent mixing of different groundwater flows creates a mixture of component waters that is characterized by a bimodal age distribution. Samples collected from pumping wells or springs are susceptible to even further turbulent mixing right in the discharge conduit where the sample is collected.

CHARACTERISTICS OF IDEAL TRACERS

An ideal groundwater age tracer should exactly replicate the transport and mixing of the groundwater with which it flows. As such, an ideal tracer (1) should not be subject to chemical retardation with respect to the flow of the water, (2) should undergo mechanical dispersion identically to the water molecules (and thus duplicate the frequency distribution of groundwater age) and (3) should undergo molecular diffusion identically to the water molecules. An ideal groundwater tracer suitable for dating must then also change its concentration as a known and defined function of time from a defined initial condition to the location at which it can be sampled. The initial conditions for a tracer-model age should be obtainable and should be established in the same location where the idealized groundwater age is zero. All these attributes should result in the tracer, at the sampling location, having a tracer-model age frequency distribution that follows from the groundwater age frequency distribution (i.e., for a radioactive tracer, this would correspond to the groundwater age distribution multiplied by the appropriate amount of decay for each age). In this context, the available choices of geochemical tracers suitable to dating needs are narrowed considerably; they are characterized by simple solubility controls, limited reactivity and known radioactive reaction rates for either ingrowth or decay (or in the case of stable tracers such as CFC’s (IAEA, 2006), known variability in the initial condition, simple geochemistry and “no” loss terms). With a known initial condition and a known reaction (e.g., radioactive
decay or known production), the measured concentration of a tracer in a groundwater sample at location x,y,z,t can be converted into a tracer-model age through a defined mathematical formula with specific assumptions.

However, the tracer-model age is subject to interpretation (and potential complication) as a result of both dispersion-controlled mixing and convergence-controlled mixing. The interpretation of the tracer-model age is functionally dependent upon whether the reaction term is linear, concave, or convex vs. distance/time and the timescale of the tracer.

For the case of a linearly changing (under ideal conditions, possibly $^4\text{He}$) tracer concentration with time (see Fig. 3.4a), a mixture of young and old waters will create a mixture whose combined frequency distribution of groundwater ages accurately reflects the mixing and the relative weighting of the old and the young water. However, for a tracer with exponential decay (e.g. $^{14}\text{C}$ or $^{36}\text{Cl}$), the mixing of an old and a young groundwater will create a tracer mixture that is interpreted as younger than the weighted mean of the separate tracer ages of young and old water would imply (see Fig. 3.4b). Dispersion-controlled mixing for tracers with concave functions such as radioactive decay will therefore always create conditions under which the tracer-model age is an underestimate of the mean groundwater age; the degree of underestimation being a function of the degree of mixing and the decay constant. For convergence-controlled mixing, the component end members are likely more widely disparate in their groundwater age distributions and the impact of convergent mixing on the tracer will result in a greater difference between the mean (or mode) of the groundwater age distribution and the tracer-model age, again with the tracer-model age being younger than the correctly interpreted mixture of component end members. Tracer reaction rates and mixing end members must therefore be considered in the interpretation of tracer-model ages. For cases where the mean of the age distribution is not equal to the mode for the age distribution (e.g., Fig. 3.1D), or the case where the age distribution is bimodal (Fig. 3.1E), an interpretation of the tracer-model age and its relation to the mean or mode of the age distribution becomes more complex.

**ADDITIONAL LIMITATIONS ON TRACER-MODEL AGES**

Under favorable circumstances, groundwater age can be characterized by some central measure (mean, median, mode) of the frequency distribution of groundwater ages within the groundwater sample (e.g., Fig. 3.1b-e). However, because a groundwater sample has been aggregated (naturally or by some bias in the sampling protocol) via distinct and separate processes, interpreting some central tendency of the distribution requires information on the nature of the distribution function. Such information is difficult to obtain for real-world (as opposed to simulated, mathematically-modelled) groundwater systems and this greatly limits the ability to interpret single values of tracer-model ages. To some extent, one can obtain information on the nature of the age distribution by methods such as classical input-output analysis (Kirchner et al., 2000; McGuire et al., 2005; McGuire and McDonnell, 2006), interpretation of multiple tracers, especially radionuclides with a wide range of half-lives (Castro et al., 2000), or numerical simulation of the system (Park et al., 2002; Weisman et al., 2002; Castro and Goblet, 2003) and use these to help interpret individual tracer-model ages,
but even so the interpretations will still have significant uncertainty associated with
them.

It is also to be appreciated in groundwater dating that a single tracer-model age
is in fact a calculation that has associated with it a specific location/time (x,y,z,t), a
specific initial condition and a specific Δs and Δt that delimit interpretation constraints.
This means that only bulk properties between two flow-connected sampling points can
be quantified unless additional information is available from well tests, additional
sampling, other tracers, other dating methods, etc. This implies that multiple measures
along a flow path will provide more and better information if interpreted together rather
than individually. It has been noted (Bethke and Johnson, 2008) that plots of tracer-
model age vs. distance yield slopes in units of inverse velocity. Such plots can be used
to support the existence of a continuous flow line as well as discontinuities in flow
velocity.

If the conditions for appropriate application of a geochemical tracer for the
calculation of a tracer-model age can be confirmed and appropriate samples can be
obtained, the calculation of the tracer-model age must still be interpreted with caution.
A tracer-model age is an interpretation and an approximation that acknowledges all of
the assumptions, idealizations and limitations of the tracer as well as the comparability
of the tracer to the processes that determine the groundwater age. Due to aquifer
heterogeneity, dispersive mixing, and other physical and chemical processes, the
macroscale groundwater age distribution cannot be defined by the tracer-model age.
Still, tracer-model ages provide information that helps constrain the age distribution and
generalities of flow in groundwater systems.

TRACERS IN THIS BOOK

For times scales of greater than 1000 years, the tracers available for application
and interpretation in terms of tracer-model ages are limited. $^4$He, $^{14}$C, $^{36}$Cl, $^{81}$Kr and U-
Th-series analyses provide valuable information and are discussed in the chapters that
follow. However, the value of a tracer-model age is increased when two or more
methodologies can be compared and contrasted in order to understand the relation
between the generally simplified assumptions inherent in the tracer models and the
more complex real system (see Chapter 9).

The geochemical groundwater tracers discussed in this book ($^4$He, $^{36}$Cl, $^{14}$C, $^{81}$Kr,
U-Th-series ratios) have been be used to calculate tracer-model ages in multiple
groundwater systems with sufficient cross checks to ensure at least a minimal level of
confidence in the results. In the following chapters, tracer-specific processes will be
defined and discussed that contribute to the calculation of tracer-model ages as well as
how various processes affect the interpretation of these tracer-model ages. We will refer
to the “tracer-model age” as a generality and in specific cases refer to, for example, the
$^{14}$C-model age" or the "$^4$He-model age" to differentiate which specific tracer has been
used and what specific model has been used to calculate the tracer-model age.

The case studies discussed in the following chapters reinforce the principle that
multiple sampling points with multiple tracers including temperature, water chemistry,
hydraulic head, stable isotopes and well-bore tests will provide information that is
generally necessary for adequately characterizing groundwater basins. These can then
be interpreted with the aid of detailed mathematical reaction and transport models.
("flow-model ages"). Additional constraints often can be imposed on the interpretation by optimizing hydraulic models to best simulate the tracer transport data (Berger, 2008). Yet even for the best tracers and the simplest groundwater systems, the system of equations describing reaction and transport in the groundwater system will be under-constrained. In order to solve the equations that describe flow in a groundwater basin, assumptions and simplifications must be made with regard to the structure of the basin, the heterogeneity of the basin properties and the evolution of the basin as a steady-state or unsteady-state flow system subject to temporally controlled uplift and erosion. Given this complexity, simple physics-based flow-models (e.g., Torgersen and Ivey, 1985; Castro, et al, 2000) that include transport and mixing of groundwater as well as the source and sink functions that control the tracer distribution (Zhao et al, 1998; Bethke et al. 1999, 2000; Castro et al. 1998ab; Castro and Goblet, 2003; Bethke and Johnson, 2008) are useful in evaluating the controls on groundwater movement and flow times.

Flow in groundwater systems typically is dependent on a complex spatial distribution of hydraulic properties. Data to constrain this distribution are generally sparse. The spatial distribution of hydraulic head is relatively insensitive to the distribution of hydraulic properties unless the materials of differing properties are arrayed in continuous layers of strongly contrasting values (Gomez-Hernandez and Gorelick, 1989). It is within this context that estimates of the groundwater age via tracer-model ages can provide significant constraints on the structure of the system. However, even given this additional information, groundwater systems are always under-constrained with regard to the data requirements and the resulting models are always non-unique. To some extent this limitation can be overcome by employing geostatistically-based multiple conditional simulations, but even this computationally intensive approach provides only an indication of the possible range of behavior of the system. It benefits the conclusions of a study when groundwater scientists maintain an appropriate sense of the complexity in the natural systems they study.

REFERENCES


Idealized groundwater age $A_{id}$

$$\lim_{\Delta z \to 0, \Delta x \to 0} \Delta t(p_1 - p_0) = A_{id}$$

Probability distribution of idealized groundwater ages
Fig. 3.1: The concept of groundwater dating represents levels of complexity. (A) An “idealized groundwater age” ($\Delta t$) would imply an elapsed time between the time the water left the unsaturated zone (when it entered the groundwater) and the time at which the water was sampled in a specific position (x,y,z,t) at a specific distance ($\Delta s$) downstream in the groundwater basin. (B) However, even for 1-D systems, groundwater (even at the most minute sampling scale) represents a collection of water molecules that have individually undergone transport and mixing reactions along multiple transport paths as a result of, for example, longitudinal dispersive processes that create water samples that alter any “idealized groundwater age” to a frequency distribution. (C) For more realistic 2-D and 3-D systems, additional transverse dispersion and finite sampling volumes may mix pathways of different lengths (possibly different recharge entryways) with the same velocity; or pathways with identical path lengths but with different velocities. The net impact of 2-D and 3-D transverse dispersion is to create mixtures and increase the standard deviation about the mean of the frequency distribution of groundwater ages. (D) Transverse dispersion will also ultimately mix (very, very old) aquitard groundwater with the (old) aquifer groundwater. Because aquitard groundwater will be characterized by a distinctly older groundwater age, it will induce a long asymmetric tail on the old-side of the sample frequency distribution of groundwater ages. (E) And, the process of convergent mixing of different groundwater flows creates a mixture of component waters that is characterized by a bimodal probability distribution.
Fig. 3.2: A depiction of the role of dispersion in creating multi-path routes from recharge to discharge in a 3-D groundwater system. Flow down the hydraulic head gradient produces decision points upon each encounter with the host grains of the aquifer. This probabilistic process creates dispersion in groundwater age arriving at position ($\Delta x$) downstream (Fig. 3.1B).
Fig. 3.3: The results of Goode (1996) showing a direct simulation of groundwater ages within a very simple aquifer where the upper 30m of the aquifer has a hydraulic conductivity of $10^{-5}$ m s$^{-1}$ and the lower 70m has $10^{-6}$ m s$^{-1}$. (a) shows the hydraulic head contours (0.2m contours) and the velocity vectors. (b) shows the streamlines from recharge to discharge. (c) shows the simulated age contours for the advection only condition (no dispersion) with a 10yr contour interval. (d) shows the simulated age contours with dispersion. See Goode (1998) for a complete description of the simulation. From Goode (1998, reproduced by permission of American Geophysical Union.)
Fig. 3.4: The groundwater age of a water sample can be represented by some central measure of the frequency distribution of ages (Fig. 3.1B,C). In an ideal world, the tracer-model age (determined by some geochemical method) would be a true reflection of the frequency distribution of groundwater age. (a) For the case of a tracer that increases (or decreases) linearly with time (e.g., possibly $^4$He or a tracer whose input is linearly changing as a function of time), a mixture of groundwaters with different ages would produce a mixed water whose tracer-model age would be in agreement with the weighted mix of groundwater ages. (b) However, for a tracer whose variability with time is nonlinear (typically exponential with time: $^{14}$C, $^{36}$Cl, etc.), the effect of mixing (in this specific case) groundwaters with different ages would produce a tracer-model age that does not agree with the weighted mix of groundwater ages. Without independent knowledge of what was mixed, and in what proportions, it is not possible to interpret a tracer-model age unequivocally as a measure of the central tendency of the frequency distribution of groundwater age.
HELIUM (AND OTHER NOBLE GASES) AS A TOOL FOR THE UNDERSTANDING LONG TIME-SCALE GROUNDWATER TRANSPORT

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INTRODUCTION

$^4$He is the alpha-decay product from the radioactive decay of U-, Th-series elements that occur naturally in the Earth. As both U and Th have long half-lives in comparison to typically anticipated groundwater ages, the accumulation of $^4$He along a groundwater flowpath has long been explored and evaluated as a groundwater dating tool. A simple age, $\Delta t$, can be defined in the following way:

$$\Delta t = \frac{\Delta C}{\Sigma I}$$

where $\Delta C$ is the change in concentration of $^4$He with respect to an initial condition and $\Sigma I$ is the sum of inputs of $^4$He to the groundwater parcel. $\Delta t$ is usually called the $^4$He-model age, which using certain assumptions under favorable conditions can be interpreted with respect to an idealized water age. It should then be possible to estimate e.g. flow velocities provided there is some additional evidence that the suite of $^4$He samples are along a flowline. However, because $^4$He diffusion coefficients are higher than that of water, and because groundwater is an open system with regard to both locally-produced $^4$He (which can accumulate or be lost) supplied on the grain scale as well as externally imposed sources and sinks for $^4$He which can exert influences on the >kilometer scale, the methodology becomes considerably more complex.

This paper presents the $^4$He methodology as a geochemical construct and then illustrates how such information can be interpreted and applied to problems of basin scale groundwater flow. The goal is to enable a valuable groundwater tracer ($^4$He and other noble gases) to be understood from a practical standpoint and interpreted in the realistic environment.

THE GEOCHEMICAL CONSTRUCT FOR APPARENT $^4$HE TRACER AGES

$^4$He is present in the atmosphere at levels of 5.24ppm and is sparingly soluble in water (Ozima and Podosek, 2002). As water accumulates near the water table, it equilibrates with soil gas (idealized as air) and acquires an initial concentration of $^4$He. When the vertical recharge velocity of the groundwater isolates the water parcel from the atmosphere (e.g. the recharge velocity moves the water parcel away from the groundwater table faster than diffusion-like exchange can re-equilibrate the water parcel with the soil gas; Peclet number, $(v\Delta x/D) > 1$), the water is initialized to a concentration of $^4$He controlled by the partial pressure of He at the water table, temperature, salinity, and the dissolution of soil air bubbles due to water table fluctuations (‘excess air’). For systems such as $^{36}$Cl, the assumption is that the water parcel then acts as a closed system and looses $^{36}$Cl by radioactive decay without mixing with other water parcels.
The comparable assumption for $^4\text{He}$ would be that radioactive decay of dissolved U, Th-series elements produces alpha particles ("$^4\alpha$") which then accumulate in the water parcel. However, for most systems, the contribution from dissolved phase U, Th-series alpha decay is insignificant and the idealized geochemical construct must be altered to allow $^4\text{He}$ sources from the solid phase (which changes as a function of time/space as determined by the groundwater flow velocity). The simplifying assumptions are that the solid phase composition and its porosity are homogeneous along the flowpath. But, given this is an open system, $^4\text{He}$ sources from outside the moving water parcel and outside the sample collection space ($\Delta x\Delta y\Delta z$) can contribute to the accumulation of $^4\text{He}$ within the water parcel. Thus, the calculation of a $^4\text{He}$-model age for the water parcel is dependent upon specific knowledge of an open system for which the source and sink terms for $^4\text{He}$ are known. Inadequate knowledge of the open system sources and sinks (potentially heterogeneous in time and space) will limit the interpretability or applicability of the $^4\text{He}$-model age in addition to the conditions discussed above. Thus, the calculation of an appropriate $^4\text{He}$-model age in a groundwater parcel is dependent upon:

(1) definition of a known initial condition including:
   a. initial solubility equilibrium
   b. excess air incorporated during the water table initialization process
   c. possible gas loss (by e.g. bubble ebulition in situ)
(2) specific knowledge of the local, grain scale source strengths for $^4\text{He}$ in the solid phase (which is changing as the water parcel moves) and how such sources vary in time and space with:
   a. the volume of solid phase associated with the water parcel (as determined by the porosity, $\Phi=f(x,y,z,t)$)
   b. direct release of alpha particles from the solid phase (which may vary in space and time) to the fluid phase
   c. diffusive release of solid-phase accumulated-$^4\text{He}$ and its variability over time/space,
   d. weathering release of solid-phase accumulated-$^4\text{He}$ and its variability over time/space by the dissolution of the solid phase during chemical reaction (a function of $x,y,z,t$)
   e. mechanically or thermally induced fracturing and subsequent diffusion of solid-phase accumulated-$^4\text{He}$ to the pore space (this term is applicable on both the microscale and the macroscale)
(3) specific knowledge of the external sources (and loss terms) for $^4\text{He}$ to the porespace groundwater and how such external sources (and loss terms) vary with time/space including:
   a. fluxes across local aquifer/aquitard boundaries (sources and losses)
   b. sources from fluxes that permeate the crust and degas to the atmosphere
   c. magma–based sources as evidenced by excess $^3\text{He}$ attributable to mantle sources and the $^4\text{He}$ that accompanies such a source
   d. tectonically controlled $^4\text{He}$ fluxes and their variability that induce $^4\text{He}$ fluxes as a result of extension, intrusion, volcanism and basin deformation

The above forms a conceptual outline for the following discussion. As a part of the discussion, it will become apparent that calculation of a $^4\text{He}$-model age requires measures of gases in addition to $^4\text{He}$ (e.g., Ne, $^{36}\text{Ar}$, Kr, Xe, N$_2$) some of which can also be used to provide temporal constraints with differing sensitivities to sources, sinks and variability (e.g. $^{40}\text{Ar}$, fissionogenic $^{136}\text{Xe}$, $^{84}\text{Kr}$ and nucleogenic ($\alpha,n$) $^{21}\text{Ne}$ and ($n,\alpha$)$^3\text{He}$). Details on these other gases are provided elsewhere (Ozima and Podosek, 2002; Matsuda, 1994; Porcelli et al. 2002) and only those details especially pertinent to the discussion of $^4\text{He}$ will be addressed. Information is also included on sampling techniques, instrumentation and mass spectrometric constraints to enable intelligent negotiation when seeking collaborative $^4\text{He}$ analyses.
**SAMPLING AND ANALYSIS**

**Sampling Methods**

Sampling groundwater for $^4$He requires collection of in situ water that is (1) not subject to gas loss by the sampling process and (2) not subject to air contamination during the sampling process. Additionally, $^4$He diffuses through typical glass/plastic containers with/without special caps on a timescale (hours to weeks) that is typically incompatible with shipping samples to the laboratory and mass spectrometer analysis schedules. $^4$He also diffuses through borosilicate glass on a timescale of hours to weeks even when closed by flame sealing (Suckow et al., 1990). Consequently, the traditional method for collecting $^4$He samples has been in ~1 cm outer diameter crimped copper tubes (Weiss, 1968). Soft refrigeration-type (dehydrated) copper tubing is used to avoid contamination by tritiogenic $^3$He and loss of gas (the crimping device creates a cold weld as opposing walls of the copper tube are pressed together). Such sampling devices are also suitable for other (non-reactive) gases although the volumes required for some gases may be larger so multiple samples would need to be collected. In such cases, it is necessary to ensure that samples represent “duplicates” of the groundwater and at least one gas should be measured in both sampling devices. Even for the case of He,Ne-only, replicate copper tube samples are often taken to evaluate the sampling procedure and the suitability of the well/borehole preparation.

The most common sampling approach for wells is to use a submersible pump connected via pressure-tight tubing to a tee. One branch leads to an outflow that can be regulated and acts as a bypass. The other branch is connected to the copper tube with a clear piece of tubing and a needle valve on the other end. By adjusting the pump rate and the flow rates in the two outflows, it is usually possible to set the pressure in the copper tube to a level larger than the sum of the partial pressures of all dissolved gases to avoid degassing. The clear tube can be monitored for signs of bubbles indicating leaks or degassing (for details see, e.g., [http://water.usgs.gov/lab/3h3he/sampling/](http://water.usgs.gov/lab/3h3he/sampling/)). Many old groundwaters are free of dissolved oxygen and a simple O$_2$ measurement with the chemical kit or an O$_2$ sensor can place an upper limit on contamination with atmospheric air during sampling. For wells with short screens, several bore volumes should be pumped out before a sample is collected. Wells with long screens should be packed-off at appropriate intervals to avoid cross-flow self-contamination (well-bore induced mixing). Alternatives to submersible pumps include borehole fluid samplers that can be used to retrieve water at depth (e.g. Kuster sampler, Solbau et al. 1986). If wells tap into artesian aquifers, flow at the surface is often sufficient to ensure a good sample but depressurization as water flows up the well may induce bubble formation which can strip gases from the fluid. As wellhead conditions are often not known before sampling and return visits are often not possible, back-up sampling systems and variations on the sampling procedure are common and creativity in the field is required.

Copper tube sampling has been shown to be robust and samples can be shipped with minimal concern and stored for considerable time prior to analysis. The most common shipping problem is loss of the crimped/exposed end of the copper tube which may lead to crimp failure and leakage of $^4$He or may create sample processing issues if one or both ends are lost (connection to vacuum processing line becomes difficult). As only the gas within the water parcel needs to be collected, some investigators have relied on gas-only sampling in the field. Sanford et al. (1996) describe a vacuum extraction technique. Sheldon (2002) and Loose et al. (2009) summarize techniques in which the dissolved gases are equilibrated with a sample host across a gas permeable membrane. After equilibrium is achieved, the sampler is removed and the equilibrium head space in the sampler can be analyzed. Sanford et al. (1996) describes the use of a semi-permeable silicon tubing to sample for dissolved gases. Dyck and Silva (1981) and Gascoyne and Sheppard (1993) used ping-pong balls to collect gases for $^4$He analysis (but these cannot be stored for long periods and require measurement in the field). Spalding and
Watson (2006) used silicon tubing attached to a syringe for sampling and direct injection of samples analyzed for H₂, O₂, and CO₂. Gardner and Solomon (2008) recently described a passive headspace diffusion sampler that maintains the total dissolved gas pressure. In cases where wells are not available or the specific yield of the formation is too small, rock samples have been collected and stored in evacuated stainless steel vessels. Over time (often weeks to months) gases dissolved in the pore fluids accumulate in the headspace and can subsequently be extracted for measurement (Osenbruck et al., 1996, 1998; Ali et al., 2010).

**Laboratory Processing Methods**

Typical extraction procedures for the laboratory involve attaching the free end of the crimped copper tube to the processing line, opening the crimp or container into an evacuated processing system, degassing of the water under vacuum (or vacuum boiling) and isolation of the extracted gases on the downstream side of a fine capillary (Torgersen, 1977; Rudolph, 1981). The capillary allows a large flow rate of water vapor so that gases of interest cannot effectively back-diffuse against the large scale advection of water vapor. The isolated gases are then cleaned of water vapor and unwanted gases (CH₄, CO₂, O₂, etc) with a series of traps that may retain gases (e.g. water vapor), adsorb gases or react gases to absorbable species (e.g. Smith and Kennedy, 1983; 1985). Gases are then quantitatively transferred into a sample container or directly into the mass spectrometer, originally by a toepler pump (e.g., Torgersen, 1977), but now most commonly with a set of one or two cryogenically cooled traps used to accumulate the gases and separate the He/Ne fraction from the other gases. Reactive gases are removed using Titanium(heated sponge or filament), Cu/CuO or alloy (ST101 or 707) getter pumps either right after extraction and removal of water vapor; or after desorption from the cryogenic traps. Sample aliquots can be stored for analysis at a later time in all metal containers; or in flame sealed borosilicate (Ne, Ar, Kr, Xe), Corning 1720 or Pb (He) glass ampoules. The diffusion coefficients of He in these specific glasses are sufficiently low that samples can be stored for years at temperatures typically <0°C (depending on gas and glass type, Suckow et al., 1990). In recent years, more and more analysis systems have been automated at least from the water sample extraction step onward, which has improved the reproducibility of the measurements and the sample throughput.

**Mass Spectrometry**

⁴He and noble gases are measured mass spectrometrically and require specialized machines with defined resolution. For helium, measurement of ⁴He and ³He are often necessary (identification of mantle sources and tritiogenic ³He). Clear measurement of ³He requires separation of the HD⁺ peak from the ³He⁺ peak and thus machine resolution of over 630 is required. If only measures of ⁴He are required, much simpler mass spectrometers can be employed and very high concentrations can be measured with gas chromatography. However, unless the field site and the problem are well determined, ⁴He “dating” in the research mode usually requires the use of a well-equipped and specialized noble gas mass spectrometer which can produce (at a minimum) ³He, ⁴He, Ne, ³²Ar, ⁴⁰Ar, Kr and Xe measures. Measures of the complete noble gas suite aid in the definition of the initial condition and the recharge temperature. The better laboratories can additionally provide measures of ²⁰,²¹,²²Ne (to potentially support ⁴He-model ages times with nucleogenic Ne-model ages); and Ar, Kr and Xe isotopes (to potentially support ⁴He-model ages with ³⁶Ar-model ages as well as fissionogenic ¹³⁶Xe- and ⁸⁴Kr-model ages). A suite of noble gas isotopic measures is also important in the identification of mass dependent fractionation as an analytical problem. For analytical detail, the reader is referred to Clarke et al. (1976), Torgersen (1977), Rudolf (1981), Smith and Kennedy (1983, 1985), Mamyrin and Tolsthikin, (1984), Bayer et al. (1989), Stute, (1989), Ludin et al. (1998), and Beyerle et al. (2000).
IDENTIFYING MULTIPLE \(^4\)HE COMPONENTS FROM MEASUREMENTS

The total \(^4\)He in a measured sample is a composite of \(^4\)He from multiple sources as well as sampling-induced \(^4\)He additions and losses (e.g. degassing in situ or during sampling). These components can be generally expressed for any noble gas (\(\text{Ng}\)) as:

\[ i\text{Ng}_{\text{tot}} = i\text{Ng}_{\text{eq}} + i\text{Ng}_{\text{exc}} + i\text{Ng}_{\text{rad}} + i\text{Ng}_{\text{nuc}} + i\text{Ng}_{\text{fiss}} + i\text{Ng}_{\text{ter}} + i\text{Ng}_{\text{fiss}} + i\text{Ng}_{\text{ter}} - \Sigma L \]  

(2)

where the subscripts \(\text{tot}\), \(\text{eq}\), \(\text{exc}\), \(\text{rad}\), \(\text{nuc}\), \(\text{fiss}\), \(\text{man}\) indicate total (=measured), equilibrium with air, excess air, radiogenic, nucleogenic, fissiogenic (only relevant for Ne, Kr, and Xe), and mantle origin, which correspond to the various source (sum of inputs, \(\Sigma I\)) terms as well as potential gas losses which are included as \(\Sigma L\) (sum of loss terms). All components marked “\(\text{is}\)” (or \(\text{in situ}\)) represent sources inside the water parcel (contained within a mobile \(\Delta x\Delta y\Delta z\)) while those with \(\text{terr}\) have their origin outside. For \(^4\)He, the rad term is U-,Th-series alpha decay and for \(^3\)He the rad term is \(^3\)H decay, often termed \(^3\)He\(_{\text{ri}}\). Fissiogenic He is not relevant, and nucleogenic \(^5\)He is produced by the reaction \(^6\text{Li}(n,\alpha)^3\text{H}(\beta^-)^3\text{He}\). He of mantle origin can often be found in areas affected by tectonic activity. The \(^3\)He/\(^4\)He ratio of radiogenic and mantle He is of the order \(10^{-8}\) or \(10^{-5}\), respectively. For He, separation of components in the total measured gas by source/production process is easier than by origin (\(\text{in situ}\) or \(\text{terrigenic}\)). Additionally, the analysis must be able to recognize and correct for several gas loss (\(L\)) possibilities that presumably reduce each Ng component via equilibrium fractionation or bulk non-fractionating loss. Calculation of a \(^4\)He-model age is based on \(\text{in situ}\) and terrigenic components.

Equilibrium with Air, \(^4\)He\(_{\text{eq}}\)

\(^4\)He\(_{\text{eq}}\) is governed by the solubility of noble gases in water as a function of Henry’s Law. As solubility is a function of temperature, pressure and salinity, most calculations of \(i\text{Ng}_{\text{eq}}\) are generalized from a limited suite of laboratory measurements. Weiss (1970, 1971) and Weiss and Kyser (1978) provide empirical equations that yield solubility concentrations from air. Clever (1979a,b;1980) provide mole fraction solubilities which Aeschbach-Hertig et al. (1999) have combined with the salting-out coefficients (Smith and Kennedy, 1983) to provide solubilities as a function of pressure, temperature and salinity. Table 8.1 (from Kipfer et al., 2002) provides the equations by which to calculate noble gas solubilities.

It should be noted that calculation of \(i\text{Ng}_{\text{eq}}\) requires the definition of an assumed recharge elevation and pressure. Additional assumptions are required with regard to changes in temperature and salinity that may occur along the flow path from recharge to the sampling point. It is often assumed that recharge occurs and \(i\text{Ng}_{\text{eq}}\) is established at the mean annual temperature and pressure of the (assumed) recharge zone and that subsequent changes in temperature (as a result of heat gain along a geothermal gradient) have no impact on this initial equilibrium solubility. Changes in “salinity” as a result of weathering and/or opening of fluid inclusions may also be assumed to have no impact on this initial equilibrium solubility. But changes in salinity by mixing from different sources and/or halite dissolution cannot be viewed in such a simplistic sense: strong increases in salinity by halite dissolution were demonstrated to impact transport of noble gases (Suckow and Sonntag, 1993). It is unknown to what extent mixing of waters impacts Ng concentrations vs. the impacts that are the result of in situ increases in T, P. Some correlations between Cl and \(^4\)He could be the result of progressive NaCl addition by halite dissolution whereas other changes in Cl could be the result of weathering and release of fluid inclusions (presumably rich in Cl). Ballentine et al. (2002) provide a discussion of the background theory. Nonetheless, the isolation and quantification of \(i\text{Ng}_{\text{eq}}\) and \(^4\)He\(_{\text{eq}}\) requires a suite of assumptions not all of which have been checked and not all of which can be checked. This is a theme that will continue.
Excess “Air” Components, $^4\text{He}_{\text{exc}}$

$^4\text{He}_{\text{exc}}$ is the result of soil processes by which excess air is occluded in the recharge process and is eventually dissolved as pressure increases. Bulk dissolution of unfraccionated air is one possibility that requires the use of a Ng tracer that is controlled primarily by dissolution of air (e.g. Ne) rather than in situ and external sources (e.g. $^4\text{He}$). Early research used a definition of the Ne components in groundwater to define the excess air component of Ne which for unfraccionated air could then be scaled to the $^4\text{He}_{\text{exc}}$. Rewriting eqn (2) for Ne:

$$N_{\text{e tot}} = N_{\text{e eq}} + N_{\text{e exc}} - \Sigma L$$

and assuming no losses:

$$N_{\text{e exc}} = N_{\text{e tot}} - N_{\text{e eq}}$$

allows the excess $^4\text{He}$ component to be calculated as:

$$^4\text{He}_{\text{exc}} = N_{\text{e exc}} \left( \frac{He}{Ne} \right)_{\text{air}}$$

Because Ne solubility is the least temperature sensitive of the noble gases, such an assumption and calculation was tenable. However, this assumes that air is in excess and that its process of dissolution is non-fractionating and non-equilibrating. Cross-checking these assumptions with the noble gas suite have shown this to be oversimplified (e.g. Aeschbach-Hertig et al., 1999). Yet, in most cases, the $N_{\text{e exc}}$ component is less than 30% and thus the calculated $^4\text{He}_{\text{exc}}$ is also small especially considering that the $^4\text{He}_{\text{eff}}$ and the $^4\text{He}_{\text{rad}}$ are often orders of magnitude larger. Because mass spectrometric measurement of $^4\text{He}$ usually also acquires Ne, analytical costs can often be reduced by making these assumptions and acquiring He,Ne concentrations only.

If measures of the complete noble gas suite are acquired, such measures can be evaluated in terms of the paleorecharge temperature that has found application in paleoclimate research (e.g. Stute et al., 1992a; 1995ab). Considerable research has been devoted to evaluating the 'Ne$_{\text{exc}}$ component in order to best fit the 'Ne$_{\text{eq}}$ components to a recharge temperature. Stute et al. (1995ab) explored partial re-equilibration (PR) where an initial air bubble was dissolved and partial re-equilibration occurred by molecular processes across the water table. Peeters et al. (2002) suggested the use of $^{20}\text{Ne} / ^{22}\text{Ne}$ ratios to test the partial re-equilibration model but where measures have been made, no significant diffusive fractionation of the isotopes has been uniquely identified. Kipfer et al. (2002) propose a multi-step re-equilibration (MR) model that would allow for large excess air (accommodated at pressure well beyond the water table). However, as MR reduces to PR in the limiting case and the lack of evidence for diffusive fractionation of $^{20}\text{Ne} / ^{22}\text{Ne}$ (Peeters et al., 2002), such a model is also less than adequate. The closed system equilibration (CE) model (Aeschbach-Hertig et al., 1999, 2000, 2001) appears to allow direct physical interpretation of the excess air component and its variance across the Ng suite in most cases. Direct verification of a mechanistic link between excess Ne and water table fluctuations is not available (Kipfer et al., 2002) but experiments with sand columns appear to support the basic mechanistic possibilities (Holocher et al., 2002). A widely used Excel/Matlab routine can be downloaded from http://www.eawag.ch/organisation/abteilungen/wut/schwerpunkte/umweltisotope/methoden/interp_EN.

Radiogenic Production, $^4\text{He}_{\text{rad}}$
$^4$He$_{rad}$ is due to radiogenic production via alpha decay of U-, Th-series elements. Other sources of alpha particles (e.g. Nd decay) and $^4$He as a result of (n,α) interactions can be considered quantitatively insignificant. Under the assumption that U-, Th-series elements have reached radio-equilibrium, the $^4$He production rate from rock can be expressed as:

$$^4$$He cm$^3$STP g$^{-1}$yr$^{-1} = J'_{He} = 0.2355 \times 10^{-12} \{[U](1+0.123([Th]/[U]-4)) \}$$

(6)

$$^4$$He atoms g$^{-1}$yr$^{-1} = J'_{He} = 2.688x10^{19}(0.2355x10^{-12} \{[U](1+0.123([Th]/[U]-4)) \}$$

(7)

where [U] and [Th] are concentrations expressed in ppm (Craig and Lupton, 1976; Torgersen, 1980). For groundwater calculations, it is then necessary to quantify how much of this in situ production becomes available to the fluid phase. This has been generalized as a release factor $\Lambda_{He}$ and the accumulation of $^4$He in the fluid phase can be calculated as:

$$^4$$He cm$^3$STP g$^{-1}$H$_2$O yr$^{-1} = J_{He} = J'_{He}(\rho \Lambda_{He}((1-\Phi)/\Phi))$$

(8)

where $\rho$ is the density of the solid (g cm$^{-3}$) and $\Phi$ is the porosity (cm$^3$ H$_2$O cm$^{-3}$ total). Quantification of $\Lambda_{He}$ is a challenge. Fig. 8.1 (modified from Torgersen, 1980) shows schematically the various mechanisms by which $^4$He can enter the porespace from the solid phase: (1) direct recoil, (2) rapid diffusion in imperfections, (3) slow diffusion in the solid phase, and (4) weathering or dissolution.

**Mechanism 1: Direct Recoil**

The recoil pathlength of an alpha particle in silicate material ($R_{\alpha}$) is of the order 30-100 microns (Andrews, 1977) and the direct recoil loss of $\alpha$ particles by the solid phase has been evaluated by Flugge and Zimens (1939) and summarized by Torgersen (1980). From the grain size and the recoil pathlength, $\Lambda_{He}$ can be calculated as:

$$\Lambda_{He} = \frac{3R_{\alpha}}{4r} - \frac{1}{16} \left( \frac{R_{\alpha}}{r} \right)^3$$

for $2r \geq R_{\alpha}$

(9)

$$\Lambda_{He} = 1$$

for $R_{\alpha} > r$

(10)

where $r$ is the grain radius and $R_{\alpha}$ is the recoil pathlength. Most aquifer grain sizes (order mm) are large compared to the recoil pathlength (order 0.1mm) and $\Lambda_{He}$ can be approximated as:

$$\Lambda_{He} = \frac{3R_{\alpha}}{4r}$$

for $R_{\alpha}/r < 0.5$

(11)

Calculations indicate that direct recoil release of $\alpha$ particles should be low ($\Lambda_{He}$ order 0.075) yet it is often observed (e.g., Torgersen and Clarke, 1985; Heaton, 1984) that $^4$He in the porewater increases AS IF $\Lambda_{He}=1$ (see Fig. 8.2). The implication of this common assumption ($\Lambda_{He}=1$) implies that the diffusive (rapid or slow) loss of $^4$He from the solid phase to the fluid phase is balanced by the production of $^4$He in solid phase by radio-production of $^4$He. This is equivalent to the assumption that the grain has reached a condition of diffusive (rapid or slow) equilibrium with the local porewater. Note that the timescale on which diffusive equilibrium is reached is much shorter for fast diffusion (mechanism 2) than for slow diffusion (mechanism 3) (see Fig. 8.1).
Mechanism 2,3: Rapid and Slow (molecular) Diffusion Release

Using an idealized spherical geometry and the solution of Carslaw and Jaeger (1957, page 244, Fig. 32), a condition of diffusive (rapid or slow) equilibrium with the local porewater occurs in a grain with an initial concentration of $^4$He=0 at a scaled time of $D_{\text{solid}}t/\Delta x^2>0.5$ (For spherical geometries, such as a sand grain $\Delta x$ is equivalent to the radius). As a generalization, the diffusive timescale $Dt/\Delta x^2>0.5$ implies that >50% change has been achieved. With the (slow) molecular diffusion coefficient of $^4$He in silicate material of the order $10^{-18}\text{cm}^2\text{s}^{-1}$ to $10^{-22}\text{cm}^2\text{s}^{-1}$ (typical crustal minerals, Lippolt and Weigel, 1988; Trull et al. 1991), the “steady state” condition (production in the grain = loss from the grain) can apply to a 0.1cm grain on the timescale of $10^8\text{yrs}$ ($10^{18}\text{cm}^2\text{s}^{-1}$) (see Fig. 8.3). However, when grains are laced with imperfections, it is important to differentiate the screened grain size from the effective grain size (Torgersen, 1980; Ballentine et al., 2002). For the effective grain size, internal defects, imperfections, dislocations and microfractures render the distance to a porespace-available boundary to be significantly less than the screen-sorted grain size (the rapid diffusion case of Torgersen, 1980; see Fig. 8.1). For example, an effective grain size of 0.01cm will reach steady state (production = loss) on a timescale order $10^6\text{years}$ ($10^2$x faster) if transport time in the “imperfection pathway” is not considered significant. Additionally, the (slow) diffusion coefficient of $^4$He in grains may increase with time due to radiation damage, microfracturing, etc. and the effective grain size may therefore decrease with time. As this loss of $^4$He from a grain is typically not measureable in the laboratory on a reasonable timescale, a measure of loss at a higher temperature can often be scaled to the in situ lower temperature (Mamyrin and Tolstikhin, 1984). Although such measures are possible, this laboratory measure of $D_{\text{solid}}$ will only reflect conditions now rather than conditions over the timescale of the $^4$He-model age (time over which solid material contributed to the fluid parcel). Of additional concern is the possibility of variability in $\Lambda_{^4\text{He}}$ in space or time. Is the rock sample you acquire representative of the “average” rock the water parcel has seen over its residence time? As effective grain sizes in aquifers are typically small and the diffusion coefficients for $^4$He in the solid phase are typically large, an in situ production rate equivalent to $\Lambda_{^4\text{He}}=1$ is often assumed.

Mechanism 4: Bulk Dissolution or Weathering

Bulk dissolution or weathering of grains should also result in the release of $^4$He accumulated within the grain (see Fig. 8.1). Because grains dissolve from the outside and diffusion will create gradients in the solid phase that decrease the concentration toward the outside of grains, quantification of a priori dissolution release of $^4$He is difficult. Both Torgersen and Clarke (1985) and Heaton (1984) calculate a simple rate for dissolution release of $^4$He based on an assumed uniform concentration of $^4$He in the grain. These concentrations are usually based on the metamorphic or depositional age of the formation and hence represent a maximum value. Both Torgersen and Clarke (1985) and Heaton (1984) calculate the rate of “weathering” release of $^4$He from their systems to be <1% of the $\Lambda_{^4\text{He}}=1$ condition and thus weathering release may be unimportant. However, it is still to be determined if this is a general condition.

Heaton (1984) estimates a bulk rate of surface chemical weathering from the chemistry of world rivers to be $3\text{mg}_{\text{rock}}\text{kg}^{-1}_{\text{rock}}\text{yr}^{-1}$. Simplistically, this is equivalent to a timescale for dissolution of 0.3Myr. However, Heaton (1984) advises that subsurface dissolution will be order $0.1-0.01x$ slower indicating subsurface timescales for dissolution of order 3-30Myr. This “dissolution timescale” can be compared to the timescale for solid phase loss of $^4$He by molecular diffusion. Using a “fast” molecular diffusion coefficient ($10^{-18}\text{cm}^2\text{s}^{-1}$) for grains of 0.1cm, yields order 300Myr as timescale for loss (Fig. 8.3). Thus one might expect weathering release or chemical dissolution to be an important release mechanism. However, the observation that release equivalent to $\Lambda_{^4\text{He}}=1$ is often observed suggests that effective grain sizes for diffusion might be as small as $0.5x10^{-3}\text{cm}$ ($\Delta x=(D\Delta t)^{0.5}$ where $D=10^{-18}\text{cm}^2\text{s}^{-1}$ and...
These arguments suggest that $^4$He release via chemical dissolution should be considered but may often be dismissed.

**Effective Release at Low Rates ($\Lambda_{He} < 1$)**

Under conditions where $D_{solid}/\Delta x << 0.5$, the solid phase can release $^4$He at a rate that is equivalent to $\Lambda_{He} < 1$. However, the authors are aware of no documented cases for which $\Lambda_{He} < 1$ has been unequivocally shown. This condition may require formation of new grains from new material (authigenic material) with no pre-existing $^4$He which is likely an artificial case.

**Enhanced Release ($\Lambda_{He} > 1$) by Comminution, Micro-, Macro-Fracturing**

The case where $\Lambda_{He} > 1$ can and does occur as a result of a decrease in effective grain size by comminution, micro- and macro-fracturing. In such a case, a large effective grain size (>1cm) may retain most of its in situ production of $^4$He but release that $^4$He when the grain size is reduced. In the case of the Sturgeon Falls site in Ontario, Canada, Solomon et al. (1996) hypothesized that Precambrian Canadian Shield rocks (>1Byr) that occur in large blocks (fracture to fracture spacing of order 1-10m) were reduced by glacial action to the 1mm grains that comprise the aquifer. The accumulated $^4$He would then be released from 1mm grains on a timescale order $10^8$ years ($10^{-16}$cm$^2$/s) to $10^9$ years ($10^{-20}$cm$^2$/s); see Fig. 8.3. Such release ($\Lambda_{He}$ order 100) was confirmed by laboratory measures (Solomon et al., 1996). Based on a comparison of groundwater $^4$He accumulation rates and independently estimated travel times (see Fig. 8.4), this scenario (glacially-produced comminution and $\Lambda_{He} > 1$) may be common at high latitudes. The enhanced release of $^4$He ($\Lambda_{He} > 1$) can continue for considerable time (see Fig. 8.5) and may provide a dominant $^4$He input within an aquifer.

This concept of comminution/fracturing is scalable. Honda et al. (1982) have shown in laboratory experiments that rock fracturing can lead to the release of $^4$He. In the 1D case, Torgersen and O'Donnell (1991) have shown that fracturing creates large gradients and surface areas that lead to high $^4$He fluxes ($\Lambda_{He} > 1$) (see Fig. 8.6). The resultant ‘pieces’ continue to loose $^4$He ($\Lambda_{He} > 1$) for timescales of the order $2 < Dt/\Delta x^2 < 5$ depending on the initial condition. Note that the flux from the slab (Fig. 8.7) is reduced by half in the timescale defined by $Dt/\Delta x^2 = 1$ but that in some cases the flux remaining to be released may still be larger than in situ production. Thus, increased stress leading to micro-fracturing can result in $\Lambda_{He} > 1$ through new surfaces and/or the creation of imperfections and microcracks which creates shorter routes and higher gradients to enable high transport rates to imperfections. At the larger scale, (1-1000m) it has been shown that 1km of uplift or downdrop will result in thermal stresses sufficient to produce stresses approaching the yield strength of rock (Knapp and Knight, 1977; Savage, 1978). The 1D modeling of Torgersen and O'Donnell (1991) shows stress-induced macro-fracturing leads to large fluxes from blocks ($\Lambda_{He} > 10^4$) and although such fluxes decrease with time, they can produce $\Lambda_{He} > 1$ for timescales of the order $2 < Dt/\Delta x^2 < 5$ (see Fig. 8.7). The net result of micro-scale fracturing coupled to larger scale (km) macro-fracturing is that retention of $^4$He in the crust becomes difficult and there can be a resultant significant flux of $^4$He from the crust to the atmosphere.

**Crustal Fluxes of $^4$He$_{rad}$ ($^4$He$_{terr}^{rad}$)**

The concentration and residence time of $^4$He in the atmosphere suggest that on a continental space scale and a million year time scale, the flux of $^4$He from the Earth’s crust to the atmosphere is comparable to the net in situ production by U-, Th-series elements alpha-decay in 30-40km of crust (Torgersen, 1989; Torgersen, 2010). This is not equivalent to a steady-state loss of $^4$He from the crust to the atmosphere as implied by Ballentine et al. (2002) as any measure of flux contains within it a characteristic time and space scale whereas steady-state implies that the flux is constant in time and space. However, the implication of the atmospheric $^4$He mass balance is that in situ crustal production of $^4$He must both be released to
a mobile phase (see above discussion of $\Lambda_{\text{He}}$) and that mobile phase must be transportable to the Earth's surface on timescales of order 1Myr although it may take longer ($10^9$ yr) for that flux to be established (see Fig. 8.8).

With regard to the interpretation of $^4\text{He}$ in groundwater systems, the issue becomes one of a possible dominant flux of $^4\text{He}$ into a water parcel from external sources rather than the internal production terms encountered in the space $\Delta x \Delta y \Delta z$ (acknowledging that $\Delta x \Delta y \Delta z$ is heterogeneous and that the solid phase remains in place while the water flows). Table 8.2 shows the measured $^4\text{He}$ degassing flux in locations around the world. Although the analysis of Torgersen and O'Donnell (1991) suggests fluxes from individual blocks can be $10^4$ in situ production and that $\Lambda_{\text{He}} < 1$ remains an unobserved possibility, it is of note that area- and time-weighted mean flux ($3.3 \times 10^{10} \text{He atoms m}^{-2} \text{s}^{-1}$) is approximately equivalent to the mean crustal production. When the fluxes of Table 8.2 are evaluated with respect to their log normal mean ($4.18 \times 10^{10} \text{He atoms m}^{-2} \text{s}^{-1}$), the variability in measured $^4\text{He}$ flux is approximately ±1.5 orders of magnitude (Torgersen, 2010; see also Fig. 8.9). It is acknowledged that the fluxes of Table 8.2 represent fluxes distributed over an area appropriate to the measurement. For instance, the quantified external flux into the Great Artesian Basin (Torgersen and Clarke, 1985) is roughly equivalent to whole crustal production and is influxed to the base of the aquifer over the space/time scale of the basin. This, of necessity, means that the flux above the aquifer directly from the soil to the atmosphere is very low. Furthermore, the net flux to the atmosphere in the discharge zone would be locally very large since it reflects the input of crustal production over the whole basin and not just the discharge zone. These measures of the degassing fluxes of $^4\text{He}$ must therefore be carefully interpreted with respect to their applicable time and space scale. For the range of basin scale fluxes to be this constrained, vertical transport must be not only relatively rapid but also relatively pervasive.

Figure 8.9 shows a simple analysis of the U prospecting data of Clarke and others (Clarke et al., 1977; Top and Clarke, 1981; Clarke et al., 1983) for 271 lakes for which only one sample is obtained per lake. Although such data only captures order 0.5yr of $^4\text{He}$ flux over a specific lake area and is likely subject to errors of the order 3x due to the assumptions necessary (the assumptions also suggest the estimate is too high by ~50%), the mean flux measured by these lakes is $4.57 \times 10^{10} \text{He atoms m}^{-2} \text{s}^{-1}$ (log normal mean with a standard deviation of a factor of 3.9x written as $^*/3.9x$). The lake regions sampled by Clarke and others is an area of the PreCambrian Canadian Shield which was depressed by about 1km due to coverage by 3km of ice sheet approximately 20kyrs ago. Thus, it is noteworthy both that the mean measured flux ($4.57 \times 10^{10} \text{He atoms m}^{-2} \text{s}^{-1}$ lognormal mean with a standard deviation of $^*/3.9x$) is not much larger than whole crustal production ($3 \times 10^{10} \text{He atoms m}^{-2} \text{s}^{-1}$; Torgersen and Clarke, 1985; Torgersen, 1989) and that the variance of the flux is consistent with the range reported from much larger basins (See Table 8.2). While the coverage of the planet with regard to crustal flux measurements remains limited, these measurements (Table 8.2; Fig. 8.9) support a hypothesis that the mean flux of $^4\text{He}$ from the continental crust is the same order as the in situ production from U,Th series decay in the continental crust. However, the variance of the crustal degassing flux is significant (a factor of $10^5$ (95th percentile) for short time (0.5yrs) and short space-scales (1km); Torgersen, 2010) and likely unpredictable thus complicating the potential use of $^4\text{He}$ as a method of groundwater "dating". Such a conclusion also requires that the net rate of vertical transport in the crust be examined.

**Vertical Transport of $^4\text{He}_{\text{in situ}}$ in the Crust**

Simple scaling arguments can be used to evaluate the necessary rates of vertical transport in the continental crust in order to achieve surface crustal fluxes equivalent to the rate of whole crustal in situ production. As the data in Fig. 8.9 and Table 8.2 represent multiple time- and space-scales, the problem is constrained by the limit: continental degassing and basin scale measures of the degassing flux (on the time-, space-scale of $10^6$yrs and 1000km) can be
approximated as equivalent to the in situ production from 30-40 km of crust but with considerable variance (Torgersen, 2010). This does not imply steady-state degassing is applicable everywhere at all times; but it does acknowledge that the range exhibited in Table 8.2 and Fig. 8.9 is relatively small. In order to achieve the crustal degassing flux in the Great Artesian Basin, Torgersen and Clarke (1985) used a timescale of 2 x 10^8 years (corresponding to a Jurassic age for the aquifer material) and assumed that most of the U, Th resided in the upper 7km of crust to calculate a scaled effective diffusion coefficient (Fig. 8.8) of 8 x 10^-6 cm^2 s^-1 for that 7km of crust. Torgersen (1989) using a solution from Carslaw and Jaeger (1957), scaled these observations to effective vertical diffusivities of 10^-5 to 10^-6 cm^2 s^-1 (Torgersen, 1989) or vertical velocities of 0.1-1 cm s^-1. Given the diffusivity of gas in water is order 10^-5 cm^2 s^-1 and that the porosity (Φ=0.1) and tortuosity effects will reduce this quiescent water to DΦ^2= 10^-7 cm^2 s^-1, it is clear that over the long time- and space-scale, continental crust must transport significant quantities of \(^{4}\)He and water at rates that are significantly faster than would be measured by typical (short time-, space-scale) well tests.

Such rates of transport are surprising when one considers the hydraulic conductivity of consolidated, non-granular rocks (Freeze and Cherry, 1976) but less surprising when the rates of metamorphic processes are considered (Etheridge et al., 1983, 1985). The low hydraulic conductivities and transport often encountered in bulk non-granular rock are measured over small timescales (<yr) with small space scale (order cm) pieces of rock. In contrast, metamorphic processes reflect the transport in the crust on the larger time/space-scales. This conclusion of rapid transport and high volumes of water is consistent with the requirements of the observed products in metamorphic geology (e.g. Etheridge et al., 1983, 1985).

Metamorphic rock structure also suggests that fluid transport is episodic with periods of “no transport” followed by periods of very high transport. Thus, the effective degassing of continental crust is supportive of and supported by the fluid transport required by metamorphic processes. When the time/space-scale for transport is large, the effective rate of crustal scale transport is higher than might be predicted. However, any specific quantification of vertical transport in the crust may yield numbers which suggest that such crustal scale transport is not viable. This feature was specifically addressed by the Torgersen and Clarke (1992) study at Cajon Pass drillhole where the vertical transport measured by borehole tests showed rates of 10^-5 cm yr^-1 while effective rates estimated from the apparent \(^{4}\)He tracer ages of the fluid implied vertical rates of 0.04-0.6 cm yr^-1. Vertical transport in the continental crust must therefore be episodic (as required by metamorphic geology; Etheridge et al., 1983, 1984) with long periods of slow transport and short periods with very high transport rate. Thus, what is “seen” in the crustal scale transport of \(^{4}\)He is comparable to travel in city subway systems: one can travel by subway from downtown Manhattan to uptown in a specific period of time (effectively several km/hr) but when viewed in detail, this transport is accomplished by a series of stops (velocity of zero km/hr) interrupted by bursts of high speed (tens of km/hr) travel. It would thus not be surprising for the external flux of \(^{4}\)He (\(^{4}\)He_{terr}) to become quite important in many aquifer systems. For a more detailed discussion of vertical transport of \(^{4}\)He_{terr} see Torgersen (2010).

In Situ Production of \(^{3}\)He

Radiogenic production of \(^{4}\)He is accompanied by a small but important nucleogenic production of \(^{3}\)He as a result of thermal neutron interactions with \(^{6}\)Li in the solid phase:

\[
\text{\(^{6}\)Li(n,\alpha)\(^{3}\)H(\beta-)\(^{3}\)He}
\]  

\(^{3}\)He produced according to eqn (12) is defined as nucleogenic \(^{3}\)He whereas radiogenic (tritiogenic) \(^{3}\)He is produced by an atmospheric source of \(^{3}\)H. To initiate the reaction (eqn 12), the production of neutrons in the solid matrix by (α,n) reactions and spontaneous fission neutrons must be calculated:
\[ n = (\alpha, n)U + (s_f, n)U + (\alpha, n)Th \]  

(13)

The dominant target elements for the \((\alpha, n)\) reactions are Na, Mg, Al, Si, C (although water is also a viable and variable sink for neutron capture) and the net production of thermal neutrons \((n, \text{neutrons g}^{-1} \text{yr}^{-1})\) can be expressed as (Ballentine and Burnard, 2002):

\[ n = 0.01[U](13.8[Na] + 5.4[Mg] + 5.0[Al] + 1.3[Si] + 2.0[C]) + 0.4788[U] + 0.01[Th](6.0[Na] + 2.45[Mg] + 2.55[Al] + 0.56[Si] + 0.83[C]) \]

(14)

where \([U], [Th]\) are in ppm and the remaining components are in per cent. These thermal neutrons are captured by further interactions with the solid phase where typical slow neutron path lengths in silicate are order 1m. This suggests that the bulk solid phase composition can be used to estimate \(^3\)He production. Such calculations are well developed. Based on the initial work by Morrison and Pine (1955) and Feige et al. (1968), the fraction of the thermal neutron flux captured by \(^6\)Li \((F_{Li}^{Thn})\) can be calculated (e.g Andrews and Kay, 1982; Andrews, 1985):

\[ F_{Li}^{Thn} = \frac{\sigma_i N_i}{\sum \sigma_i N_i} \]

(15)

where \(\sigma_i\) is the thermal neutron cross section and \(N_i\) is the molar abundance for important components of the rock composition (see Table 8.3). Combining eqn (14) and (15) yields the rate of production of \(^3\)He which can be further combined with eqn (7) to calculate the \(^3\)He/\(^4\)He production ratio. Note, the rate of \(^3\)He production is based on the neutron production rate which is a function of \([U],[Th]\) but the \(^3\)He/\(^4\)He production ratio is determined by the rock composition and is a function of the Li/U, Th ratio.

Table 8.4 shows the \(^3\)He/\(^4\)He production ratio for average crust as well as selected rock types based on specific rock compositions from the literature. While there is a large degree of agreement, the observed differences and variability are significant. Table 8.4 further shows that differences between the observed \(^3\)He/\(^4\)He production rate and the calculated \(^3\)He/\(^4\)He production rate are also significant. Because \((\alpha, n)\) reactions occur within one alpha pathlength (0-40microns) of the decaying nuclei, inhomogeneities in rock chemistry on the space scale of 40microns can impact the specific \(^3\)He yield. Furthermore, the assumption of homogeneous rock over the space scale of 1m may be problematic for the thermal neutron capture and the relative siting/separation of the trace elements U, Th, Li, Gd, Sm (the last two elements have very large cross sections) or the relative presence of water may significantly impact the specific \(^3\)He yield. Such issues were discussed by Martel et al. (1990) who investigated the Carnmenellis granite \(^3\)He/\(^4\)He production (see also discussion by Ballentine and Burnard, 2002). Chazal et al. (1998) revisited the Stripa granite and found a measured \(^3\)He/\(^4\)He ratio was 4x the calculated ratio. Specific causes for the differences between the observed/measured \(^3\)He/\(^4\)He ratios and calculated production ratios have not been unequivocally identified but the data of Table 8.4 and analysis of studies mentioned above serve to provide context for the use of calculated \(^3\)He/\(^4\)He production ratios and an interpretation of the errors that might be appropriate to that value. Based on the data of Table 8.4 and the discussion of Martel et al. (1990), Ballentine and Burnard (2002), and Tolstikhin et al. (1996) it would appear that a calculated \(^3\)He/\(^4\)He production ratio is likely good to no better than one significant figure or may be as poor as 10x. The best way to determine the \(^3\)He/\(^4\)He production ratio is by collecting a number of \(^3\)H free groundwater samples from the aquifer and use the component separation process described below.
Separation of He Components

As multiple He sources are likely in groundwater systems and each source may have a different isotope composition, separating the various components and specifically identifying the He isotope ratio associated with that component can improve the analysis of He. Transforming the isotopic mass balances for $^{4}\text{He}$ and $^{3}\text{He}$ (e.g., eqn 2) to a measured ratio:

$$
\left(\frac{^{3}\text{He}}{^{4}\text{He}}\right)_{\text{tot}} = \left(\frac{^{3}\text{He}}{^{4}\text{He}}\right)_{\text{measured}} = \frac{^{3}\text{He}_{eq} + ^{3}\text{He}_{exc} + ^{3}\text{He}_{terr} + ^{3}\text{He}_{is}}{^{4}\text{He}_{eq} + ^{4}\text{He}_{exc} + ^{4}\text{He}_{is} + ^{4}\text{He}_{terr}}
$$

(16)

where $^{3}\text{He}_{tri}$ is tritogenic $^{3}\text{He}$ and $^{3}\text{He}_{is}$ and $^{3}\text{He}_{terr}$ represent in situ produced and terrigenic contributions, respectively. The latter two contain He of radiogenic, nucleogenic, and sometimes mantle origin. Using the method of Weise (1986; see also Weise and Moser, 1987; Stute et al., 1992b, Castro et al., 2000) yields an equation in the form of $(y)=\left[m\right]\times+b$.

$$
\left(\frac{^{3}\text{He}_{tot} - ^{3}\text{He}_{exc}}{^{4}\text{He}_{tot} - ^{4}\text{He}_{exc}}\right) = \left[ \frac{^{3}\text{He}_{eq}}{^{4}\text{He}_{eq}} + \frac{^{3}\text{He}_{terr}}{^{4}\text{He}_{terr}} \right] \cdot \frac{^{4}\text{He}_{eq}}{^{4}\text{He}_{tot} - ^{4}\text{He}_{exc}} + R_{is,terr}
$$

(17)

where $R_{is,terr}$ represents the $^{3}\text{He}^{4}\text{He}$ ratio originating from both in situ and terrigenic sources. We merge them into one isotope ratio, because they are difficult to separate based on field measurements only.

$$
R_{is,terr} = \frac{^{3}\text{He}_{is,terr}}{^{4}\text{He}_{is,terr}} = \frac{^{3}\text{He}_{is} + ^{3}\text{He}_{terr}}{^{4}\text{He}_{rad} + ^{4}\text{He}_{terr} + ^{4}\text{He}_{man}}
$$

(18)

Because radiogenic and mantle helium may both contribute to in situ and terrigenic $^{4}\text{He}$, the graphical determination of the ratio $R_{is,terr}$ provides specific information regarding the source of non-atmospheric $^{4}\text{He}$ in the system. The y-axis is the measured $^{3}\text{He}^{4}\text{He}$ isotope ratio corrected for the excess air addition; the x-axis measures the relative importance of $^{4}\text{He}_{eq}$ to the other $^{4}\text{He}$ components minus $^{4}\text{He}_{exc}$. $^{3}\text{He}_{exc}$ can be either derived from Ne measurements using eqn (5) or by using concentrations of all stable noble gases and the inverse model as discussed above (Aeschbach-Hertig et al., 2000, 2001).

Data plot along linear (He component) mixing lines if $R_{is,terr}$ is constant for the data set and if the amount of $^{3}\text{He}_{eq}$ is constant or negligible (Fig. 8.10a). If $^{3}\text{He}_{tri}$ is present, data will scatter somewhat around the mixing line, because the variable $^{4}\text{He}_{eq}$ is part of the slope in eqn (17). However, the temperature and recharge elevation dependence of $^{4}\text{He}_{eq}$ is small and slopes typically do not vary by more than 2% due to this effect. The addition of mantle-derived helium (assuming $R_{man} = 1.2 \times 10^{-5}$, e.g. Craig and Lupton, 1981) increases the y-axis intercept, while the presence of $^{3}\text{He}_{tri}$ anchors the right end of the mixing lines (Fig. 8.10a). If $R_{is,terr}$ is variable in a data set and $^{3}\text{He}_{eq}$ is present and variable, He components cannot be separated in a unique way. Assuming that the pre-nuclear bomb $^{3}\text{H}$ concentrations in precipitation were fairly constant, a $^{3}\text{H}$ measurement on the samples can be used as an indicator of anthropogenic $^{3}\text{He}_{tri}$ and serve as a flag for those cases where a separation may be more complicated or impossible. It should be noted that the area underneath the lowest mixing line in Fig 8.10a is a forbidden area because no known process can produce data that fall into this domain. Similar appearing graphs can be obtained by plotting $^{3}\text{He}^{4}\text{He}_{tot}$ versus Ne$^{4}\text{He}_{tot}$ or just versus $^{4}\text{He}_{tot}$. However,
because of variable amounts of \(^{4}\)He\(_{\text{exc}}\) it is not possible to draw accurate mixing lines in these diagrams.

As an example of the component separation, the He data set from the Great Hungarian Plain aquifers (Stute et al., 1992b) is discussed. For the purpose of this paper, He\(_{eq}\) and Ne\(_{eq}\) were calculated using the solubility data of Weiss (1971), assuming an elevation of the recharge area of 200m and an average recharge temperature of 6±6°C, which covers the glacial/interglacial temperature range derived from noble gas temperatures in the Great Hungarian Plain (Stute, 1989; Stute and Deák, 1989). He\(_{\text{exc}}\) was then determined with eqn (5) by using Ne concentration data.

Samples from recharge areas (characterized by a downward hydraulic gradient) and samples containing \(^{3}\)H>1 TU at the time of sampling (1985) are highlighted by open symbols (Fig. 8.10b). Error bars reflect 1σ analytical errors and the uncertainty in recharge temperature. The inverse model (Aeschbach-Hertig et al., 2000, 2001, discussed above) was also used to determine He\(_{\text{exc}}\) from all the noble gas concentrations. It yields slightly smaller error bars, but the two plots (not shown) are identical within the error bars of Fig. 8.10b.

Assuming \(^{3}\)He\(_{\text{tri}}\) = 0, the upper limit of R\(_{\text{is,terr}}\) may be estimated by placing an envelope line below the data points (Fig. 8.10b). The resulting intercept with the y-axis, \((4±4) \times 10^{-6}\) is consistent with isotope ratios of He released from sediments (e.g. Mamyrin and Tolstikhin, 1984) and is our best estimate for the \(^{3}\)He\(_{\text{nuc}}/^{4}\)He\(_{\text{rad}}\) ratio in the Great Hungarian Plain. If R\(_{\text{is,terr}}\) is assumed to be constant, data points above the lower line in Fig. 8.10b have to contain either \(^{3}\)He\(_{\text{tri}}\) or \(^{3}\)He\(_{\text{man}}\). There are no \(^{3}\)H data for many of the deeper samples. However, they can be assumed to not contain \(^{3}\)H because of their low radiocarbon contents (Stute and Deák, 1989; Stute et al., 1992b). Samples from the recharge areas plot slightly above the lower envelope line and are unlikely to contain significant amounts of mantle He. \(^{3}\)H measurements indicate that samples are of pre-nuclear bomb test origin. The sum of derived \(^{3}\)He\(_{\text{tri}}\) (1.6±1.7TU) and measured \(^{3}\)H (0.5±0.2TU) is (2.1±1.7)TU, providing an estimate of the natural \(^{3}\)H in recharge before anthropogenic \(^{3}\)H was added to the hydrologic cycle. This value is lower than the pre-bomb estimate by Roether (1967) of (5±1.5) TU, possibly as a result of partial loss of \(^{3}\)He\(_{\text{tri}}\) across the water table due to low recharge rates in Hungary (Schlosser et al., 1989; Stute et al., 1992b). Samples from the recharge areas plot slightly above the lower envelope line and are unlikely to contain significant amounts of mantle He. \(^{3}\)H measurements indicate that samples are of pre-nuclear bomb test origin. The sum of derived \(^{3}\)He\(_{\text{tri}}\) (1.6±1.7TU) and measured \(^{3}\)H (0.5±0.2TU) is (2.1±1.7)TU, providing an estimate of the natural \(^{3}\)H in recharge before anthropogenic \(^{3}\)H was added to the hydrologic cycle. This value is lower than the pre-bomb estimate by Roether (1967) of (5±1.5) TU, possibly as a result of partial loss of \(^{3}\)He\(_{\text{tri}}\) across the water table due to low recharge rates in Hungary (Schlosser et al., 1989; Stute et al., 1992b). Assuming \(^{3}\)He\(_{\text{nuc}}/^{4}\)He\(_{\text{rad}}\) = 4±4 \times 10^{-6}, \(^{3}\)He\(_{\text{tri}}\) = 1.6±1.7TU and R\(_{\text{man}}\) = 1.2±0.1 \times 10^{-5} are representative for the Great Hungarian Plain, the mantle component \((^{4}\)He\(_{\text{man}}/^{4}\)He\(_{\text{is}}+^{4}\)He\(_{\text{terr}}\)) yields values up to 16%, consistent with the geologic history of the Pannonian Basin undergoing extension. A detailed discussion of this He data set can be found in Stute et al. (1992b).

**Nucleogenic and Fissionogenic Noble Gases: \(^{1}\)Ng\(_{\text{nuc}}\) \(^{1}\)Ng\(_{\text{fiss}}\)**

The contribution of nucleogenic and fissionogenic processes in the production of other noble gas isotopes can be an important diagnostic for \(^{4}\)He. In particular, nucleogenic \(^{20,21,22}\)Ne and fissionogenic \(^{83,84,86}\)Kr and \(^{129,131,132,134,136}\)Xe can be produced although only the dominant isotopes can be observed in very old groundwater systems (Lippman et al., 2002; Kennedy et al., 2002). In such cases, the nucleogenic isotope and fissionogenic isotope accumulation can be compared to the accumulation of \(^{4}\)He. IF the release factor for each noble gas isotope is assumed to be \(\Lambda_{\text{Ng}}=1\), then apparent \(^{21,22}\)Ne, \(^{86}\)Kr and \(^{136}\)Xe tracer-model ages should concur with apparent \(^{4}\)He tracer-model ages. However, because D\(_{\text{Ng}}\) decreases with increasing atomic mass, the release factor for each noble gas is likely to follow the order \(\Lambda_{\text{He}} > \Lambda_{\text{Ne}} > \Lambda_{\text{Kr}} > \Lambda_{\text{Xe}}\) (Drescher et al., 1998), and one might expect the simple noble gas tracer-model age (\(\tau_{\text{Ng}}\)) to reflect the order \(\tau_{\text{He}} > \tau_{\text{Ne}} > \tau_{\text{Kr}} > \tau_{\text{Xe}}\). Such diagnostics can be critical in the evaluation of noble gas model ages from very old groundwaters (e.g. Lippman et al., 2002).
including the aquitard. $^{3}\text{He}/^{4}\text{He}$ ratios can often suggest a terrigenic (external) contribution to the groundwater especially where aquitard rock has significantly different bulk compositions than the aquifer rock although the reader is cognizant of the error in calculation of the $^{3}\text{He}/^{4}\text{He}$ production ratio. However, because the external terrigenic sources are not known a priori, a comparison to the possible production ratio calculated for an adjacent rock may not constrain the problem when the observed anomalous isotopic composition could also be explained by a mixture between local aquifer rock and an external “exotic” rock. While one could feel fairly confident regarding the input of a mantle source of $^{3}\text{He}$, calculation of a per cent mantle contribution is potentially misleading because the mantle endmember has inherent variability (hot spots have $^{3}\text{He}/^{4}\text{He}$ ratios of 4-35Ra where Ra is the ratio in air Ra=1.384x10$^{-6}$, Clarke et al., 1976) and such ratios will also vary with the age (time since eruption; Torgersen, 1993; Torgersen et al., 1994). This suggests that evidence of a non-local contribution (Ng$^{\text{terr}}$) based on measured isotopic ratios should be seen as evidence to evaluate and model several different mechanisms by which such observations could be produced and observed in situ. The calculation of the per cent mantle $^{3}\text{He}$ contribution when that mantle source is order millions of years old begins to lose meaning.

**The Special Case of $^{40}\text{Ar}$**

The above discussion can be generalized to include $^{40}\text{Ar}_{\text{rad}}$ which is the decay product of $^{40}\text{K}$. The production rate for $^{40}\text{Ar}_{\text{rad}}$ (atoms g$^{-1}$ yr$^{-1}$) is:

$$^{40}\text{Ar}_{\text{rad}} = 102.2[K]$$

where [K] is the concentration of potassium in ppm. The $^{4}\text{He}_{\text{rad}}/^{40}\text{Ar}_{\text{rad}}$ production ratio can be derived from eqn (19) and eqn (7) to give:

$$^{4}\text{He}_{\text{rad}}/^{40}\text{Ar}_{\text{rad}} = \{3.242 \times 10^6[U] + 7.710 \times 10^5[Th]\}/\{102.2[K]\}$$

In many cases, $^{40}\text{Ar}_{\text{rad}}$-model ages can be calculated for comparison to $^{4}\text{He}$-model ages. For the calculation of $\Lambda_{^{40}\text{Ar}_{\text{rad}}}$, the above criteria generally apply. However, note that K is typically associated with major phases within the rock whereas U-,Th- series elements are associated with minor phases. In this sense, K may be located in very large grains and/or U,Th may be associated with the surface of grains. Thus, it is often encountered that release factor for $^{40}\text{Ar}_{\text{rad}}$ ($\Lambda_{^{40}\text{Ar}_{\text{rad}}}$) is less than release factor for $^{4}\text{He}$ ($\Lambda_{^{4}\text{He}_{\text{rad}}}<\Lambda_{^{40}\text{Ar}_{\text{rad}}}$). This has been confirmed by the experiments of Krishnaswami and Seidemann (1988) and is intuitive with regard to the difference in their respective diffusion coefficients (D$_{\text{Ar}}$/D$_{\text{He}}$=10$^{-5}$-10$^{-6}$, see Ballentine and Burnard, 2002; their Table 9 for calculating diffusion coefficients). Alternatively, the combination of grain size and diffusion coefficient may have enabled $^{4}\text{He}$ to reach steady-state after comminution whereas the slower loss of $^{40}\text{Ar}_{\text{rad}}$ may still impose a local input of $^{40}\text{Ar}_{\text{rad}}$ that is significantly in excess of local production (Torgersen and O’Donnell, 1991). Thus, $^{40}\text{Ar}_{\text{rad}}$-model ages can be non-confirmatory of $^{4}\text{He}$-model ages but yet still provide knowledge about process within the aquifer system. This separation of $^{4}\text{He}$ and $^{40}\text{Ar}_{\text{rad}}$ can be explicitly seen as noble gases accumulate in oil production reservoirs (see Fig. 8.11). Initially, with short times suggested by low concentrations of $^{4}\text{He}$ or small $^{40}\text{Ar}/^{36}\text{Ar}$ ratios, $^{4}\text{He}/^{40}\text{Ar}_{\text{rad}}$ ratios are far in excess of in situ production. However with time and the integrated accumulation of the late release of $^{40}\text{Ar}_{\text{rad}}$, the $^{4}\text{He}/^{40}\text{Ar}_{\text{rad}}$ ratio approaches that typical of crustal production (~ 5, Torgersen et al., 1989).

In the case where $^{40}\text{Ar}_{\text{rad}}$ and $^{4}\text{He}$ may both have viable external (to the aquifer) sources ($^{40}\text{Ar}_{\text{rad}}^{\text{terr}}$ and $^{4}\text{He}_{\text{rad}}^{\text{terr}}$), the above possibilities with respect to relative release factors in the external source apply. Additionally, diffusive transport into the local water parcel may
separate $^{40}\text{Ar}_{\text{rad}}$ and $^4\text{He}_{\text{rad}}$. Torgersen et al. (1989) found that the Great Artesian Basin was dominated by external fluxes of $^4\text{He}_{\text{rad}}$ and $^{40}\text{Ar}_{\text{rad}}$ both of which were approximated by the whole crustal rate of in situ production (with some degree of variation). Yet Torgersen et al. (1989) emphasize that $^{40}\text{Ar}_{\text{rad}}$ has spatial heterogeneity not apparent in $^4\text{He}_{\text{rad}}$. Additionally, Castro et al. (1998ab) found that diffusive separation of $^4\text{He}_{\text{rad}}$ and $^{40}\text{Ar}_{\text{rad}}$ across aquitards within the Paris Basin created differing and contrasting mechanisms of $^4\text{He}_{\text{rad}}$ or $^{40}\text{Ar}_{\text{rad}}$ accumulation in different layers. Thus, a comparison of terrigenic $^{40}\text{Ar}_{\text{rad}}_{\text{terr}}$ and $^4\text{He}_{\text{rad}}_{\text{terr}}$ may again not be confirmatory and $^{40}\text{Ar}_{\text{rad}}$ requires additional boundary and initial conditions that make any solution non-unique.

SUMMARY

The various components that contribute to the total measured $^4\text{He}$ in a groundwater sample show noble gas isotopic measures in addition to $^4\text{He}$ are a requirement for the separation of components. Furthermore, the overall complexity of noble gas groundwater processes suggest any tracer-model age calculation should be cross-checked with other methods (e.g., $^{36}\text{Cl}$, $^{40}\text{Ar}_{\text{rad}}$). It is then necessary to use such information within a simplified basin flow model (Fritzel, 1996; Zhao et al., 1998; Castro et al., 1998ab, 2000; Bethke et al., 2002; Castro and Goblet, 2003; Bethke and Johnson, 2008;) to arrive at the best conceptualization of the aquifer and its timescale of transport which may still provide a non-unique solution.

CASE STUDIES

Setting the Stage

In spite of the potential for the application of $^4\text{He}$-model ages to groundwater transport, it was recognized early that the method raises considerable questions. Geochemists are of necessity skeptical of direct application of concepts and have rightly devoted considerable time to testing the underlying assumptions for the use of $^4\text{He}$ in groundwater systems. Marine (1979) evaluated $^4\text{He}$-model ages in groundwater based on assumptions regarding $\Lambda_{^4\text{He}}$ but cross-checked $\Lambda_{^4\text{He}}$ with measures from the solid phase indicating $0.73 < \Lambda_{^4\text{He}} < 0.97$. However, his analysis did not include external, open system sources of $^4\text{He}$ (large fluxes from the crust and/or aquitards) that could transport $^4\text{He}$ into the system. (Note that solid phase measures indicating $\Lambda_{^4\text{He}} \sim 1.0$ almost demands a resultant crustal flux.) Andrews and Lee (1979) evaluated $^4\text{He}$-model ages in groundwater based on assumptions regarding $\Lambda_{^4\text{He}}$ but cross-checked such ages with $^{14}\text{C}$ analysis. The results indicated significant excess $^4\text{He}$ ($4x$) and excessively large $^4\text{He}$-model ages. Torgersen (1980) evaluated $^4\text{He}$-model ages based on only-local sources from gas wells, geothermal systems and groundwater and found $^4\text{He}$-model ages order 1000x in excess of $^3\text{H}$-$^3\text{He}$ model ages for cold springs. Heaton (1984) compared $^4\text{He}$-model ages to $^{14}\text{C}$-model ages for two aquifer systems and found only-local source $^4\text{He}$-model ages were 10-100x the calculated $^{14}\text{C}$-model ages. Heaton (1984) calculated the rate of $^4\text{He}$ addition due to weathering (dissolution) input of $^4\text{He}$ (see Torgersen, 1980) but dismissed that source as insignificant. Torgersen and Clarke (1985) also evaluated a $^4\text{He}$ source associated with weathering input and also found that source to be insignificant. Notable in the Heaton (1984) and Torgersen and Clarke (1985) studies was an increase in the rate of $^4\text{He}$ accumulation down the presumed flowline (assuming a flow model). These studies clearly demonstrated an inherent complication in the calculation of $^4\text{He}$-model ages in groundwater that had yet to be specifically identified although Heaton (1984) did note that an external flux of $^4\text{He}$ from below the aquifer could be an important source.

Simple Open System Aquifer Models
In a study of the Great Artesian Basin (GAB) in Australia, Torgersen and Clarke (1985) and Torgersen and Ivey (1985) had the good fortune of evaluating a well-defined system with existing and available hydraulic ages (flow-model ages based on Darcy’s Law), $^{14}$C-model ages and $^{36}$Cl-model ages (Airey et al., 1979, 1983; Bentley et al., 1986). After evaluating local $^4$He production and its downflow variability via $^{222}$Rn, in situ U-,Th-series abundances and possible sources via weathering release from the solid phase, Torgersen and Clarke (1985) concluded $^4$He in the Great Artesian Basin must have a dominant external source from outside (below) the aquifer. A key component in this analysis is that simple local-source-only $^4$He concentrations agree with $^{14}$C-model ages and hydraulic flow-model ages for timescales less than 40kyrs. Yet for longer timescales, $^4$He concentrations exceed the local-source-only $^4$He concentration by 74x (see Fig. 8.2). Within this largely uniform aquifer, the local-source-only production rate is likely to be constant throughout the aquifer without large scale variation and this was confirmed with $^{222}$Rn analyses (Torgersen and Clarke, 1985). Torgersen and Ivey (1985) used a simple, piston–flow, 2D model adapted from Carslaw and Jaeger (1957) which included a 2D aquifer of uniform vertical diffusion and uniform horizontal velocity:

$$v_x \frac{\partial C}{\partial x} = D_z \frac{\partial^2 C}{\partial z^2} + I \quad (21)$$

With $v_x$, $D_z$ and I constant, a constant flux across the bottom boundary and zero flux across the top boundary, Torgersen and Ivey (1985) were able to evaluate the variability of $^4$He as a tracer of groundwater processes rather than as a groundwater dating methodology. They demonstrated the change in the apparent rate of $^4$He accumulation with time/distance along the aquifer was related to the time needed to diffuse a bottom boundary flux vertically through the aquifer. Secondly, they were able to demonstrate that the external bottom flux dominated the sources of $^4$He at long timescales. Although the simple Torgersen and Ivey (1985) model did not allow a loss term for the $^4$He flux out the top of the aquifer, their analysis shows that such a flux would be minimal on the timescale of the GAB system. Their analysis proceeded to evaluate simply the parameter sensitivity of the tracer flow model (from Carslaw and Jaeger,1957) by evaluating the sensitivity of the $^4$He measures obtained with regard to relative depth within the aquifer, aquifer thickness, aquifer porosity and the vertical rate of diffusion/dispersion. The model was also applied to the Aoub sandstone data of Heaton (1981) which was much thinner and much younger and allowed a sensitivity analysis of the impact of the bottom boundary input flux. Castro et al. (2000) ultimately re-sampled and re-evaluated the (Stampriet) Aoub aquifer (Heaton, 1981, 1984) and obtained a bottom boundary $^4$He flux ~2x larger than estimated by Torgersen and Ivey (1985). Castro et al. (2000) additionally quantified the Carrizo aquifer in Texas and the Ojo Alamo and Nacimiento aquifers (San Juan Basin, New Mexico). These crustal fluxes are reported in Table 8.2. Torgersen et al. (1989) showed the accumulation of $^{40}$Ar$_{rad}$ from an external bottom boundary flux of $^{40}$Ar$_{rad}$ in the GAB system also dominated in situ production of $^{40}$Ar$_{rad}$ in the aquifer. The key contribution of these papers is the transition from a theoretical calculation of a $^4$He-model age to the incorporation of $^4$He into simplified groundwater flow models as a component subject to reaction and transport in the groundwater systems. As such, $^4$He allows finer scale tuning of knowledge about transport, mixing, sources and sinks to/in aquifer systems. The disadvantage is that some prior knowledge about the structure of the aquifer system is required.

Stute et al. (1992b) use a 2D model of flow in the Great Hungarian Plain with a bottom boundary flux equivalent to 0.25x the value of Torgersen and Ivey (1985; equivalent to whole crustal production) but allowing flux out the top boundary. Fitting the observed $^4$He and $^3$He concentrations to the 2D model, Stute et al. (1992b) were able to constrain vertical flow velocities in this aquifer system and provide an estimate of groundwater turnover in the system.
to be order $10^5$ yrs. An important contribution of this work is the ability to examine the discharge region of an aquifer system in terms of the Peclet number ($\Delta zv_z/D_z$) which defines the basic transport of the system. Castro et al. (2000) further evaluated the model of Torgersen and Ivey (1985) for the Carrizo aquifer system and verified the basic assumptions of the system including the assumption of a topmost no-flux boundary. Although emphasizing that fluxes across boundaries can be the result of advection, dispersion and diffusion, they conclude that many systems are sufficiently young or short to operate AS IF there was no flux across the top boundary. The corollary to this observation is that $^4$He fluxes measured at the land surface will be highly variable; for such an aquifer, the flux leaving the ground surface to the atmosphere will be very low while the $^4$He flux to the atmosphere at the discharge zone will be very high. The transport properties and mechanisms of the continental crust dictate a high degree of spatial variability.

$^4$He as a component in Groundwater flow Models Evolves

Fritzel (1996) and Zhao et al. (1998) inserted $^4$He (and $^3$He) within established (Bethke, et al., 1993) groundwater flow models. Zhao et al. (1998) show (Fig. 8.12) that for a base case (in situ production plus a large basal bottom flux; Fig. 8.12.2), $^4$He in the vertical section of the aquifer increases from the top to the bottom reflecting the importance of the basal flux. However, for the exemplar case in which the bottom boundary flux is insignificant (Fig. 8.12.3), the $^4$He concentration in the aquifer increases from the top to bottom reflecting the importance of “old water” in the upper confining shale as a source of high $^4$He concentration. The Zhao et al. (1998) examination of an irregular basal flux (Fig. 8.12.4) shows that if $^4$He basal flux is confined to an area 1/10 the original and is 10x the original, then $^4$He decreases downstream of the basal flux region as a result of hydrodynamic dispersion and mixing. As shown by both Torgersen and Ivey (1985) as well as Zhao et al. (1998), increasing the vertical rate of dispersion/mixing results in a shorter period of local in situ production dominance, less vertical variation and a system dominated by horizontal variability over vertical variability (Fig. 8.12.5). Zhao et al. (1998) also evaluate the impact of subregional flow cells induced by basin topography as a control on aquifer $^4$He distribution (Fig. 8.12.6). These studies show how the quantification of large scale average aquifer transport properties can be fine-tuned with the inclusion of $^4$He in reaction and transport models even under conditions where the details of the basal flux variability may not be explicitly defined.

Bethke et al. (1999) re-evaluated the $^4$He data of Torgersen and Clarke (1985) with the helium capabilities of the enhanced basin flow model (Bethke et al., 1993). They show that $^4$He measurements obtained in the upper 20% of the aquifer vertical section are controlled not only by the lateral flow ($v_x$) and the vertical mixing ($D_z$) of the basal flux up into the aquifer, but also by the vertical water velocity encountered in the recharge area and the discharge area, a subject that was also addressed in simpler form by Stute et al. (1992b). Such dependency is not discernable in the simplistic model of e.g. Torgersen and Ivey (1985) because it is based on a piston flow concept. Significantly, Bethke et al. (1999) were able to address the high concentrations and variability of $^4$He in this GAB aquifer system without resorting to stagnant zones (Mazor, 1995). This did much to reconcile the geochemical concepts of $^4$He inputs, sources and accumulation with established concepts of flow in large aquifer systems. Bethke et al. (2000) combined the use of $^{36}$Cl and $^4$He to conclude that isotope distributions can be used to obtain internally consistent descriptions of deep groundwater flow directions and rates.

Castro et al. (1998ab) used a finite element code model of transport in the Paris Basin (Wei et al., 1990) with multiple aquifers arranged vertically. Within this study, Castro et al. (1998ab) examined the vertical flux of not only $^4$He and $^3$He but also $^{40}$Ar$_{rad}$ and $^{21}$Ne. This study demonstrated the potential for diffusive separation of noble gases as they are transported across various aquitards in the system (very small Peclet numbers). While this analysis is not disputed here, Castro et al. (1998) admit “the model is extremely sensitive to parameter
variations, in particular to changes in flow rate and permeability”. Given the degree of structural complexity in the model, the sheer number and spatial variability of parameters that control water flow and noble gas transport; together with the relatively few noble gas measures and aquifer transport parameter measures from the Paris Basin, the question is raised as to whether the conclusion (diffusion controlled separation of $^4$He and $^{40}$Ar$_{rad}$) is unique. Sensitivity to parameter choice/variability is an important constraint in modeling and the tests run by Zhao et al. (1998) (see Fig. 8.12) and Bethke et al. (2000) provide for greater interpretation around the conclusions. The study of Castro and Goblet (2003) in the Carrizo aquifer system suggests that $^4$He can and often does constrain the conceptual transport model for the aquifer system as only one of five conceptual models of the Carrizo successfully captured the $^4$He distributions that had been measured. Berger (2008; reported in Bethke and Johnson, 2008) used the Paris Basin model and optimized the flow field with constraints provided by $^4$He, head, salinity and temperature.

Bethke and Johnson (2008) discuss in detail the use of $^4$He, $^{36}$Cl etc. as tracers in groundwater modeling and assimilate a rigorous definition of groundwater age. Because groundwater flow systems are subject to lateral dispersion/diffusion, vertical groundwater velocity distributions resulting from recharge area downflow and discharge area upflow as well as convergence and divergence of streamlines, the concept of groundwater age incorporates many complexities as discussed in Chapter 3. The interpretation of e.g. a$^4$He-model age as an idealized groundwater age is thus specific and limited. The most important of the groundwater flow field complexities is the mixing of water parcels. Such issues of groundwater mixing are well established in short timescale groundwater flow where multiple tracers ($^3$H-$^3$He, CFC, bomb $^{14}$C, etc) are often used to quantify both $v_x$ and $D_x$ in a 1D system (e.g. Ekwurzel et al, 1994; Plummer et al, 2004). This is possible because the input function for $^3$H is much different than e.g. the input function for CFCs and a comparison of the distribution of both tracers enables the quantification of two controlling parameters. In very old groundwater systems, the viable groundwater “dating” methods are $^{14}$C, $^4$He, $^{81}$Kr and $^{36}$Cl. Since $^4$He is typically controlled by (1) an internal production of $^4$He that is often constant and (2) a large external flux that may be assumed to be constant, the use of combined dating methods of e.g. $^4$He and $^{36}$Cl (with its exponential decay control) provides a powerful means by which to constrain the parameter values describing flow and mixing in aquifer systems although model optimization with other tracers including temperature (Berger, 2008) are possible and enlightening.

**SUMMARY**

The concept of using $^4$He to derive an idealized groundwater age has largely been abandoned in favor of the use of $^4$He (other noble gas isotopes, $^{36}$Cl and $^{81}$Kr) as a component in groundwater reaction and transport models to constrain the complexity of transport in specific aquifers. The inclusion of $^4$He in standard groundwater transport models has the ability to constrain the fundamental aquifer flow conceptualization as well as to refine the quantification of the controlling flow parameter values and their distribution. Building such conceptual transport models of aquifer systems requires some degree of fore-knowledge about the basic aquifer structure, the general transport properties of the structure (hydraulic conductivity of the aquitards vs. hydraulic conductivity of the aquifer) as well as the in situ $^4$He production (concentration of U, Th and porosity) of the basin structural components. In such cases, the use of $^4$He and adequate samples of $^4$He across the groundwater flow system can provide significant constraints on flow. Still to be addressed however, are systems for which little structural information is known and for which the basic parameters controlling flow are poorly known in space/time. These issues are exemplified by drillhole sampling that present unique opportunities and problems.
CONCEPTUAL $^4$He MODEL AGES AS A CONSTRAINT ON GROUNDWATER “AGE”

The material presented above shows the simple concept of $^4$He-model ages as a proxy for idealized groundwater age is likely inapplicable in most systems. This does not negate the value of $^4$He tracer applications, but it does imply that the physical meaning of the $^4$He-model age must be evaluated. Simple $^4$He-model age calculations in the idealized 1D system (piston flow and vertical gradients of $^4$He as a result of bottom flux) demonstrate that direct comparison of 1D piston flow-model ages and $^4$He-model ages are inappropriate at best. And, the possibility that a bottom boundary flux could also be lost out the top of the control volume further indicates that the $^4$He-model age calculated is applicable only to $^4$He and that it has no parallel in groundwater flow.

The calculation of a $^4$He-model age in most cases will involve the amount of $^4$He in a control volume (atoms m$^{-3}$) as well as fluxes (atoms m$^{-2}$ s$^{-1}$) across boundaries of that control volume. This necessitates the definition of a layer thickness to which the $^4$He concentration measures apply. Even if one can obtain closely spaced $^4$He concentrations to define a gradient, one would be pressed to define whether the influx across the bottom boundary is advection controlled or diffusion controlled and knowledge of $v_z$ and/or $D_z$ would require additional knowledge about the aquifer structure, its composition and its transport properties. The calculation of $^4$He-model age as a proxy for groundwater age thus becomes a geochemical “artform”.

Calculations of the $^4$He-model age are more specifically generalized as:

$$
\tau_{He} = \left[ \Lambda_{He} J'_{He} \rho_{rock} \frac{1 - \Phi}{\Phi} + \frac{\Sigma F_{He}}{\rho_{H2O} \Phi z} \right]^{-1}
$$

(22)

where $J'_{He}$ is the internal rate of $^4$He production from U-,Th-series decay (eqn 6,7) $\rho_{rock}$ is rock density, $\rho_{H2O}$ is water density, $\Phi$ is porosity, $\Sigma F_{He}$ are the boundary fluxes of $^4$He into/out-of the system (atoms m$^{-2}$ yr$^{-1}$) of thickness $z$ (m). The first term in the (…)$^{-1}$ bracket represents the local source of $^4$He as a result of local U-,Th-series element decay and the second term in the (…)$^{-1}$ bracket represents the external flux to the system across a (bottom) boundary. The “artform” comes not only in choosing $\Lambda_{He}$, $F_{He}$ and $z$ but also in explicitly defining meaning for $\tau_{He}$ in relation to a $^4$He-model age and an idealized groundwater age. One example is the case where the vertical flux through the system has reached a steady state and the flux into the bottom is equal to the flux out the top. $\Sigma F_{He}$ for this case is zero but the concentration in the vertical position is linearly variable giving linearly variable $^4$He-model ages in the vertical. The loss terms will be specifically avoided in the following analysis for this reason. Nonetheless, the concept of a $^4$He-model age calculation is worth exploring in unique opportunities.

$^4$He fluxes determined by vertical borehole variation in $^3$He/$^4$He

Sano et al. (1986) examined natural gas wells in Taiwan and identified a $^3$He/$^4$He ratio that decreased as samples approached the surface. This scenario can be modeled if the base of the system is “tagged” with mantle $^3$He ($^3$He/$^4$He $\sim 10^{-5}$) signature, the system is vertically controlled and in situ production by radioactive decay of U-,Th-series elements in the layer (thickness=$z_i$) between measures supplies an input of crustal He of known ratio ($^3$He/$^4$He $\sim 10^{-6}$) that dilutes the mantle $^3$He flux with crustal production as it is transported vertically in the rock column. For a horizontally homogeneous system with both a $^3$He-enriched component at depth and an in situ production of helium, the flux of helium from the top of the layer ($F_1$) is (generalized from Sano et al., 1986):
and the flux into the bottom of a layer \((F_2)\) is:

\[
F_2 = \frac{P_i z_i (R_1 - R_i)}{(R_2 - R_i)}
\]  

where \(P_i\) is the production rate of \(^{4}\text{He}\), \(R_1\) and \(R_2\) are the isotopic ratios of \(^{3}\text{He}/^{4}\text{He}\) at the top and bottom of the layer respectively and \(R_i\) is the production ratio of \(^{3}\text{He}/^{4}\text{He}\) in the layer, and \(z_i\) is the thickness of a layer. If the system contains multiple layers with differing rates of in situ production, the appropriate equations are:

\[
F_i = \frac{\sum P_i z_i R_1 - \left[ \sum P_i z_i \right] R_2}{(R_1 - R_2)}
\]

\[
F_2 = F_i - \sum P_i z_i
\]  

where \(P_i\) is the in situ production of individual layers between the surfaces defining \(F_1\) and \(F_2\). Using eqn (23,24), Sano et al. (1986) quantified the fluxes of \(^{4}\text{He}\) in two Taiwan natural gas to be \(2.7 \pm 0.6 \times 10^{10}\) atoms \(^{4}\text{He}\) m\(^{-2}\) s\(^{-1}\) and \(2.4 \pm 0.8 \times 10^{10}\) atoms \(^{4}\text{He}\) m\(^{-2}\) s\(^{-1}\) (Table 8.2). These continental degassing fluxes are in agreement with measures from the Great Artesian Basin (Torgersen and Clarke, 1985; Torgersen and Ivey, 1985) and the atmospheric mass balance (Torgersen, 1989) and could have been used to calculate apparent \(^{4}\text{He}\)-model ages as per eqn (22). Torgersen and Marty (unpublished) applied such relations to the Paris Basin and obtained ages that were roughly 10x larger for the Dogger aquifer than have been obtained by Castro et al. (1998ab) using a full scale hydrologic flow model. These results suggest that although the mathematics of the approach is appealing, the underlying assumptions are likely too restrictive to apply to the general case. It would be interesting to apply eqn (23-26) to modeled results of (e.g.) Zhao et al. (1998) to determine when/if these simple relations have meaning.

**Cajon Pass**

Torgersen and Clarke (1992) evaluated the \(^{4}\text{He}\)-model age for waters collected in the Cajon Pass scientific drillhole to constrain groundwater flow and heat transport in and around the San Andreas Fault. Samples were collected with a downhole sampler (Solbau et al. 1986) after the drillhole had been given over wholly to fluid inflow during a prolonged period of no drilling (due to lack of funds). The drillhole was pumped and water remaining was spiked with fluorescein to differentiate contaminant water from fracture water inflow. Specific intervals were packed-off to define layers of fracture water inflow that were allowed to accumulate over periods of months. Careful sampling enabled some vertical structure in the inflow water to be defined but the evaluation of \(^{4}\text{He}\) tracer-model ages were based on bulk concentrations of the fluorescein (contaminate)-corrected inflow water \(^{4}\text{He}\) concentration.

CASE (1) calculations in Torgersen and Clarke (1992) assumed \(F_{\text{He}} = 0\); used a \(\Lambda_{\text{He}}\) value quantified by the \(^{222}\text{Rn}\) concentration after the method of Torgersen (1980); and calculated the source function from U,Th-series decay \((\eta_{\text{He}})\) from estimated rock composition. The resultant apparent \(^{4}\text{He}\)-model age was 0.9-5 Myrs which implies a vertical fluid velocity of
0.04-0.2 cm yr\(^{-1}\) (\(v = \Delta z / \Delta t\) where \(\Delta z = 2000\) m). CASE (2) calculations in Torgersen and Clarke (1992) assumed a release factor of \(\Lambda_{\text{He}} = 1\). The resultant \(^{4}\text{He}\)-model age was 33-330 kyr implying a vertical fluid velocity of 0.6-6 cm yr\(^{-1}\). They further evaluated the possibility of a non-steady state source (loss of \(^{4}\text{He}\) as a result of fracturing (Torgersen and O'Donnell, 1991) which possibly mimics the \(\Lambda_{\text{He}} > 1\) defined by Solomon et al. (1996) and concluded that \(\Lambda_{\text{He}} = 1\) was a good approximation. This gives a range for the vertical fluid velocity of 0.04-6 cm yr\(^{-1}\). We add to their analysis CASE (3) where it is assumed the accumulation of \(^{4}\text{He}\) in the Cajon Pass groundwater was dominated by the crustal degassing flux. Assuming an externally imposed degassing flux equivalent to the whole crustal production and assuming the concentration measured at ~2000 m applies to the whole layer from 0-2000 m depth, a \(^{4}\text{He}\)-model age of 1667 yrs would be calculated giving a vertical fluid velocity of 120 cm yr\(^{-1}\). Torgersen and Clarke (1992) show that excess heat generated by fault zone friction is not significantly removed by vertical fluid flow estimate for CASE (1,2) demonstrating that the San Andreas Fault system is likely a low strength/low coefficient of friction system. Furthermore, the vertical fluid velocity estimated from \(^{4}\text{He}\)-model ages were compared to drillhole well tests that estimate vertical fluid velocities of 10\(^{-5}\) cm yr\(^{-1}\). If one assumes that both quantifications represent reality but over different timescales (the drillstem test provides an estimate of fluid velocity on the timescale of months for a space equivalent to the open hole section; and the \(^{4}\text{He}\) tracer age-based velocity is applicable over the residence time (tracer age) and the 2000 m depth of the sample), then the comparison suggests that fluid transport is episodic with short intervals of rapid fluid transport and longer timescales of very slow fluid transport. Such a conclusion is in agreement with metamorphic geology literature and the mechanisms of fluid transport suggested by Nur and Walder (1990). Adding the CASE (3) does not change the conclusion with regard to episodic transport but it does enable hydrothermal heat flow (estimate < 65-130 W m\(^{-2}\)) to remove any Fault Zone generated heat (estimate < 85-90 W m\(^{-2}\)) IF such a vertical fluid transport rate can be verified. Thus, the principles of \(^{4}\text{He}\)-model age calculations can be applied to constrain systems for which little information is available.

South African Ultra-deep Mine Waters

Lippman et al. (2003) evaluated the noble gas isotope composition of groundwaters collected from seeps in the ultradeep mines of South Africa. They calculated noble gas tracer ages based on \(^{4}\text{He}\), \(^{40}\text{Ar}_{\text{rad}}\), \(^{134}\text{Xe}\) and \(^{138}\text{Xe}\) on the basis of the generalization of eqn (22) from \(^{4}\text{He}\) to other noble gases. Scenario #1 calculations were based on in situ local-only sources of noble gas isotopes (\(\Sigma F_{\text{He}}=0\)) with an assumed \(\Lambda_{\text{He}} = 1\) and \(\Lambda_{\text{Ar}} = 1\). For Xe isotopes, \(0.1 < \Lambda_{\text{Xe}} < 0.5\) was artfully fit based upon a much smaller recoil distance involved in the fissionogenic production of these isotopes. Scenario #2 includes the possibility of a whole crustal production degassing flux (\(F_{\text{He}}=8 \times 10^9\) atoms \(^{4}\text{He}\) cm\(^{-2}\) s\(^{-1}\); see Table 8.2) applicable over the layer from the surface to the depth of sampling. Their calculations indicate noble gas tracer-model ages of the order 10-100 Myrs (scenario #1) and 0.1-20 Myrs (scenario #2). Given that \(^{36}\text{Cl}\) measures in the same water indicate \(^{36}\text{Cl}\)-model ages in excess of 1.5 Myrs, the noble gas estimated ranges for tracer age can be used as a zero order estimate of the idealized groundwater age. The vertical fluid velocities estimated (sample depth is order 2000-3000 m) from these noble gas tracer ages are 0.003-0.02 cm yr\(^{-1}\) which are consistent with hydraulic conductivity in tight rock (Freeze and Cherry, 1978; unfractured metamorphic and igneous rocks assuming hydrostatic gradients) as well as in situ measures of vertical transport rates at Cajon pass (California; Coyle and Zoback, 1988; Torgersen and Clarke, 1992).

Deep Borehole Sampling

Osenbruck (1996) explored a new sampling method for deep borehole rock in which either inflow of water was minimal and/or the restrictions of the drilling schedule/cost were such that direct groundwater sampling was not feasible. The method (Osenbruck, 1996) depends
upon the relatively slow diffusion of noble gases in the matrix porefluids of intact rock (hours) to enable rock sampling (drillcore retrieval) that preserves noble gas concentrations from matrix porefluids recovered from depth. The principle assumption is that matrix porefluids are equivalent to fracture filling porefluids which are likely the major mode of transport. In a typical sampling operation, drillcore is recovered at the surface within hours of being cut and intact rock is subcored to avoid rock on the exterior of the drillcore that had already been micro-fractured and had begun to release porefluids. The subcored rock is then introduced into a vacuum container, purged of air and left either under low N₂ pressure or vacuum for an extended period of time. The natural relaxation of the rock then causes expansion, dilatation and draining of porefluids into the sealed container. The container may be maintained at room temperature or at elevated temperatures (e.g. equivalent to in situ temperatures) to increase the diffusivity in water and thus speed the release of porefluid to the container (Ali et al., 2007, 2008, 2010). Opening the container to the mass spectrometer will then enable measures of the amount of water released as well as the noble gases contained in those porefluids.

Using the method of Osenbruck (1996) to obtain porefluid samples, Osenbruck et al. (1998) explored the tracer-model ages in a potential nuclear waste repository in Morsleben, Germany. Their results show a profile of ⁴He in porefluids that is consistent with vertical diffusive transport in a horizontally homogeneous system. They assume that transport occurs at a rate determined by tortuosity- and porosity-corrected molecular diffusivity and calculate a diffusion coefficient of D=2 x 10⁻⁶ cm²s⁻¹. Using this diffusion coefficient and the measured gradient in porefluid ⁴He concentration, they calculate a vertical flux of 2x10⁻⁷ccSTP⁴He cm⁻² yr⁻¹ which is in agreement with other measured fluxes (see Table 8.2). Using the characteristic timescale for such a steady-state profile to be obtained (from Carslaw and Jaeger, 1957):

\[ \tau = 4 \frac{\Delta x^2}{\pi^2 D} \] (27)

they calculate a lower limit on the porewater age of 6Myr. Here the tracer-model age based on the ⁴He concentration and the sum of the in situ production and the crustal flux can be calculated for comparison. For depths of 300-700m where ⁴He is approximately constant at 4 x 10⁻⁴ ccSTP⁴He g⁻¹H₂O, the tracer-model age is given by eqn (22). The data of Osenbruck et al. (1998) yield 7.5Myr using their calculation of the local crustal flux (which is circular reasoning) or 4.3Myr if the local ⁴He crustal flux is equivalent to the whole crustal production as estimated from the measures of Table 8.2.

The Osenbruck (1996) methodology for sampling porefluids opens the more general case for dating deep borehole porefluids. Drescher et al. (1998) collected deep borehole rock samples from the KTB project (depths from 100-9000m) and measured the solid phase concentration of ⁴He, ⁴⁰Ar rad, ²¹Ne, ⁸⁴,⁸⁶Kr and ¹³⁴,¹³⁶Xe. These are converted to an effective noble gas tracer-model age of the rock which can be compared to the metamorphic age of the rock as determined by e.g. ⁸⁷Sr/⁸⁶Sr, ⁴⁰Ar rad/K and/or other dating methods. The release fraction for each noble gas to the porefluid can then be quantified as (Drescher et al., 1998):

\[ \Lambda_{\text{meas}}^{\text{Ng}} = 1 - \frac{\tau_{\text{rock}}^{\text{Ng}}}{\tau_{\text{meta}}} \] (28)

Direct measurements and eqn (28) (Drescher et al., 1998) indicate the release factor from the KTB borehole rock to be \( \Lambda_{\text{meas}}=0.88±0.11 \) (Fig. 8.13) which is in agreement with the generally assumed value of \( \Lambda_{\text{meas}}=1.0 \). Similar values can be obtained from the case study of Tolstikhin et al. (1996). Assuming the rock samples of Drescher et al. (1998) are representative of the crust,
they imply a crustal flux of 0.88x whole crustal production with similar estimates for \(^{21}\)Ne, \(^{40}\)Ar\(_{\text{rad}}\) and \(^{136}\)Xe (Fig. 8.13). Note that the depth at which these samples were collected removes a significant fraction of the crust as a contributor to the net crustal flux. The approach can be further generalized.

These simple measures of \(\tau_{\text{rock}}\) need to be corrected for the time necessary to establish a gradient through which to diffuse the in situ production. \(\tau_{\text{rock}}\) therefore establishes a minimum constraint on the true value of \(\Lambda_{\text{He}}\) and a best estimate for \(\Lambda_{\text{He}}\) might be:

\[
1 - \frac{\tau_{\text{rock}}}{\tau_{\text{meta}}} < \Lambda \left[ \frac{\text{meas}}{\text{rock}} \right] < 1 - \frac{\tau_{\text{rock}}}{\tau_{\text{meta}}} - \Delta x^2 / D_{\text{He}} \frac{\tau_{\text{cor}} - \tau_{\text{rock}}}{\tau_{\text{meta}}}
\]

where \(\Delta x\) is the effective grain size and \(D_{\text{He}}\) is the diffusion coefficient of He in the grain. Since \(D_{\text{He}} > D_{\text{Ne}} > D_{\text{Ar}} > D_{\text{Xe}}\), the correction will be relatively more important for the heavier noble gases.

Dresher et al. (1998) were unable to collect porefluid samples from the KTB by the method of Osenbruck et al. (1998) but this analysis can proceed in the theoretical sense. Parts of this analysis are applied to Ali et al. (2010). Any one sample obtained at depth can be evaluated with respect to local or external sources with measures of \([\text{Ng}]_{\text{H}_2\text{O}}\) and \([\text{Ng}]_{\text{rock}}\) and a metamorphic age of the rock. If it is assumed that the sample operated as a closed system, then conservation of mass indicates:

\[
[\text{Ng}]_{\text{rock}} \cdot (1 - \Phi) + [\text{Ng}]_{\text{H}_2\text{O}} \cdot \Phi = J_{\text{internal}} \cdot \rho \cdot \tau_{\text{meta}} (1 - \Phi)
\]

and all (e.g.) \(^4\)He produced in the metamorphic age of the rock (at which time it was assumed that \(^4\)He was initialized to zero) is contained in either the rock or the pore fluid. Rearranging eqn (30) and including the internal production from the solid phase with regard to the release fraction gives:

\[
\frac{[\text{Ng}]_{\text{rock}}}{J_{\text{internal}} \cdot \rho} + \frac{[\text{Ng}]_{\text{H}_2\text{O}}}{\Lambda_{\text{Ng}} J_{\text{internal}} \cdot \rho} \cdot \frac{\Phi}{(1 - \Phi)} = \tau_{\text{meta}}
\]

or

\[
\tau_{\text{rock}} + \tau'_{\text{H}_2\text{O}} \Lambda_{\text{Ng}} = \tau_{\text{meta}}
\]

where \(\tau'_{\text{H}_2\text{O}}\) is the \(^4\)He tracer-model age in the water calculated with the assumption that (eqn 22) \(F_{\text{He}} = 0\) and the appropriate solution should be bracketed by corrected (eqn 29) and uncorrected values of \(\tau_{\text{rock}}\). Thus, for the closed system sample volume \(\Delta x \Delta y \Delta z\), the e.g. helium age of the rock (\(\tau_{\text{rock}}\)) plus a portion (\(\Lambda_{\text{He}}\)) of the \(^4\)He tracer-model age in the fluid (\(\tau'_{\text{H}_2\text{O}}\)) is equal to the metamorphic age of the rock (as determined by \(^{40}\)Ar and/or \(^{87}\)Sr/\(^{86}\)Sr dating of specific mineral separates). Clear indications of an open system with respect to e.g. \(^4\)He in the volume \(\Delta x \Delta y \Delta z\), but with distinctly different meanings, are expressed as:

\[
\tau_{\text{rock}} + \tau'_{\text{H}_2\text{O}} \Lambda_{\text{Ng}} < \tau_{\text{meta}} \quad \text{open system, 'no' external source}
\]

\[
\tau_{\text{rock}} + \tau'_{\text{H}_2\text{O}} \Lambda_{\text{Ng}} > \tau_{\text{meta}} \quad \text{open system, significant external source}
\]
For the inequality expressed by eqn (32b), there has been a net loss of Ng from the local crustal volume $\Delta x \Delta y \Delta z$. The most likely means to loose $^4$He (or $^{40}$Ar) is by transport in the fluid phase. Thus, $\tau'_{H2O}$ (eqn (22) with the assumption $F_{He}=0$) provides a first order estimate of the age of fluids within the matrix porosity in the sample and the tracer model age. With the assumption that matrix porefluids have equilibrated in situ with the fracture-filling and transporting porefluids, the Ng tracer-model ages and the transport in the deep crust can be estimated.

For the inequality expressed by eqn (32c), there is a clear indication of an external source of noble gas to the system (or noble gas enrichment due to phase separation and re-dissolution which must be handled in an alternative manner). Again, the mechanism of transport is most likely to be via the fluid phase in fractures and as was seen above, the first order estimate of the external flux is $3.63 \times 10^{10}$ $^4$He atoms m$^{-2}$s$^{-1}$ with a variability of 36x. The methods discussed in this section are actively being applied for samples recovered from the San Andreas Fault Observatory at Depth (Stute et al., 2007; Ali et al., 2007, 2008, 2010).

**SUMMARY**

The application of $^4$He-model ages in groundwater as a proxy for the idealized groundwater age and a method for groundwater “dating” has proven to be difficult to apply but ultimately valuable. The most common complication is the dominance of external fluxes of noble gas which occurs as the result of small- and large-scale transport within the crust. Estimates of the crustal flux of $^4$He range from 0.03x to 36x the whole crustal in situ production and have been documented in a number of areas. It is to be appreciated that such crustal fluxes have associated with them a specific time- and space-scale. Furthermore, it is to be recognized that these fluxes are generally conceptualized as near-uniform over the basin in question. Hence, a flux into an aquifer may result in little vertical flux to layers above as well as a concentrated outflux at the discharge zone.

Over the past several decades, research has moved the application of $^4$He-model ages from the case where individual samples might be “datable” to the case where large suites of samples are utilized and $^4$He is incorporated as a constituent tracer in large scale reaction and transport models. Such models then optimize the groundwater transport parameters and the $^4$He tracer distributions relative to the various in situ production and crustal flux terms. However, the field has also enlightened the subject to the degree that open system methodologies for placing bounds on groundwater ages using $^4$He are possible and may be applicable. This is especially true in the field of deep borehole sampling where the number of samples is limited and samples are limited to vertical profiles.
REFERENCES


Table 8.1: Noble Gas Solubilities

The equilibrium concentrations of He, Ne, Ar, and Kr can be calculated as:
\[
C_{eq}^i = \exp \left\{ t + t2(100 / T) + t3(\ln(T / 100) + t4(T / 100) + S[s1 + s2(T / 100) + s3(T / 100)^2]} \right\} \left( \frac{p_{tot} - e_{w}}{p_{norm} - e_{w}} \right) ^{1000}
\]

The equilibrium concentrations of Xe can be calculated as:
\[
C_{eq}^{Xe} = \exp \left\{ x1 + x2(100 / T) + x3 \cdot \ln(T / 100) \right\} \cdot 0.00011 \exp \left\{ S \cdot (x4 + x5(100 / T) + x6 \cdot \ln(T / 100)) \right\}
\]

Solubilities of $^3$He and $^4$He expressed as a function of the $^3$He/$^4$He ratio ($R_{eq}$):
\[
R_{eq} = 1.384 \cdot 10^{-6} \left[ \exp \left( (r1 + r2 / T + r3 / T^2) \right) \cdot (1 + r4 S) \right]^{-1}
\]

The following definitions apply:
- $C_{eq}^i$, $C_{eq}^{Xe}$: concentration of noble gas, cm$^3$STP g$^{-1}$
- $ptot$, $pnorm$: local and reference (1atm) atmospheric pressure (atm)
- $e_{w}$: water vapor pressure
- $T$, $S$: water temperature (K) and salinity (g$_{salt}$ kg$^{-1}$)

The coefficients are given as:

<table>
<thead>
<tr>
<th>$R_{eq}$</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
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<td>$t_1$</td>
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<td>-167.2178</td>
<td>-170.6018</td>
<td>-178.1725</td>
<td>-112.684</td>
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<td>$t_2$</td>
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<td>216.3442</td>
<td>225.1946</td>
<td>251.8139</td>
<td>153.5817</td>
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<tr>
<td>$t_3$</td>
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<td>139.2032</td>
<td>140.8863</td>
<td>145.2337</td>
<td>74.469</td>
</tr>
<tr>
<td>$t_4$</td>
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<td>-22.6202</td>
<td>-22.629</td>
<td>-22.2046</td>
<td>-10.0189</td>
</tr>
<tr>
<td>$s_1$</td>
<td>---</td>
<td>-0.044781</td>
<td>-0.127113</td>
<td>-0.038729</td>
<td>-0.011213</td>
</tr>
<tr>
<td>$s_2$</td>
<td>---</td>
<td>0.023541</td>
<td>0.079277</td>
<td>0.017171</td>
<td>-0.001844</td>
</tr>
<tr>
<td>$s_3$</td>
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<td>-0.0129095</td>
<td>-0.0021281</td>
<td>0.0011201</td>
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<tr>
<td>$r_1$</td>
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<td>$r_2$</td>
<td>19.8715</td>
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<td>$r_3$</td>
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<td>$r_4$</td>
<td>0.000464</td>
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<tr>
<td>$x_1$</td>
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<td>---</td>
<td>---</td>
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<tr>
<td>$x_2$</td>
<td>---</td>
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<td>$x_3$</td>
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<td>$x_4$</td>
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<tr>
<td>$x_5$</td>
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<tr>
<td>$x_6$</td>
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</tr>
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</table>

after Kipfer et al. (2002)
Table 8.2: The helium flux from continental regions

<table>
<thead>
<tr>
<th>region</th>
<th>(^{4}\text{He} \text{ flux} \times 10^{10} \text{ atoms m}^{-2} \text{ s}^{-1})</th>
<th>Method</th>
<th>plotted, evaluated flux, \times 10^{10} \text{ atoms m}^{-2} \text{ s}^{-1})</th>
<th>time scale</th>
<th>space scale</th>
<th>reference</th>
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<tbody>
<tr>
<td>continents</td>
<td>2.8</td>
<td>calculation from U,Th</td>
<td>2.8</td>
<td>2Myr</td>
<td>&gt;5000km</td>
<td>1,2,3</td>
</tr>
<tr>
<td>Great Artesian Basin</td>
<td>3.1</td>
<td>measured accum in GW</td>
<td>3.1</td>
<td>1Myr</td>
<td>500km</td>
<td>2</td>
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<tr>
<td>Great Hungarian Plain</td>
<td>0.07-0.45</td>
<td>measured accum in GW</td>
<td>0.2</td>
<td>1Myr</td>
<td>200</td>
<td>7</td>
</tr>
<tr>
<td>Great Hungarian Plain</td>
<td>8</td>
<td>measured accum in GW</td>
<td>8</td>
<td>1Myr</td>
<td>200</td>
<td>8</td>
</tr>
<tr>
<td>Paris Basin</td>
<td>0.4-4</td>
<td>measured accum in GW and model</td>
<td>1</td>
<td>10kyr</td>
<td>100-500km</td>
<td>11,12,13,14</td>
</tr>
<tr>
<td>Paris Basin</td>
<td>0.4</td>
<td>measured accum in GW</td>
<td>0.4</td>
<td>10kyr</td>
<td>100-500km</td>
<td>11</td>
</tr>
<tr>
<td>Molasse Basin</td>
<td>0.2</td>
<td>measured accum in GW</td>
<td>0.2</td>
<td>250kyr</td>
<td>50km</td>
<td>9</td>
</tr>
<tr>
<td>Carrizo Aquifer, TX</td>
<td>1</td>
<td>measured accum in GW and model</td>
<td>1</td>
<td>100kyr</td>
<td>75km</td>
<td>23</td>
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<tr>
<td>Black Sea</td>
<td>1.3</td>
<td>profile and model</td>
<td>1.3</td>
<td>440</td>
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<td>26</td>
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<td>San Juan Basin,NM</td>
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<td>measured accum in GW and model</td>
<td>0.8</td>
<td>40kyr</td>
<td>40km</td>
<td>23</td>
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<tr>
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<td>10kyr</td>
<td>75km</td>
<td>15</td>
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<td>Auob Sandstone</td>
<td>0.09-3</td>
<td>measured accum in GW</td>
<td>1</td>
<td>20kyr</td>
<td>50km</td>
<td>5</td>
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<td>measured accum in GW and model</td>
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<td>20kyr</td>
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<td>Caspian Sea</td>
<td>1.9-5.9</td>
<td>lake profile</td>
<td>4</td>
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<td>Lake Baikal</td>
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<td>lake profile</td>
<td>21</td>
<td>10</td>
<td>177km</td>
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<td>Lake Huron</td>
<td>not detectable</td>
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<td>0.5yr</td>
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<td>Lake Erie</td>
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<td>0.5yr</td>
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<td>Lake Van</td>
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<td>lake profile, volcanic area</td>
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<td>2</td>
<td>60</td>
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<tr>
<td>Lake Taupo</td>
<td>3</td>
<td>lake profile, volcanic area</td>
<td>3</td>
<td>10yrs</td>
<td>15km</td>
<td>19, 28</td>
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<tr>
<td>Lake Nyos</td>
<td>30000</td>
<td>lake profile, volcanic area</td>
<td>30000</td>
<td>18yrs</td>
<td>1</td>
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<tr>
<td>Lake Lugano</td>
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<td>lake profile</td>
<td>4.8</td>
<td>12yrs</td>
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<td>600</td>
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<td>Crater Lake</td>
<td>55</td>
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<td>3yrs</td>
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<td>8</td>
<td>1yrs</td>
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<td>Lake Mashu</td>
<td>92</td>
<td>lake profile, Kz, volcanic area</td>
<td>92</td>
<td>2yrs</td>
<td>5</td>
<td>22</td>
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<td>811</td>
<td>10yrs</td>
<td>1km</td>
<td>16, 28</td>
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<td>Lake 120</td>
<td>14</td>
<td>lake profile</td>
<td>14</td>
<td>3y</td>
<td>0.5km</td>
<td>17, 28</td>
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<td>Lac Pavin</td>
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<td>60</td>
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<td>271 lakes, 1 sample each</td>
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<td>profile</td>
<td>0.1</td>
<td>500yrs</td>
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<tr>
<td>ocean flux</td>
<td>0.04-0.26</td>
<td>theory</td>
<td>0.1</td>
<td>510yrs</td>
<td>22609</td>
<td>27</td>
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</tbody>
</table>

1) O’Nions and Oxburgh 1983  
2) Torgersen and Clarke 1985  
3) Torgersen and Ivey 1985  
4) Craig et al 1975  
5) Heaton 1984  
6) Sano et al 1986  
7) Stute et al 1992  
8) Martel et al 1989  
9) Andrews et al, 1985  
10) Tolstikhin et al 1996  
11) Marty et al 1993  
12) Pinti and Marty 1995  
13) Pinti et al 1997  
14) Castro et al 1998  
15) Dewonick et al 2001  
16) Torgersen et al 1981  
17) Campbell and Torgersen, 1980  
18) Torgersen and Clarke 1978  
19) Torgersen 1983  
20) Torgersen et al 1977  
22) Kipfer et al 2002  
23) Castro et al 2000  
24) Stute et al, 1995  
26) Top and Clarke, 1983  
27) Torgersen 1989  
28) this study

* the flux is <10^{9} \text{4He atoms m}^{-2} \text{ s}^{-1}; the flux is chosen to best estimate symmetric log normal error bounds
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<th>element</th>
<th>MW</th>
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<td>Gd</td>
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<td>49000</td>
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after Andrews and Kay, 1982

Table 3: Parameters for calculation of $^3\text{He}/^4\text{He}$ production ratios
### Table 8.4: \(^{3}\text{He}/^{4}\text{He} \) Production Ratios

<table>
<thead>
<tr>
<th>Material</th>
<th>(^{3}\text{He}/^{4}\text{He} ) calculated (x10^8)</th>
<th>(^{3}\text{He}/^{4}\text{He} ) measured (x10^8)</th>
<th>Reference</th>
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<tr>
<td>Upper Continental Crust</td>
<td>3.90</td>
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<td>Torgersen &amp; Clarke, 1987; Torgersen, 1989</td>
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<tr>
<td>Lower Continental Crust</td>
<td>0.21</td>
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<td>Torgersen &amp; Clarke, 1987; Torgersen, 1989</td>
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<td>Upper crust</td>
<td>1.08</td>
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<td>Ballentine &amp; Burnard, 2002</td>
</tr>
<tr>
<td>Middle crust</td>
<td>0.40</td>
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<td>Ballentine &amp; Burnard, 2002</td>
</tr>
<tr>
<td>Lower crust</td>
<td>0.37</td>
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<td>Ballentine &amp; Burnard, 2002</td>
</tr>
<tr>
<td>Oceanic crust</td>
<td>0.029</td>
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<td>Torgersen &amp; Clarke, 1987; Torgersen, 1989</td>
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<td>Basalt</td>
<td>1.3</td>
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<td>Andrews, 1985</td>
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<tr>
<td>Ultramafic</td>
<td>0.114</td>
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<td>Andrews, 1985</td>
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<tr>
<td>Hooray Sandstone</td>
<td>2.2-3.3</td>
<td>---</td>
<td>Torgersen &amp; Clarke, 1987</td>
</tr>
<tr>
<td>Sandstone, UK</td>
<td>2.23</td>
<td>---</td>
<td>Andrews, 1985</td>
</tr>
<tr>
<td>Sandstone, avg</td>
<td>0.58</td>
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<td>Andrews, 1985</td>
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<tr>
<td>Clay and shale</td>
<td>1.99</td>
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<td>Andrews, 1985</td>
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<td>Limestone</td>
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<td>Torgersen et al., 1981</td>
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<td>Limestone, UK</td>
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<td>Limestone, avg</td>
<td>0.23</td>
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<td>Andrews, 1985</td>
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<tr>
<td>Typical Granite</td>
<td>5-15</td>
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<td>Fiege et al., 1968</td>
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<td>Granite</td>
<td>2.23</td>
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<td>Andrews, 1985</td>
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<tr>
<td>WR, Stripa</td>
<td>0.594</td>
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<td>Andrews et al., 1989</td>
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<td>Whole rock</td>
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<td>Orthoclase</td>
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<td>Biotite</td>
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<td>Plagioclase</td>
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<td>Gerling et al., 1971; samples from Rapakiwi</td>
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<td>1-whole rock</td>
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<td>1.6</td>
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<td>2-whole rock</td>
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<td>43-whole rock</td>
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<td>0.8</td>
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<td>27-whole rock</td>
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<tr>
<td>SS1-WR</td>
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<td>SS1-mica</td>
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<td>0.0084</td>
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After Ballentine et al., 2002
Fig. 8.1: Mechanisms for the release of alpha-decay $^4$He from rock. (1) recoil of the alpha particle (30-100 microns); (2) recoil followed by rapid diffusion along recoil damage tracks, grain imperfections and microfractures; (3) molecular diffusion in the solid state with no advantages from recoil damage or grain imperfections; (4) weathering and dissolution release. After Torgersen (1980).
Fig. 8.2: Helium concentrations vs. groundwater hydraulic (flow-model) age (as supported by $^{36}$Cl-model ages) for the Great Artesian Basin, Australia. For groundwaters younger than 40 krys, the accumulation rate is $4.6 \times 10^{-12}$ ccSTP$^4$He cm$^{-3}$ H$_2$O yr$^{-1}$ which agrees with the calculated rate ($\Lambda_{He}=1$) of $3.95 \times 10^{-12}$ ccSTP$^4$He cm$^{-3}$ H$_2$O yr$^{-1}$. For groundwaters greater than 100 kys, the rate of accumulation is $2.91 \times 10^{-10}$ ccSTP$^4$He cm$^{-3}$ H$_2$O yr$^{-1}$ or 74x in situ production. An external bottom boundary flux provides the best explanation for the source and the timescale over which it can be seen (from Torgersen and Clarke, 1985).
Fig. 8.3: Simple scaled rates of diffusion for various grain sizes as a function of diffusion coefficient. The timescale $\Delta x^2/2D$ approximates the timescale for loss of the solid-phase-accumulated $^4$He; Significant fluxes (>10% of max) would be observable at timescales of $0.1\Delta x^2/2D$ and all initial $^4$He would be effectively lost by $3\Delta x^2/2D$. Note that $D_{He}/D_{Ar}\sim10^5-10^6$ and therefore closure for Ar is maintained for far longer timescales than closure for $^4$He.
Fig. 8.4: The accumulation of $^4$He in various groundwater aquifers as a function of travel time (flow-model age) from Solomon et al. (1996). Typical in situ production is 0.18 micro-cc/kg over 60 yrs. The data indicate rates >100x the expected in situ production via radiodecay. This enhanced source is the result of slow release of solid-phase-accumulated $^4$He (accumulated over the metamorphic age of the rock) that occurs as a result of comminution of large blocks/grains into smaller grains. The source is exemplary of mechanism (3) of Fig. 8.1. From Solomon et al. (1996), reproduced by permission of American Geophysical Union.
Fig. 8.5: Model calculations (from Solomon et al 1996) showing the timescale over which solid phase accumulated $^4$He can be released into the groundwater. The fluxes from the solid phase to the groundwater are a function of the grain size (labeled on various curves), the initial $^4$He concentration before comminution (metamorphic age of the solid; compare initial concentration $60 \text{ micro- cm}^3 \text{ g}^{-1}$ to $6 \text{ micro- cm}^3 \text{ g}^{-1}$) and the diffusion coefficient for $^4$He in the solid (graphs present the case for only a single diffusion coefficient $D_{^4\text{He}} = 4.5 \times 10^{-21} \text{ cm}^2 \text{ s}^{-1}$). From Solomon et al. (1996), reproduced by permission of American Geophysical Union.
Fig. 8.6: The bulk fracturing model of Torgersen and O'Donnell (1991) illustrated the 1D case for simple comminution. Before fracturing, the slab of thickness L can acquire a noble gas concentration that is (initial condition 1) 0.005x the steady-state or (initial condition 2) the steady state concentration of $A_0 L^2 D^{-1}$. Fracturing then reduces the slab thickness from L to l. Fracturing is quantified as the ratio L/l and can have any value >1. Note that the higher L/l, the larger the surface area available for diffusion into the porespace. From Torgersen and O'Donnell (1991), reproduced by permission of American Geophysical Union.
Fig. 8.7: The flux of noble gas (y-axis) to the porespace relative to in situ production as a function of diffusion time, $Dt/l^2$ (from the general case $Dt/\Delta x^2$). Dashed lines are calculated for the IC1 (0.005x steady state concentration at time of fracturing) and solid lines are calculated for IC2 (steady state concentration at time of fracturing). The results show that fracturing/comminution can result in large local sources of $^4$He to the porespace that can persist for characteristic timescales of $1 < Dt/l^2 < 5$ but $Dt/l^2=0.5$ marks the point where approximately half the accumulated noble gas has been lost to the porespace. Given that $D_{He}/D_{Ar} \sim 10^5$, the entire accumulated $^4$He could be lost from the slab while $^{40}$Ar loss continues for considerably longer. Note that the concentration in the porefluid is governed not only by the flux from the slab but also by the residence time in the post-fractured system. From Torgersen and O’Donnell (1991), reproduced by permission of American Geophysical Union.
Fig. 8.8: The effective time for diffusive transport as a function of layer thickness and effective diffusion coefficient. The timescale $\Delta x^2/2D$ approximates the timescale for diffusive exchange of produced/accumulated $^4$He. Significant fluxes into the layer and/or out of the layer (~20% of max) would be observable at timescales of $0.1\Delta x^2/2D$ and all exchangeable species would be effectively lost/gained in $3\Delta x^2/2D$. 
Fig. 8.9: A statistical analysis of the measured flux of $^4$He into 271 Canadian Shield lakes using the data of Clarke et al. (1977, 1983) and Top and Clarke (1981). These data typically provide one sample per lake including both a measure of excess $^4$He and the $^3$H-$^3$He model age. The calculation assumes the depth of sampling (most often below the thermocline) is an approximation of the mean lake depth. The calculation likely has an error based on assumptions that is order 3x. Also shown are fluxes based on the data of Table 8.2 for which both an area x time weighted mean has been calculated as well as a log normal mean and deviation. The agreement between the mean and std deviation for the Clarke lakes and the Table 8.2 data suggest the magnitude of the crustal degassing flux is approximately equivalent to whole crustal production with variance of a factor of 44.6x or 1.5 orders of magnitude. One therefore has a 68% probability of measuring a flux between $0.1 \times 10^{10}$ and $186 \times 10^{10}$ atoms $^4$He m$^{-2}$ s$^{-1}$ during any one study. The analysis suggests a strong spatial and temporal variability in the measured flux.
Fig. 8.10: Graphical Separation of the individual He components. a) outlines the meaning of the various mixing lines with their endmembers, b) shows the data from the Great Hungarian Plain (Stute et al., 1992b). Samples containing more than 1TU of tritium and samples collected in recharge areas (with vertical downward hydraulic gradient) are highlighted with open circles. After Stute et al. (1992b).
Fig. 8.11: The $^{4}\text{He}/^{40}\text{Ar}_{\text{rad}}$ ratio measured in gas/oil reservoirs which reflect the accumulation of local and crustal degassing sources and their mode of release from the solid phase production. Note that as time increases (as defined by increasing $^{4}\text{He}$ or $^{40}\text{Ar}/^{36}\text{Ar}$) the $^{4}\text{He}/^{40}\text{Ar}_{\text{rad}}$ ratio decreases from values well above the production ratio to values that integrate and approach the production ratio. From Torgersen et al. (1989).
Fig. 8.12: The utilization of He data in the quantification of groundwater flow and transport problems (from Zhao et al., 1998) in the Great Artesian Basin, Australia. In all cases the (A) figure shows $^4\text{He}$ concentrations in units of $10^{-5}$ cm$^3$STP$^4\text{He}$ cm$^{-3}$H$_2$O while the (B) figure shows the $^3\text{He}/^4\text{He}$ ratio in units of $10^{-8}$.

1. the conceptual model for numerical simulations: 1000km basin with a basin tilt of 0.7km/1000km and an aquifer thickness of 1km.

2. the base case scenario prescribed with a basal flux from Torgersen and Ivey (1985) showing (12.2A) an increase in $^4\text{He}$ along flowlines and from top to bottom of the aquifer and (12.2B) a decrease in $^3\text{He}/^4\text{He}$ ratio downstream that is the result of both in situ dilution of the air-saturated initial condition with in situ production as well as the basal flux which has been set to have a greater $^3\text{He}/^4\text{He}$ than in situ production.

3. the condition where the basal flux is zero shows (12.3A) the $^4\text{He}$ concentration decreasing with increasing depth in the aquifer as a result of input from the overlying shale aquitard and (12.3B) a lower $^3\text{He}/^4\text{He}$ ratio resulting from the lower in situ production ratio.

4. the condition where the basal flux is highly localized (1/10th the area but at 10x the flux). (12.4A) shows the localized basal flux is significantly diluted downstream by dispersion.

5. the variability of the $^4\text{He}$ concentration as a result of different dispersivities (12.5A) used assumes no mechanical dispersion, (12.5B) shows the condition for a longitudinal dispersivity of 100m and transverse dispersivity of 10m (Note that (12.2A) shows the intermediate case of longitudinal dispersivity 10m and a transverse dispersivity of 1m.

6. the variability of $^4\text{He}$ under the influence of subregional flows cells imposed by regional topography.

7. A comparison of the $^4\text{He}$ concentrations along the top of the aquifer and the bottom of the aquifer for each illustrated case. Note that all cases show a general increase with distance but that variability along the flow path can be identified with specific cause/effect hypotheses that are model testable.

Unless otherwise specified, the model is defined with:

- aquifer length, 1000km; aquifer thickness, 1km; topographic slope 700m/1000km
- Permeability sandstone: 1micro-m$^2$
- Permeability shale: 5x10$^{-5}$ micro-m$^2$
- Dispersivity longitudinal: 10m
- Dispersivity transverse: 1m
- Diffusion coefficient: 3x10$^{3}$ cm$^2$ yr$^{-1}$
- In situ production of $^4\text{He}$, sandstone: 3.07x10$^{-13}$ cm$^3$STP$^4\text{He}$ cm$^{-3}$H$_2$O yr$^{-1}$
- In situ production of $^4\text{He}$, shale: 8.78x10-12 cm$^3$STP$^4\text{He}$ cm$^{-3}$H$_2$O yr$^{-1}$
- Basal Flux: 0.14x10-5 cm$^3$STP$^4\text{He}$ cm$^{-2}$tot yr$^{-1}$
- $^3\text{He}/^4\text{He}$ meteoric recharge: 138.6x10$^{-8}$
- $^3\text{He}/^4\text{He}$ production in sandstone: 1.80x10$^{8}$
- $^3\text{He}/^4\text{He}$ production in shale: 1.85x10$^{8}$
- $^3\text{He}/^4\text{He}$ of basal flux: 3.5x10$^{-8}$
Fig. 8.13: The release fraction $\Lambda_{\text{Ng}}$ as determined from whole rock samples recovered from the KTB borehole by Drescher et al. (1998). The results represent an analysis of rock based on eqn (36) and the results confirm the general trend of $\Lambda_{\text{He}} > \Lambda_{\text{Ne}} > \Lambda_{\text{Ar}} > \Lambda_{\text{Xe}}$ as would be expected from their respective diffusion coefficients in the solid phase. From Drescher et al. (1998)
METHODS FOR DATING VERY OLD GROUNDWATER: EASTERN AND CENTRAL GREAT ARTESIAN BASIN CASE STUDY

T. Torgersen

Introduction

The Great Artesian Basin (GAB) extends across 1.7 \( \times 10^6 \) km\(^2\) or one-fifth of the Australian continent. Annual rainfall ranges from 100mm in the arid western parts to a maximum of 600mm near the main recharge areas along the eastern basin margin. Average annual runoff is less than 10mm and generally less than 5mm. Ephemeral rivers dominate the land surface of the basin, except for a few perennial rivers in the most northern, tropical parts of the region. Most interior rivers drain into Lake Eyre (a dry salt pan at 12m below sea level) however the river waters often evaporate or infiltrate before reaching Lake Eyre because of the long distances. With little or no surface water present in the dry, hot and harsh climate of Australia’s interior, the ability of the early settlers to explore and exploit the resources of this region were limited.

Artesian water was discovered in this vast interior region in the late 1870s and eventually most of the 4700 flowing artesian waterbores were drilled into the artesian aquifers in the Cadna-owie Formation and Hooray Sandstone aquifers, the main exploited confined aquifers in the Lower Cretaceous-Jurassic sedimentary sequence (Habermehl, 1980, 2001). In addition, the overlying Cretaceous aquifers are tapped by 20,000 pumped waterbores. This degree of exploitation led to a significant drawdown of the artesian groundwater levels and by 1970-2000 only 3100 wells remained flowing under artesian pressure and many of the artesian bores which ceased flowing were pumped, usually by windmills (Habermehl, 1980, 2001; Radke et al., 2000). Recent estimates of the artesian groundwater in storage in the Great Artesian Basin (8.70 \( \times 10^{12} \) m\(^3\) to 1.0 \( \times 10^{15} \) m\(^3\)) make it one of the largest artesian aquifers in the world (Radke et al., 2000). Investigations including the geology, groundwater hydrology and borehole measurements have been conducted since the early 1900s, but a significantly increased scientific effort has been in effect beginning in the early 1970s to understand the hydrogeology, hydrodynamics, hydrochemistry and isotope hydrology characteristics of this system, as well as its recharge, discharge and groundwater movement.

In the following sections, a case study is developed to demonstrate how the Eastern and Central GAB was studied, quantified and evaluated. This case study deals predominantly with the structure and components of the scientific study of very old groundwater and places this in a logical framework so the knowledge, precedents and the lessons of the GAB can be applied to other systems.

The GAB comprises multiple subsystems or three sedimentary basins which are hydraulically connected, the Eromanga, Surat and Carpentaria Basins (Fig. 13.1) with each system subject to differing developmental pressures as well as unique recharge flow and discharge conditions. Jack (1923) recognized the convergence of two separate flow systems near longitude 138E characterized by high alkalinity waters from the east and high sulfate waters from the west. In this case study, the focus will be on the primary, long time-scale flow within the Central Eromanga Basin portion of the Great Artesian Basin. The primary groundwater use in the Central Eromanga Basin is the pastoral industry with an emphasis on cattle for beef and sheep for wool. Additionally, the artesian groundwater is also the vital supply for town water and homesteads and for the petroleum (since the 1960s) and mining (since the 1980s) industries. The driving economics of the Basin are utilization of a sustainable resource, with conservation, rehabilitation and/or removal of some waterbores. As the artesian groundwater in this part of the GAB has some of the longest flowlines and some of the slowest flow rates, it provides an endmember for the application, analysis and evaluation of methods for dating very old groundwater.
Habermehl (1980, 2001) and Habermehl and Lau (1997) set the stage for detailed scientific investigations of the GAB system and the individual studies discussed below. The discussion in the following sections is largely an overview of the information contained within the individual studies with a historical context to elucidate how dating methods and field sampling were guided by existing information. The reader is referred to these primary literature sources for greater detail. Radke et al. (2000) provide details about the field sampling and detailed interpretations of the combined geological, hydrogeological, hydrodynamics, hydrochemical, radiochemical and isotopic analyses and is an example of how information can be combined, integrated and utilized for the fullest understanding of very old groundwater basins.

Deposition, Structure and Hydrogeology of the Eastern GAB

The primary deposition of the sediments comprising the aquifers and the aquitards of the GAB began with an intracratonic downwarp (Veevers, 1984; Shaw, 1990) of the eastern Australian continent. During Jurassic-Cretaceous (200-100 Ma) time, fluvial and fluvio-lacustrine sediments were deposited in the three constituent sedimentary basins of the Great Artesian Basin (the Eromanga, Surat and Carpentaria Basins; Senior et al., 1978), as a result of drainage from the east, west and south. Rising sea levels in the Early Cretaceous deposited shallow marine sediments over much of the previous fluvio-lacustrine sequences from the north with maximum marine inundation around 120-110Ma (Struckmeyer and Brown, 1990). Major uplift of the continent commenced around 95Ma ago and reached 200m over a time span from 110-60Ma (Gurnis et al., 1998). These fluvio-lacustrine and marine sediments were converted to a hydrogeologic groundwater system by regional uplift along the eastern margins of the continent between 10-15Ma (Senior and Habermehl, 1980) and 5Ma ago (Toupin et al., 1997). The eastern margin of the present GAB was marked by Jurassic and Cenozoic volcanism (Duncan and McDougal, 1989). The present hydrogeologic structure of the GAB is shown in Fig. 13.2.

This hydrogeologic history is important in the subsequent evaluation because the residence times of groundwaters in the GAB (order 1Myr) may or may not have had time to flush connate waters from the Cadna-owie Formation and Hooray Sandstone and/or from the overlying marine and continental connate waters in the Cretaceous aquifers. Secondly, because Cenozoic volcanism was common along the eastern margin of the GAB, specific locales have been “spiked” with components representing contact with the volcanic centers including low \(^{87}\text{Sr}/^{86}\text{Sr}\) groundwater (Collerson et al, 1988) and high \(^3\text{He}/^{4}\text{He}\) ratios (Torgersen et al., 1987).

After the uplift of the eastern margins, it is likely that Australia was latitudinally positioned to benefit from coastal rains in summer along the northeast slopes of the Great Dividing Range that include parts of the eastern recharge zone as well as monsoon rains that provide precipitation for the main recharge areas on the western slopes of the Great Dividing Range and that can penetrate deeper into the arid continental interior. The palaeoclimate records of Lake Eyre (Magee et al., 2004) and the fluvial records of the interior (Nanson et al., 1992; Nanson and Price, 1999) suggest a clear trend toward aridity from 130 Ka to the present. The analysis of Torgersen et al. (1985, 1988) suggests that Pleistocene-Holocene climates in the Gulf of Carpentaria region (northern parts of the GAB) were similar to the present.

Setting the Stage

The synthesis of Habermehl (1980) summarized the geology and hydrogeology of the GAB, its primary aquifers, and its fundamental chemical characteristics. Hydraulic conductivities of the aquifers are found to be generally in the range of 0.1 to 10m d\(^{-1}\) with transmissivities of the order 1-2000m\(^2\) d\(^{-1}\). Artesian pressure heads had been mapped and the 1970 potentiometric contours defined the drawdown of potentiometric head and the loss of storage relative to the reconstructed 1880 (predevelopment) potentiometric head (Fig. 13.3).
This reconstruction and the bore-measured hydraulic conductivities enabled the numerical groundwater flow model of Seidel (1980); and the interpretation and definition of artesian groundwater flow directions (Fig. 13.4) and estimates of flow velocities for broad sections of the GAB. Regional scale applications of the model were developed (Habermehl and Seidel, 1979) and model application and calibration were reported in Seidel (1980). Subsequent updates of artesian groundwater flow models have preserved these basic characteristics while defining details. The basic bidirectional artesian groundwater flow pattern that defines the eastern and central GAB from the western GAB was confirmed by the distribution of water chemistry types and confirmed the preliminary analysis of Jack (1923) and in more detail by Habermehl (1986). The original hydrodynamic model of Seidel (1980) was subsequently replaced by (steady-state and transient) MODFLOW models described by Welsh (2000), Welsh and Doherty (2005) and Welsh (2006).

**Stable Isotope and ¹⁴C Measurements**

Airey et al (1979) reported stable isotope (D, ¹⁸O) measurements from bores within the eastern part of the GAB and showed that the composition was consistent with a rainwater source and minimal interaction with the host rock. The minimal variation in the stable isotope ratios along apparent flowlines indicated a minimal climate signal over the timescale represented by the transect and the time interval allowed by the bore spacing. Transects of Na, Cl and HCO₃ indicated some co-variation down flow lines (Fig. 13.5) that may or may not have resulted from rainfall variations (Kershaw 1978; see also Kershaw 1994, Kershaw and Nanson, 1993). ¹³C ratios were shown to co-vary with HCO₃ (Calf and Habermehl, 1984). This variation was interpreted as a two-component system where HCO₃ introduced during recharge increasingly reacts with and is diluted by dissolved CaCO₃ of marine origin along the flow path.

**The 1982 Field Work:**

**Stannum-to-Innamincka and Bonna Vista-to-Thargomindah**

The above studies set the stage for the field work in the GAB during 1982 which focused on sampling bores located along artesian groundwater flowlines (Fig. 13.6) identified by the potentiometric head and previous chemistry and stable isotope profiles. This field effort included sampling for ¹⁴C, ³⁶Cl and ⁴He that had the potential to quantify groundwater ages and flow rates within the eastern and central GAB in addition to chemistry and stable isotopes.

Stable isotope measurements from the 1982 field work (Airey et al., 1983, Calf and Habermehl, 1984) confirmed flow lines inferred from potentiometric heads (Habermehl, 1980) (Fig. 13.7). Specifically, the deuterium contours show tongues of isotopically heavier water (Airey et al 1983) that are consistent with those flow directions. Numerous ¹⁴C samples collected along the flowlines near the recharge areas confirmed the presence of relatively young groundwaters (for the GAB) that contained measurable modern carbon (>1%; Calf and Habermehl, 1984). The transects of ¹³C generally confirmed flow directions inferred from the reconstructed potentiometric surface when the effects of increasing down gradient dissolution of marine carbonates identified in earlier work (Airey et al., 1979) were included. Bentley et al. (1986b) tested the ³⁶Cl groundwater dating method and developed its potential. Extensive ¹⁴C samples taken in and near the recharge area were used to define the initial condition for ³⁶Cl within the confined portion of the basin. Hydrologic ages were used to select bores to define the recharge condition for ³⁶Cl; ¹⁴C was used to confirm the appropriateness of those bores.

The evaluation by Bentley et al. (1986b) of the ³⁶Cl samples taken in 1982 identified dissolution of “dead” Cl (presumably from ancient marine deposits) and/or addition of Cl from other sources to be a significant diluent for ³⁶Cl. Consequently, ³⁶Cl ages are calculated by one of three end-member equations. The comparison in Fig. 13.8 generally confirms the validity of the hydraulically calculated groundwater ages through the calculation of the isotope tracer ages. It is noted however, that the interpreted ³⁶Cl tracer ages do not account for mixing of waters via
flow convergences and it is noted that the artesian groundwater flow lines used for the 1982 expedition were specifically selected to minimize flow convergence.

The helium isotope collection of 1982 sought to verify the potential for $^4$He dating of groundwater as proposed by e.g. Davis and DeWiest (1966) and within the background of work that had already been conducted by e.g. Marine (1976, 1979), Andrews (1977) Andrews and Lee (1979), Heaton and Vogel (1979) and Torgersen (1980). Torgersen and Clarke (1985), working with knowledge that the apparent hydraulic groundwater ages had been confirmed by $^{36}$Cl measures, showed that (relatively) “young” groundwaters of the GAB increased their $^4$He concentration at a rate that was consistent with a $^4$He source derived from local sources within the aquifer sandstones. However, farther along flowlines in “older” groundwaters, the rate at which $^4$He increased was up to 74x the rate of in situ production (Fig. 13.9). $^{222}$Rn measurements in the 1982 groundwater samples showed no significant increase in the $^{222}$Rn activity in the older portion (high $^4$He flux region) of the flow line and thus no evidence that a stronger, local, in situ source of $^4$He was acting to increase the rate of $^4$He introduction. These helium results indicated the predominance of an external source of $^4$He that was consistent with a basal flux derived from U, Th series decay in the Earth’s crust beneath the GAB. Most importantly, the inference of a large basal flux of $^4$He was supported by the simple hydraulic flow model of Torgersen and Ivey (1985) that accounted for the delay time (see Fig. 13.9) before the enhanced rate of $^4$He accumulation (the basal flux) was observed. Because of the predominance of this external $^4$He source, the $^4$He tracer ages were never calculated from the GAB $^4$He measurements.

Helium isotope measurements from the 1982 and 1985 expeditions (Torgersen et al. 1987) showed the isotope ratio of helium accumulating along most flow paths was consistent with the calculated in situ production ratio and was additionally indistinguishable from an expected deep crustal production ratio (both order $10^{-8}$; Fig. 13.10). However, some paths showed $^3$He/$^4$He ratios that were significantly elevated (Fig. 13.10) and suggested a mantle source of helium ($^3$He/$^4$He ratios order $10^{-5}$). These data suggest a point source input of a $^3$He-rich component that is diluted along the groundwater flowpath by mixing and addition of helium from the basal fluxes to the in situ production. This stable helium tracer thus defines a unique source region within the recharge area that can be tracked downstream to define a flow path. This $^3$He-rich tracer thus further defines and supports the flow paths inferred by Habermehl (1980) from the potentiometric surface. In addition, Collerson et al. (1988) showed that recharge area groundwaters were “spiked” with low $^{87}$Sr/$^{86}$Sr ratios (and a higher Ca/Sr ratio) as a result of Cenozoic volcanic intrusions and Jurassic and younger volcanic activity that was active in and along the eastern margin of the sedimentary basin of what would become the GAB (Fig. 13.11). The downstream dilution of this recharge area $^{87}$Sr/$^{86}$Sr “spike” again serves to strongly support the validity of the flow lines identified from potentiometric surfaces.

Torgersen et al. (1989) show that $^{40}$Ar results appear to follow the same dynamics as $^4$He in the Great Artesian Basin and are also consistent with in situ production followed by input from an external basal flux. The $^4$He and $^{40}$Ar data are generally explained by similar processes but the $^3$He/$^{40}$Ar ratio remains quite variable. This suggests that these deep crustal noble gas fluxes are decoupled. Decoupling of $^4$He and $^{40}$Ar from their U, Th-series and K sources is likely accomplished by processes at the grain scale including recoil, diffusive release and dissolution as well as large scale fracturing that will additionally separate $^4$He and $^{40}$Ar (Torgersen and O’Donnell, 1991). Given the relative signal strengths, the $^{40}$Ar results suggest that $^4$He is more useful for basins with very old groundwater.

The 1985 Field Work:
Fairlight Trust-to-Clayton, Athol-to-Mutti Mutti and Mt. Crispe-to-Curdimurka

Continuing to build a knowledge base of the flow paths and flow rates of the eastern GAB, field work in 1985 addressed additional flow lines in the eastern and central GAB as well
as a flow line in the western GAB that is not included in this discussion. The flow lines sampled explore the northern area of the basin and the role of converging flowlines as a complication in the application and use of tracer age calculations.

Torgersen et al (1991) identified an increase in Cl and SO$_4$ down the flowline for the Athol-to-Mutti Mutti group which also showed $^{36}$Cl ages on the high side of hydraulic ages (see Fig. 13.12). A discontinuous $^{36}$Cl evolution is distinct near Meerabooka where the East-West transect possibly intersects the North-South transect. Distinct addition of Cl is also evident near the end of the North-South transect at Clayton bore, as flowing groundwater rises from depth and is subject to convergent mixing. The impact of such mixing on the calculated tracer age was estimated based on linear mixing along an exponential decay curve. For this flow line, convergent mixing was suspected to cause minimal offset of the apparent tracer age.

Torgersen et al. (1992) combine the helium isotope data of 1982 and 1985 fieldwork and show the area of highest He concentration to be coincident with the oldest water and the lowest (and near radioequilibrium) $^{36}$Cl concentration (compare Fig. 13.13 and Fig. 13.14). The helium data also show the impact of the western recharge area and the limited recharge along the northwestern recharge margin.

**Modelling $^{36}$Cl and $^4$He**

The results of the 1982 and 1985 fieldwork for both $^{36}$Cl and $^4$He presented new data and new methods for the evaluation of very old groundwater. Discussion in the literature regarding the approach, assumptions and necessary conditions for the application of new methods (Bentley et al., 1986a) is common. Andrews and Fontes (1992, 1993; see also Fontes and Andrews, 1993 and Mazor, 1992) presented an evaluation of GAB $^{36}$Cl data that explained spatial variations in $^{36}$Cl as the result of mixing between groundwaters along flowlines and deep, $^{36}$Cl “dead” waters but presented no mechanisms by which (near instantaneous) mixing could occur over such a broad region. Torgersen and Phillips (1993) and Phillips (1993) countered their argument showing that the conditions necessary to generate the mixing lines proposed by Andrews and Fontes (1993) necessitated unreasonable endmembers and permitted virtually no radiodecay of recharge-water $^{36}$Cl and thus allowed no time for it to be transported. The exchange highlighted the need to evaluate the role of mixing in the interpretation of apparent $^{36}$Cl ages. Bethke et al. (2000), Park et al. (2002) and Radke et al. (2000) included such effects in their models.

Mazor (1995) and Mazor and Nativ (1992; 1994) suggested that helium in the “older” portions of the GAB could be explained as the result of water trapped in stagnant compartments of the aquifer. However, among a number of points raised by Torgersen (1994), such stagnation is inconsistent with the continuing evolution of $^{87}$Sr/$^{86}$Sr (Collerson et al., 1988) and would require not only that flow stopped in stagnant zones but also that geochemical processes of mineral dissolution were halted in a unique increasing sequence. The discussion highlights the need to examine all the ancillary physical, chemical and isotopic data available including the progression in geochemical reactions, stable isotopes, and tracers, to establish a means to validate the basic assumptions used for calculating groundwater flow velocity and age. This synthetic approach to analysis (all together) was adopted by Radke et al. (2000) for their benchmark analysis of the Great Artesian Basin.

Zhao et al. (1998) evaluated the effect of hydrodynamic flow in a typical confined aquifer on the distribution and accumulation of $^4$He in the flowing groundwaters. Their modelling suggests that flow divergence and convergence and especially upflow in a discharge zone can induce significant mixing (see also Goode, 1996). The Zhao et al. (1998) study thus begins the process of questioning the application of piston flow mechanics to either hydraulic ages or groundwater dating methods. Bethke et al. (1999, 2000) undertook full-scale modelling of the Great Artesian Basin groundwater flow system including the $^4$He accumulation and concluded that the distribution of $^4$He is controlled not only by lateral flow but also by upflow and downflow.
regions that develop in response to basin topography and structure. This modelling effort showed that the spatial distribution of $^4$He can be quantitatively reconciled with groundwater flow patterns using 3D modelling framework. Similar modelling of the $^{36}$Cl dynamics (Park et al., 2002) again confirmed the need to consider 3D flow in aquifer systems and the role of upflow, downflow, and convergent flow in the reconciliation of hydraulic ages with tracer-based ages. The summary manuscript (Bethke and Johnson, 2008) reiterates these principles.

**Geochemical Modelling of Groundwater Reaction Paths**

Herczeg et al. (1991) conducted a detailed analysis of the groundwater geochemistry from the 1985 field work using PHREEQE (Parkhurst et al. 1980). That study explained the increase in total dissolved solids (TDS) along flowlines and distinct chemical differences between the Eastern GAB (Na-HCO$_3$ type) and the Western GAB (Na-SO$_4$-Cl type) waters. Figs. 13.15 and 13.16 show clearly the strong increase in alkalinity, DIC and $\delta^{13}$C along eastern GAB groundwater flowlines as well as the slowly increasing Na, Cl and TDS and the decreasing Ca and Mg. Herczeg et al. (1991) discussed the increase in TDS as a result of (1) mixing of flowline groundwaters with saline waters within the deeper portions of the basin, (2) ion filtration through mudstone membranes and (3) dissolution of evaporates, carbonate minerals or other minerals in situ. They inferred that saline waters most likely originated from the overlying Cretaceous marine sediments and were introduced by downward by diffusion into the aquifers of the Cadna-owie Formation and Hooray Sandstone. However, given the upwards leakage of artesian groundwater from the deeper, stratigraphically lower aquifers to the stratigraphically higher Cretaceous aquifers, that mixing is likely to be slight. Herczeg et al. (1991) further inferred that ion filtration is likely to be minimal based on the $^{36}$Cl studies of Bentley et al. (1986b) and concluded that variable evapotranspiration in the recharge areas in combination with mineral dissolution along flowlines represented the most plausible mechanism for the chemical evolution observed in Figs. 13.15 and 13.16.

The eastern GAB flowline trends of increasing Na alkalinity and DIC together with the decreasing Ca and Mg were evaluated (Herczeg et al., 1991) in terms of a model proposed by Blake (1989) which includes (1) dissolution of carbonate minerals resulting in increased Ca, Mg and HCO$_3$ (2) cation exchange of Ca and Mg for Na in clay minerals, followed by (3) a reaction of Na with kaolinite to produce Na-smectite. Reasoning that the downgradient flow increase in alkalinity can only be accomplished by carbonate dissolution in the presence of high pCO$_2$, they concluded that CO$_2$ respiration by plants in the recharge zone can drive the $\delta^{13}$C of DIC resulting from these reactions from an initial -15‰ to approximately -12‰. However, to enable the reactions to continue requires the addition of CO$_2$ as a result of anaerobic fermentation and reduction of CO$_2$ to methane.

**The 2000 Benchmark and Synthesis**

Following the seminal paper of Habermehl (1980), the publication by Radke et al. (2000) is a compilation and synthesis of the hydrogeology, hydrochemistry and isotope hydrology of the Great Artesian Basin. It is based largely on samples and laboratory results of the fieldwork by Habermehl and others during the 1970s, 1980s and 1990s, with some additions of analyses and results from Queensland and South Australia. This benchmark paper synthesized groundwater flow models, geochemical reaction and transport models and the dating of the artesian groundwater in the aquifers of the Cadna-owie Formation and Hooray Sandstone to infer the timescale of recharge and the in situ flow rates. It further utilized distinctive hydrogeochemical anomalies to infer details of groundwater flow in these aquifers. In the few paragraphs that follow, their findings are summarized especially as they relate to this case study and the additional detail they deduce through the use of modern hydrodynamic and hydrogeochemical codes.
The mapped (Radke et al., 2000) spatial distributions of modern $^{14}$C (Fig. 13.17) and $^{36}$Cl (Fig. 13.14) are consistent with previous work. The location of very old groundwater (near equilibrium values of $^{36}$Cl) is consistent with the mapped regions of very high $^4$He (Fig. 13.13). Recharge, flow direction and discharge zones (Fig. 13.18 and 13.19) reported by Radke et al. (2000) were similar to the original diagrams of Habermehl (1980). Recharge is estimated to be of the order $10^{12}$ L yr$^{-1}$ with an unknown proportion distributed between rainfall and river infiltration. This current recharge rate may be enhanced as a result of the previous century of drawdown. Natural discharge is order $0.5 \times 10^{12}$ L yr$^{-1}$ with most discharge via upward leakage and minimal discharge via outlet springs (see Table 13.1). The range of estimates for GAB storage of water is significant (Table 13.1) leading to vastly different simple estimates of groundwater residence times (storage volume divided by input rate (or output rate)). The climate reconstructions of e.g. Magee, et al. (2004) suggest a decline in rainfall over Pleistocene time and discharge springs have experienced a significantly reduced head over the past century. Thus, it is not anticipated that discharge rates contribute significantly to this residence time discrepancy. Using the Habermehl and Seidel (1979) estimated storage ($10^{18}$ L) would yield recharge-based and discharge-based residence times of 1Myr and 2Myr which are in general agreement with estimates from $^{36}$Cl and hydraulic estimates. The precision and the precise meanings of these differences in storage are not clear but it may be the difference between in situ storage and recoverable storage.

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<th>Table 13.1 Water Balance for the Great Artesian Basin, Australia</th>
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TheEastern GAB is characterized by increasing TDS and alkalinity along flow lines. Chemical anomalies are noted along the Birdsville-Diamantina Track (BTR) with additional high Cl anomalies along the Eulo-Nebine Ridge area. Groundwater temperatures increase with depth of the aquifers and anomalous geothermal gradients throughout the basin (Habermehl and Pestov, 2002; Habermehl et al. (2002) and the Central Eromanga Basin show a distinct increase in Na especially when expressed as sodium excess (e.g., $[\text{Na}] - [\text{Cl}]$). High fluoride concentrations occur over basement highs where the aquifer is possibly in contact with igneous and metamorphic basement rocks. The stable isotopic signature of the groundwater suggests
heavy monsoon rainfall in the eastern recharge zone is responsible for a majority of recharge although evapotranspiration before recharge may be significant. Stable isotopes throughout the basin (Radke et al., 2000) show little variation. This apparent lack of any palaeoclimatic signature that may be the result of minimal climatic variation and/or attenuation by dispersive mixing. Hydrodynamic models of groundwater flow calibrated against $^{14}$C in and near the recharge areas suggest flow rates range from 1.4 to 2.9m yr$^{-1}$ (Radke et al., 2000). Flow rates calculated by hydrodynamic models and estimates of the $^{36}$Cl controls indicate several areas with artesian groundwater flow rates as low as 0.03-0.3m yr$^{-1}$ (see Fig. 13.18). Very slow flow regions are areas of predominate water loss via upward leakage although the hydrochemical signatures in low flow areas also indicate the possibility of downward diffusion of some ions from overlying Lower Cretaceous aquitards into the Lower Cretaceous-Jurassic aquifers (Fig. 13.19). It would appear that discharge from artesian springs (11%) is small compared to discharge via upward leakage (89%) for a total natural discharge of 0.5 x 10$^9$ L yr$^{-1}$. However, spring discharges might have been much larger in past geological times (Prescott and Habermehl, 2008). Anthropogenic discharge (0.57 x 10$^9$ L yr$^{-1}$) is estimated to currently be slightly in excess of natural discharge.

Overall, the benchmark paper of Radke et al. (2000) is in general agreement with earlier studies including the flow rate and age of groundwater inferred from $^{14}$C, $^{36}$Cl and $^{4}$He studies. However, their detailed analysis appears to identify high flow regimes with lower salinities in shallow-depth-of-burial regions. NETPATH (Plummer et al., 1994) modelling of GAB geochemistry produced results in agreement with the overall net reactions postulated by Herczeg et al. (1991) but suggested that carbonate dissolution reactions are the primary driving mechanism rather than smectite-kaolinite transformations. Thermal convection (Pestov, 2000) has not been substantiated.

Continuing Work in the GAB

As a result of the large data base available for the GAB, several anomalies have been identified within the recharge areas (e.g. Torgersen et al. 1987; Collerson et al 1988), and the TACEM anomalies (anomalies near wellbores named Tambo, Augathella, Charleville, Eddystone, and Mitchell; Radke et al. 2000) as well as along artesian groundwater flow paths. The groundwaters in the central and western Queensland and northern South Australia portions of the GAB (and in particular along the Birdsville Track) are characterized by higher temperatures than anticipated (Habermehl and Pestov, 2002). Total dissolved solids are low along the Birdsville Track compared to central and western Queensland and South Australia. This trend is inferred to be the result of mixing induced by the rapid rise in elevation of the crystalline bedrock based on geothermometry studies of Pirlo (2004). Evidence for this mixing of waters is provided by the discord among silica geothermometers and cation geothermometers. Because silica geothermometers re-equilibrate relatively quickly compared to cation geothermometers, the low Si temperatures and the high cation temperatures indicate mixing from deeper, hotter (faster reactions) regions and shallow regions.

O'Shea and Jankowski (2007) have performed hierarchical cluster analysis on the chemical compositions in the Coonamble Embayment (southeastern GAB and an area in New South Wales not discussed above) and compared them with traditional Piper diagrams (Piper, 1944), Durov diagrams (Chiligar, 1956) and a Chada (1999) modification of a Piper analysis. Their cluster analysis indicates three main geochemical water types that can be associated with processes of ion exchange, precipitation and mixing from different sources. They were also able to identify an anomalous sample that is suspected to be influenced by magmatic sources of CO$_2$. This indication of magmatic CO$_2$ is consistent with the location of other anomalies observed in $^{87}$Sr/$^{86}$Sr (Collerson et al., 1988) and $^{3}$He/$^{4}$He Torgersen et al. (1987) that are geographically associated with the eastern recharge zone that was subject to considerable Cenozoic and pre-Cenozoic volcanism (Duncan and McDougal, 1989).
Recharge, recharge processes and rates, detailed hydrochemistry and isotope studies, including stable (δD, δ18O and δ13C) and radioactive (14C, 36Cl) isotopes have been carried out in the Queensland (Kellett et al., 2003) and New South Wales (Habermehl et al., 2009) parts of the GAB and recharge rates range from 0.5 to 10mm yr⁻¹, with some higher values. A detailed study of recharge along the western margin and discharge in the southwestern region of the GAB commenced in 2009.

Shimada et al. (1997, 1998, 1999) sampled several transects in the Coonamble Embayment in 1996 and interpreted the hydrochemistry, stable (δD, δ18O and δ13C) and radioactive (14C, 36Cl) isotope results for this southeastern part of the GAB, which has its own recharge area.

Extensive sampling of flowing artesian waterbores tapping the aquifers in the Cadnawie Formation and Hooray Sandstone was carried out in 2002 and 2003 along transects similar to the 1982 and 1985 transects, with additional transects in the Queensland, South Australia and Northern Territory parts of the GAB. This was followed in 2004 and 2005 by the construction of fully cored drill-holes through the Lower Cretaceous aquitards into the aquifers near the northeastern recharge area and the southwestern discharge area. Laboratory results on hydrochemistry, stable isotopes (δD, δ18O and δ13C), radioactive isotopes (14C, 36Cl) and noble gases (4He, 3He/4He, Ne) were analyzed and interpreted and confirm the results of earlier studies. Additional 36Cl and 4He measures continue to show they remain useful indicators for groundwater residence times of very old groundwater (Hasegawa et al. 2009, Mahara et al., 2009).
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Fig. 13.1: The Great Artesian Basin of Australia from Radke et al. (2000). The basin is composed of several sub-basins that are both hydrologically and structurally identifiable. The recharge areas, the reconstructed 1880 potentiometric surface and the inferred flow directions are also shown.
Fig. 13.2: The regional geologic and hydrogeologic structure of the Great Artesian Basin of Australia. From Radke et al. (2000). Note that north is to the left.
Fig. 13.3: Regional drawdown (meters) of the potentiometric surface of the Cadna-owie-Hooray aquifer following development during the period 1880-1970 (from Habermehl, 1980; copyright Commonwealth of Australia)
Fig. 13.4: Recharge, natural spring discharge areas and directions of regional groundwater flow in the primary Cadna-owie-Hooray aquifer of the Great Artesian Basin based on 1980 data sources (from Habermehl, 1980; copyright Commonwealth of Australia). These inferred flowlines were used to guide the sampling locations for the 1982 and 1985 field work. Compare to Fig. 13.1.
Fig. 13.5: Chemical profiles along multiple flow lines within the Central Eromanga Basin of the eastern GAB. (a) Chloride, (b) sodium, (c) bicarbonate, (d) initial bicarbonate based on a $^{13}$C balance. The solid lines indicate 8-point moving averages of all wells except those in parentheses. Differing symbols represent various flowlines within the central Eromanga Basin. The insert in part (a) shows the variation of rainfall for the region over the last 120kyrs. These data (from Airey et al., 1979) provided guidance for 1982 field work.
Fig. 13.6: Sampling locations and bores numbers for both the 1982 and the 1985 field work. Discussion of flow line evolution is typically discussed in terms of first and last waterbore (from Torgersen et al., 1992).
Fig. 13.7: Contours of deuterium isotopes (top) show a tongue of isotopically heavy water following the trends in flow directions seen in Fig. 13.4. Contours of $^{13}\text{C}$ isotopes (bottom) reflect the trend in flow directions and the dominate geochemical dissolution of marine carbonates (from Airey et al., 1983)
Fig. 13.8: $^{36}\text{Cl}/\text{Cl}$ vs. $^{36}\text{Cl}$ concentration for the Great Artesian Basin (top) and the comparison (bottom) of apparent $^{36}\text{Cl}$ tracer ages to apparent groundwater ages calculated from hydraulic properties (from Bentley et al., 1986, reproduced by permission of American Geophysical Union.)
Fig. 13.9: Helium concentrations vs. groundwater hydraulic age (as supported by $^{36}$Cl dates, Bentley et al., 1986) for the Great Artesian Basin, Australia as deduced from the 1982 field work. For groundwaters younger than 40kyrs, the accumulation rate is $4.6 \times 10^{-12}$ ccSTP $^4$He cm$^{-3}$ H$_2$O yr$^{-1}$ which agrees with the calculated rate ($\Lambda_{He}=1$) of $3.95 \times 10^{-12}$ ccSTP $^4$He cm$^{-3}$ H$_2$O yr$^{-1}$. For groundwaters greater than 100kyrs, the rate of accumulation is $2.91 \times 10^{-10}$ ccSTP $^4$He cm$^{-3}$ H$_2$O yr$^{-1}$ or 74x in situ production. An external bottom boundary flux provides the best explanation for the source and the timescale over which it can be seen (from Torgersen and Clarke, 1985).
Fig. 13.10: Mantle $^3$He is identified in portions of the two flow lines of the GAB, (Fairlight Trust to Wilfred Downs and Juanbong to Bonna Vista; lower left; number in parentheses indicate bore number for cross referencing with the top two figures) based on the occurrence of the high ratio in $^3$He/$^4$He as seen by the slope of the line. The occurrence of Cenozoic volcanism (top left) in the area of recharge and the groundwater flow lines (top right) show how this signal is carried into the interior of the GAB (from Torgersen et al., 1987, reproduced by permission of American Geophysical Union.)
Fig. 13.11: The evolution of dissolved $^{87}\text{Sr}/^{86}\text{Sr}$ within two flowlines of the GAB (north is Stannum-to-Innamincka and south is BonaVista-to-Thargomindah). The low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is acquired in the recharge zone likely via contact with Cenozoic volcanics (see Fig. 13.9 and note also the acquired $^3\text{He}$ signature). As the flowing groundwaters dissolve the host rock ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7111$) and marine carbonates ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.709234$) in situ, that endmember is steadily acquired in the dissolved phase (after the measurements of Collerson et al. 1988).
Fig. 13.12: $^{36}$Cl measures along Fairlight Trust-to-Clayton flow line show a distinct discontinuity at Meerabooka possibly indicating flow line mixing as deduced by both the $^{36}$Cl/Cl vs. $^{36}$Cl plot (bottom) and the tracer $^{36}$Cl age vs the hydraulic groundwater age (top) (from Torgersen et al., 1991, reproduced by permission of American Geophysical Union.)
Fig. 13.13: Contours of $^4$He in the Great Artesian Basin compiled from the 1982 and 1985 fieldwork. High $^4$He concentrations clearly delineate the regions of oldest water within the southern Central Eromanga Basin (from Torgersen et al., 1992) and concur with the $^{36}$Cl contours (Fig 13.14).
Fig. 13.14: Contours of $^{36}\text{Cl}$ from Radke et al. (2000). The primary recharge areas (high $^{36}\text{Cl}$) are clearly delineated as is the locale for very old groundwater (low $^{36}\text{Cl}$). The agreement between the areas of low $^{36}\text{Cl}$ and high $^4\text{He}$ (older) and between high $^{36}\text{Cl}$ and low $^4\text{He}$ (younger) (Fig. 13.13) is clear.
Fig. 13.15: Evolution of Na and K chemistry and TDS along the 1985 sampling lines as reported by Herczeg et al. (1991). Note that the Western GAB (Mt.Crispe-to-Curdimurka) is distinct from the Eastern GAB and that mixing with the Eastern GAB flow is apparent at the end of the western flow line.
Fig. 13.6: Evolution of alkalinity, $^{13}$C, Ca$^{+2}$ and Mg$^{+2}$ chemistry along the 1985 sampling lines as reported by Herczeg et al. (1991). Note that the Western GAB (Mt Crispe-to-Curdimurka) is distinct from the Eastern GAB and that mixing with the Eastern GAB flow is apparent at the end of the western flow line.
Fig. 13.17: Contours of $^{14}$C (in per cent modern) from Radke et al. (2000). The primary recharge areas are clearly delineated and the loss of $^{14}$C in the older regions of the GAB is clear.
Fig. 13.18: Benchmark synthesis of flow rates and chemical evolution of the Great Artesian Basin (from Radke et al. 2000)
Fig. 13.19: Benchmark synthesis of the Great Artesian Basin showing flow rates, upward leakage and chemical evolution (increasing salinity; blue to orange) displayed over the basal structure of the Cadna-owie-Hooray aquifer (from Radke et al. 2000).