Quartz–Helium Method to Estimate Fluid Flow in Thick Aquitards, Gunnedah Basin, Australia

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Abstract
The hydraulic integrity of aquitards is generally assumed and relies on a few core-scale permeability measurements, drill-stem tests, or textbook values. This approach is because hydraulic data across the full aquitard thickness is generally lacking. Proper assessment of aquitard integrity should be studied at the formation (spanning its entire thickness at a single point) or regional (formation properties at multiple locations throughout the basin) scale. One formation-scale approach uses environmental tracers and advection-dispersion modeling to constrain fluid flow rates. This study demonstrates the use of helium concentrations in quartz as a method of constraining the rate of fluid flow in a 520-m thick aquitard in the Gunnedah Basin, NSW, Australia. Quartz was separated from existing core samples in the Watermark and Porcupine Formations at depths from 750 to 1200 m. The helium was released from these samples by heating and select samples were impregnated with helium to determine the rate of helium diffusion through the quartz. One-dimensional advection-dispersion modeling of the helium profile accounting for diffusive helium exchange between quartz and pore water revealed, that (1) vertical fluid velocity has been on the order of 0.02 mm/year or less for tens to thousands of years, (2) helium is in equilibrium between quartz and pore water, and (3) the helium profile is transient indicating that helium concentrations in the underlying Maules Creek Formation has varied over geological time. Further modeling identified aquitard conditions (thickness and temperature) for which equilibrium exists, a precondition for deriving formation-scale permeability.

Introduction
The subsurface containment or migration of hydrocarbons and other fluids is dependent on the integrity of the geological units that separate the reservoir from adjacent aquifers. In most conventional hydrocarbon reservoirs, the overlying cap rock or aquitard has very low permeability (mD to nD range). This, among other factors such as wettability, limit hydrocarbon migration from the reservoir throughout geological time. However, in unconventional hydrocarbon reservoirs, such as those producing coal bed methane (CBM; also known as coal seam gas [CSG]), the integrity of the overlying aquitard can be questionable. This is because the sorption of hydrocarbons and hydrostatic head has limited their migration (Dallegge and Barker 2000; Moore 2012) and the overlying geological unit may not be impermeable. Groundwater extraction for hydrocarbon production or agricultural and industrial use leads to a reduction in reservoir pressure, thereby desorbing gas from the coal cleats. Taking these conditions into account, there is a greater need to assess hydrogeological properties of aquitards within CBM producing basins. In particular, there is a need to assess to what degree there are hydraulic connections between the target reservoirs and overlying aquifers. The latter may be utilized for irrigation, stock and municipal water supply. Hydraulic connections in this case refers to faults, fractures, and changes in lithology (Cartwright et al. 2007). Other hydraulic connections may include wells that are leaky, improperly decommissioned, or have existed beyond their engineered lifespan (Wu et al. 1998, 2016; Dusseault and Jackson 2014). These wells all carry the risks of potentially significant impacts (Kell 2011), but will not be considered here, as the investigation techniques discussed in this study are insensitive to these modern changes in fluid flow and mass transport.

While aquitards in deep basins are usually tens to hundreds of meters thick, their permeability is usually...
assessed on the scale of centimeters. This is the scale at which traditional permeability assessment techniques (e.g., diamond coring and triaxial permeametry or well test interpretation) are undertaken (Butler et al. 2007; Yu et al. 2013). Such small-scale analyses are unable to characterize the influence of formation-scale features such as faults, fractures and heterogeneous lithology (Clauser 1992; Schulze-Makuch et al. 1999).

An alternative approach is to assess fluid flow at the formation scale (van der Kamp 2001). Because rates of fluid flow in aquitards are typically very low (possibly significantly less than mm/year), the assessment of fluid flow at this scale requires the use of environmental tracers, which have been present in aquitards for millennia. If the sources, sinks and transport properties of the environmental tracers can be constrained, it is possible to use them to infer fluid velocity at the formation scale (Mazurek et al. 2011). Figure 1 shows how the distribution of a tracer through an aquitard depends on the dominant transport method (i.e., advection versus diffusion) and the direction of advection.

Numerous tracers have been used to assess fluid flow rates in aquitards (Gimmi et al. 2007; Hendry et al. 2011; Mazurek et al. 2011; Gardner et al. 2012; Smith 2015). The present study examines the use of helium ($^3$He), which is completely inert and is produced in the radioactive decay of uranium (U) and thorium (Th). Isolation from the atmosphere during regional groundwater flow and fluxes from deeper resources result in helium concentrations increasing by orders of magnitude (Ballentine and Burnard 2002; Kaudse et al. 2016; Stute et al. 1992). Measuring helium in aquitard pore water proves difficult because helium is readily lost from core samples due to its low solubility and therefore, core samples must be immediately preserved using specialized methods (Osenbrück et al. 1998).

An alternative method to assess helium concentrations in pore water is to use helium contained in quartz as a proxy (Lehmann et al. 2003). The majority of sedimentary rocks contain quartz and helium readily diffuses into the mineral’s intragranular porosity (Wood et al. 1990). Following an extended period of contact and elevated in situ temperatures, the helium will equilibrate between the quartz and pore water (Lehmann et al. 2003). In core samples held at ambient temperatures, helium concentrations are believed to be retained in quartz grains for a period of at least several decades (Smith et al. 2013). As such, specialized preservation methods (Osenbrück et al. 1998) are not required. Furthermore, archived core samples are generally readily available from core libraries—a more economic option than drilling a new corehole. By measuring helium concentrations in quartz from a vertically distributed set of samples, it is possible to constrain a solute transport model (Mazurek et al. 2011; Gardner et al. 2012).

In this study, helium concentrations in quartz grains were measured in 12 samples from one drill core across approximately 500-m thick aquitard sequence in the Gunnedah Basin, NSW, Australia. Diffusion testing and numerical modeling were performed to determine whether helium had equilibrated between quartz and pore water. The vertical transport of helium through the aquitard sequence was simulated to estimate formation-scale hydraulic properties. Further modeling was undertaken to identify aquitard thicknesses and temperatures that are conducive to allow helium equilibrium between pore water and quartz. This information could provide additional evidence that fluid flow in low permeability formations has been negligible over millennia in the Gunnedah Basin.

Methods

Study Area
Core samples for quartz-helium analysis come from the Slacksmith 1 corehole in the Gunnedah Basin, NSW, Australia. The corehole was drilled in 2009 and core was collected from 101 to 1410 m depth (Santos Pty Ltd 2009); samples from the 696 to 1213 m depth interval ($n = 12$; Figure 2) were obtained from the Londonderry Drillcore Library, NSW.

Geology and Hydrogeology
The Gunnedah Basin is a structural trough containing Permian and Triassic sediments (Tadros 1993). CBM targets are in the Hoskisson’s Coal in the Black Jack Group (600 to 700 m deep; Figure 2) and coal seam in the Maules Creek Formation (850 to 1000 m deep). Interburden of the Black Jack Group and Maules Creek Formation
probably has low permeability (CDM Smith 2014). Low permeability formations of interest to the present study are the Permian Watermark and Porcupine Formations, which separate the Pamboola Formation of the Black Jack Group from the underlying Maules Creek Formation.

At Slacksmith 1, the Watermark Formation contains an upward-coarsening sequence of silt grading to fine-grained sandstone (Santos Pty Ltd 2009). The Porcupine Formation contains an upward-finining conglomerate containing sandstones, siltstones and a few igneous intrusions (Santos Pty Ltd 2009). The combined thickness (L) of these two formations is over 520 m. Downhole temperatures of these aquifers increases with depth from 46 to 64°C.

**Sample Preparation and Analysis**

**Mineral Separation and Helium Analysis**

Quartz was separated from other minerals using a combination of physical and chemical treatments which were similar to previously described methods (Smith 2015). The samples were disaggregated through crushing and then purified through subsequent steps utilizing nitric acid, sieving (45 to 150 μm), magnetic separation and heavy liquid separation. The final sample contained quartz, some fraction of feldspars and possibly clay coatings on these grains. Additional processing to remove feldspars and clay coatings is possible using hydrofluoric acid, but this was avoided as it would partially dissolve the quartz. The helium contributions of feldspar and clay coating and their effects on the diffusion rates has not been quantified but was assumed to be negligible. However, quantification of these effects in future studies is warranted.

Quartz samples were heated at 290°C for 6 days to release the helium from the quartz grains. Helium (4He) concentrations were measured at the CSIRO Waite Campus, Urrbrae, South Australia using a quadrupole mass spectrometer system designed for the measurement of noble gases (Poole et al. 1997).

To determine the effective solubility of the quartz, which varies between samples, the quartz was impregnated with pure helium. Samples were then heated to release the helium and then reanalyzed. This effective solubility is known as the helium accessible volume (HAV; Lehmann et al. 2003). The helium pore water concentration (\(H_{\text{eq}}\)) is calculated using the initial helium concentration, HAV and the air-water solubility of helium (Crovetto et al. 1982; Lehmann et al. 2003).

**Helium Diffusion Rate in Quartz**

The reliability of quartz-derived pore water helium concentrations depends on equilibrium exchange of helium between the two domains (i.e., quartz and pore water). At ambient and moderately elevated temperatures (i.e., 20 to 60°C), the diffusion of helium in quartz requires millennia to achieve equilibrium conditions (Trull et al. 1991). We will show that temperatures found at our study area are high enough to achieve equilibrium. At elevated temperatures (i.e., 290°C; as used above), the diffusion rate increases dramatically and equilibrium exchange occurs in hours to days. However, observed rates of diffusion have varied considerably between studies (Trull et al. 1991; Shuster and Farley 2005), which may be a function of grain damage and/or the presence of fluid inclusions (Smith et al. 2013). To quantify the diffusion rate of helium in quartz at the study site, step-heating diffusion experiments were conducted.

Quartz separates from three Slacksmith 1 core samples were sieved to 60 to 75 μm and impregnated with helium at approximately 150 Torr (760 Torr = 1 atm). After impregnation, the samples were transferred to new sample containers and evacuated. The samples were then heated to 290°C for increasingly longer time steps of 2 to 1438 min. Each time step corresponds to an expected helium release of 10% of the total helium. This was calculated using an analytical solution to the diffusion equation that assumes spherical quartz grains and a diffusion coefficient of 2.86 × 10⁻¹⁴ m²/s (Crank 1975; Trull et al. 1991).

**Modeling Methods**

Helium transport was modeled for two reasons: (1) to verify equilibrium (or at least quasi-equilibrium) between quartz and pore water at the pore scale using a diffusive first-order mass-exchange model and (2) to estimate vertical fluid velocities at the formation scale using a one-dimensional advection-dispersion model. These two transport mechanisms were then combined

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Figure 2. Stratigraphic units, hydrogeological classification (white = probably low permeability, gray = low permeability and black = coal seam) (CDM Smith 2014), subsample depths, and downhole temperature and gamma at Slacksmith 1, Gunnedah Basin, NSW.
into a single model to account for formation-scale helium transport and the equilibrium of helium between quartz and pore water to infer if the helium concentrations in quartz were representative of helium concentrations expected in the pore water. The transport of helium was simulated using a numerical method. The model allowed temperature, and thus rates of diffusion, to vary with depth. Modeled concentrations were calibrated to observed concentrations through the estimation of transport parameters, including vertical fluid velocity. The degree of model-to-measurement misfit for each model was quantified using a normalized sum of least squares metric. Further description of modeling methods is found in the Supporting Information.

The transport of helium in a low permeability formation greatly depends on the effective diffusion coefficient, which can be defined using the temperature-dependent free-water diffusion coefficient \( D_{0,w} \) (Jähne et al. 1987), which is multiplied by the aquitard porosity accessible to the tracer \( n \) and flow path tortuosity \( \tau \):

\[
D_e = D_{0,w} n \tau
\]  

(1)

Because flow path tortuosity is typically not a well-constrained parameter, \( D_e \) is instead commonly approximated as:

\[
D_e = D_{0,w} n^m
\]  

(2)

where \( m = 2 \) is the maximum expected porous media diffusion coefficient for helium (Mazurek et al. 2011).

**Testing the First-Order Rate Model**

Analytical solutions for spherical diffusion include time-varying boundary conditions, but these are limited in their application (Crank 1975). Alternatively, a transient form of the partial differential equation (PDE) for advective-diffusive transport (including spherical diffusion) can be solved using a standard numerical solver, such as the pdepe solver for MATLAB® (MathWorks, Natick, Massachusetts, USA), which solves various initial-boundary value problems for systems of parabolic and elliptic PDEs. Initial testing showed the pdepe solution matched the analytical solution given a constant boundary condition. The suitability of the first-order rate model was then tested against the pdepe solver for models featuring step-change boundary conditions.

**Results**

**Helium Transport and Production Parameters**

Gas-porosity, bulk density, and vertical hydraulic conductivity measurements were available for each sample (Turnadge et al. 2016). Bulk density and an assumed mineral density of 2.7 g/cm³ where used to estimates total porosity \((n_T)\), whereas gas-porosity estimates represent effective porosity \((n_e)\). Total porosities are 4.9 to 13% with a mean of 10%. Effective porosities are 0.4 to 2.3% with a mean of 0.9%. Vertical hydraulic conductivity values range from 0.9 to \(30 \times 10^{-7} \) m/day with a harmonic mean of \(2.1 \times 10^{-7} \) m/day.

Mean concentrations of U and Th are 1.9 and 4.8 ppm, respectively and are similar between the Watermark and Porcupine Formations. Mean concentrations of U and Th give a helium production rate of \(1.16 \times 10^{-20} \) cm³ STP/g/s, where STP is the standard temperature and pressure and \( r \) denotes rock.

**Helium Concentrations**

Helium concentrations in quartz, HAVs and helium concentrations in groundwater are given in Figure 3. Error bars represent analytical uncertainties. Standard error propagation was used where appropriate. Helium concentrations in quartz increase with depth by a factor of 3 and reach a maximum in the middle of the aquitard. Concentrations then decrease slightly before increasing near the base of the aquitard. HAV values have no trend with depth and have a mean of \(1.6 \times 10^{-3} \) cm³He/cm³ quartz. Applying sample-specific HAVs partially removes the vertical trend in helium concentration. Therefore, the average HAV (dashed line in Figure 3b) was used to calculate the helium concentrations in pore water.

**Rates of Helium Diffusion in Quartz**

**Spherical Numerical Model**

Helium release rates during step-heating diffusion experiments were higher than expected, with approximately 60% of total helium released during the first 290°C heating step (i.e., after 2 min). Therefore, there are no data to constrain diffusion rates at earlier times. While the total heating time was initially expected to exceed 24 h, all helium was released in less than 3 h.

Calculated diffusion coefficients at 290°C for a median grain diameter of 68 μm are given in Table 1 and the helium release data was adequately fitted using two diffusion rates \(D_1\) and \(D_2\) \((\Sigma x^2 = 0.07\) to 0.32; Table 1). At 290°C and for a median grain diameter of 150 μm, the calculated equilibration of helium between pore water and quartz occurs within 8 to 11 h. At 40°C, the equilibration time increases to 54 to 76 × 10⁴ years (Crank 1975).

**First-Order Analytical Model**

First-order diffusion modeling of the step-heating data produced a good fit to the data when two or more rates were used \((\Sigma x^2 = 0.09\) to 0.46; Table 1). Table 1 shows that the inclusion of two rates \(k_1\) and \(k_2\) produces an acceptable fit to observed data. However, this first-order model does not match the spherical model. This is because there are no data to constrain the model at early times (i.e., \(r < 2\) min) and the first-order model does not adhere to the spherical geometry of the quartz. Therefore, to improve the performance of the first-order model, it was fitted to synthetic data derived from the spherical two-parameter diffusion model, which required at least three first-order rates \((k_1, k_2,\) and \(k_3\)) to produce a good fit to the synthetic data \((\Sigma x^2 = 0.09\) to 0.46; Table 1).

To related the quartz diffusion coefficient to the modeled first-order rates \((k; 1/T)\), it is divided by the
Figure 3. Helium results: (a) measured helium concentration in quartz, (b) measured (circles) and mean (dashed line) helium accessible volume of quartz, and (c) calculated helium concentration in pore water.

Table 1
Optimized Diffusion Coefficients from Step-Heating Experiments for One-, Two-, and Three-Rate Diffusion Models

| Depth (m) | One Rate | Two Rates | First-Order |
|-----------|----------|-----------|-------------|
|           | $D/a^2$ (10^{-4}) | $D_1/a^2$ (10^{-4}) | $D_2/a^2$ (10^{-4}) | $D_3/a^2$ (10^{-4}) | $k_1$ (10^{-4}) | $k_2$ (10^{-4}) | $k_3$ (10^{-4}) | $\Sigma \chi^2$ |
| 696       | 4.13     | 29.1      | 12.2       | 0.9     | 0.14     | 148        | 9.46        | 0.16     | 4090    | 186   | 13.1   | 0.64 |
| 1137      | 1.91     | 20.6      | 6.55       | 0.73    | 0.32     | 110        | 8.17        | 0.46     | 1820    | 97.1  | 9.07   | 0.29 |
| 1213      | 2.97     | 11.4      | 6.79       | 0.97    | 0.07     | 114        | 10.6        | 0.09     | 2630    | 133   | 15.1   | 0.43 |

$D/a^2$ and $k$ are rates at 290 °C and have the units 1/s.

$D_1/a^2$, $D_2/a^2$, and $D_3/a^2$ are the diffusion coefficients for the three-rate model.

$\Sigma \chi^2$ is the sum of the squares of the deviations from the fit.

Grain radius squared ($D_q/a^2$; 1/T). The parameters $D/a^2$ and $k$ were then related by ratios that are independent of temperature.

Figure 4 shows an example comparison between pdepe model results and the first-order analytical model. The first-order model generally matches the pdepe model, with some discrepancies occurring shortly after the rapid change in boundary condition. The omission of spherical grain geometry from transport modeling warrants consideration as a loss of fine-scale detail occurs when the distribution of helium within quartz grains is lost. Complex helium gradients within quartz grains can result in rates of diffusion that cannot be characterized using the first-order model. Inset diagrams in Figure 4 show the helium concentration versus grain radius relationship derived from the numerical spherical transport model and compares it to the concentration derived from the three-parameter first-order analytical model. At all steps, the concentration at the center of the sphere only changes slightly, whereas the concentrations in the outer third of the sphere change most significantly. For example, at approximately 90 years, the boundary concentration has decreased to zero (i.e., helium concentration in the pore water becomes zero). The helium that previously diffused into the sphere will now diffuse outwards towards the lower concentrations at the boundary, but will also continue to diffuse towards the lower concentration at the center of the sphere. This multidirectional diffusion generates nonuniform concentration profiles within quartz grains; these are conditions that cannot be accurately modeled by the simple first-order analytical model.

While these complex diffusion patterns could be important under certain circumstances (especially at microscopic scale), for the purpose of this modeling...
Figure 4. Comparisons between PDE and first-order models with a step change in boundary condition. The median quartz grain diameter was specified as 70 μm. Example of the loss of fine-scale detail caused by the linearization of helium diffusion can be seen in the subset figures (grain centers are located at \( r/a = 0 \) and interfaces between grain surface and pore water are at \( r/a = 1 \)).

(and given that larger sources of uncertainty exist), the simplification resulting from use of a first-order model is considered minor and should not significantly impact the modeling of quartz—pore water partitioning at the formation scale. Therefore, the first-order analytical model is used for quartz-helium equilibrium in all subsequent formation-scale advection-dispersion modeling.

**Modeled Pore Water Velocity**

Total porosity \( (n_T) \) is appropriate for modeling helium transport because helium’s small size, neutral charge and high diffusivity, which allows it to access the total porosity (Mazurek et al. 2011). However, based on the steady-state numerical model, the modeled helium pore water concentrations are too high to match observed data in the Porcupine Formation (Figure 5). This suggests that the effective diffusion coefficient is larger than the values based on Equation 2 (using \( n = n_T = 0.1 \), \( m = 2 \), and \( D_{0,w} = 9.96 \times 10^{-9} \) m\(^2\)/s at 46 to 64°C).

The factor \( m \) in Equation 2 is based on the assumption that flow path tortuosity can be calculated as a power function of rock porosity using the coefficient \( m \) (Jury et al. 1991), rather than being directly estimated. When analyzing core samples from the San Andreas Fault Zone, California, United States, Ali et al. (2011) calculated the effective diffusion coefficient of helium in pore water at the core scale and determined that tortuosity was a factor of approximately 2.0 to 4.3 times higher than the porosity. Use of a tortuosity value four times greater (\( \tau = 0.4 \); Equation 1) than the mean total porosity \( (n_T = 0.1) \) resulted in an adequate model to measurement misfit for the Watermark Formation, but resulted in helium concentrations in excess of measured values for the Porcupine Formation. This discrepancy is discussed below.

**Steady-State Modeling**

A numerical solution of the advection-dispersion equation (Equation S1.1) is used to produce steady-state distributions of helium in the pore water and quartz of an aquitard. Figure 6 shows calculated steady-state helium distributions in the pore water for a range of upward and downward flow velocities. The model results compare well to the observed helium concentrations in the Watermark Formation when the vertical flow velocity is 0.02 mm/year or less and either upward or downward. Conversely, steady-state model results compare poorly to observed helium concentrations for the Porcupine Formation. This suggests that the helium profile in the latter unit is not at steady-state, which may be the result of transient helium concentrations in the underlying Maules Creek Formation. Potential causes of such transient helium concentrations include changes in groundwater flow velocities owing to climate change, bursts of mantle-derived helium associated with tectonic events (Williams et al. 2013), and so on. At present, this is an important uncertainty that needs further corroboration.

**Transient Modeling**

For the purposes of transient numerical modeling, the helium concentration at the base of the Porcupine Formation (i.e., the lower boundary condition) was assumed to vary in time according to the following sine function:

\[
C = \left( 2 + \sin \left( \frac{t}{2 \times 10^5} \right) \right) \times 10^{-5} \tag{3}
\]

The initial parameters of this model were chosen rather arbitrarily, and subsequently adjusted manually.
until they allowed a better description of the nonuniform helium profile. This resulted in input concentrations that ranged from 1 to $3 \times 10^{-5}$ cm$^3$ STP/g with a period of $1.26 \times 10^6$ years. Using this boundary condition, and for both upward and downward flow velocities of 0.02 mm/year, resulted in solutions that were in acceptable agreement with observed data (Figure 7). Decreasing the vertical flow velocity by one order of magnitude produced comparable results. Greater decreases in vertical flow velocity had negligible effect on the vertical profile of helium as transport was dominated by diffusion. In all scenarios, quartz-helium concentrations are in quasi-equilibrium with pore water helium (Figure 7).

Increasing the vertical flow velocity by one order of magnitude produced a vertical profile that was in good agreement with observed data when upward flow was considered. Conversely, when downward advection was considered, a poor match was achieved. None of the numerical model solutions were found to fit the data perfectly. Calibration fits could potentially be improved by modeling additional combinations of vertical flow velocity and boundary condition variations. However, lacking an independent data to constrain the boundary conditions, the results given here remain somewhat general.

In summary, it is suggested that the most pertinent result of the present study is that the modeling presented, which was constrained by analyses of aquitard core samples, was used to constrain pore water velocities to be in the order of 0.02 mm/year or less. Modeling results suggest that velocities may be up to one order of magnitude higher or several orders of magnitude lower. Furthermore, transient transport modeling using time-varying source boundary conditions indicate that helium concentrations remain equilibrated between pore water and quartz grains.

**Discussion**

**Comparison with Independent Estimates**

Measured core-scale vertical hydraulic conductivities for the Watermark and Porcupine Formation ranged between 0.9 and $30.0 \times 10^{-7}$ m/day (1.0 to $34.7 \times 10^{-12}$ m/s) while the groundwater model estimated modern hydraulic gradient ranged between 0.001 and 0.015 m/m (Turnadge et al. 2016). Using the measured mean effective porosity of 0.9%, the modern pore water velocity therefore ranged between $1 \times 10^{-5}$ m/day (0.00365 mm/year) and $5 \times 10^{-6}$ m/day (1.8 mm/year). The lower end of this range is comparable to those derived from helium transport modeling (i.e., 0.002 to 0.02 mm/year). Both methods suggest that the Watermark/Porcupine aquitard features very low permeability at this location and, given its thickness (i.e., exceeding 500 m in some locations), it is reasonable to assume that leakage across these formations is very low under natural pressure and depressurization due to CBM development.

However, it should be noted that these hydraulic gradients are not constrained by any directly observed data and represent modern conditions for specific areas of the Gunnedah Basin. Because hydraulic conditions have likely varied over millennia, the modern hydraulic gradients are not necessarily representative of that in which the vertical profile of helium initially developed. Therefore, it is likely that estimates of aquitard vertical hydraulic conductivity derived using the present day hydraulic gradient coupled with vertical profiles of helium may have underestimated the formation-scale pore water velocity. It is less likely that the velocity would have been overestimated, as even lower values than the 0.002 to 0.02 mm/year range derived here would not materially affect the helium distribution across the profile any further (Figure 6).

Under the very low fluid velocities predicted, mass transport across the aquitard will be dominated by diffusion. This is confirmed by Péclet numbers ($Pe = v \times L/D_e$) of 0.07 to 0.7, given that Péclet numbers of less than one indicate diffusion-dominated transport (Mazurek et al. 2011).
A similar study by Hendry et al. (2011) using vertical profiles of the $\delta^{2}$H of pore water collected across a 120 m thick aquitard yielded advection rates of 1 m per 10k years. Lower advection rates were obtained in our study (0.2 m per 10k years) and in those of Harrington et al. (2013) (0.009 m per 10k year) and Mazurek et al. (2011) (0.6 to 0.03 m per 10k year), indicating higher sensitivity in the latter studies. Factors that determine sensitivity of the modeling approach include (1) lack of clear concentration gradients across the profiles, (2) overall quality of the data in the profiles, including gaps in the profile, and (3) limited independent information regarding paleo-hydrogeological evolution to constrain the model (Mazurek et al. 2011).

Using the quartz-helium technique, a reasonably well-constrained vertical hydraulic conductivity ($K_v$) was derived. The associated uncertainty of approximately one order of magnitude (or larger if $K_v$ values lower than the current minimum of $0.9 \times 10^{-7}$ m/day are considered) may seem large, but for such low $K_v$ values this uncertainty is considered acceptable because interaquifer leakage would be negligible in this range. We did not pursue deriving a quantitative uncertainty about $K_v$ because transient helium distributions greatly complicates the modeling procedure such that Monte Carlo-type randomization approaches similar to those of Smith (2015) has proven beyond the scope of this project.

Transience in vertical profiles of aquitard helium concentrations has previously been observed in other groundwater basins, including the Eromanga Basin, Australia (Gardner et al. 2012) and the Adelaide Plains Basin, Australia (Bresciani et al. 2015). Continental helium fluxes are known to be spatially and temporally variable (Torgersen 2010), which may explain the seemingly transient distribution of helium observed in the Gunnedah Basin. Intrusions, which may be releasing helium, have been identified in the lower Porcupine Formation and underlying Maules Creek Formation.

Application of the quartz-helium method to other parts of the Gunnedah Basin to derive estimates of aquitard $K_v$ would require carefully selection of aquitard thickness, temperature and hydraulic properties to ensure that equilibria between quartz and pore water helium concentrations could be expected. For example, in the present study, aquitard core samples from the Slacksmith 1 corehole were selected because the Watermark and...
Porcupine Formations were quite deep at this location; therefore, subsurface temperatures were sufficiently high to enhance helium diffusion in quartz and thereby establish equilibrium conditions required for analysis.

In the previously mentioned Eromanga Basin study (Gardner et al. 2012), pore water helium was used to obtain best-fit formation-scale hydraulic conductivities that ranged from \( \leq 1 \times 10^{-12} \) to \( 2 \times 10^{-9} \) m/s with corresponding fluid fluxes ranging from \( \leq 0.003 \) to 3 mm/year. The high range of variability was due to finding anomalously high helium concentrations in shallow samples. These results indicate that substantial preferential flow paths exist and local vertical fluid fluxes through the aquitard could be up to 1000 times higher than in competent core profiles. In the present study, it is therefore important to stress that extrapolating the results of a few core profiles to a large area cannot be justified without an associated regional sampling campaign.

Future Usage and Limitations

This study shows that helium can be considered to be in equilibrium between quartz and pore water in the Watermark and Porcupine Formations at the Slacksmith 1 corehole. At this location, the formations are considerably thick (i.e., \( > 500 \) m) and occur at significant depths within the basin (i.e., \( \sim 700 \) m); therefore, a sufficiently high temperature is present to enhance diffusion. To assess whether equilibrium conditions are present in other parts of the basin where these aquitards are thinner and occur shallower in the basin, hypothetical helium transport modeling was undertaken. Three temperature profiles and three thicknesses were considered. All temperature profiles featured gradients of \( 25^\circ \text{C}/\text{km} \) with maximum temperatures of 20, 40, and \( 60^\circ \text{C} \) located at the base of the profile. The three aquitard thicknesses tested were 5, 50, and 500 m. The total simulation period of each model run was \( 10^2 \), \( 10^4 \), and \( 10^6 \) years, with longer times selected to be appropriate for thicker formations, in which more time is required to approach a steady-state helium distribution in pore water. Pore water velocities were chosen as 2, 0.2, and 0.02 mm/year for increasingly thick aquitards. This choice maintained a constant Péclet number \( (Pe = 0.5) \).

The initial pore water and quartz-helium concentration distribution across the formation is a
Figure 8. Hypothetical modeling of helium transport and equilibrium between pore water and quartz grains for 5, 50, and 500-m thick aquitards at 20, 40, and 60 °C; vertical fluid flow direction is upward and decreases with thickness to maintain the same Péclet number; only select time steps are shown and these time steps increase with increasing aquitard thickness; solid and dashed lines show helium concentration versus depth in pore water and quartz, respectively; background color shows the disequilibrium between phases versus time; calculation of $D_e$ uses $\tau = 4n$; quartz grain diameter is 46 to 150 μm and is weighted to equal mass per grain size.
linear profile between the following boundary concentrations: $4 \times 10^{-5}$ cm$^3$ STP/g at the base and $0.1 \times 10^{-5}$ cm$^3$ STP/g at the top. At $t > 0$, the boundary concentration at the base shift to $2 \times 10^{-5}$ cm$^3$ STP/g; the boundary concentration at the top of the profile shifts to $1 \times 10^{-5}$ cm$^3$ STP/g. This allows the observation of equilibrium of helium between pore water and quartz via the numerical model.

For a 5-m thick aquitard, equilibrium between domains does not occur at any temperature and the highest disequilibrium is observed at the boundaries (Figure 8). The disequilibrium is defined by $|C_q/C_w - 1|$, where $C_q$ and $C_w$ are the pore water helium concentrations derived from quartz and directly from pore water, respectively. The observed disequilibrium is not surprising because helium can be transported quickly through a relatively thin aquitard. The pore water helium distribution can therefore reach an equilibrium state much faster than quartz grains can gain or lose helium. This suggests that the quartz-helium method is not suitable for applications to thin aquitards as it is unlikely that equilibrium conditions exists in such contexts. Alternatively, application of the method in thin aquitards requires an independent indication that helium boundary conditions have not varied significantly over recent geological time.

The results from the 50-m model show that quasi-equilibrium conditions can be expected only at high temperatures (Figure 8). This greater degree of equilibrium can be attributed to the greater thickness, which means helium transport is slower because helium has larger distances to diffuse, which also means the helium gradients are lower. The longer time required for pore water helium to approach steady-state also results in more time for helium to diffuse in and out of the quartz.

For the 500-m thick aquitard, most scenarios show complete or nearly complete equilibration of helium concentrations. Similar to the results of the 50-m thick model, the increased thickness and longer transport time across the formation result in a system that is slow to react to changes in boundary conditions; therefore, sufficient time elapses to enable the equilibration between domains. Although equilibrium conditions may be expected in thick aquitards, this does not guarantee that conditions will be suitable for the estimation of pore water velocities. This is because changes in boundary conditions have lasting effects within the aquitard, which may result in helium distributions that are not readily interpretable, at least without requiring some assumptions with regards to temporal changes in boundary conditions. As previously stated, there is no way to independently estimate initial helium concentrations (Mazurek et al. 2011), which in turn means there is no way to independently estimate transient boundary conditions. However, formation-scale pore water velocities, and possibly hydraulic conductivities, may be estimated by trialing various initial conditions and boundary conditions. Because hydraulic conductivity values vary over orders of magnitude, the ability to constrain $K_v$ estimates to within a single order of magnitude represents a significant scientific advance, particularly when no reliable alternative analyses currently exist by which to estimate fluid flow at the formation scale.

In the ideal situation, pore water helium is directly measured and compared with quartz-helium estimates. However, the scarcity of specially preserved core samples requires the estimation of equilibrium to give confidence in the quartz-helium estimates. Measuring and modeling pore water helium is by no means the ultimate solution in characterizing aquitards, but it does provide valuable information on aquitards that may be data poor. The quartz-helium method should be considered in addition to other methods such as stable isotopes of water in pore water, geophysical methods, and core-scale permeametry.

Conclusions

The quartz-helium method was successfully applied to core samples of the Watermark-Porcupine aquitard sequence from the Slacksmith 1 corehole. Numerical helium transport models were used to estimate a pore water velocity of 0.02 mm/year or less, which generally agrees with independent core-scale gas permeametry measurements. A transient vertical distribution of helium in the Porcupine Formation suggests that helium concentrations have been variable in the underlying source unit (i.e., the Maules Creek Formation) over recent geological time. The existence of transient conditions means that it is difficult to estimate the uncertainty of the derived pore water velocities and associated vertical hydraulic conductivities.

Laboratory measurements of diffusion in quartz were undertaken and subsequently included in a formation-scale advection-dispersion helium transport model. Model results indicate that pore water and quartz grain helium concentrations should currently be in equilibrium at the Slacksmith 1 corehole. Furthermore, modeling results also indicate that helium concentrations in quartz grains are a suitable proxy for helium concentrations in pore water, provided that the aquitard of interest is adequately thick (i.e., tens to hundreds of meters) and subsurface temperatures are at least 40°C. It is recommended that the suitability of the quartz-helium method be evaluated on a case-by-case basis.

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Supporting Information
Additional supporting information may be found online in the Supporting Information section at the end of the article. Supporting Information is generally not peer reviewed.

Appendix S1 Diffusion modeling methods. A description of the advection-dispersion model and the helium diffusion in quartz model.

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