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EDITORIAL

Can argillaceous formations isolate nuclear waste? Insights from isotopic, noble gas, and geochemical profiles

ABSTRACT

There is considerable interest in the use of thick argillaceous geologic formations to contain nuclear waste. Here, we show that diffusion can be the controlling transport process in these formations and diffusional time scales for $\delta^{18}O$ and $\delta^{2}H$ in water, dissolved He, and Cl transport in shale-dominated aquitards are typically over 10^6 years, well exceeding the regulatory requirements for isolation in most countries. Our scientific understanding of diffusive solute transport processes through argillaceous formations would benefit from the application of additional isotopic tracers (e.g., using new ^4He sampling technology), multidimensional diffusive-dispersive modeling of groundwater flow and diffusive-dispersive solute transport over long geologic time scales, and an improved understanding of spatial heterogeneity as well as time-dependent changes in the subsurface conditions and properties of argillaceous formations in response to events such as glaciation. Based on our current isotopic and geochemical understanding of transport, we argue that argillaceous formations can provide favorable long-term conditions for isolating nuclear wastes.

Key words: aquitard, conservative tracers, nuclear waste disposal

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In the United States, the current halt on the Yucca Mountain disposal site for spent nuclear fuel has again brought the use of argillaceous formations as a potential host rock for nuclear waste disposal into consideration (Neuzil 2013; Shaw 2014). Many other countries, including France, Switzerland, Belgium, Japan, and Canada, are considering thick argillaceous (clay aquitard) formations as candidates for disposal and containment of their nuclear wastes. European countries, in particular France, Switzerland, and Belgium, have been conducting research programs into the suitability of argillaceous formations as host rocks for nuclear waste for some time. France, for example, commenced their research program in 1996, and their studies are presented in an array of papers in the scientific literature.

Thick, low-permeability argillaceous formations are widespread throughout the world, both as surficial deposits (e.g., glacial tills/glacio-lacustrine deposits) or consolidated or unconsolidated units within sedimentary basins (e.g., mudstones and shales). Knowledge of the hydrogeology and hydrologic history of argillaceous formations is critical to predict their ability to act as effective barriers to contaminant migration. Moreover, the low permeability and high sorption capacity of argillaceous aquitards make them attractive as host formations for containment of radioactive wastes and other hazardous materials. As noted by Neuzil (2013), thick sedimentary shales may be characterized by anomalous, subhydrostatic 'fossil' pressures (Vinard *et al.* 2001; Normani & Sykes 2012), resulting in inwardly directed hydraulic gradients lasting over geologic timescales. In glaciated regions, these underpressures could have developed due to unloading as the last glacial maximum (Bense & Person 2008). Here, we summarize our current understanding with respect to isotopic, noble gas, and geochemical profiles, identify key knowledge gaps regarding solute movement through thick argillaceous geologic formations, and suggest future research directions that might better inform decisions about the viability of these geologic deposits for nuclear waste isolation (e.g., Shaw 2014). This summary was motivated by the outcome of an International Atomic Energy Agency sponsored consultants' meeting on the isotope hydrology of diffusion-dominated hydrologic systems held December 2013.

Currently, nuclear regulatory agencies generally require that radionuclides in a buried waste repository remain isolated from the surface for at least 10^6 years. This criterion effectively requires a demonstration that solute or

radionuclide transport away from the proposed repository is by the slowest means possible: molecular diffusion. Diffusive transport can only be reliably established through the analysis and interpretation of naturally occurring isotopic and geochemical tracer profiles in porewaters, including dissolved solutes (e.g., Cl^-, Br^-, He), naturally occurring stable (e.g., $\delta^{18}O$, δ^2H) and radioactive (e.g., ^{14}C, ^{36}Cl, ^{81}Kr, ^{129}I) isotopes, and radiogenic noble gases (^4He, ^{40}Ar). Interpretation of geochemical tracer profiles in several argillaceous formations shows that their solute transport is controlled by diffusion and suggests that clay formation thicknesses of >100 m can satisfy the isolation criterion.

Natural geochemical and isotopic tracer profiles in aquitards have been collected and interpreted for near surface (Quaternary deposits) and deeper shales and claystones (Cretaceous to Triassic) around the world, mostly within the past 20 years. The most common tracers used in these studies are the stable isotopes of the water molecule ($\delta^{18}O$, δ^2H) and dissolved species such as Cl^-. The shapes of vertical and interformational geochemical profiles in many clay deposits reveal that molecular diffusion is the dominant transport mechanism. Regionally consistent depth profiles suggest long-term diffusion-dominated migration of solutes through argillaceous formations can be highly predictable. The goodness of fit of one-dimensional transport modeling to tracer profiles supports molecular diffusion as the predominant solute transport mechanism (advection being negligible), with many clay sites revealing distinctive geochemical and isotopic profiles over vertical distances of tens to hundreds of meters and indicating transport over time scales of 10^5 to 10^6 years. However, obtaining a quantitative and precise understanding of the long-term transport history of natural tracers in argillaceous deposits is difficult and will yield nonunique solutions because the modeling of individual tracer profiles is necessarily dependent on imperfectly known initial and/or boundary conditions as well as transport parameters that may or may not be well documented in climatological or geological literature. Because different geochemical tracer profiles in clay porewater develop as a result of different initial and boundary conditions, as well as transport parameters, estimates of the long-term migration of solutes in these deposits should therefore be based on a consistent and harmonized interpretation of as many disparate isotopic and geochemical tracers as possible, and further informed by hydraulic studies (e.g., pressure anomalies). Examples of $\delta^{18}O$ or δ^2H and ^4He depth profiles at drill sites and best-fit model simulations are presented in Fig. 1.

The profiles presented in Fig. 1 reflect the excellent progress made toward our scientific understanding of hydrologic transport through clay-rich aquitards over the past 20 years. They also highlight research opportunities that exist to refine and better constrain site-specific conditions that can improve our level of confidence in defining the controls on the long-term transport of solutes as a prerequisite for nuclear waste repository siting. These opportunities include the following: (i) the development and testing of new tracer methods and the intercomparison of methods to obtain isotopic and geochemical profiles in clay; (ii) characterizing the impacts of temporal boundary conditions and spatial variability in thicknesses on solute transport; and (iii) evaluating the potential for *in situ* gas production, the presence of a free-gas phase, and its impact on solute transport. These tracers and new ways to characterize how they are distributed within formations are reviewed briefly below.

Estimating solute transport in argillaceous formations requires the application of analytical and field methods that are markedly different in technique, effort, and level of care from that applied to traditional hydrogeologic investigations of aquifers. Studies show that detailed isotopic and geochemical profiles through argillaceous deposits are critical to obtain sufficient tracer data for developing well-constrained predictive advective–diffusive transport models. In practice, the required stable isotopic ($\delta^{18}O$ and δ^2H) profiles in argillaceous formations must be obtained through the use of fresh core samples rather than monitoring wells. Obtaining detailed $\delta^{18}O$ and δ^2H porewater profiles from core samples (and processing a requisite large number of samples) remains technically challenging (e.g., due to drill fluid contamination), particularly from cores in formations with low porosities and permeabilities. Currently, there are three leading techniques for obtaining the stable isotopic composition ($\delta^{18}O$, δ^2H) of pore water: direct liquid–vapor equilibration, heated vacuum and cryogenic distillation, and high pressure mechanical squeezing. Such techniques have been applied successfully, but are rarely compared. All warrant further testing and development but most important is the intercomparison and consistency of varied methods across a well-characterized thick argillaceous formation.

Sampling for dissolved gases such as radiogenic ^4He in aquitards is particularly challenging because the pore water must remain isolated from the atmosphere and at a pressure greater than the total dissolved gas pressure; some emerging gas tracers such as ^{81}Kr (Lu *et al.* 2014) also require large fluid volumes. Profiles of ^4He concentration have been obtained by placing freshly collected core samples in containers in which they degas (Osenbrück *et al.* 1998), using passive headspace samplers in piezometers (Sheldon *et al.* 2003; Hendry *et al.* 2005), and measuring He in quartz as a surrogate for pore water (Smith *et al.* 2013). However, all of these methods have limitations, and refinements and/or new methods are needed.

Consideration of geologic heterogeneities in space and time must be made for rigorous long-term predictions of transport in argillaceous formations. Spatial variability in

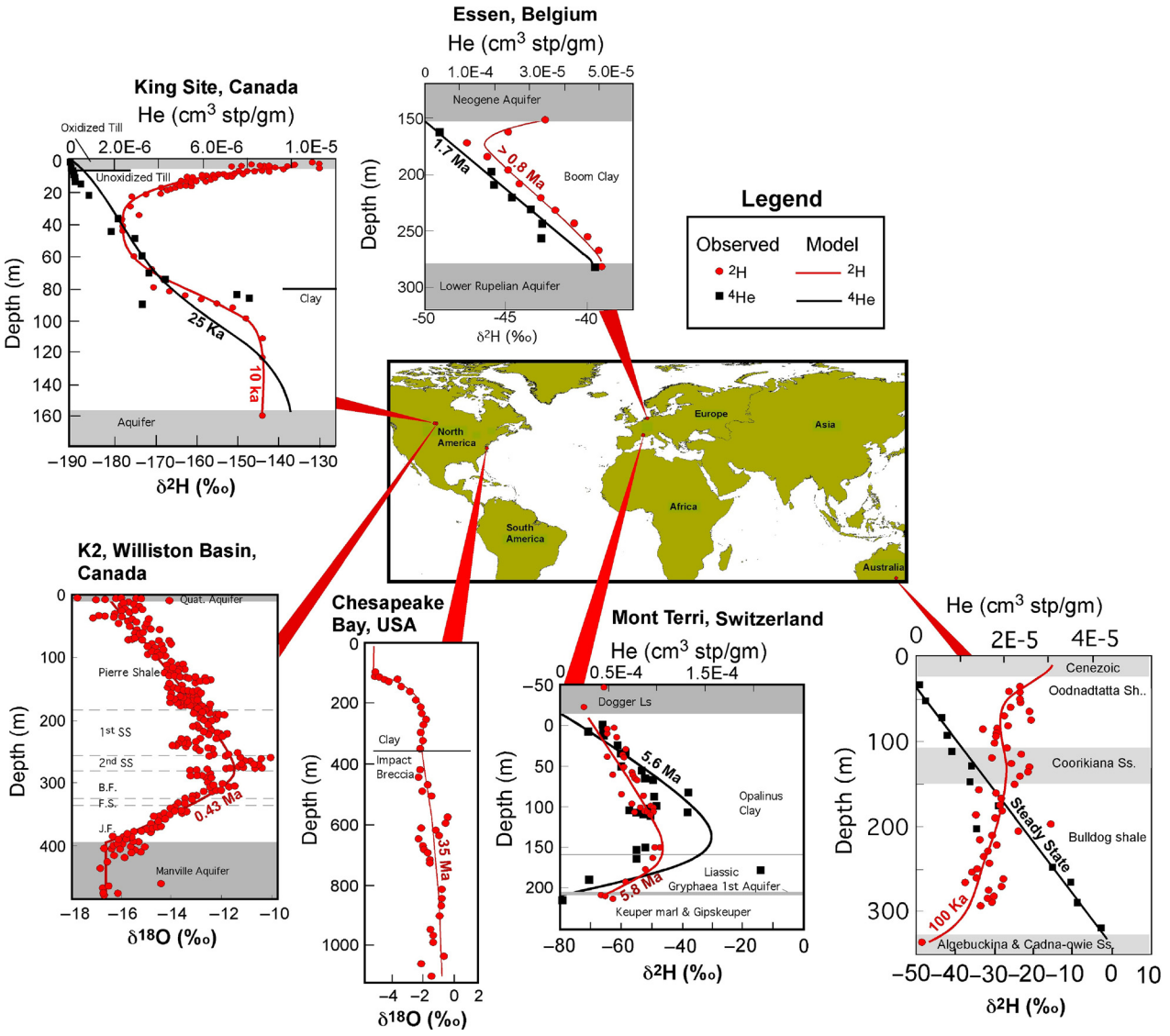

Fig. 1. Location of selected examples of geochemical and isotopic profiles through low permeability argillaceous formations (after T.A. Al, I.D. Clark, R. Mohapatra, L. Kennell, M. Jensen, K.G. Raven, submitted; Clark *et al.* 2013; Gardner *et al.* 2012; Harrington *et al.* 2013; Hendry & Wassenaar 1999; Hendry *et al.* 2005, 2013; Hasegawa *et al.* 2013; Mazurek *et al.* 2011 (and references therein), Sanford *et al.* 2013). The solid lines denote best-fit numerical models of diffusion-dominated solute transport.

solute transport in aquitards can be attributed to permeable fractures, faults (Cartwright *et al.* 2007), blowout/collapse structures, and primary sedimentation features (Christiansen *et al.* 1982; Grasby *et al.* 2000; Christiansen & Sauer 2001, 2002). The potentially great impact of small geologic heterogeneities on solute transport in diffusion-dominated aquitards remains largely unknown, and their presence currently limits confidence in findings extrapolated from individual boreholes to a larger regional scale. This is demonstrated by significant regional variability in the aquitard flux of ^{4}He measured in a shallow phreatic aquifer overlying the laterally continuous aquitard unit in the Great Artesian Basin, Australia (Gardner *et al.* 2012). Observational methods to interpolate borehole data to the regional scale with higher confidence could include the application of two- and three-dimensional geophysical surveys (e.g., Cartwright *et al.* 2007) and sampling aquifers bounding argillaceous formations located between boreholes. When present, pressure anomalies also provide valuable constraints on heterogeneity (e.g., Neuzil 2013).

Over long geological time scales, solute transport in aquitards may vary temporally as a result of natural events such as seismicity, tectonic stresses, glaciation and deglaciation, the dissolution of underlying evaporite or carbonate units (Cartwright *et al.* 2007), or even anthropogenic

activities such as mining or drilling. Further, the timing of activation of faults or blowout structures related to glacial loading (e.g., Grasby *et al.* 2000) can impact isotopic and geochemical distributions.

Numerical reconstructions of isotopic, salinity, and/or noble gas composition in thick aquitard formations have generally been limited to one-dimensional studies. The use of isotopic tracers in numerical modeling requires realistically defined initial and boundary conditions (transient or static) over long periods of geologic time, which is especially problematic. In glaciated regions, continental ice sheets affect the isotopic composition of land surface boundary conditions through time. Typically, continental ice sheet meltwater has a distinctive (highly depleted) isotopic signature for water isotopes. The major difficulty in imposing glacial boundary conditions on clay till formations is the lack of detailed information on the position of ice sheets prior to the most recent glaciations. Further, the impact of permafrost ahead of ice sheets on recharge under cold climate conditions is unknown (Edmunds 2001). In glaciated regions, variations in the isotopic composition of aquifers at the base of argillaceous sediments (Fig. 2) likely vary through time. In coastal areas, sea level changes can influence the upper boundary condition (chemical and isotopic) over geological time scales (Plummer *et al.* 2012). While considerable insights can be gained by one-dimensional studies of fluid flow (Neuzil & Provost 2014) and solute transport, the application of multidimensional numerical models represents a promising quantitative approach to assessing spatial and temporal variations in the boundary condition at the base of thick aquitards resulting from lateral advection-dominated transport in aquifers at depth over geologic time scales (e.g., Cohen *et al.* 2010; Bea *et al.* 2011, 2014; McIntosh *et al.* 2011). However, such multidimensional modeling requires the measurement of regional tracer profiles throughout the aquitard extent as well as in adjacent formations; this is a costly effort. It also requires estimates of ice sheet thickness through time as well as hydrogeologic and geomechanical formation properties (e.g., Lemieux *et al.* 2008), which are uncertain at best. Rock properties can also change through time due to glacial loading. Time-dependent permeability changes and pressure adjustments in thick shales associated with glacial loading represent an important yet still unresolved issue (Belitz & Bredehoef 1988; Bea *et al.* 2011, 2014; Manga *et al.* 2012; Neuzil 2012).

A major uncertainty in modeling solute transport in argillaceous aquitards is the potential presence and impact of a free-gas phase; this is of particular relevance for noble gas tracers. Archaeal and bacterial activity in some organic rich argillaceous geologic materials is known to produce CH_4 and CO_2 at concentrations sufficient to cause gas exsolution (Martini *et al.* 2003, 2008; I.D. Clark, D. Ilin, R.E. Jackson, M. Jensen, L. Kennell, H. Mohammadzadeh, A. Poulain, K.G. Raven, Y.P. Xing, submitted). The prediction and measurement of partial gas saturation conditions is therefore critical to characterize pore pressure changes and solute transport in shales. The presence of a separate gas phase in shales would greatly complicate liquid-phase diffusion due to gas-fluid partitioning and decreases in the liquid cross-sectional area and connectivity as well as the collection and interpretation of gas tracers due to phase partitioning. Lee & Deming (2002) proposed that multiphase effects associated with the presence of gas within shale units led to ultra-low effective permeabilities responsible for the preservation of anomalous hydraulic heads on time scales of 10^7 years or more within the Anadarko Basin, USA. An important parameter controlling gas saturation in geologic formations is the organic carbon content, which can act as a substrate for the sorption of

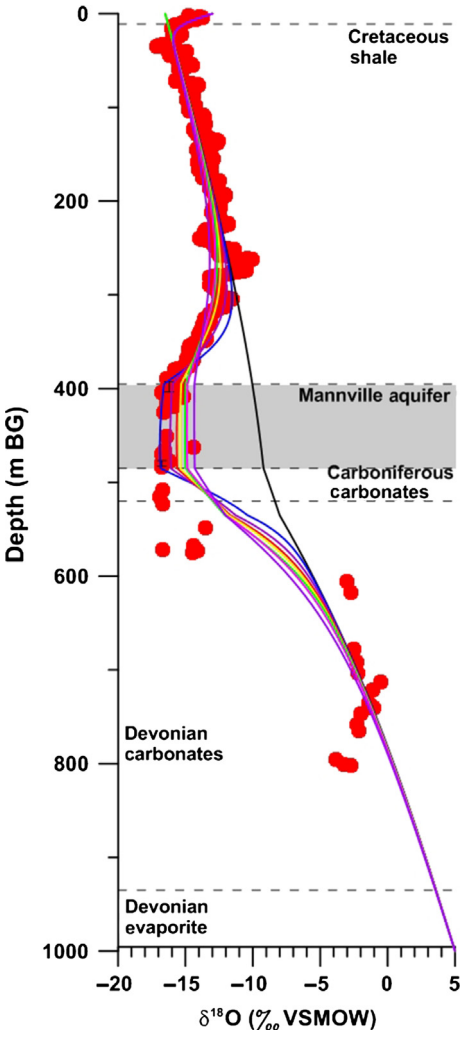

Fig. 2. Best-fit match of stable isotope composition within Cretaceous shales, Saskatchewan, Canada. The timing of the influx of low salinity glacially derived meltwater into a mid-level aquifer was varied in the model runs (after Hendry *et al.* 2013).

gases. For a given pore volume with a gas concentration exceeding porewater solubility constraints, the amount of gas sorbed on the organic carbon fraction can affect the formation of a free-gas phase. *In situ* gas production beyond the solubility/pressure conditions for the porewaters can also generate a secondary gas phase.

In summary, more than 20 years of research has shown that solute transport in thick argillaceous formations is often largely diffusion-dominated over timescales relevant to nuclear waste repository performance criteria. The diffusive time scales of solute transport in thick argillaceous formations have been shown to approach and even exceed 10^6 years. However, better characterization of the impacts of heterogeneity and long-term (hydro)geologic events is warranted. This will require the development of new methods to obtain appropriate isotopic and geochemical profiles and models to gain a clear understanding of the impacts of temporal and spatial variability on solute transport as well as the potential for gas production, the presence of a free-gas phase, and impacts on solute transport. In addition to these areas of research, important research questions related to the impact of waste disposal on the diffusive transport of solute through the argillaceous formations need to be resolved. These include multicomponent reactive transport, waste-derived gas migration, and thermal effects on transport.

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