Influence of partial gas saturation on solute transport: Michigan Basin, Southwest Ontario

Clark[1], I.D., Al[2], T.A., Jackson[3], R.E. & Raven[3], K.

[1]Department of Earth Sciences, University of Ottawa, Ottawa, ON Canada, K1N 6N5, idclark@uottawa.ca

[2]Department of Geology, University of New Brunswick, Fredericton, NB Canada, E3B 5A3, tal@unb.ca

[3]Intera Engineering Ltd. 200-1 Raymond Street, Ottawa, ON K1R 1A2

Introduction

The Nuclear Waste Management Organization (NWMO) is conducting investigations of the 840 m thick Paleozoic sedimentary sequence beneath the Bruce nuclear site, located near Tiverton, Ontario, as part on an on-going Environmental Assessment into the suitability of the site to host a Deep Geologic Repository (DGR) for Ontario Power Generation's (OPG) Low and Intermediate Level Radioactive Waste.   Multi-disciplinary studies conducted as part of a 3-year site characterisation program have involved laboratory-diffusion measurements on shale and carbonate rock core samples, as well as, hydrogeochemical investigations of groundwater and rock matrix pore fluids to provide constraints on processes and mechanics governing long-term hydrogeochemical evolution and mass transport. This paper examines evidence for the potential role of partial gas saturation in the generation of a barrier to diffusive transport and stability of the deep hydrogeologic system within the Ordovician sediments proposed to host the DGR.

Methods

Effective diffusion coefficient (D_e) measurements were conducted on brine-saturated samples using steady-state through-diffusion or radiography techniques as described by Cavé et al (2009). Inter-laboratory comparisons of diffusion measurements have been conducted among three labs, and detailed comparisons have been conducted among different methods, each with excellent correspondence. The relative brine and gas saturations of the Paleozoic dolostone, shale and limestone were estimated by petrophysical testing using both Dean Stark and NMR/He(g) procedures.

The geochemical characteristics of the porewater and groundwater that underly the Bruce nuclear site are obtained by direct sampling in the case of groundwater, and by a variety of porewater extraction techniques in low-permeability rocks. Drill core samples were vacuum packed in the field, with prior nitrogen flushing, and stored at temperatures below 8 ºC before shipping to the University of Ottawa. The extraction of CO_2 was carried out during vacuum distillation at 150 °C for 6 hours. The CO_2 released from the rock sample during heating was trapped in vials with water vapour at liquid N_2 temperature. Following vacuum distillation, each vial was warmed to release the condensed CO_2. Methane was extracted from crushed core samples using 500 mL plastic iso-jars. The headspace contained air at atmosphere pressure, and a correction was made for the minor contamination from 2 ppm atmospheric CH_4. Concentrations and $\delta^{13}C$ of extracted CO_2 and CH_4 were analyzed on a Finnigan MAT Delta XL continuous flow mass spectrometer interfaced with a GC to purify the gas. Standard gas mixtures were used to generate a calibration curve for concentration measurements.

Results and Discussion

A total of 141 diffusion measurements have been completed on samples collected across the Ordovician and Silurian stratigraphy. With the exception of just a few samples from the Upper

Silurian, the measured D_e values are in the range of 10^{-12} m^2/s or lower (Fig. 1). The highest values occur in the Upper Silurian Salina B, C, E and F units, with values greater than 10^{-11} m^2/s in the silty shale of the Salina B. The lowest values, on the order of 10^{-14} m^2/s are obtained in the gypsum-anhydrite layers of the Salina A0-A2 units, in the carbonate "hardbeds" within the lower Queenston and upper Georgian Bay Formations, and several limestone samples in the Gull River Formation. The majority of the data are in the range $10^{-13} < D_e < 10^{-11}$ m^2/s, with Lower Silurian and Upper Ordovician shale samples representing the higher end of this range because of their relatively high porosity (7 to 9 %). The lower porosity of the Middle Ordovician limestones (< 2%) results in lower D_e values which cluster in the range $10^{-13} < D_e < 10^{-12}$ m^2/s, with just a few samples displaying values greater than 10^{-12} m^2/s.
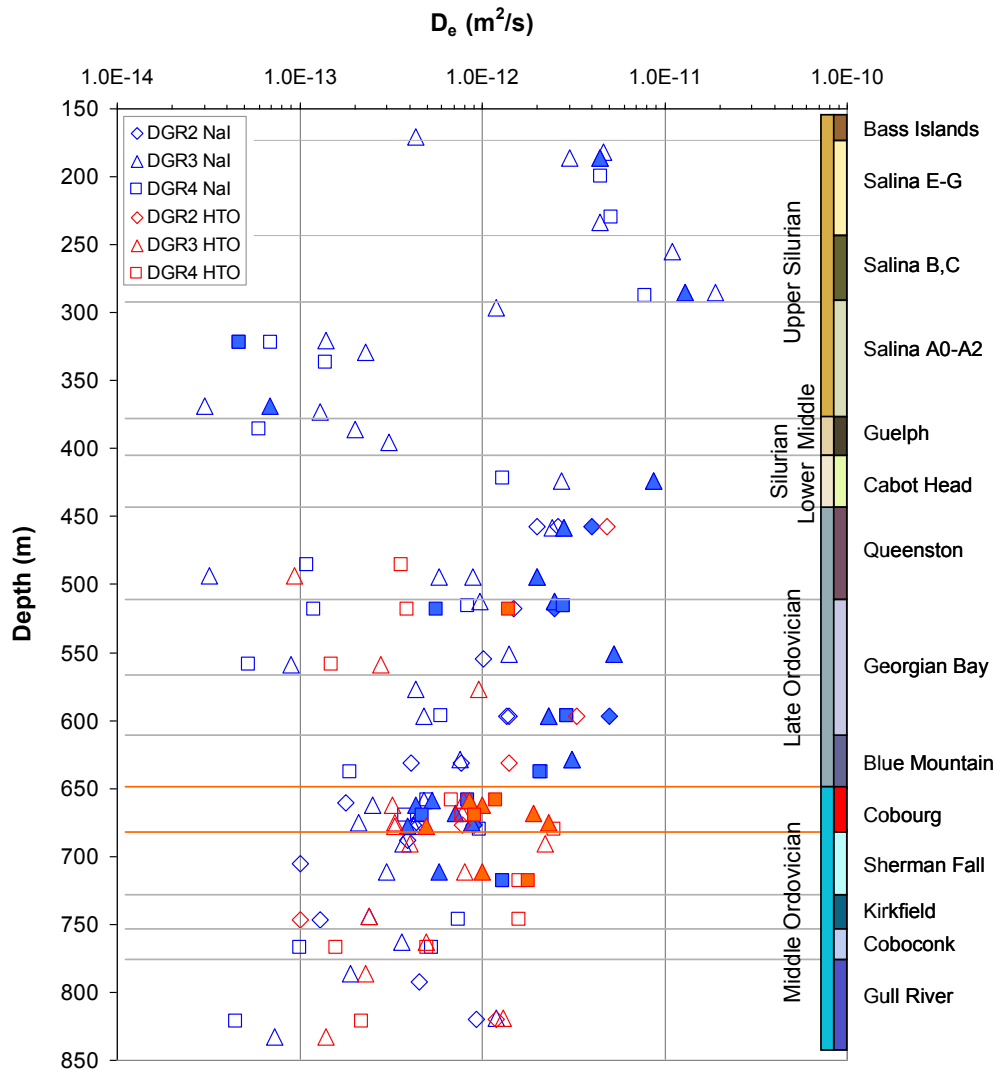

Figure 1: Plot of effective diffusion coefficients (D_e) versus depth. Open symbols represent measurements in the orientation normal to bedding, and filled symbols represent measurements parallel to bedding.

The petrophysical testing indicates that median gas saturation estimated for the Silurian rocks is 14%, for the Ordovician shale it is 11%, and it is 9% for the Ordovician limestone and the

Cambrian dolostone/sandstone. The gas content in the pore space is expected to contribute to a lowering of the *in-situ* D_e such that the laboratory measurements may overestimate the *in-situ* D_e values by one or two orders of magnitude in stratigraphic intervals where partially saturated conditions exist due to gas generation (Sarapalli et al. 2002).

Concentration data for CH_4 (Fig. 2) are presented in terms of the mass of gas per mass of water. This approach does not provide an accurate measure of dissolved gas content in cases where the pore space may contain a discrete gas phase. However, the reported "aqueous" gas concentrations can be compared to expected solubility limits, and values in excess of solubility limits provide additional evidence for the presence of a separate gas phase.

Focussing on the Ordovician, the CH_4 content increases gradually downward through the Ordovician Queenston Formation shale and then reaches a near constant value through the Georgian Bay Formation shale. There is a pronounced increase in the CH_4 content in the interval represented by the Blue Mountain Formation shale and the Cobourg Formation. The CH_4 content in the Middle Ordovician limestone and the underlying Cambrian sandstone is low relative to the overlying Blue Mountain shale and the Cobourg argillaceous limestone. The solubility limit for CH_4 in brine as a function of pressure and temperature has been investigated by Duan and Mao (2006). Their calculations indicate a maximum solubility of approximately 0.02 mol/kgw at the pressure and temperature conditions of the Ordovician sedimentary rocks, thus 0.02 mol/kgw could be considered an upper limit on CH_4 solubility. In the absence of a third liquid petroleum phase, the occurrence of CH_4 in excess of this value provides additional evidence that a separate gas phase exists in most samples from the Upper Ordovician shale and the Cobourg Formation. If a liquid petroleum phase is present in any of the samples it would be expected to absorb CH_4 and add additional uncertainty to the estimation of an upper limit on CH_4 solubility.

The stable isotope data (Fig. 2) provide important insight into the origin of the CH_4. The $\delta^{13}C$ and δ^2D data for CH_4 define two fields, one for CH_4 of biogenic origin in the Upper Ordovician shale, and a second for CH_4 of thermogenic origin in the Middle Ordovician limestone. This interpretation is supported by the $\delta^{13}C$ data for CO_2, which is enriched in $\delta^{13}C$ in the Blue Mountain Formation shale and the Collingwood Member of the Cobourg Formation, corresponding to the inferred zone of biogenic CH_4 formation. Hydraulic measurements demonstrate that the hydraulic conductivity in the shale and limestone units is on the order of 10^{-13} m/s or lower, suggesting that solute transport is dominated by diffusion. The clear separation of the biogenic CH_4, above, and thermogenic CH_4, below, suggests that there is no significant cross-formational mixing. This may be explained, in part, by a decrease in D_e values due to partial saturation, and by the fact that a discontinuous gas phase maintains saturation with respect to CH_4 in the brine, thereby creating a near uniform aqueous CH_4 concentration versus depth with no concentration gradient to drive diffusive transport.
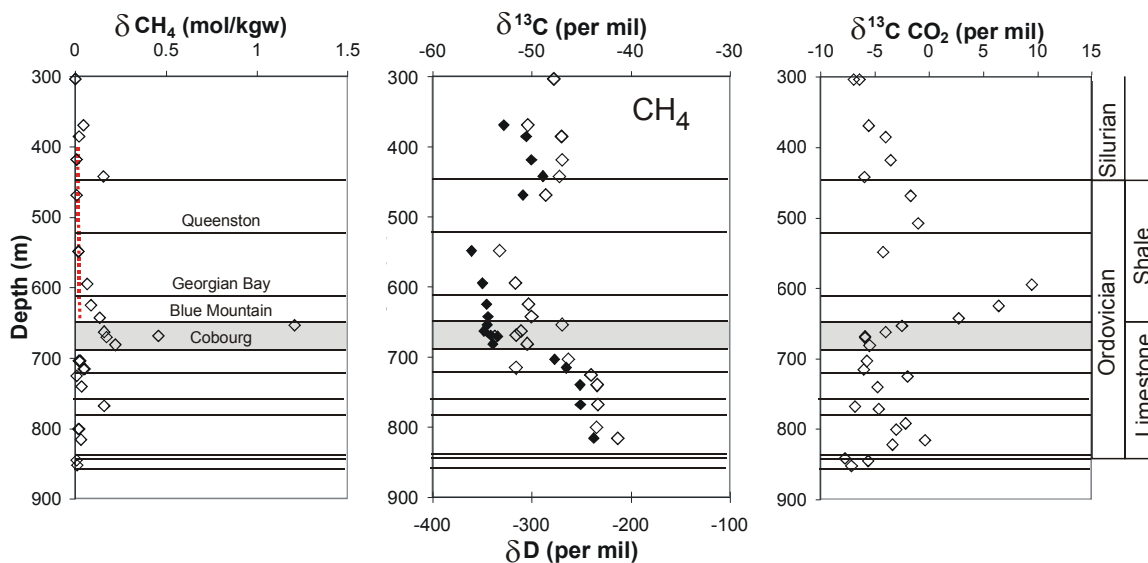
Figure 2: Depth profiles of concentration and isotopic data for gases CH_4 and CO_2. The estimated solubility limit for CH_4 of 0.02 mol/kgw is indicated by the red dotted line. Open symbols in the CH_4 isotope plot represent $\delta^{13}C$. The shaded Cobourg formation is the proposed host formation for the deep geological repository.

Conclusions

Stable isotope data for CH_4 and CO_2 collected from low permeability (< 10^{-13} m/s)shale and limestone indicate that little or no cross-formational mixing has occurred between stratigraphic intervals containing CH_4 of differing origin – biogenic and thermogenic. Petrophysical testing on rock core and inferences based on CH_4 solubility support a situation in that the low porosity Ordovician shales (7 to 9%) and carbonates (<2%) are partially saturated with brine (300 g/L) and gas. Combined, this evidence reveals a discrete vertical barrier to solute migration within the near horizontally bedded Ordovician sediments, one in which partial gas saturation may decrease in-situ D_e values by as much as one or two orders of magnitude from the range measured in the laboratory on saturated samples (10^{-12} m/s^2 or less).

Acknowledgements

References

Cavé, L.C., AI, T.A., Xiang, Y. and Vilks, P. 2009, A technique for estimating one-dimensional diffusion coefficients in low permeability sedimentary rock using X-ray radiography: Comparison with through-diffusion measurements: Journal of Contaminant Hydrology, 103, 1-12.

Duan, Z. and S. Mao 2006, A thermodynamic model for calculating methane solubility, density and gas phase composition of methane-bearing aqueous fluids from 273 to 523 °K and from 1 to 2000 bar: Geochimica Cosmochimica Acta, 70, 3369–3386.

Saripalli, K.P., Serne, R.J., Meyer, P.D. and McGrail, B.P. 2002, Prediction of diffusion coefficients in porous media using tortuosity factors based on interfacial areas, Ground Water, 40, 346-352.