



**Improvements to the
direct vapor
equilibration laser
spectroscopy method**

M. J. Hendry et al.

**Determining the stable isotope
composition of pore water from saturated
and unsaturated zone core:
improvements to the direct vapor
equilibration laser spectroscopy method**

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Abstract

A method to measure the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ composition of pore waters in saturated and unsaturated geologic core samples using direct vapor equilibration and laser spectroscopy (DVE-LS) was first described in 2008, and has since been widely adopted by others. Here, we describe a number of important methodological improvements and limitations encountered in routine application of DVE-LS over several years. Generally, good comparative agreement and accuracy is obtained between core pore water isotopic data obtained using DVE-LS and that measured on water squeezed from the same core. In complex hydrogeologic settings, high-resolution DVE-LS depth profiles provide greater spatial resolution of isotopic profiles compared to long-screened or nested piezometers. When fluid is used during drilling and coring (e.g., water rotary or wet sonic drill methods), spiking the drill fluid with ^2H can be conducted to identify core contamination. DVE-LS analyses yield accurate formational isotopic data for fine-textured core (e.g., clay, shale) samples, but are less effective for cores obtained from saturated permeable (e.g., sand, gravels) geologic media or on chip samples that are easily contaminated by wet rotary drilling fluid. Data obtained from DVE-LS analyses of core samples collected using wet (contamination by drill water) and dry sonic (water loss by heating) methods were also problematic. Accurate DVE-LS results can be obtained on core samples with gravimetric water contents $< 5\%$ by increasing the sample size tested. Inexpensive ZiplocTM gas sampling bags were determined to be as good as, if not better, than other, more expensive bags. Sample storage in gas tight sample bags provides acceptable results for up to 10 days of storage; however, measurable water loss and evaporitic isotopic enrichment occurs for samples stored for up to 6 months. With appropriate care taken during sample collection and storage, the DVE-LS approach for obtaining high resolution pore water isotopic data remains a promising alternative to study the hydrogeology of saturated and unsaturated sediments. Eliminating analytical interferences from volatile organics remains a challenge.

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1 Introduction

The stable isotope composition of pore water ($\delta^2\text{H}$, $\delta^{18}\text{O}$) in unsaturated and saturated zone geologic media is an important hydrologic tracer used to determine the origin, rate of water movement, and mixing of different waters; this method has been applied to studies evaluating resources, the water cycle, and groundwater contamination, as well as those determining soil vapor fluxes (e.g. Clark and Fritz, 1997; Gimmi et al., 2007; Mueller et al., 2014). Traditional approaches for obtaining pore water stable isotope depth profiles from geologic media generally require the installation of wells or piezometers (saturated zone) or suction lysimeters (unsaturated zone) to obtain liquid water samples for offline isotopic assays (Freeze and Cherry, 1979). Although piezometers, wells, and lysimeters are useful for characterizing physical and chemical pore water transients in the subsurface, they generally lack detailed vertical depth resolution (< 1 m scale to detect transients) or may be too expensive to install and monitor over large spatial scales or over detailed vertical profiles. Other water isotope techniques use physical extraction of pore water from sub-samples of saturated or unsaturated cores, such as high-speed centrifugation (Allison and Hughes, 1983; Gimmi et al., 2007; Ingraham and Shadel, 1992; Kelln et al., 2001), mechanical squeezing (Kelln et al., 2001), cryogenic microdistillation (Araguas-Araguas et al., 1995), and azeotropic distillation (Allison and Hughes, 1983; Revesz and Woods, 1990). In general, physical extraction methods are laborious and have the potential for evaporative isotopic fractionation caused by storage, multistep procedures, or by incomplete recovery of the water or evaporative loss during handling. Alternative methods for obtaining pore water isotopes from cores include radial diffusion mass-balance mixing cells (Altinier et al., 2007; Bensenouci et al., 2013; Rubel et al., 2002; Savoye et al., 2006; van der Kamp et al., 1996) or direct equilibration of the pore water in core subsamples using helium- CO_2 or a He- H_2 catalyst mixtures with headspace gas-water equilibration (Hendry et al., 2004; Kelln et al., 2007; Koehler et al., 2000).

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et al., 2013; Mueller et al., 2014; Stumpp and Hendry, 2012), to intermediate depths (< 100 m depths; Hendry et al., 2011a), and on deep geological cores at basinal scales (< 500 m depths; Harrington et al., 2013; Hendry et al., 2013). Since the original DVE-LS publication (Wassenaar et al., 2008), we have applied this method in a number of field studies and made a number of important adaptations gained from the experience of thousands of pore water isotopic analyses. We also discovered unforeseen constraints with the DVE-LS method.

Here, we describe some of the improvements and caveats that were unforeseen at the time of method development. We assess and evaluate several aspects, including: (1) the accuracy of high-resolution isotopic depth profiles by DVE-LS, (2) contamination impacts from a range of drilling and sample collection methods, (3) the effects of long-term sample storage in plastic gas sampling bags and approaches to correct for it, (4) alternate gas sampling bag materials, with the aim of increasing the storage time with no loss of sample integrity, (5) water content limits for obtaining accurate isotopic data; and (6) spectral contamination by petroleum organics. These topics are addressed in separate sections, including a discussion of relevant materials, results, and outcomes. The known issue of high salinity (e.g., cores from deep brines) is considered exceptional to most hydrogeologic water resource studies, and is discussed elsewhere (Brand et al., 2009; Koehler et al., 2013; West et al., 2010).

2 High-resolution DVE-LS profiles vs. pore waters from squeezed cores and piezometers

The ability of the DVE-LS method to produce accurate, high-resolution depth profiles of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of pore water has not been the subject of rigorous testing to date. Only Bourke et al. (2015) compare pore water δ values measured using DVE-LS with water samples obtained by squeezing core samples, finding that both sets of data yield comparable isotopic results. We conducted a similar comparative test at a hydrogeologically complex site having a greater range in pore water δ values. We compared the

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files reflect the dynamic nature of lateral advective transport within the coarse textured zones and diffusion-dominated transport within the finer textured zones (based on the shape of the vertical profiles; however, further discussion of the definition of solute transport based on $\delta^2\text{H}$ and $\delta^{18}\text{O}$ depth profiles is beyond the scope of this paper and the reader is referred to Hendry et al. (2015) for details). The results of isotopic analyses of water samples collected from piezometers also support the general shape of the high-resolution isotopic profiles above. However, the piezometers clearly fail to capture the true hydrogeologic (and isotopic) complexity of the site, and do not reveal the actual isotopic depth profiles obtained from DVE-LS (or squeezing), likely due to spatial variability of sand layers. Thus, an interpretation of the hydrogeology at this site based solely on isotopic data obtained from piezometers would lead to completely erroneous conclusions; the complex hydrogeology is best defined using high-resolution isotopic profiling.

3 Contamination from rotary drilling and coring methods

In the original DVE-LS paper (Wassenaar et al., 2008), continuous saturated and unsaturated core samples were collected to 30 m depth in glacial till using a split spoon sampler advanced through hollow stem augers. Since that study, split spoon core sampling techniques have been successfully used with both solid and hollow stem augers or direct push drilling methods to obtain high-resolution profiles through a range of other near-surface glacial till, glaciolacustrine, and fluvial sediments (< 15 m BG) (Bourke et al., 2015; Hendry and Wassenaar, 2009; Stumpp and Hendry, 2012; Turchenek, 2014). Grab samples from surficial (< 1.5 m BG) sediments collected using a hand auger have also been successfully analyzed (Stumpp and Hendry, 2012).

Auger drilling and hand sample collection methods have major depth and media limitations. Because it is often difficult using auger drilling to collect solid samples at depths > 30 m or in highly consolidated geologic media, rotary drill methods that employ drilling fluids and split spoon core barrels are required to obtain core samples

core barrel (3 m long × 13.8 cm outside diameter (OD)). These samples were immediately trimmed and placed in sealed gas sampling bags in the field. Spiked drill water samples were collected every 10 m of drilling.

The $\delta^2\text{H}$ values of pore waters from intact core samples, trimmed chips, and wiped chips from the Cretaceous shales and drill fluid were plotted vs. depth (Fig. 4). These data clearly reveal that drilling fluid readily contaminated most of the chip samples, regardless of the cleaning method used. The depth profile also revealed that the degree of contamination of chip samples increased with contact time between the chips and the drilling fluid (i.e., contamination was worse in samples from deeper in the core hole due to the longer contact time). In short, DEV-LS analyses of chip samples using rotary drill methods should be avoided.

4 Use of sonic drilling methods for saturated and unsaturated coring and DVE-LS analysis

Sonic drilling differs from mud (water) rotary drilling in that the drill bit is physically vibrated vertically while being pushed down and rotated. It is generally used to collect continuous core samples to depths of 100 m. The effect of wet (using deuterium oxide spiked drill water) vs. dry (no fluid added) sonic core sampling for DVE-LS analyses was tested at a natural saturated site and an unsaturated waste rock pile near Sparwood, British Columbia.

Coring was conducted using a truck-mounted sonic drill rig with a 0.15–0.18 m internal diameter (ID) casing and 0.10 m ID (and occasionally 0.15 m ID) 3.05 m long core tube. The core tube was advanced 3.05 m before extraction of the core and advancement of the casing. Core samples were collected at 1 m intervals and, in the case of the wet drilling, D_2O spiked drill water samples were collected from the drill rig water tank when it was full and half empty. Geologic descriptions of the core were made in the field. The isotopic composition of pore waters in core samples and the drilling fluid were analyzed using DVE-LS (Wassenaar et al., 2008). Sonic drilling can rapidly heat

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texture was predominately sandy but contained cobble-dominated layers in the upper 13 m of the profile. A water table was observed at 65 m BG (Fig. 6). Isotope plots of $\delta^2\text{H}$ for the dry and wet sonic methods are presented in Fig. 6. Contamination by drill fluid during wet coring was evident in a large number of samples, as shown by elevated $\delta^2\text{H}$ values and with depth (49 % of wet core samples were measurably contaminated). The temperature measured in both wet corehole samples (mean = 28.9 ± 8.1 °C, max = 48 °C, min = 19 °C; $n = 37$) and in dry corehole samples (mean = 50.7 ± 21.4 °C, max = 85 °C, min = 16 °C; $n = 59$) were elevated with respect to in situ temperature profiles (mean = 11.2 ± 4.3 °C, max = 29.3 °C, min = 1.4 °C; $n = 187$; unpublished data) measured by thermocouples installed from 0.0–81.3 m BG. As was the case for the wet and dry corehole data from the natural site, the elevated core temperatures in the unsaturated waste rock were attributed to heating during sonic coring. The temperature of the unsaturated dry core samples increased with increased depth or rock strength, often reaching 60–80 °C. Opening core sleeves to collect subsamples often resulted in a rapid loss of water vapor from the unsaturated core (Fig. 7). In some cases, loss of water vapor resulted in kinetic isotope fractionation of the pore water as evidenced by a large number of samples that plotted along an evaporitic fractionation line, with the slope of the line defined by the relative humidity in the atmosphere during sampling (Fig. 8). Although dry sonic coring eliminated the potential for sample contamination by drilling fluid, the kinetic isotope fractionation that can occur as a result of water loss from the core samples complicates interpretation of these isotope measurements, even though the depth profile can incorrectly suggest otherwise (Fig. 6). A method to correct for this isotope fractionation is presented by Barbour et al. (2015).

5 Minimum water content required for DVE-LS analyses of core samples

Based on original water content experiments with DVE-LS, Wassenaar et al. (2008) note that the accuracy of isotopic data obtained by DVE-LS became markedly and progressively positively biased for 60 g samples with < 5 % gravimetric water con-

on samples with GWC > 5% (see details in the figure captions), consistent with the requirement established by Wassenaar et al. (2008).

6 Effects of long-term sample storage in gas sampling bags

In the original DVE-LS method (Wassenaar et al., 2008), core samples were immediately placed in plastic gas sampling bags and the isotopic composition of the headspace measured as soon as possible. In many field-based programs, however, core samples must be stored for extended periods of time or shipped before isotopic analysis is possible. The impact of evaporative water loss, leakage, and subsequent isotopic fractionation during transport or sample storage in gas sampling bags was evaluated by conducting a series of tests to determine the effect of long-term storage on DVE-LS isotope values. Tests were conducted on core samples of glacial till collected at different times from sites near Weyburn, Saskatchewan. Samples were collected using mud rotary drilling methods, trimmed, and bagged as described by Wassenaar et al. (2008). All samples were analyzed using DVE-LS as outlined above and GWC determined within 14 d of collection. The samples were stored in 47 L coolers at room temperature. Selected core samples were taken and analyzed after 6, 17, and 25 months of storage.

Core samples analyzed for stable isotopes by DVE-LS within 14 d of sample collection all plotted along the Local Meteoric Water Line (Fig. 10), indicating these samples were unaffected by short-term storage evaporative effects. However, samples analyzed 6, 17, and 25 months after collection plotted farther along an evaporation line ($y = 3.0 \times -87$; Fig. 10a). Plots of the changes in δ values over time (Fig. 10b and c) indicate a linear increase in the isotopic composition. GWC analyses show water losses from the initial values of $9.1 \pm 8.8\%$ after 6 months, $12.0 \pm 7.0\%$ after 17 months, and $15.0 \pm 9.6\%$ after 25 months. These data reveal that storage of the samples in plastic gas sampling bags for 6 months or more greatly alters the isotopic signature of the pore water, and support the requirement to perform DVE-LS analyses as soon as possible

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after sampling. These findings are consistent Wassenaar et al. (2008), who report isotope values of core samples show evidence of evaporative isotopic enrichment after 12 d of storage.

The fact that the samples fall along a well-defined evaporitic line suggests that these values can be corrected to in situ values using fractionation theory. Although details are not provided in this paper, the slope of the evaporitic line at laboratory temperatures (20°C) and average indoor relative humidity for Saskatoon (35%) is approximately 3.

7 Use of alternative gas sampling bag materials

The inability to store core samples for DVE-LS analyses for long periods in plastic gas sampling bags poses a major limitation to field-based studies (Sect. 6). In an attempt to find a gas sampling bag material that could increase the storage time of core samples for DVE-LS without loss of sample integrity, tests were conducted on gas sampling bags manufactured from alternate materials. The range of gas sampling bag materials included (1) crystal clear, plastic bags with zippered tops, (2) black bags with zippered tops, (3) mylar foil bags, (4) silver foil bags, and (5) IsoPaks™. The crystal clear and black bags were supplied and manufactured by Pacific Bag Inc. (<http://www.pacificbag.net>), the mylar bags and silver pouches (composed of polyester resin) were supplied and manufactured by sorbent systems (<http://www.sorbentsystems.com/ironshield.html>), and the IsoPaks™ were supplied by IsoTech Labs (<http://www.isotechlabs.com>). For comparative purposes, the original low-cost Ziploc™ gas sampling bags were also assessed.

For these tests, 5.0 mL of USGS 47 standard water ($\delta^2\text{H} = -150.2\text{‰}$, $\delta^{18}\text{O} = -19.8\text{‰}$) were placed into 30 Ziploc™ bags, crystal clear bags, black bags, silver pouches, and mylar bags and into 12 IsoPaks™. The top of the crystal clear bags, black bags, and IsoPaks™ were sealed with the zipper seals and, to ensure a complete seal, an additional heat sealing was placed above the zipper. The mylar bags and silver pouches were heat sealed (these bags do not have zipper seals). Heat sealing

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was performed using an American International Electric Inc. Double Impulse sealer. Triplicate samples of Ziploc™, crystal clear packs, black bags, and mylar bags were gravimetrically weighed and analyzed for stable isotopes by DVE-LS at $t = 0$ (after 1 h of sealing), and after 1, 5, 10, 15, 30 and 50 d. Duplicate samples of the IsoPaks™ were tested on all days except day 50. All samples were analyzed by DVE-LS. The headspace gas phase in each bag was also analyzed for light hydrocarbons (C_1 - C_6) after vapor isotope analysis on day 0 and 1 using an Agilent 7890 Gas Chromatograph to check for potential material-derived spectral interferences that would affect the laser isotope analyzer. The precision of hydrocarbon analyses was $< 5\%$. No measurable hydrocarbons were detected on day 0 or 1 in the Ziploc™ bags, crystal clear bags, and IsoPaks™; however, hydrocarbons were detected in the black and mylar bags and silver pouches on day 0 and 1. Based on these findings, hydrocarbon analyses were performed on the black and mylar bags and silver pouches on day 5, 10, 15, 30, and 50.

Water loss in the bags over time is presented in Fig. 11a. Over 50 days of testing, the average water loss from the Ziploc™, crystal clear, and IsoPak™ bags was considerable at 0.61 ± 0.07 , 0.87 ± 0.10 , and 0.26 ± 0.18 g, respectively. In contrast, water loss from the mylar, black bags, and silver pouches over the test period was negligible at 0.02 ± 0.01 , 0.05 ± 0.02 , and 0.27 ± 0.03 g, respectively. Water loss in the Ziploc™ bags, crystal clear bags, and IsoPaks™ was also reflected in considerable evaporitic isotope fractionation (Fig. 11b and c). For example, the mean isotopic enrichments over the test period ranged up to $+11.4\%$ and $+4.5\%$ for δ^2H and $\delta^{18}O$, respectively in the crystal clear bags. The negative deviation of δ^2H and $\delta^{18}O$ in mylar and black bags on day 0, 1, 5, 10, 15, 30, and 50 and in silver pouches on day 15, 30, and 50 was consistent with the presence of volatile organic contaminants that can cause isotopologue interferences with laser-measured δ^2H and $\delta^{18}O$ (see Sect. 8, below). The presence of organic contaminants in these bags was confirmed by the presence of hexane (and presumably other organics) (data not presented). In summary, water loss measured in the Ziploc™ bags, crystal clear bags, and IsoPaks™ resulted in consid-

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the hydrocarbons (having unknown but generally isotopically depleted ^2H content) adversely affected the corresponding pore water results. Further, because oxygen atoms in the sample H_2O vapor exchange oxygen atoms through the CuO catalyst and O_2 at high temperatures, $\delta^{18}\text{O}$ values for pore waters were not possible with this approach (cf. Koehler and Wassenaar, 2012). In summary, a catalytic oxidation interface could potentially overcome some organic gas interferences, provided hydrocarbons are not present at concentrations > 5 vol%, but this methodological addition only allows for pore water $\delta^2\text{H}$ measurements.

9 Summary, conclusions, and future research

The stable isotopes of pore water ($\delta^2\text{H}$, $\delta^{18}\text{O}$) in unsaturated and saturated zone geologic media are important hydrologic tracers that can be used to determine the origin, movement, and flux of water in resource evaluations; inform water cycle studies; evaluate groundwater contamination; and determine soil vapor fluxes. A method of measuring the stable isotope composition of pore water ($\delta^2\text{H}$, $\delta^{18}\text{O}$) obtained from unsaturated and saturated zone geologic media using direct vapor equilibration laser spectroscopy (DVE-LS) was recently developed by Wassenaar et al. (2008) and is now in widespread use. Since its development, our research team has used the DVE-LS method on thousands of samples from a variety of media. This study summarizes some of our testing that informs use of the method.

A good comparative agreement was obtained between core pore water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values obtained using DVE-LS and conventionally squeezed samples. In complex hydrogeologic settings, high-resolution DVE-LS depth profiles provide superior isotopic data compared to long-screened or nested piezometers.

When drilling allows, core samples collected below the water table for DVE-LS analyses are best collected without the use of drill water (e.g., dry sonic) because it can contaminate the pore water isotope signature. In cases where drill fluids are required for drilling, spiking the drill fluid with a $\delta^2\text{H}$ tracer has proven to be of value in defining

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core contamination. Core samples collected using water rotary or wet sonic methods from less permeable zones (e.g., tills and shales) are generally not impacted by drill fluids. In contrast, core samples collected from permeable zones (e.g., sands) should be analysed and the resulting data interpreted with caution because they can be contaminated by drill water. Further, the use of chip samples collected during water rotary drilling for DVE-LS analyses should be avoided because the samples can be quickly contaminated by drill fluids. DVE-LS analyses on core samples collected from thick unsaturated zones using wet and dry sonic methods should be avoided due to contamination by drill water and heating during sonic coring resulting in kinetic fractionation, respectively.

Ziploc™ bags were determined to be as good for DVE-LS analyses, if not better, than other sample bags tested. They are also cost effective and readily available. Core testing showed that core samples should be trimmed and bagged in the field as soon after collection as possible. Ideally, DVE-LS analyses should be undertaken within 10 d of sampling, as loss of water and evaporitic effects on DVE-LS analyses were evident after about 6 months of storage. DVE-LS results can be obtained on samples containing more than 3 g of water when analyzed in 1 L sample bags.

Additional methodological studies to find a gas-sampling bag that can be used to store core samples from extended periods of time as well as a method to remove hydrocarbons from vapor samples without altering the $\delta^{2}\text{H}$ and $\delta^{18}\text{O}$ values are warranted and are being conducted by our group.

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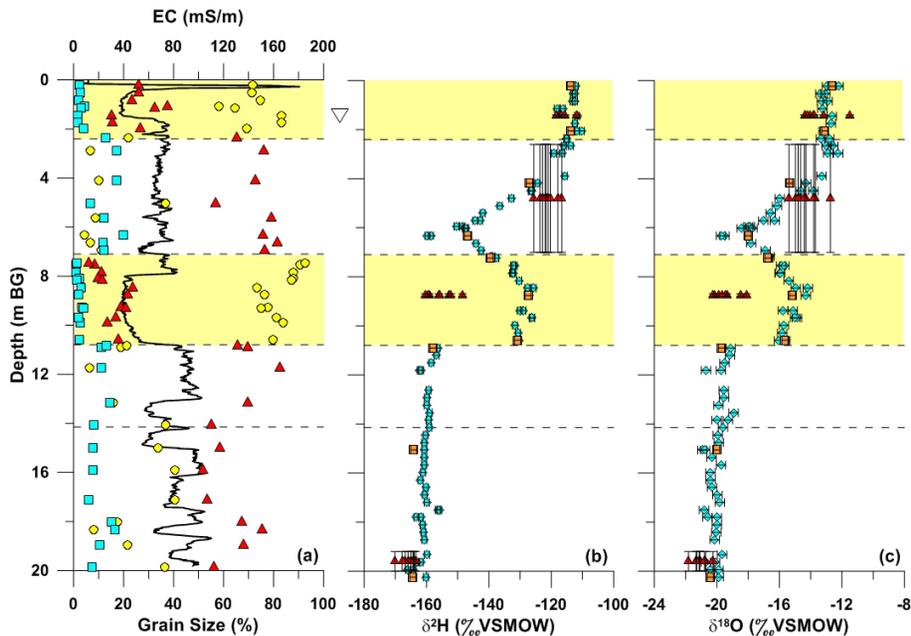


Figure 1. High-resolution profiles vs. elevation above sea level for **(a)** percent sand, silt, and clay and electrical conductivity (EC; measured using a direct push EC log), **(b)** $\delta^2\text{H}$, and **(c)** $\delta^{18}\text{O}$ near Lethbridge, Alberta, Canada. The sand, silt, and clay size fractions in **(a)** are presented as yellow circles, red triangles, and light blue squares, respectively. The vapor, mechanical squeezed, and piezometer values in **(b)** and **(c)** are presented as blue diamonds, orange squares, and red triangles, respectively. The vertical lines for the piezometer values represent the length of the sand pack around the screened zone. The location of the water table is presented as an inverted triangle in **(a)**. Gravimetric water content of all samples ranged from 18–32% ($n = 59$).

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Figure 3. Evaluation of core cuttings as an alternative sample source for DVE-LS: **(a)** sieved chip samples after washing, and **(b)** wiped chip samples (typically 25 mm × 15 mm) prior to placement in Ziploc™ bags.

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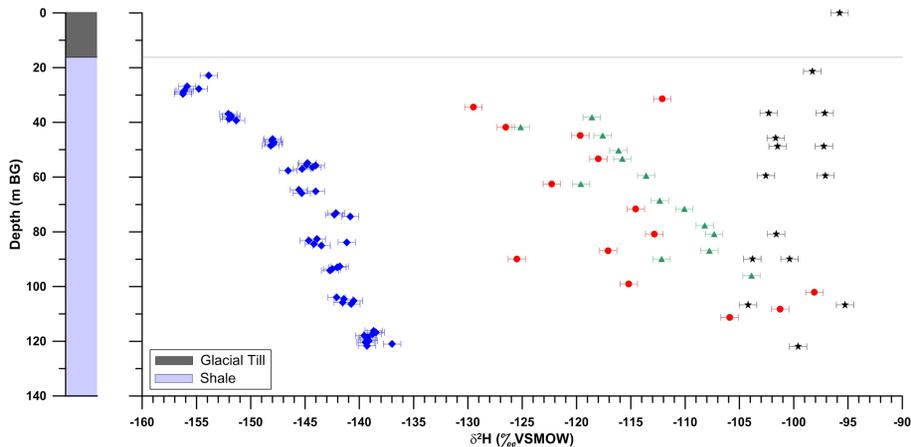


Figure 4. $\delta^2\text{H}$ values vs. depth for pore waters measured via vapor equilibration on core samples (solid blue diamonds), trimmed chip samples (solid red circles), and wiped chip samples (solid green triangles) from Cretaceous shale at a site near Luck Lake, Saskatchewan, Canada. The $\delta^2\text{H}$ values of the drill fluid are presented as solid black stars. The analytical error is presented as horizontal bars. Gravimetric water content of all samples ranged from 15.5–42.2% ($n = 80$).

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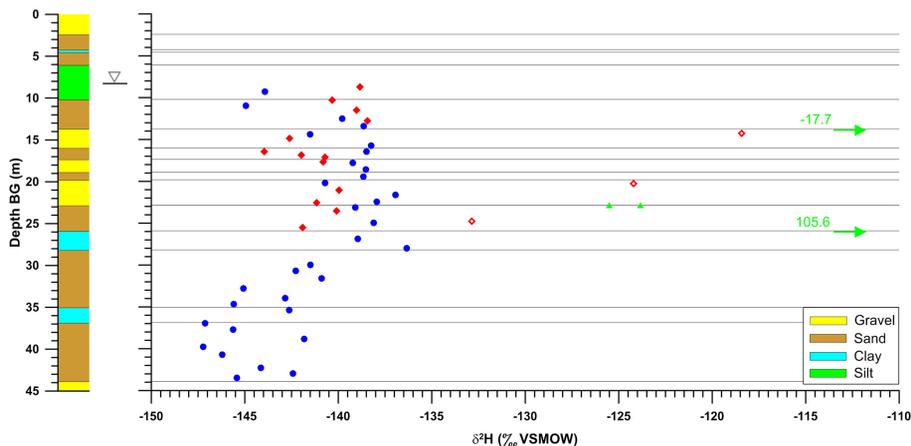


Figure 5. $\delta^2\text{H}$ depth profiles of pore water from a complex, saturated natural geologic media located in the Elk Valley, British Columbia. Values for samples collected via dry sonic coring are represented by solid blue circles, via wet sonic and not showing evidence of contamination (or minimally so) are represented by solid red diamonds, and via wet sonic and visibly contaminated by drill fluid are represented by open red diamonds. The $\delta^2\text{H}$ values of the drill fluid samples are represented by solid green triangles. The location of the water table is identified by inverted triangles. The mean gravimetric water content of samples from adjacent wet and dry sonic core samples from the complex, saturated, natural site were $9.9 \pm 5.1\%$ ($n = 19$) and $12.6 \pm 5.1\%$ ($n = 34$), respectively.

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Figure 7. Vapour condensation on the inside of plastic sampling sleeve at ground surface. Core temperature at ground surface was 85 °C.

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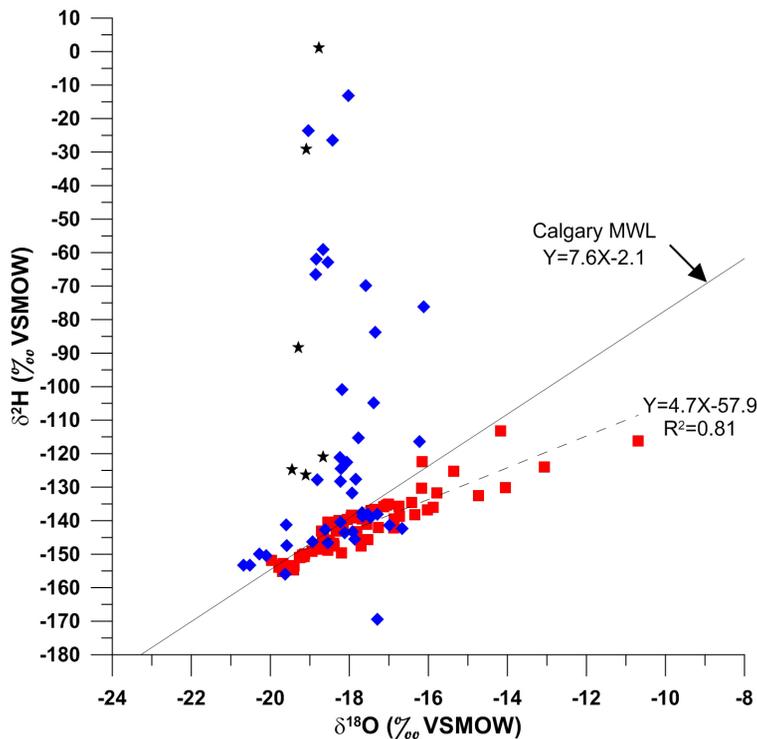


Figure 8. Cross-plot of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of pore waters from core samples collected at two adjacent sites on an unsaturated waste rock pile near Sparwood, British Columbia. Coring was conducted using wet (solid blue diamonds) and dry (solid red squares) sonic drilling. Values for spiked drill mud are presented as solid black stars. The local meteoric water line for Calgary (Peng et al., 2004) and the best-fit (evaporitic fractionation) line for the dry sonic data set are presented as solid and dashed lines, respectively.

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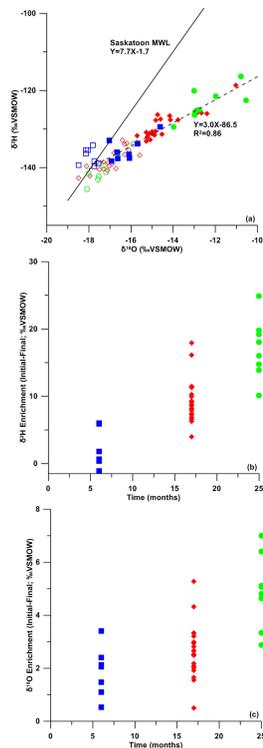


Figure 10. Effect of storage time on $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of pore water in cores stored in ZiplocTM bags: **(a)** cross plot of $\delta^2\text{H}$ and $\delta^{18}\text{O}$, **(b)** $\delta^2\text{H}$ enrichment (initial minus final value) of pore water vs. storage time, and **(c)** $\delta^{18}\text{O}$ enrichment (initial minus final value) of pore water vs. storage time collected from samples of glacial till. All samples were analyzed within 10 d of sampling (open symbols), and after 6, 16, and 22 months of storage (solid blue squares, red diamonds, and green circles, respectively). The solid and dashed lines in **(a)** represent the Saskatoon Meteoric Water Line (MWL) and the best-fit evaporation line to all data, respectively.

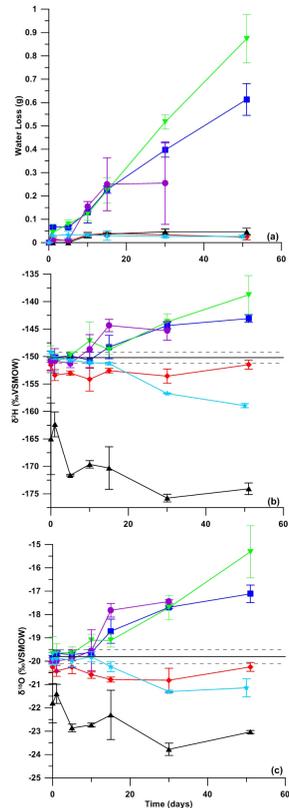


Figure 11. Analytical results (mean and standard deviation of triplicate samples) of **(a)** water loss, **(b)** $\delta^2\text{H}$, and **(c)** $\delta^{18}\text{O}$ in pore water with time for each bag tested. Types tested included Ziploc™ bags (blue squares), crystal clear bags (green inverted triangles), mylar bags (red diamonds), black bags (black triangles), IsoPaks™ (purple circles), and silver pouches (pale blue stars). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of the test pore water are presented as horizontal solid lines, with the associated standard errors presented as dashed lines ($\delta^2\text{H} = \pm 0.8\text{‰}$; $\delta^{18}\text{O} = \pm 0.3\text{‰}$).