

1 **Determining the stable isotope composition of pore**  
2 **water from saturated and unsaturated zone core:**  
3 **Improvements to the direct vapor equilibration laser**  
4 **spectrometry method**

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17  
18 **Abstract**

19 A method to measure the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  composition of pore waters in saturated and  
20 unsaturated geologic core samples using direct vapor equilibration and laser spectrometry  
21 (DVE-LS) was first described in 2008, and has since been rapidly adopted. Here, we  
22 describe a number of important methodological improvements and limitations encountered  
23 in routine application of DVE-LS over several years. Generally, good comparative  
24 agreement and accuracy is obtained between core pore water isotopic data obtained using  
25 DVE-LS and that measured on water squeezed from the same core. In complex  
26 hydrogeologic settings, high-resolution DVE-LS depth profiles provide greater spatial  
27 resolution of isotopic profiles compared to long-screened or nested piezometers. When  
28 fluid is used during drilling and coring (e.g., water rotary or wet sonic drill methods),  
29 spiking the drill fluid with  $^2\text{H}$  can be conducted to identify core contamination. DVE-LS  
30 analyses yield accurate formational isotopic data for fine-textured core (e.g., clay, shale)  
31 samples, but are less effective for cores obtained from saturated permeable (e.g., sand,

32 gravels) geologic media or on chip samples that are easily contaminated by wet rotary  
33 drilling fluid. Data obtained from DVE-LS analyses of core samples collected using wet  
34 (contamination by drill water) and dry sonic (water loss by heating) methods were also  
35 problematic. Accurate DVE-LS results can be obtained on core samples with gravimetric  
36 water contents <5 % by increasing the sample size tested. Inexpensive Ziploc™ gas  
37 sampling bags were determined to be as good as, if not better, than other, more expensive  
38 specialty bags. Sample storage in sample bags provides acceptable results for up to 10 days  
39 of storage; however, measureable water loss and evaporitic isotopic enrichment occurs for  
40 samples stored for up to 6 months. With appropriate care taken during sample collection  
41 and storage, the DVE-LS approach for obtaining high resolution pore water isotopic data  
42 is a promising alternative to study the hydrogeology of saturated and unsaturated  
43 sediments. Eliminating analytical interferences from volatile organics remains a challenge.

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## 45 **1 Introduction**

46 The stable isotope composition of pore water ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ) in unsaturated and saturated zone  
47 geologic media is an important hydrologic tracer used to determine the origin, rate of water  
48 movement, and mixing of different waters; this method has been applied to studies  
49 evaluating resources, the water cycle, and groundwater contamination, as well as those  
50 determining soil vapor fluxes (e.g. Clark and Fritz, 1997; Gimmi et al., 2007; Mueller et  
51 al., 2014). The method of core sampling and subsequent isotope analysis ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) is  
52 best applied when the objective of a study is to characterize vertical and spatial variability  
53 of the stable isotopes of water rather than temporal variability. Traditional approaches for  
54 obtaining pore water stable isotope depth profiles from geologic media generally require  
55 the installation of wells or piezometers (saturated zone) or suction lysimeters (unsaturated  
56 zone) to obtain liquid water samples for offline isotopic assays (Freeze and Cherry, 1979).  
57 Although piezometers, wells, and lysimeters are useful for characterizing physical and  
58 chemical pore water transients in the subsurface, they generally lack detailed vertical depth  
59 resolution (<1 m scale to detect transients) or may be too expensive to install and monitor  
60 over large spatial scales or over detailed vertical profiles. Other water isotope techniques  
61 use physical extraction of pore water from sub-samples of saturated or unsaturated cores,  
62 such as high-speed centrifugation (Allison and Hughes, 1983; Gimmi et al., 2007;

63 Ingraham and Shadel, 1992; Kelln et al., 2001), mechanical squeezing (Kelln et al., 2001),  
64 cryogenic microdistillation (Araguas-Araguas et al., 1995; West et al., 2006; Koeniger et  
65 al., 2011; Orolowski et al., 2013), azeotropic distillation (Allison and Hughes, 1983;  
66 Revesz and Woods, 1990) and microwave-distillation (Munksgaard et al., 2014). In  
67 general, physical extraction methods are laborious and have the potential for evaporative  
68 isotopic fractionation caused by storage, multistep procedures, or by incomplete recovery  
69 of the water or evaporative loss during handling. Alternative methods for obtaining pore  
70 water isotopes from cores include radial diffusion mass-balance mixing cells (Altinier et  
71 al., 2007; Bensenouci et al., 2013; Rubel et al., 2002; Savoye et al., 2006; van der Kamp et  
72 al., 1996) or direct equilibration of the pore water in core subsamples using helium–CO<sub>2</sub>  
73 or a He–H<sub>2</sub> catalyst mixtures with headspace gas-water equilibration (Hendry et al., 2004;  
74 Kelln et al., 2007; Koehler et al., 2000).

75 Wassenaar et al. (2008) proposed a novel method for measuring the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of pore  
76 water in saturated and unsaturated geologic (core, soil) samples by using a direct vapor  
77 equilibration laser spectrometry (DVE-LS) approach. The DVE-LS method is based on the  
78 principle that a geologic sample containing pore water in a closed-system (e.g., a flexible  
79 gas sampling bag) will quickly equilibrate with the available head space, coming to 100 %  
80 relative humidity (RH) at ambient pressures and temperatures and undergoing isotopic  
81 fractionation consistent with equilibrium fractionation within a closed system. The  
82 equilibrated H<sub>2</sub>O headspace is dynamically and quickly sampled by a laser spectrometer  
83 for online isotopic analysis. By strictly controlling the temperature and the time of  
84 H<sub>2</sub>O<sub>porewater</sub>-H<sub>2</sub>O<sub>headspace</sub> equilibration, the isotopic composition of headspace H<sub>2</sub>O vapor is  
85 measured from directly equilibrated saturated or unsaturated core. The well-known  
86 temperature dependent isotopic equilibrium fractionation factors (Majoube, 1971) can be  
87 used to calculate the pore water oxygen and hydrogen isotopic composition; however, it is  
88 generally more accurate and easier to evaluate the fractionation from liquid to vapor by  
89 concurrently running identically equilibrated laboratory water standards of known isotopic  
90 values that span the expected range of the samples using DVE-LS (Wassenaar et al., 2008).  
91 The final isotope composition of the pore water sample is then normalized and reported  
92 according to the Vienna Standard Mean Ocean Water–Standard Light Antarctic  
93 Precipitation (VSMOW-SLAP) scales.

94 The analytical precision of the DVE-LS method for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  ( $\pm 0.4$  ‰ for  $\delta^{18}\text{O}$  and  
95  $\pm 2.1$  ‰ for  $\delta^2\text{H}$ ) is comparable to or better than the aforementioned extractions and isotope  
96 ratio mass-spectrometry (IRMS)-based direct equilibration methods (Kelln et al., 2001;  
97 Morrison et al., 2001), and significantly better than those reported for physical and  
98 chemical water extractions (Allison and Hughes, 1983; Revesz and Woods, 1990).  
99 Accuracy is assured through the application of Identical Treatment (IT) approaches, using  
100 controls and standards and, where available, by field comparison with isotopic data from  
101 piezometers or by other extraction methods.

102 The DVE-LS method has since been adopted and modified to obtain high-resolution  
103 isotopic profiles to define solute transport mechanisms, timing of hydrogeologic events,  
104 and sources of waters in near surface environments such as soils and the unsaturated zone  
105 (<15 m depths; Garvelmann et al., 2012; Hendry and Wassenaar, 2009; Klaus et al., 2013;  
106 Mueller et al., 2014; Stumpp and Hendry, 2012; Sprenger et al. 2015), to intermediate  
107 depths (<100 m depths; Hendry et al., 2011a; Filippini et al., 2015), and on deep geological  
108 cores at basinal scales (<500 m depths; Harrington et al., 2013; Hendry et al., 2013). Since  
109 the original DVE-LS publication (Wassenaar et al., 2008), we have applied this technique  
110 to a number of field studies and made a number of important technical adaptations gained  
111 from the experience of thousands of pore water isotopic analyses. We also discovered some  
112 unforeseen constraints with the DVE-LS method.

113 Here, we describe some of the improvements and caveats that were not anticipated at the  
114 time of method development. We assess and evaluate several aspects, including: (1) the  
115 accuracy of high-resolution isotopic depth profiles by DVE-LS; (2) contamination impacts  
116 from a range of drilling and sample collection methods; (3) the effects of long-term sample  
117 storage in plastic gas sampling bags and approaches to correct for it; (4) alternate gas  
118 sampling bag materials, with the aim of increasing the storage time with no loss of sample  
119 integrity; (5) water content limits for obtaining accurate isotopic data; and (6) spectral  
120 contamination by petroleum organics. These topics are addressed in separate sections,  
121 including a discussion of relevant materials, results, and outcomes. The known issue of  
122 high salinity (e.g., cores from deep brines) is considered exceptional to most hydrogeologic  
123 water resource studies, and is discussed elsewhere (Brand et al., 2009; Koehler et al., 2013;

124 West et al., 2010).

## 125 **2 High-resolution DVE-LS profiles versus pore waters from squeezed cores** 126 **and piezometers**

127 The ability of the DVE-LS method to produce accurate, high-resolution depth profiles of  
128 the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of pore water has not been the subject of rigorous testing to date. Only  
129 Bourke et al. (2015) compare pore water  $\delta$  values measured using DVE-LS with water  
130 samples obtained by squeezing core samples, finding that both sets of data yield  
131 comparable isotopic results. We conducted a similar comparative test at a  
132 hydrogeologically complex site having a greater range in pore water  $\delta$  values. We  
133 compared the high-resolution (cm scale) isotopic depth profiles of pore water determined  
134 by DVE-LS to liquid water samples obtained by both squeezing duplicate core samples  
135 and collection from four site piezometers. DVE-LS was performed on continuous core  
136 taken from the water table (about 0.50 m below ground surface; BG) to 20 m BG at a site  
137 near Lethbridge, Alberta, Canada. Core samples were collected using a split spoon hollow  
138 stem auger at depth intervals of 30 cm (n=60). The percentages of sand, silt, and clay size  
139 particles were determined on core samples taken 10 cm above the DVE-LS core samples  
140 using the method outlined in Sperazza et al. (2004). Electrical conductivity (EC) was  
141 determined using a direct push (D-P) EC logger. Samples were analyzed for pore water  
142 stable isotopes using the DVE-LS method within 14 d of field sampling. Duplicate core  
143 samples (n=9) were targeted to select a wide  $\delta$  range in the corehole, and were squeezed  
144 using a mechanical squeezer at 50 MPa for 24 h within 30 d to obtain liquid water samples.  
145 Water samples were also collected from four standpipe piezometers installed at the drill  
146 site and analyzed for stable isotopes nine times over a three-year period. The DVE-LS  
147 analyses were conducted on core samples using a Picarro 2120i analyzer. Liquid water  
148 samples collected from squeezed samples or piezometers were analyzed by conventional  
149 liquid water laser spectrometry as described by Lis et al. (2008).

150 The geology of the depth profile was determined from logging, grain-size analyses, and  
151 EC logging (Figure 1a), and consisted of a sequence of sand-rich layers (0-2.4 and 7.1-10.8  
152 m BG) and silt-rich layers (2.4-7.1 and >10.8 m BG) (Figure 1a). The water table was at  
153 0.46 m BG at the time of coring, but seasonally ranged from 0.15 to 0.89 m BG.

154 High-resolution pore water isotopic depth profiles obtained by DVE-LS are shown in  
155 Figures 1b and 1c. H and O isotopes exhibited the same depth trends. The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$   
156 values obtained by DVE-LS are in good comparative agreement with the squeezed pore  
157 water sample values, falling within  $\pm 2.0$  ‰ and  $\pm 0.2$  ‰ (n=9), respectively. Good  
158 agreement between these two methods is supported by the observed isotopic discontinuity  
159 for both DVE-LS and squeezed pore water samples across the base of the sand layer at 10.8  
160 m BG. The complex vertical depth trends of squeezed and DVE-LS profiles reflect the  
161 dynamic nature of lateral advective transport within the coarse textured zones and  
162 diffusion-dominated transport within the finer textured zones (based on the shape of the  
163 vertical profiles; however, further discussion of the definition of solute transport based on  
164  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  depth profiles is beyond the scope of this paper and the reader is referred to  
165 Hendry et al. (2015) for details). The results of isotopic analyses of water samples collected  
166 from piezometers also support the general shape of the high-resolution isotopic profiles  
167 above. However, the piezometers clearly fail to capture the true hydrogeologic (and  
168 isotopic) complexity of the site, and do not reveal the actual isotopic depth profiles obtained  
169 from DVE-LS (or squeezing), likely due to spatial variability of sand layers. Thus, an  
170 interpretation of the hydrogeology at this site based solely on isotopic data obtained from  
171 piezometers would lead to completely erroneous conclusions; the complex hydrogeology  
172 is best defined using high-resolution isotopic profiling. The piezometer installed in the  
173 second sand layer in particular (8.75 m BG) shows an offset (-28.5 and -5.1 ‰ for  $\delta^2\text{H}$  and  
174  $\delta^{18}\text{O}$ , respectively) between results obtained from piezometers and those obtained from  
175 DVE-LS and squeezing. This difference was attributed to a recent rapid change in source  
176 water in this sand layer, as evidenced by the sharp isotopic interface across the lower  
177 boundary of the sand.

### 178 **3 Contamination from rotary drilling and coring methods**

179 In the original DVE-LS paper (Wassenaar et al., 2008), continuous saturated and  
180 unsaturated core samples were collected to 30 m depth in glacial till using a split spoon  
181 sampler advanced through hollow stem augers. Since that study, split spoon core sampling  
182 techniques have been successfully used with both solid and hollow stem augers or direct  
183 push drilling methods to obtain high-resolution profiles through a range of other near-

184 surface glacial till, glaciolacustrine, and fluvial sediments (<15 m BG) (Bourke et al., 2015;  
185 Hendry and Wassenaar, 2009; Stumpp and Hendry, 2012; Turchenek, 2014). Grab samples  
186 from surficial (<1.5 m BG) sediments collected using a hand auger have also been  
187 successfully analyzed (Stumpp and Hendry, 2012).

188 Auger drilling and hand sample collection methods have major depth and media  
189 limitations. Because it is often difficult using auger drilling to collect solid samples at  
190 depths >30 m or in highly consolidated geologic media, rotary drill methods that employ  
191 drilling fluids and split spoon core barrels are required to obtain core samples from deeper  
192 (<500 m BG) formations (Hendry et al., 2011a; Hendry et al., 2013; Schmeling, 2014). To  
193 evaluate the impact of the required drilling fluids and potential to contaminate the core pore  
194 water, a series of techniques were employed using drilling fluids spiked with D<sub>2</sub>O tracer.  
195 Estimates of potential contamination of core subsamples by drilling fluids were determined  
196 by pre-spiking the drill rig water reservoir (water was used as a drill fluid in all cases) with  
197 0.015 mL of 99 % deuterium oxide (D<sub>2</sub>O) per 1 L of water (at a cost of USD1/mL of D<sub>2</sub>O)  
198 prior to drilling to increase the  $\delta^2\text{H}$  value of the drilling water by >100 ‰ over natural  
199 values. In these tests, core subsamples were collected and quickly processed in the field in  
200 a manner consistent with Wassenaar et al. (2008). All cores were field extruded and  
201 immediately trimmed to remove drilling fluid from the outer surfaces of the core prior to  
202 bagging the core sample for further processing. Sample exposure to air following core  
203 opening was limited to a few minutes. Coring, sampling, and spiking of drill fluids used in  
204 these studies are described in Hendry et al. (2011a).

205 In the case of rotary drilling, core waters contaminated with drill mud yielded  $\delta^2\text{H}$  values  
206 that plotted far off the expected local meteoric water line (LMWL) as exemplified by data  
207 collected from a Cretaceous shale (12 to 324 m BG) at a site near Esterhazy, Saskatchewan  
208 (Figure 2a). Here, drilling water contaminated eight of the 286 core samples analyzed.  
209 Based on numerous other measurements made on core samples collected in this manner  
210 via rotary drilling at several sites across Saskatchewan, Canada, <3 % of core samples from  
211 shales collected and tested (n=637) were identified as contaminated by drilling fluid.  
212 Similarly, <9 % of Quaternary till (n=179) and <7 % of recent silt samples (n= 55) were  
213 contaminated by drill water (data not presented). These data indicate that the DVE-LS  
214 method can provide accurate formational isotopic values for fine-textured core samples

215 collected using rotary drilling methods followed by rapid core sampling and handling. Not  
216 surprisingly, this method proved largely ineffective on permeable geologic sediments  
217 obtained by rotary drilling. For example, 23 % of saturated sand cores tested (n=151)  
218 collected via rotary drilling across Saskatchewan, Canada were contaminated by drilling  
219 water (data not presented).

220 The importance of rapidly collecting, trimming, and storing core samples after rotary  
221 drilling was reflected in data obtained using an alternate collection method on core samples  
222 from Cretaceous shale (324-411 m BG) at a site located 8 km from the site in Figure 2a.  
223 Here, drilling and coring were conducted using rotary drilling (with D<sub>2</sub>O spiked drill water)  
224 using 3.04 m × 75 mm core barrels with polyvinyl chloride (PVC) liners. Unlike the  
225 sampling approach described above, entire lengths of core from each core barrel were kept  
226 in their PVC liners, but the drilling fluid was simply drained from the core tubes, and the  
227 ends of the PVC tubes capped and sealed. These core tubes were shipped to the laboratory  
228 where they were stored for 2 d before being sub-sampled at 1 m resolution (n=85) for  
229 isotopic analyses. In contrast to the samples extruded and trimmed immediately onsite  
230 (Figure 2a), 84 % of these samples fell above the LMWL indicating extensive  
231 contamination derived from the spiked drill water persisting in the tube (Figure 2b). These  
232 data show that minimizing core exposure time to drilling fluid is critical; core samples  
233 should be trimmed of all drilling mud immediately after collection in the field to minimize  
234 isotopic contamination.

235 In many field programs, the cost of rotary drilling may preclude the extra time required to  
236 collect and trim core samples for DVE-LS analyses and therefore only cuttings can be  
237 collected. Thus, we also examined whether core cuttings could be used as an alternative  
238 sample source. The efficacy of conducting DVE-LS analyses on cleaned drill cutting  
239 samples collected during rotary drilling was assessed in Cretaceous shale at a site near  
240 Luck Lake, Saskatchewan. A Chevron Drag bit was used to maximize the size of the chips  
241 during drilling. Chip samples were collected at 3 m depth intervals from 31-111 m BG by  
242 screening the return drilling fluid through a wire mesh strainer (Figure 3a). The drilling  
243 fluid was spiked with D<sub>2</sub>O as described above. The largest core chips (typically 25 × 15  
244 mm) were collected from the strainer (Figure 3b), and the outer surfaces immediately  
245 cleaned using one of two methods: wiping with paper towels to remove drill fluid or



246 shaving the outer 2 mm from the entire surface. Once the outer surfaces were cleaned, the  
247 chips were placed in sealed gas sampling bags. For comparative purposes, core samples  
248 were also collected at 3 m intervals using a split spoon core barrel (3 m long × 13.8 cm  
249 outside diameter (OD)). These samples were immediately trimmed and placed in sealed  
250 gas sampling bags in the field. Spiked drill water samples were collected every 10 m of  
251 drilling.

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

#### 260 **4 Use of sonic drilling methods for saturated and unsaturated coring and** 261 **DVE-LS analysis**

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

268 Coring was conducted using a truck-mounted sonic drill rig with a 0.15-0.18 m internal  
269 diameter (ID) casing and 0.10 m ID (and occasionally 0.15 m ID) 3.05 m long core tube.  
270 The core tube was advanced 3.05 m before extraction of the core and advancement of the  
271 casing. Core samples were collected at 1 m intervals and, in the case of the wet drilling,  
272 D<sub>2</sub>O spiked drill water samples were collected from the drill rig water tank when it was  
273 full and half empty. Geologic descriptions of the core were made in the field. The isotopic  
274 composition of pore waters in core samples and the drilling fluid were analyzed using  
275 DVE-LS (Wassenaar et al., 2008). Sonic drilling can rapidly heat core samples and high

276 temperatures were suspected to cause evaporation of water in core samples; hence, the  
277 internal temperature of the cores was measured immediately after they were brought to  
278 surface.

279 The geology and isotopic depth profiles for the wet and dry sonic core holes at the natural  
280 site are presented in Figure 5. The geology was characterized by sands with silt-, clay-, and  
281 gravel-dominated layers. The mean temperatures ( $\pm$  standard deviation) of the wet and dry  
282 core samples were  $13.8 \pm 1.7$  °C (max=16.4, min=10.5; n=16) and  $43.7 \pm 22.3$  °C, (max=80,  
283 min=9.2; n=31), respectively. The wet core samples yielded mean temperatures typically  
284 twice that measured in standpipe piezometers installed at this site (mean= $5.0 \pm 1.5$  °C,  
285 max=7.8 °C, min=2.8 °C; n=78; Szmigielski et al., 2014). In contrast, mean temperatures  
286 measured in the dry core samples were on average 40 °C greater than the mean in the  
287 piezometers. These data show that core temperatures at natural (saturated) sites are  
288 influenced by sonic drilling methods. The  $\delta^2\text{H}$  depth profile from the dry corehole exhibited  
289 subtle but continuous trends with depth between all samples. Overall, the wet sonic profile  
290 was consistent with the dry corehole profile, although strong positive contamination  
291 excursions were noted for four isolated samples. Because these excursions trended towards  
292 the  $\delta^2\text{H}$  values of the  $\text{D}_2\text{O}$  spiked drill water (also reflected on a cross plot of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ,  
293 not presented) and three of these samples were from permeable gravel zones, it was  
294 assumed that these few anomalous values were the result of core contamination by drill  
295 fluids. Overall, the data suggest that both wet and dry sonic drilling and coring can be used  
296 with DVE-LS in most hydrogeologic environments to obtain isotopic depth profiles below  
297 the water table. The exception is permeable units, for which a dry sonic drilling and coring  
298 method should be used.

299 Although core sampling to generate isotopic depth profiles in shallow unsaturated zones  
300 has been established (see Introduction), sampling methods to generate vapor profiles of  
301  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  through thick unsaturated zones have not been assessed. We assessed the  
302 applicability of using wet and dry sonic core sampling methods through a thick unsaturated  
303 waste rock pile near Sparwood, British Columbia. The waste rock texture was  
304 predominately sandy but contained cobble-dominated layers in the upper 13 m of the  
305 profile. A water table was observed at 65 m BG (Figure 6). Isotope plots of  $\delta^2\text{H}$  for the dry  
306 and wet sonic methods are presented in Figure 6. Contamination by drill fluid during wet

307 coring was evident in a large number of samples, as shown by elevated  $\delta^2\text{H}$  values and with  
308 depth (49 % of wet core samples were measurably contaminated). The temperature  
309 measured in both wet corehole samples (mean=28.9±8.1 °C, max=48 °C, min=19 °C;  
310 n=37) and in dry corehole samples (mean=50.7±21.4 °C, max=85 °C, min=16 °C; n=59)  
311 were elevated with respect to *in situ* temperature profiles (mean=11.2±4.3 °C, max=29.3  
312 °C, min=1.4 °C; n=187; unpublished data) measured by thermocouples installed from 0.0-  
313 81.3 m BG. As was the case for the wet and dry corehole data from the natural site, the  
314 elevated core temperatures in the unsaturated waste rock were attributed to heating during  
315 sonic coring. The temperature of the unsaturated dry core samples increased with increased  
316 depth or rock strength, often reaching 60-80 °C. Opening core sleeves to collect subsamples  
317 often resulted in a rapid loss of water vapor from the unsaturated core (Figure 7). In some  
318 cases, loss of water vapor resulted in kinetic isotope fractionation of the pore water as  
319 evidenced by a large number of samples that plotted along an evaporitic fractionation line,  
320 with the slope of the line defined by the relative humidity in the atmosphere during  
321 sampling (Figure 8). Although dry sonic coring eliminated the potential for sample  
322 contamination by drilling fluid, the kinetic isotope fractionation that can occur as a result  
323 of water loss from the core samples complicates interpretation of these isotope  
324 measurements, even though the depth profile can incorrectly suggest otherwise (Figure 6).  
325 A method for correcting these profiles for fractionation associated with core heating and  
326 water loss has been developed and will be submitted for publication in the near future.

## 327 **5 Minimum water content required for DVE-LS analyses of core samples**

328 Based on original water content experiments with DVE-LS, Wassenaar et al. (2008) note  
329 that the accuracy of isotopic data obtained by DVE-LS became markedly and progressively  
330 positively biased for 60 g samples with <5 % gravimetric water content (GWC) when tested  
331 in 1 L sample bags, despite the gas sampling bags having a 100 % RH headspace. They  
332 concluded that the DVE-LS technique was not suitable for dry sediments with low water  
333 content.

334 We estimated the minimum mass of water that would be lost from the sand to bring the  
335 headspace to a saturated vapor pressure under ambient laboratory temperatures  
336 (approximately 20 mg at 25 °C). The theoretical equilibrium isotope fractionation that

337 would have occurred was then calculated for a closed system using (Gat, 1996):

338 
$$R_f = R_0 / (\alpha - f(\alpha-1)), \quad [1]$$

339 where R is the ratio of the stable to abundant isotope in the initial (o) and final (f) water,  $\alpha$   
340 is the fractionation factor, and f is the fraction of water remaining in the liquid phase  
341 following equilibration. The theoretical isotope fractionation over the range in water  
342 content compared well with those measured by Wassenaar et al. (2008) (Figure 9),  
343 suggesting that their trends in the measured data were consistent with equilibrium isotope  
344 fractionation (reservoir effect). Minor variances between measured and calculated values  
345 in Figure 9 were attributed to inaccuracies in the estimated mass of water loss (e.g.,  
346 adsorption of water vapor to the sample bag).

347 The minimum 5 % GWC limit suggested by Wassenaar et al. (2008) was originally  
348 determined using 60 g of dry sand in a 1 L gas sampling bag. This GWC equates to a mass  
349 of water in the soil of 3 g and corresponds to an f value in equation [1] of approximately  
350 99 %. This limit suggests that isotope fractionation as a result of water loss to the headspace  
351 and bag would be minimal in geologic samples containing more than 3 g of water. Samples  
352 with GWC <5 % may be analyzed provided the total mass of geologic sample is increased  
353 to ensure that there is sufficient water present within the bag to eliminate additional  
354 fractionation. For example, if a sample with a GWC of 2 % was to be analyzed in a 1 L gas  
355 sampling bag, the total dry mass of the soil sample would have to be increased to >150 g.  
356 The only limitation to this approach is the amount of available headspace available in a 1  
357 L bag for at least 3 min of isotopic gas sampling. Note that all isotopic analyses presented  
358 in Figures 1, 2, and 4-6 were conducted on samples with GWC >5 % (see details in the  
359 figure captions), consistent with the requirement established by Wassenaar et al. (2008).

## 360 **6 Effects of long-term sample storage in gas sampling bags**

361 In the original DVE-LS method (Wassenaar et al., 2008), core samples were immediately  
362 placed in plastic gas sampling bags and the isotopic composition of the headspace  
363 measured as soon as possible. In many field-based programs, however, core samples must  
364 be stored for extended periods of time or shipped before isotopic analysis is possible. The  
365 impact of evaporative water loss, leakage, and subsequent isotopic fractionation during

366 transport or sample storage in gas sampling bags was evaluated by conducting a series of  
367 tests to determine the effect of long-term storage on DVE-LS isotope values. Tests were  
368 conducted on core samples of glacial till collected at different times from sites near  
369 Weyburn, Saskatchewan. Samples were collected using mud rotary drilling methods,  
370 trimmed, and bagged as described by Wassenaar et al. (2008). All samples were analyzed  
371 using DVE-LS as outlined above and GWC determined within 14 d of collection. The  
372 samples were stored in 47 L coolers at room temperature. Selected core samples were taken  
373 and analyzed after 6, 17, and 25 months of storage.

374 Core samples analyzed for stable isotopes by DVE-LS within 14 d of sample collection all  
375 plotted along the Local Meteoric Water Line (Figure 10), indicating these samples were  
376 unaffected by short-term storage evaporative effects. However, samples analyzed 6, 17,  
377 and 25 months after collection plotted farther along an evaporation line ( $y=3.0x-87$ ; Figure  
378 10a). Plots of the changes in  $\delta$  values over time (Figure 10b,c) indicate a linear increase in  
379 the isotopic composition. GWC analyses show water losses from the initial values of  
380  $9.1\pm 8.8$  % after 6 months,  $12.0\pm 7.0$  % after 17 months, and  $15.0\pm 9.6$  % after 25 months.  
381 These data reveal that storage of the samples in plastic gas sampling bags for 6 months or  
382 more greatly alters the isotopic signature of the pore water, and support the requirement to  
383 perform DVE-LS analyses as soon as possible after sampling. These findings are consistent  
384 Wassenaar et al. (2008), who report isotope values of core samples show evidence of  
385 evaporative isotopic enrichment after 12 d of storage and Herbstritt et al (2014) who report  
386 water loss of up to 1 g within the first 10 days of storage in Toppits<sup>®</sup> and CB400-420 bags.  
387 The fact that the samples fall along a well-defined evaporitic line suggests that these values  
388 can be corrected to *in situ* values using fractionation theory. Although details are not  
389 provided in this paper, the slope of the evaporitic line at laboratory temperatures (20 °C)  
390 and average indoor relative humidity for Saskatoon (35 %) is approximately 3.

## 391 **7 Use of alternative gas sampling bag materials**

392 The inability to store for DVE-LS analyses for long periods in plastic gas sampling bags  
393 poses a major limitation to field-based studies (Section 6). In an attempt to find a gas  
394 sampling bag material that could increase the storage time of core samples for DVE-LS  
395 without loss of sample integrity, tests were conducted on gas sampling bags manufactured

396 from alternate materials. The range of gas sampling bag materials included (1) crystal clear,  
397 plastic bags™ with zippered tops, (2) black bags with zippered tops, (3) mylar foil bags,  
398 (4) silver foil bags, and (5) IsoPaks™. The crystal clear™ and black bags were supplied  
399 and manufactured by Pacific Bag Inc. (<http://www.pacificbag.net>), the mylar bags and  
400 silver pouches (composed of polyester resin) were supplied and manufactured by sorbent  
401 systems (<http://www.sorbentsystems.com/ironshield.html>), and the IsoPaks™ were  
402 supplied by IsoTech Labs (<http://www.isotechlabs.com>). For comparative purposes, the  
403 original low-cost Ziploc™ gas sampling bags were also assessed.

404 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  
405 placed into 30 medium-sized Ziploc™ bags, crystal clear bags™, black bags, silver  
406 pouches, and mylar bags and into 12 IsoPaks™. The top of the crystal clear bags™, black  
407 bags, and IsoPaks™ were sealed with the zipper seals and, to ensure a complete seal, an  
408 additional heat sealing was placed above the zipper. The mylar bags and silver pouches  
409 were heat sealed (these bags do not have zipper seals). Heat sealing was performed using  
410 an American International Electric Inc. Double Impulse sealer. Medium-sized Ziploc  
411 freezer bags were placed inside large-sized Ziploc freezer bags and sealed during storage.  
412 Triplicate samples of Ziploc™, crystal clear bags™, black bags, and mylar bags were  
413 gravimetrically weighed and analyzed for stable isotopes by DVE-LS at t=0 (after 1 hour  
414 of sealing), and after 1, 5, 10, 15, 30 and 50 d. Duplicate samples of the IsoPaks™ were  
415 tested on all days except day 50. All samples were analyzed by DVE-LS. The headspace  
416 gas phase in each bag was also analyzed for light hydrocarbons (C<sub>1</sub>-C<sub>6</sub>) after vapor isotope  
417 analysis on day 0 and 1 using an Agilent 7890 Gas Chromatograph to check for potential  
418 material-derived spectral interferences that would affect the laser isotope analyzer. The  
419 precision of hydrocarbon analyses was <5 %. No measurable hydrocarbons were detected  
420 on day 0 or 1 in the Ziploc™ bags, crystal clear bags™, and IsoPaks™; however,  
421 hydrocarbons were detected in the black and mylar bags and silver pouches on day 0 and  
422 1. Based on these findings, hydrocarbon analyses were performed on the black and mylar  
423 bags and silver pouches on day 5, 10, 15, 30, and 50.

424 Water loss in the bags over time is presented in Figure 11a. Over 50 days of testing, the  
425 average water loss from the Ziploc™, crystal clear bags™, and IsoPak™ bags was

426 considerable at  $0.61\pm 0.07$ ,  $0.87\pm 0.10$ , and  $0.26\pm 0.18$  g, respectively. In contrast, water loss  
427 from the mylar, black bags, and silver pouches over the test period was negligible at  
428  $0.02\pm 0.01$ ,  $0.05\pm 0.02$ , and  $0.03\pm 0.03$  g, respectively. Water loss in the Ziploc™ bags,  
429 crystal clear bags™, and IsoPaks™ was also reflected in considerable evaporitic isotope  
430 fractionation (Figure 11b,c). For example, the mean isotopic enrichments over the test  
431 period ranged up to +11.4 ‰ and +4.5 ‰ for  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , respectively in the crystal clear  
432 bags™. The negative deviation of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in mylar and black bags on day 0, 1, 5, 10,  
433 15, 30, and 50 and in silver pouches on day 15, 30, and 50 was consistent with the presence  
434 of volatile organic contaminants that can cause isotopologue interferences with laser-  
435 measured  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  (see Section 8, below). The presence of organic contaminants in  
436 these bags was confirmed by the presence of hexane (and presumably other organics) (data  
437 not presented). In summary, water loss measured in the Ziploc™ bags, crystal clear bags™,  
438 and IsoPaks™ resulted in considerable evaporitic water loss and isotope fractionation (i.e.,  
439 isotopic enrichment) commencing around day 10-15, thus limiting the usefulness of these  
440 gas sampling bags for storage past this time period; this is consistent with the findings  
441 presented in Section 6. Despite limited long-term storage capabilities of the Ziploc™ gas  
442 sampling bags, they are as good as the crystal clear bags™ or IsoPaks™ for short-term  
443 sample collection and storage for DVE-LS analyses. Based on the cost of the Ziploc™  
444 bags, crystal clear bags™, and IsoPaks™ (USD26/100 bags, USD18/100 bags, and  
445 USD1,050/100 bags), the Ziploc™ bags were cost effective and readily available. Mylar  
446 bags, black bags and silver pouches (USD 41/100 bags, USD 16/100 bags, and USD 24/100  
447 bags) were not suitable for the DVE-LS method because of the possibility of contamination  
448 by volatile organics.

## 449 **8 Spectral contamination by volatile organic compounds in core samples**

450 Some geological formations, and particularly those with organic-rich sediments, may host  
451 bacterial populations that produce biogenic gases or may contain gaseous hydrocarbons  
452 that migrate from depth over geologic time scales (Brand et al., 2009; Hendry et al., 2011b;  
453 Schmidt et al., 2012). Unfortunately, a number of hydrocarbons and other volatile organic  
454 compounds are known to cause serious spectral interferences for water isotope analyzers.  
455 We encountered core samples in some Cretaceous shales that contained considerable

456 concentrations of sedimentary CH<sub>4</sub> that seriously affected equilibrium pore water isotopic  
457 measurements using the DVE-LS method (Pratt et al., 2014). While spectral corrections  
458 for the effect of some specific volatile organic compounds (e.g., methane, alcohols) are  
459 feasible up to a few vol % concentrations (Hendry et al., 2011b), it is typically not known  
460 if gaseous hydrocarbons are present in core samples.

461 Rather than attempting to resolve and post-correct for organic spectral interference, we  
462 tried several methods for sample headspace hydrocarbon removal: 1) a 21-cm long CuO  
463 quartz oxidation tube furnace interface at > 950 °C; 2) a reverse flow Nafion scrubber; and  
464 3) an activated carbon tube. Each was placed in-line between the pore water gas sampling  
465 bag and the laser spectrometer sample inlet (Pratt et al., 2014). Only the CuO oven removed  
466 100 % of the hydrocarbons at concentrations up to about 5 vol % as C<sub>1</sub>-C<sub>6</sub>. Although  
467 hydrocarbons were still combusted, at concentrations >5 vol % the impact of additional  
468 H<sub>2</sub>O derived from the burning of the hydrocarbons (having unknown but generally  
469 isotopically depleted <sup>2</sup>H content) adversely affected the corresponding pore water results.  
470 Further, because oxygen atoms in the sample H<sub>2</sub>O vapor exchange oxygen atoms through  
471 the CuO catalyst and O<sub>2</sub> at high temperatures, δ<sup>18</sup>O values for pore waters were not possible  
472 with this approach (*cf.* Koehler and Wassenaar, 2012). The Nafion gas scrubber  
473 construction and operation introduced errors in the isotopic signature. For water molecules  
474 to pass through the Nafion membrane, they must pass through the pore space in the  
475 membrane in a stacked fashion. These molecules are trapped when water vapour ceases to  
476 be passed through the tube and it was not possible to strip the trapped water vapour  
477 molecules between samples. Problems were also encountered with the flow rates of water  
478 passing through the membrane being too slow to allow laser spectrometer measurements.  
479 The Nafion tube did, however, remove 98-100 % of methane at concentrations up to <5  
480 vol %, but in so doing only provided a maximum water vapour concentration of 800 ppmv,  
481 far below the requirement for measurement on the Picarro. The measured isotopic values  
482 exhibited no correlation to the standard water value being evaluated, making the method  
483 unacceptable. The activated carbon filtration system was also successful in removing  
484 methane, but also absorbed most of the water vapour in the sample stream, causing a null  
485 measurement on the laser spectrometer. In summary, a catalytic oxidation interface could  
486 potentially overcome some organic gas interferences, provided hydrocarbons are not



487 present at concentrations >5 vol %, but this methodological addition only allows for pore  
488 water  $\delta^2\text{H}$  measurements.

## 489 **9 Summary, conclusions, and future research**

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

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

504 When drilling allows, core samples collected below the water table for DVE-LS analyses  
505 are best collected without the use of drill water because it can contaminate the pore water  
506 isotope signature. In cases where drill fluids are required for drilling, spiking the drill  
507 fluid with a  $\delta^2\text{H}$  tracer has proven to be of value in defining core contamination. Core  
508 samples collected using water rotary or wet sonic methods from less permeable zones  
509 (e.g., tills and shales) are generally not impacted by drill fluids. In contrast, core samples  
510 collected from permeable zones (e.g., sands) should be analysed and the resulting data  
511 interpreted with caution because they can be contaminated by drill water. Further, the use  
512 of chip samples collected during water rotary drilling for DVE-LS analyses should be  
513 avoided because the samples can be quickly contaminated by drill fluids. DVE-LS  
514 analyses on core samples collected from thick unsaturated zones using wet and dry sonic  
515 methods should be avoided due to contamination by drill water and heating during sonic  
516 coring resulting in kinetic fractionation, respectively. In addition, representative DVE-LS

517 analyses of core samples with gravimetric water contents <5 % can be made provided the  
518 total mass of geologic sample in the Ziploc™ bags is adequate to minimize fractionation.  
519 Ziploc™ bags were determined to be as good for DVE-LS analyses, if not better, than other  
520 sample bags tested. They are also cost effective and readily available. Core testing showed  
521 that core samples should be trimmed and bagged in the field as soon after collection as  
522 possible. Ideally, DVE-LS analyses should be undertaken within 10 d of sampling, as loss  
523 of water and evaporitic effects on DVE-LS analyses were evident after about 6 months of  
524 storage. DVE-LS results can be obtained on samples containing more than 3 g of water  
525 when analyzed in 1 L sample bags.

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

529

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## Figures

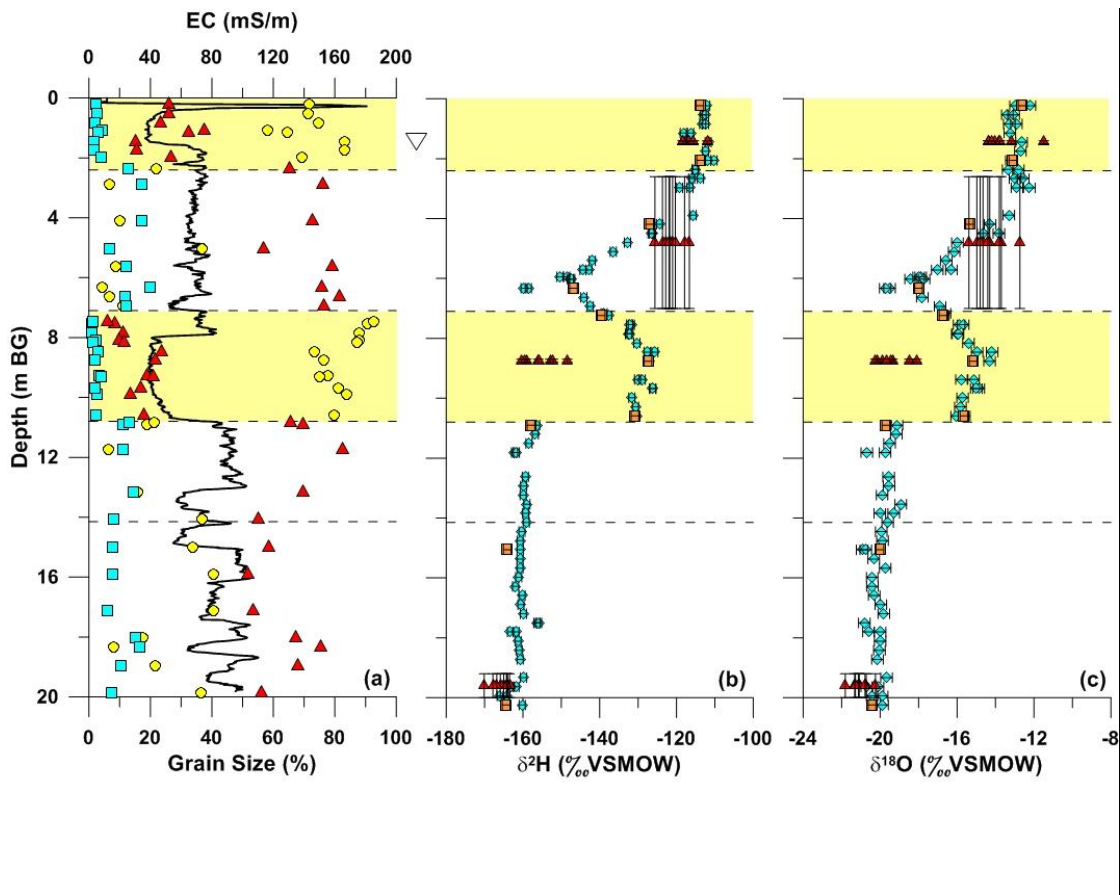


Figure 1. High-resolution profiles vs. meters below ground for (a) percent sand, silt, and clay and electrical conductivity (EC; measured using a direct push EC log), (b)  $\delta^2\text{H}$ , and (c)  $\delta^{18}\text{O}$  near Lethbridge, Alberta, Canada. The sand, silt, and clay size fractions in (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). Yellow shaded areas represent sand layers.

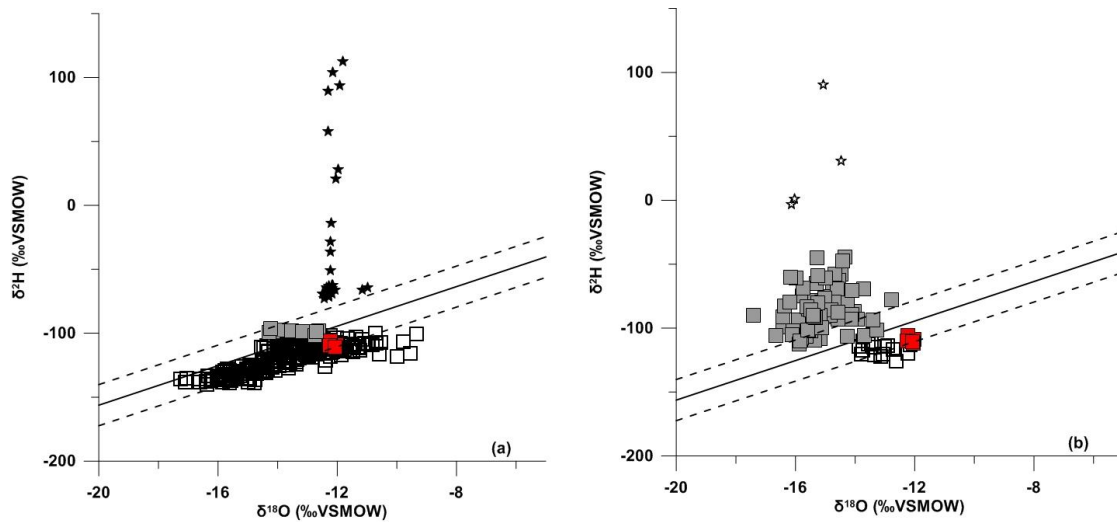


Figure 2. Cross-plot of the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of pore water from Cretaceous shales and drill fluids at two drill sites near Esterhazy, Saskatchewan, Canada. Solid grey squares and open black squares represent contaminated and uncontaminated samples, respectively, trimmed in the field (a) and trimmed in the laboratory (b). Solid red squares represent the source water for rotary drilling, and solid and open stars represent isotopically-spiked drill waters for coreholes for samples trimmed in the field and laboratory, respectively. The local meteoric water line (LMWL) for Saskatoon, Saskatchewan is also presented with associated 95 % confidence intervals (after Hendry et al., 2013). Gravimetric water content of all samples ranged from 7.8-31.3 % (n=101).



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 × 15 mm) prior to placement in Ziploc™ bags.

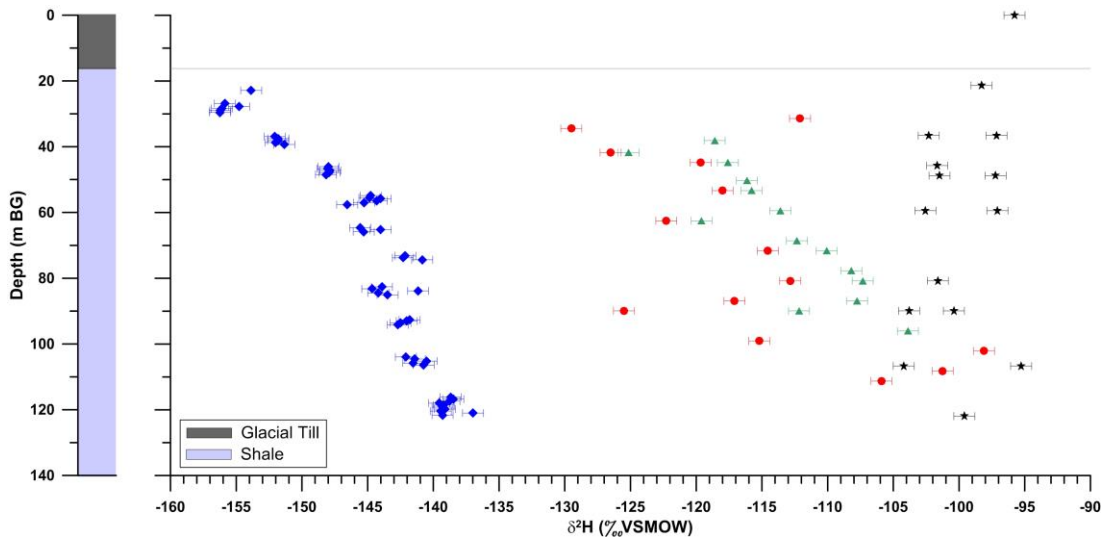


Figure 4.  $\delta^2\text{H}$  values vs. depth for pore waters measured via vapor equilibration on core samples (solid blue diamonds), trimmed chip samples (solid red circles), and wiped chip samples (solid green triangles) from Cretaceous shale at a site near Luck Lake, Saskatchewan, Canada. The  $\delta^2\text{H}$  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).

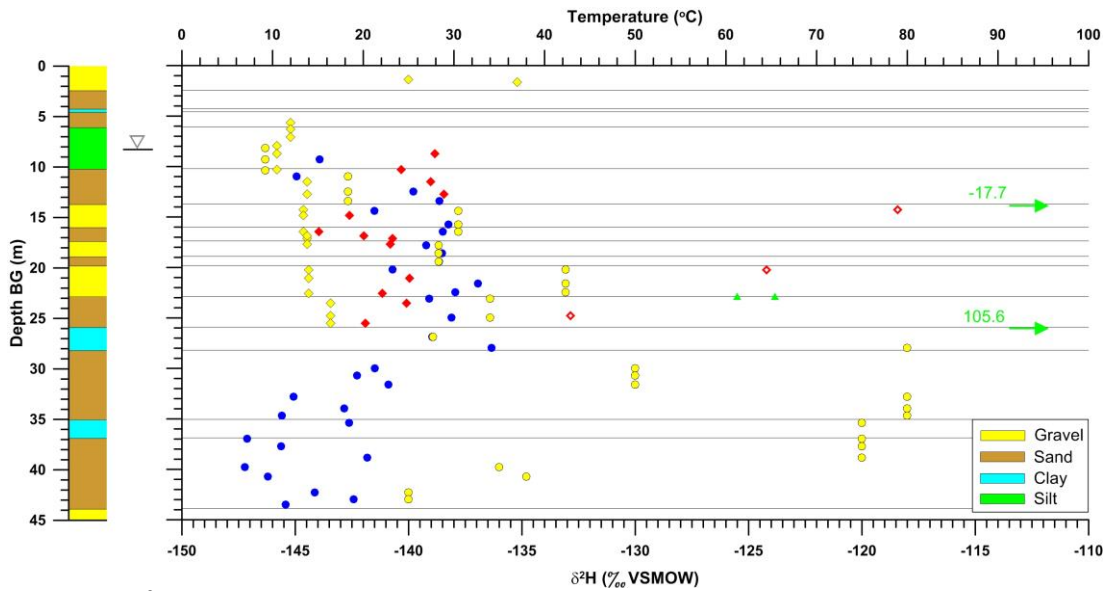


Figure 5.  $\delta^2\text{H}$  depth profiles of pore water from a complex, saturated natural geologic media located in the Elk Valley, British Columbia. Values for samples collected via dry sonic coring are represented by solid blue circles, via wet sonic and not showing evidence of contamination (or 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 temperatures of the core upon extraction are represented by yellow solid circles and yellow solid diamonds for the dry sonic and wet sonic samples, respectively. The location of the water table is identified by an inverted triangle. 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.

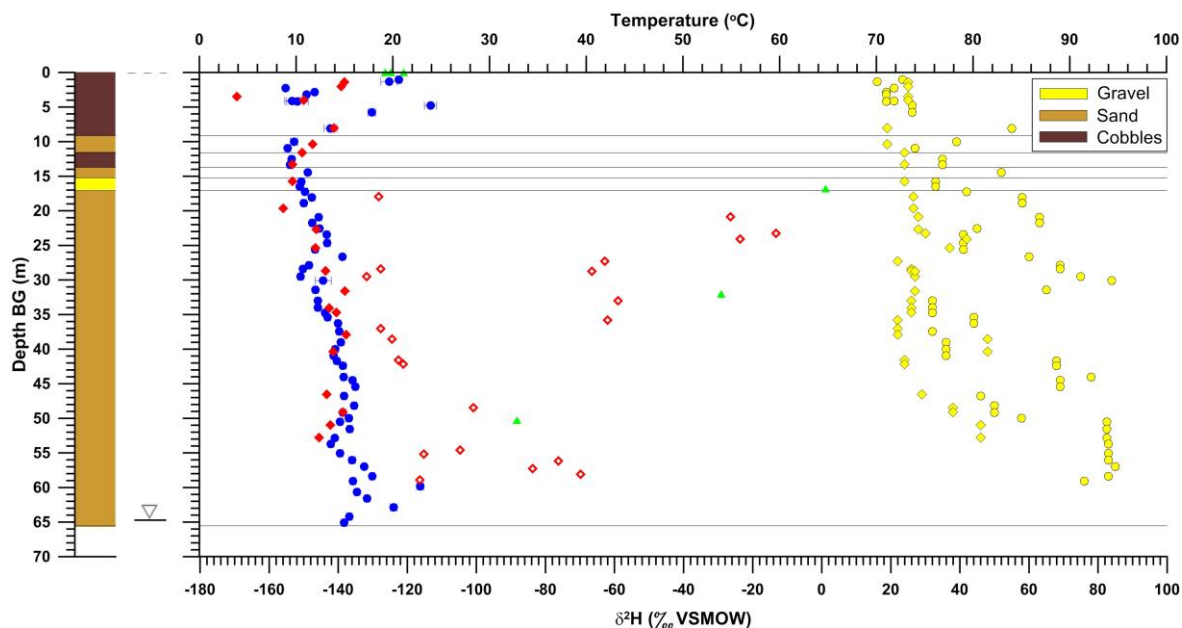


Figure 6.  $\delta^2\text{H}$  depth profiles of pore water from an unsaturated waste rock pile located in the Elk Valley, British Columbia. Samples collected via dry sonic coring are represented by solid blue circles, collected via wet sonic and not showing evidence of contamination (or minimally so) are represented by solid red diamonds, and collected 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 temperatures of the core upon extraction are represented by yellow solid circles and yellow solid diamonds for the dry sonic and wet sonic samples, respectively. The location of the water table is identified by an inverted triangle. The mean gravimetric water content of samples from adjacent wet and dry sonic core samples from the unsaturated waste rock pile were  $7.8 \pm 1.5\%$  ( $n=35$ ) and  $7.6 \pm 2.0\%$  ( $n=39$ ), respectively.



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

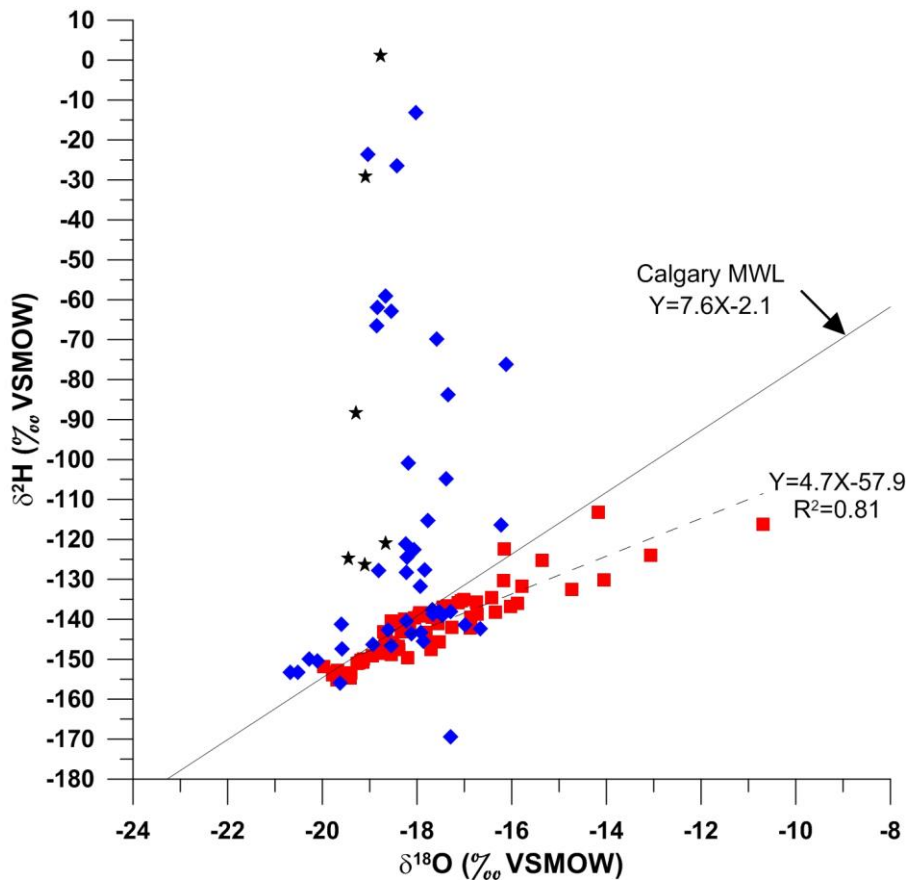


Figure 8. Cross-plot of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of pore waters from core samples collected at two adjacent sites on an unsaturated waste rock pile near Sparwood, British Columbia. Coring was conducted using wet (solid blue diamonds) and dry (solid red squares) sonic drilling. 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.



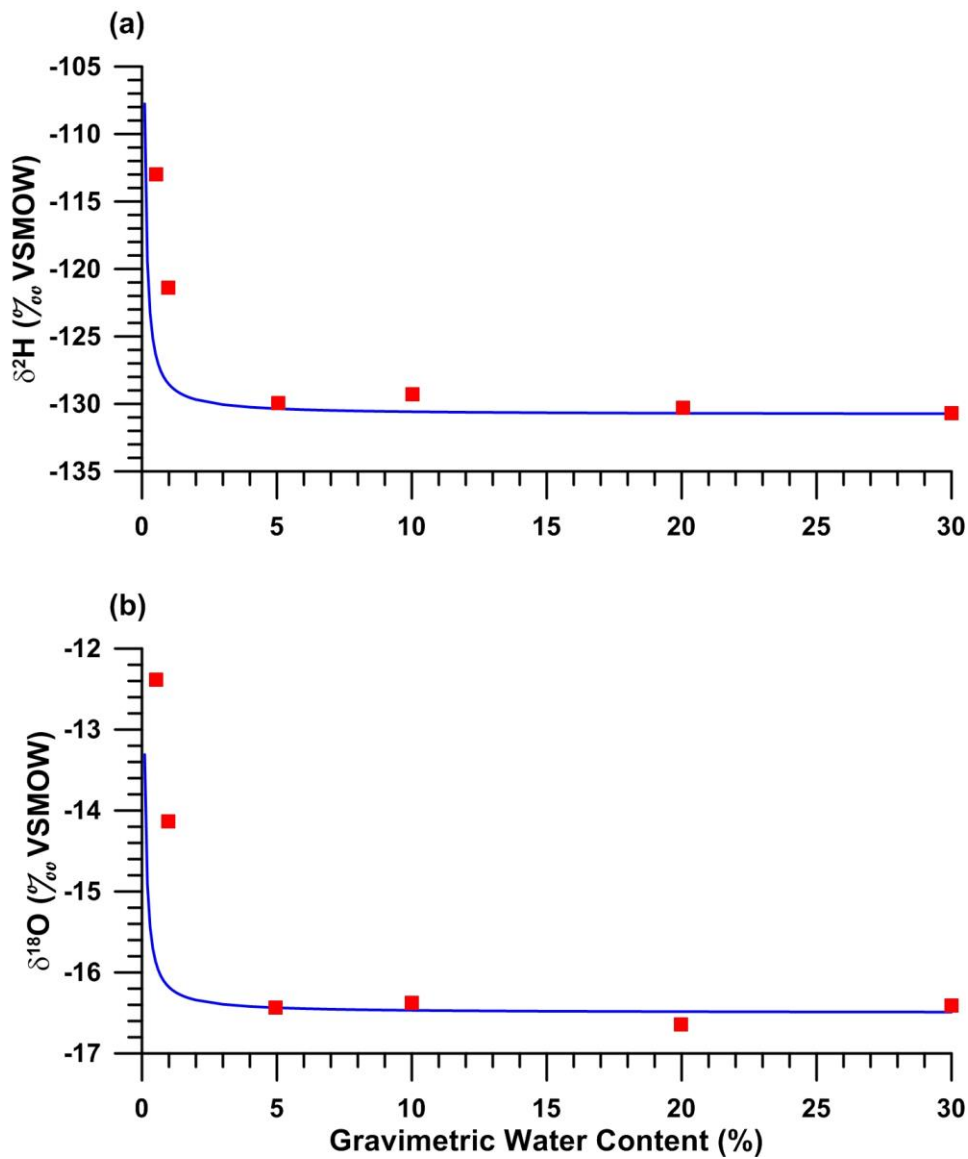


Figure 9. Calculated isotopic equilibrium fractionation of pore water in a closed system (blue line) compared to data from Wassenaar et al. (2008) measured in the headspace of Ziploc™ bags for (a)  $\delta^2\text{H}$  and (b)  $\delta^{18}\text{O}$ .

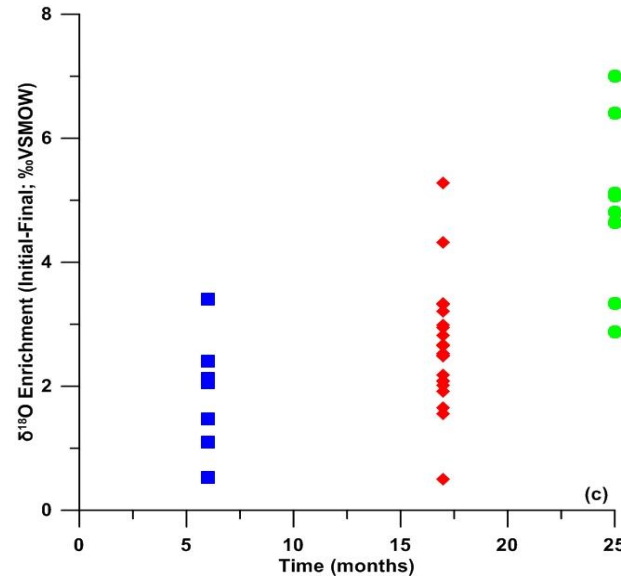
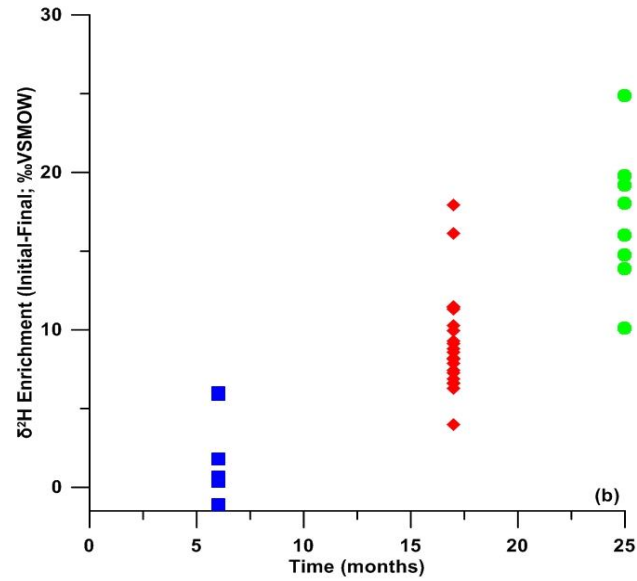
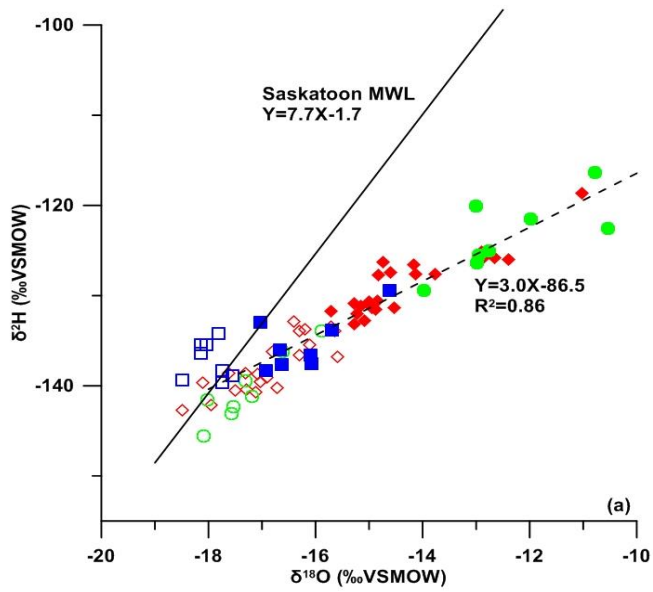


Figure 10. Effect of storage time on  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of pore water in cores stored in Ziploc™ bags: (a) cross plot of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , (b)  $\delta^2\text{H}$  enrichment (initial minus final value) of pore water vs. storage time, and (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.

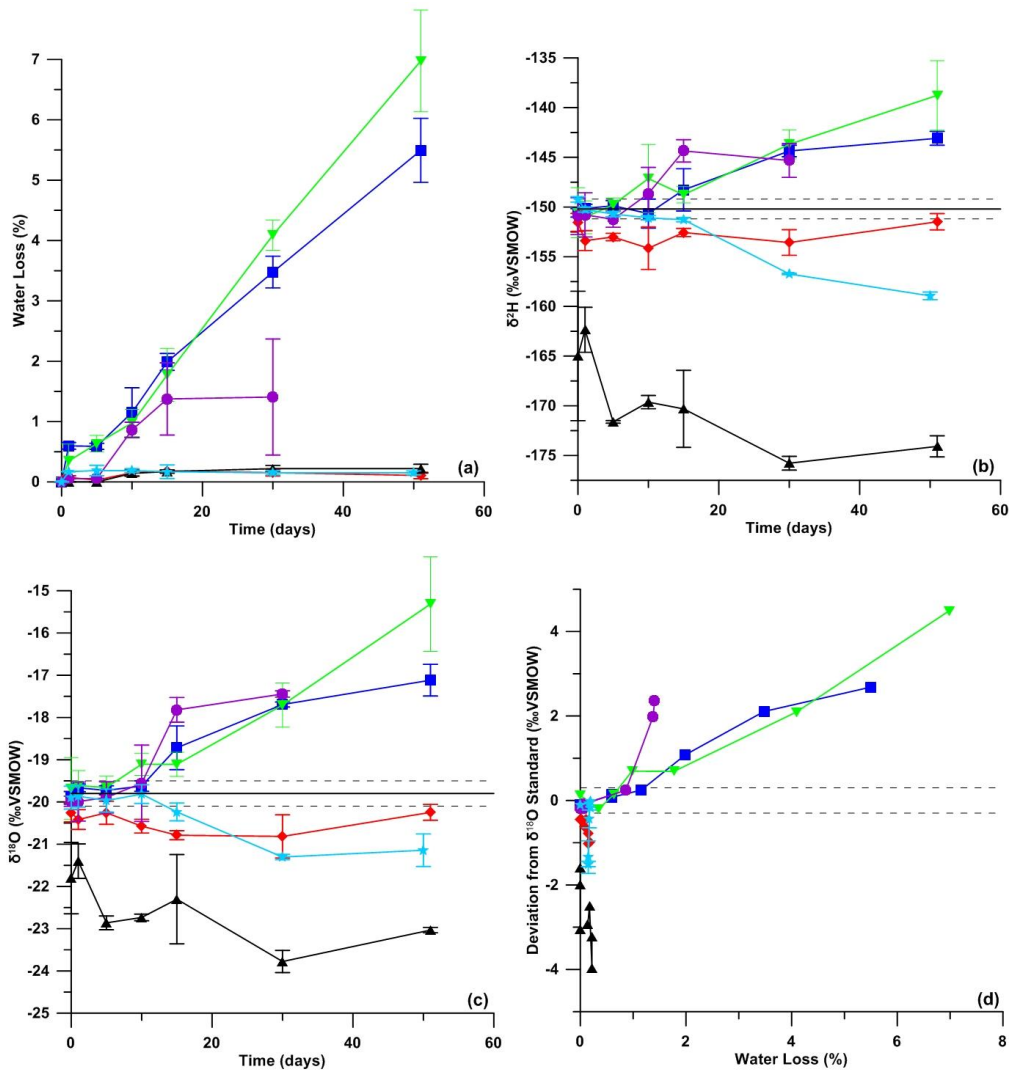


Figure 11. Analytical results (mean and standard deviation of triplicate samples) of (a) water loss, (b)  $\delta^2\text{H}$ , (c)  $\delta^{18}\text{O}$  in pore water with time for each bag tested, and (d) water loss vs. deviation from the  $\delta^{18}\text{O}$  isotope standard value. Types tested 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 ( $\delta^2\text{H}=\pm 0.8\text{‰}$ ;  $\delta^{18}\text{O}=\pm 0.3\text{‰}$ ).