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# An Automated Technique for Measuring $\delta\text{D}$ and $\delta^{18}\text{O}$ Values of Porewater by Direct $\text{CO}_2$ and $\text{H}_2$ Equilibration

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**The stable-oxygen and -hydrogen isotopic values ( $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ) of porewater in geologic media are commonly determined on water obtained by extraction techniques such as centrifugation, mechanical squeezing, vacuum heating and cryogenic microdistillation, and azeotropic distillation. Each of these techniques may cause isotopic fractionation as part the extraction process and each is laborious. Here we demonstrate a new approach to obtain automated, high-precision  $\delta\text{D}$  and  $\delta^{18}\text{O}$  measurements of porewater in geologic sediments by direct  $\text{H}_2$ - and  $\text{CO}_2$ -porewater equilibration using a modified commercial  $\text{CO}_2$ -water equilibrator. This technique provides an important and cost-effective improvement over current extraction methods, because many samples can be rapidly analyzed with minimal handling, thereby reducing errors and potential for isotopic fractionation. The precision and accuracy of direct  $\text{H}_2$ - and  $\text{CO}_2$ -porewater equilibration is comparable to or better than current porewater extraction methods. Finally, the direct equilibration technique allows investigators to obtain high-resolution (cm scale) porewater  $\delta\text{D}$  and  $\delta^{18}\text{O}$  profiles using cores from individual boreholes, eliminating the need for costly piezometers or conventional porewater extractions.**

The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of porewater extracted from geologic media have been used to determine the age and origin of porewaters,<sup>1–3</sup> and in some cases, depth trends of  $\delta^{18}\text{O}$  and/or  $\delta\text{D}$  values of porewaters have yielded long-term trends of past climatic changes.<sup>4–6</sup> To obtain detailed  $\delta^{18}\text{O}$  and  $\delta\text{D}$  profiles from geologic media, stable isotope measurements are most commonly made on porewater that has been obtained using various extrac-

tion techniques. These extraction techniques include centrifugation,<sup>7,8</sup> mechanical squeezing,<sup>9</sup> vacuum heating and cryogenic microdistillation,<sup>10–12</sup> and azeotropic distillation with an immiscible organic solvent such as toluene.<sup>13–16</sup> Each of these techniques has limitations and the potential for causing isotopic fractionation as part of a multistep extraction process. For example, mechanical squeezing and centrifugation require relatively large amounts of intact sample material (hundreds of g) and a specialized hydraulic press or high-speed centrifuge.<sup>17</sup> Porewater extractions using these methods can take 24–48 h or more and, therefore, are subject to evaporation effects. For fine-grained, low permeability geologic media in particular, mechanical extractions cannot recover all of the porewater and, again, may result in isotopic fractionation. Extraction of porewater from core samples by azeotropic distillation or other heating and cryogenic methods may be further complicated by the presence of hydrated minerals (e.g., gypsum), which can release structural water during heating. The azeotropic distillation method involves handling of toxic solvents such as toluene and requires specialized glass and fume hood apparatus.<sup>15</sup> Because of the heating and condensation steps involved, inattention during distillation can easily lead to large isotopic fractionations of the water sample. Thus, new techniques are needed to obtain reliable and detailed  $\delta^{18}\text{O}$  and  $\delta\text{D}$  profiles from porewater in geologic media.

For clay sediments, the aforementioned techniques are made more difficult due to the low permeability of the media, which frequently leads to incomplete recovery of water and results in considerable isotopic fractionation.<sup>17</sup> More recently, a radial diffusion cell (RDC) method was developed to overcome some of the limitations for determining the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  composition of

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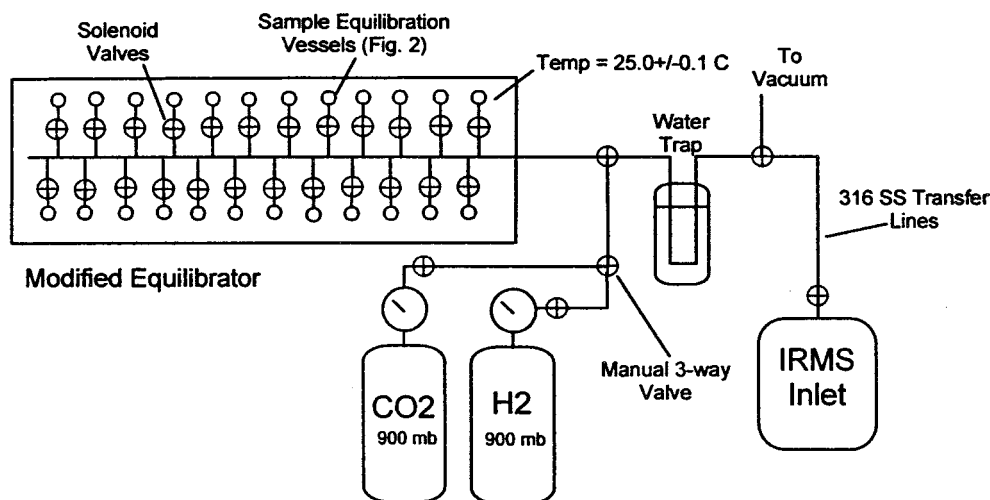


Figure 1. Simplified schematic diagram of modified Micromass CO<sub>2</sub>–water equilibrator to accommodate H<sub>2</sub>–water and direct H<sub>2</sub>–porewater equilibration.

porewater from low-permeability clay-rich core samples.<sup>18</sup> However, the RDC method requires precisely measured physical and isotopic parameters for each diffusion cell (e.g., mass, porosity, moisture content, cell geometry, and initial reservoir  $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) and requires approximately 40–60 days to complete individual samples. Therefore, the RDC technique is impractical where large numbers of samples are involved.

It is well known that CO<sub>2</sub> quickly comes to isotopic equilibrium with liquid water,<sup>19</sup> and the isotopic fractionation factor for the exchange reaction is well established.<sup>20</sup> Thus, an alternative approach to measuring the  $\delta^{18}\text{O}$  values of porewater from water-saturated geologic media is to directly equilibrate core samples with CO<sub>2</sub>, thereby avoiding the steps of having to physically extract porewater. A direct CO<sub>2</sub>–porewater equilibration approach was demonstrated for unsaturated soils and plants, provided the moisture contents are generally greater than 10%.<sup>21–24</sup> The equilibrated CO<sub>2</sub> gas is measured for its stable oxygen isotopic composition, thereby providing a measure of the  $\delta^{18}\text{O}$  of the porewater. Because the CO<sub>2</sub> equilibration technique is widely used to measure  $\delta^{18}\text{O}$  values of water, commercial equilibration devices are easily accessed and may be modified for direct equilibration of sediment samples for porewater  $\delta^{18}\text{O}$  measurements.<sup>23</sup>

Although automated equilibration of H<sub>2</sub> gas with liquid water in the presence of a Pt catalyst has been developed to determine the  $\delta\text{D}$  values of natural waters,<sup>25,26</sup> to our knowledge such an approach has not been demonstrated for direct  $\delta\text{D}$  measurements of porewaters in geologic media. A direct H<sub>2</sub>–plant–water equilibration for  $\delta\text{D}$  determinations was first attempted by Scrimgeour<sup>21</sup> using an alumina catalyst, however, the variability resulting from off-line determinations ( $\pm 15\%$ ) were deemed unacceptable for natural-abundance isotopic studies. A combined measurement of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  is often critical when evaluating porewater for sources or for processes such as evaporation or to derive climatic information.<sup>1–3</sup>

The objective of this paper was to improve and extend the direct equilibration approach to include automated, high-precision  $\delta\text{D}$  and  $\delta^{18}\text{O}$  measurements of porewater in geologic sediments. A significant advantage of this automated, direct H<sub>2</sub>– and CO<sub>2</sub>–porewater equilibration technique over conventional extraction techniques is that many samples can be analyzed with minimal

handling, thereby reducing errors and potential for isotopic fractionation and greatly increasing sample throughput. In addition, this technique allows the investigator to obtain high-resolution isotopic depth profiles from cores collected from a single borehole, instead of requiring the installation of costly, multiple piezometers or conducting conventional mechanical porewater extractions.<sup>17</sup>

#### ANALYTICAL PROCEDURES

**Equilibrator Modifications.** Minor modifications to a standard Micromass Isoprep-18 CO<sub>2</sub>–water equilibration device were required to accommodate H<sub>2</sub> equilibration for  $\delta\text{D}$  measurements of both waters and porewaters. The  $\delta\text{D}$  values of liquid water samples can be measured by equilibration with H<sub>2</sub> gas in the presence of a special Pt catalyst, commonly referred to as “Hokko beads”.<sup>25,26</sup> With the exception of the addition of a catalyst, our technique is virtually identical to standard CO<sub>2</sub>–water equilibrations and therefore is easily adapted to automated on-line systems.<sup>27</sup> The equilibrator device required only simple hardware modifications to accommodate the hydrogen equilibration technique (Figure 1). First, because the original Tygon tubing fittings on the equilibrator adsorb water and therefore could adversely affect deuterium measurements, all original Tygon transfer tubing between the equilibrator and the water trap was replaced with an equivalent outer diameter Swagelock 316 stainless steel (SS) tubing and SS flexible hose. A second modification was the addition of a second SS gas reservoir for the H<sub>2</sub> equilibration gas and a three-

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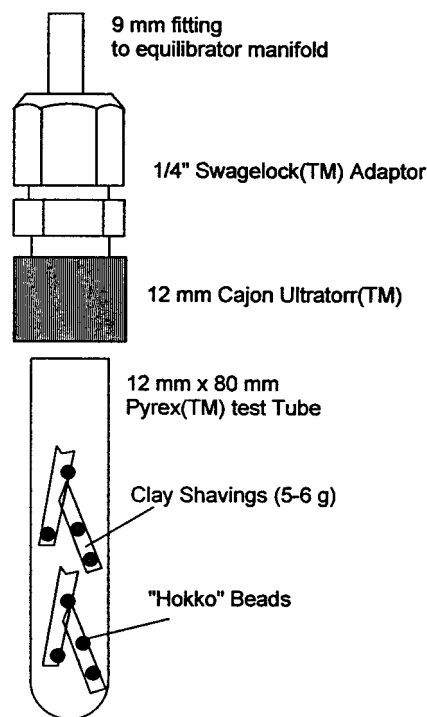


Figure 2. Sample equilibration vessel constructed for direct  $\text{H}_2$ - and  $\text{CO}_2$ -porewater equilibration of sediment samples.

way SS Swagelock valve to allow switching between automated  $\text{CO}_2$  and  $\text{H}_2$  equilibration modes (Figure 1). A 0–30 psi pressure gauge was placed between the hydrogen reservoir and the three-way valve to monitor pressure in the  $\text{H}_2$  reservoir. Research grade gases for filling the  $\text{CO}_2$  and  $\text{H}_2$  reservoirs were plumbed directly from high-pressure cylinders with copper tubing, safety valves, and regulators. Because  $\text{H}_2$  gas has a significantly lower signal per unit volume compared to  $\text{CO}_2$ , each equilibration run required the  $\text{H}_2$  reservoir to be refilled with hydrogen. We used a pressure of 900 mbar in the  $\text{H}_2$  and  $\text{CO}_2$  reservoir, which allowed sufficient gas from each equilibrated sample to reach the isotope ratio mass spectrometer (IRMS). The oscillating sample manifold, normally used to accelerate  $\text{CO}_2$ -water equilibration, was switched off for all  $\text{H}_2$ -water and  $\text{H}_2$ -core equilibrations. These simple modifications (Figure 1) allowed the Micromass IRMS software to automatically control all aspects of  $\text{H}_2$  and  $\text{CO}_2$  equilibration, sample gas transfer, and analysis.

The standard narrow-necked conical equilibration vessels used on the equilibrator system were not suitable for containing sediment samples used in direct equilibration. Custom sample equilibration tubes were constructed from 12-mm-o.d. by 80-mm Pyrex test tubes, which served as the sample equilibration vessel (Figure 2). The sample equilibration tubes containing core or sediment were attached to the equilibrator sample bench by means of 9–22-mm Swagelock UltraTorr reducing adaptors. The equilibration vessels were designed to hold a 2–10 g of sediment and  $\sim 6 \text{ cm}^3$  of  $\text{CO}_2$  or  $\text{H}_2$  at  $\sim 600$  mbar, which was sufficient to allow expansion of equilibrated gas into the inlet system of the IRMS.

**Hydrogen Isotopic Analysis of Natural Waters.** For stable-hydrogen isotope analysis, we used an in-house research grade  $\text{H}_2$  gas in the IRMS reference bellows that had a  $\delta\text{D}$  value of  $\sim -750\text{‰}$  Vienna Standard Mean Ocean Water (VSMOW), and

Table 1.  $\delta\text{D}$  Results ( $\text{‰} \pm 1 \text{ SD}$ ) of  $\text{H}_2$ -Water Equilibrations Using the Modified Isoprep Equilibrator, Compared with Known Values of Calibrated Intercomparison Waters

sample	$\delta\text{D}$ (VSMOW)	$\delta\text{D}$ known value
SSRW	$-133 \pm 0.6$ ( $n = 5$ )	$-133^a$
SSNOW	$-202 \pm 0.8$ ( $n = 5$ )	$-202^a$
USGS35000	$-395 \pm 1.0$ ( $n = 5$ )	$-395^b$
USGS39500	$-1.4 \pm 0.2$ ( $n = 5$ )	$-1.5^b$

<sup>a</sup> Based on over 60 analyses conducted over 2 years by zinc reduction at NWRI. <sup>b</sup> Intercomparison samples provided by T. Coplen (USGS, Reston, VA).

we included 4 calibrated in-house water standards for every set of 20 water or porewater analyses. Table 1 shows the results of  $\text{H}_2$ -water equilibrations, normalized to the VSMOW-Standard Light Arctic Precipitation (SLAP) standard scale. Samples measured by conventional zinc reduction and laboratory intercomparisons are also given in Table 1. External reproducibility and precision for automated  $\text{H}_2$ -water equilibration was better than  $\pm 1\text{‰}$ .

The equilibrator was first tested with a blank run of  $\leq 99.99\%$   $\text{H}_2$  gas to ensure satisfactory performance of the automated system for hydrogen. Twenty-four Pyrex conical sample equilibration vessels were loaded on the sample bench (Figure 1) but contained no water or Pt catalyst. The water trap on the equilibrator prior to the IRMS sample inlet was filled with liquid  $\text{N}_2$  and covered with a foam insert to minimize loss of liquid  $\text{N}_2$  over the course of the automated analysis of 24 samples ( $\sim 3 \text{ h}$ ). The IRMS system filled the empty sample vessels with  $\text{H}_2$  and conducted automated sample analysis at  $25^\circ\text{C}$ . Blank runs of 24 samples of  $\text{H}_2$  were made using an equilibration gas against itself ( $\sim -1000\text{‰}$  VSMOW) and against a  $\sim -700\text{‰}$  (VSMOW) reference gas. Results of two 24 automated blank sample runs were  $-1.6 \pm 0.56$  ( $n = 24$ ) and  $+371.8 \pm 0.58\text{‰}$  ( $n = 24$ ), respectively. These results showed the equilibrator did not leak  $\text{H}_2$  or otherwise cause hydrogen isotopic fractionation during gas transfers to the IRMS inlet system.

For natural water samples, the standard conical equilibration vessels were loaded with 20–40 mg ( $\sim 10$ – $20$  beads) of 1-mm-o.d. Hokko beads (Shoko Co. Ltd.), a Pt-doped styrene-divinylbenzene copolymer, followed by 3 mL of water. An automated analysis run was set up as above. The IRMS system evacuated the samples through individual capillaries for 3 min, followed by filling of the sample vessels with 100%  $\text{H}_2$ . Although complete water- $\text{H}_2$  equilibration should take as little as 1 h,<sup>27</sup> the electric solenoid valves for each sample vessel on the equilibrator bench (Figure 1) generated heat when initially opened for automatic filling of the equilibration vessels, leading to a temperature rise. The temperature rose to  $27^\circ\text{C}$  within minutes after automatically filling the equilibration vessels with  $\text{H}_2$  and slowly dissipated after  $\sim 1 \text{ h}$ ; therefore, a 4-h equilibration time at  $25 \pm 0.1^\circ\text{C}$  was found to be sufficient to achieve the thermal stability required for hydrogen equilibration of water samples.<sup>27</sup>

**Laboratory Testing of Direct Equilibration.** Samples of local clay-rich glacial till were dehydrated in a drying oven at  $110^\circ\text{C}$ , ground using a mortar and pestle, and then resaturated with water of known  $\delta^{18}\text{O}$  isotopic composition. The clay mixtures were



Table 2. Measured  $\delta^{18}\text{O}_{\text{VSMOW}} \pm \text{SD}$  ( $n$ ) of Synthetic Core Porewater, RDC Porewater, and 100% Silica Sand Porewater Measured by Direct  $\text{CO}_2$ -Porewater Equilibration<sup>a</sup>

sample	moisture content (wt %)	$\delta^{18}\text{O}_{\text{meas}}$ (‰)	$\delta^{18}\text{O}_w$ (‰)	diff (‰)
S-Core 1	27.0	$-16.8 \pm 0.3$ (18)	$-17.4 \pm 0.1$	+0.6
S-Core 2	8.5	$-16.8 \pm 0.3$ (17)	$-17.3 \pm 0.1$	+0.5
silica sand	24.0	$-16.9 \pm 0.1$ (4)	$-17.3 \pm 0.1$	+0.4
RDC	24.0	$-16.9 \pm 0.1$ (4)	$-17.3 \pm 0.1$	+0.4
mean diff				+0.5

<sup>a</sup>  $\delta^{18}\text{O}_w$  is the isotopic composition of the water used to saturate artificial cores, sand, and the RDC reservoir.

placed in a sealed piston apparatus and pressurized to uniformly saturate the clay material, forming an artificial core. Two saturated clay-rich artificial cores were made having water contents of 24 and 8.5 wt %, respectively (Table 2). A single RDC<sup>18</sup> was also tested, containing clay-rich till of mineralogical composition similar to those used in the artificial cores and the field samples (see below). The RDC had fully equilibrated<sup>18</sup> with an internal reservoir of known oxygen isotopic composition (Table 2). A small sub-sample of the equilibrated clay from the RDC was taken and tested for its  $\delta^{18}\text{O}$  isotopic composition by direct  $\text{CO}_2$  equilibration. Finally, a sample of 100% fine-grained silica sand was saturated (24% saturation) with water of known  $\delta^{18}\text{O}$  composition and its porewater was measured for  $\delta^{18}\text{O}$  by direct equilibration (Table 2).

Clay-rich core samples from two field sites (below) were obtained for determination of porewater isotopic composition by direct equilibration. For each sample, approximately 4–5 g of saturated clay material (13–20 wt %  $\text{H}_2\text{O}$ ) was required for  $\delta\text{D}$  and  $\delta^{18}\text{O}$  analysis. Working quickly to avoid evaporation and drying-out effects, cores were split open from their steel casings, and a spatula was used to obtain 4–5 g of clay shavings (~3–5 mm thick) from the center of the core. Small pebbles or rocks were discarded. Two to four individual shavings were divided using the spatula to fit the sample equilibration vessels (Figure 2). The outer edges of cores were avoided in case drilling fluids had penetrated the outer rim of the core.

We conducted experiments to determine whether Hokko beads could be used to achieve  $\text{H}_2$ -porewater isotopic exchange on saturated low-permeability clay-rich sediments. Core shavings were placed on weighing paper and two to three individual Hokko beads were gently pressed onto each shaving. The core shavings were immediately transferred to the Pyrex equilibration vessel (Figure 2) and mounted on the equilibrator sample manifold. The sample preparation and loading procedure for each sample took only a few minutes in order to avoid evaporation effects. Twenty saturated clay-rich samples and four standard waters were automatically evacuated, filled with  $\text{H}_2$  gas, and equilibrated at  $25 \pm 0.1$  °C for 4 h. Four in-house laboratory standard waters were included to normalize the core porewater results to the VSMOW/SLAP standard scale. After completion of the equilibration, the IRMS system automatically measured the  $\delta\text{D}$  of each sample. Following hydrogen isotope analysis of 24 samples, the residual  $\text{H}_2$  gas in the equilibrator was pumped away. We also conducted experiments (data not shown) that showed the absence of Hokko

catalyst on sediment samples yielded a hydrogen isotopic composition identical to the equilibration  $\text{H}_2$  reservoir for all samples, which demonstrated that sediments had no intrinsic capacity to catalyze  $\text{H}_2$ -water equilibration. The IRMS and equilibrator system was then switched to  $\text{CO}_2$  for automated  $\delta^{18}\text{O}$  analysis, using a sample equilibration time of 12 h at  $25 \pm 0.1$  °C. Following analyses, the Hokko beads and the core shavings were discarded.

All measurements for  $\delta\text{D}$  and  $\delta^{18}\text{O}$  were conducted using a Micromass Optima triple collecting IRMS. Typically, samples were first analyzed for their  $\delta^{18}\text{O}$  values followed by the equilibration with  $\text{H}_2$  to obtain  $\delta\text{D}$  values of the porewater. Results are reported as the relative difference between the  $^{18}\text{O}/^{16}\text{O}$  and D/H abundance ratios of the samples and VSMOW standard, expressed in the ‰ notation. Sample repeatability for  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of direct porewater equilibration, based on triplicate core sample analyses, was equal to or better than  $\pm 1$  and  $\pm 0.3$ ‰, respectively.

**Field Sample Testing.** Core samples were obtained from two near-surface clay-rich Late Pleistocene aquitard systems near Lanigan (51.4° N latitude, 105.4° longitude) and Colonsay (51.5° N latitude, 105.4° longitude), Saskatchewan, Canada, as part of a hydrogeologic investigation. A total of 41 Shelby core samples were taken over 0–30-m depth interval at the Lanigan site in August 1998. Five piezometers were installed at depths of 5, 9, 12, 15, and 23 m proximal to the depths of the core samples at Lanigan. Groundwater collected from these piezometers on three occasions in 1999 were analyzed for  $\delta\text{D}$  and  $\delta^{18}\text{O}$  to compare results with those obtained by direct porewater equilibration. Lanigan core samples were collected during the development of the  $\text{H}_2$  equilibration component; therefore, only 8  $\delta\text{D}$  analyses were made on Lanigan cores that had been stored for over 1 year. At Colonsay, a total of 23 core samples were collected in November 1999, from a single borehole, over a depth interval of 4.5–85 m. Due to cost restrictions, no wells were installed at the Colonsay site for comparison of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  results. All core samples were sealed in their tubes and stored cold (5 °C) until  $\delta\text{D}$  and  $\delta^{18}\text{O}$  isotopic analysis, usually within 2 weeks of field collection.

## RESULTS AND DISCUSSION

**Oxygen Isotope Results.** The  $\delta^{18}\text{O}$  values of porewater determined by direct  $\text{CO}_2$ -porewater equilibration from laboratory experiments are presented in Table 2.  $\delta^{18}\text{O}$  values determined for porewater from artificial clay samples (S-Core 1,2) were +0.5 to +0.6‰ more positive than the water used to saturate the clay. A +0.4‰ shift from the water used to saturate sediment was also observed when 100% fine-grained silica sand was used. Similarly, a +0.5‰ positive shift was also observed between the clay porewater of the RDC and its reservoir. Standard waters included in each set of core analyses did not show any isotopic shift from expected values; thus, it appeared that direct  $\text{CO}_2$  equilibration of geologic samples resulted in a relatively constant  $\delta^{18}\text{O}$  offset of  $\sim +0.5$ ‰ despite the variable mineralogy, porosity, and clay and water content.

An explanation for the small, consistent, positive shift of +0.5‰ for direct porewater  $\delta^{18}\text{O}$  determinations remains speculative. For example, Others<sup>22–24</sup> did not observe  $\delta^{18}\text{O}$  differences between the water used to wet the soils or sand and experimental results by direct  $\text{CO}_2$  equilibration. Variable moisture content was considered a potential cause, but both artificial clay core samples

of differing moisture contents yielded a similar offset (Table 2). Further, were low moisture (e.g., a low water to CO<sub>2</sub> headspace ratio) or incomplete equilibration responsible, it would result in a negative  $\delta^{18}\text{O}$  offset rather than the observed positive shift. A positive deviation could also result from evaporative enrichment during sample storage. In this case, an evaporative isotopic enrichment trend would then be anticipated for  $\delta\text{D}$ , which was not observed, even on core samples that had been stored for over 1 year (see below). A final and most likely possibility is that a small portion of the porewater is bound to active mineral surfaces and is immobile or isolated from isotopic exchange with the "bulk" porewater or CO<sub>2</sub>. Water bound to mineral surfaces cannot have the same isotopic properties as free water. The different reservoirs of water in sediment include free water occupying macropores, adsorbed water, and bound water.<sup>28</sup> In clay-rich sediment, adsorbed water is in the diffuse double layer and is considered "less" mobile than the bulk water. As a result, it may be possible that the isotopic composition of water in these different soil–water reservoirs has different equilibrium  $\delta^{18}\text{O}$  compositions. Thus, partitioning of oxygen isotopes in water between different bonding environments may be an explanation for the small difference between the direct equilibration results and piezometer data. However, this postulate is inconsistent with the findings of Stewart,<sup>10</sup> who noted that fractionation between adsorbed water and bulk water is negligible and is inconsistent with the results of previous direct CO<sub>2</sub> equilibration studies. In previous studies, however, the  $\delta^{18}\text{O}$  values of porewater were calibrated using soils wetted with standard waters (D. Yakir, personal communication), so that the isotopic composition of the pure water and porewater was never directly compared. We also note that isotopic partitioning between water reserves cannot as easily explain the similar offset in 100% silica sand (Table 1). Our results suggest that the consistent +0.5‰ offset between the measured saturation water and piezometers can be corrected for and so do not repudiate the  $\delta^{18}\text{O}$  profiles obtained by direct equilibration.

Results of direct equilibration  $\delta^{18}\text{O}$  determinations on porewater from 40 cores and 5 piezometers for the Lanigan site are shown in Figure 3 and in Table 3. The direct equilibration results for these clay-rich core samples yielded a vertical  $\delta^{18}\text{O}$  depth profile that closely approximated that from piezometer results (Figure 3). However, as observed in the laboratory experiments, direct CO<sub>2</sub> equilibration resulted in a vertical depth profile that appeared to be  $\sim +0.5\text{‰}$  more positive compared to the waters collected from the adjacent piezometers. A detailed analysis of results from four individual Shelby cores taken over a 2-m depth interval centered at 21-m depth were compared with the proximal piezometer water at 23-m depth (Table 3). Here, however, a comparison of  $\delta^{18}\text{O}$  results were within analytical error, considering the reproducibility of direct CO<sub>2</sub>–porewater equilibration ( $\pm 0.3\text{‰}$ ) and water equilibration ( $\pm 0.1\text{‰}$ ) techniques. Overall, an empirical correction of  $-0.5\text{‰}$  for direct CO<sub>2</sub> equilibration yielded  $\delta^{18}\text{O}$  results that were in keeping with experimental and field results. The slightly greater degree of variability for  $\delta^{18}\text{O}$  using this approach is overcome by the benefits of increased sampling resolution and low cost compared to other extraction techniques and the installation of piezometers. For example, using direct

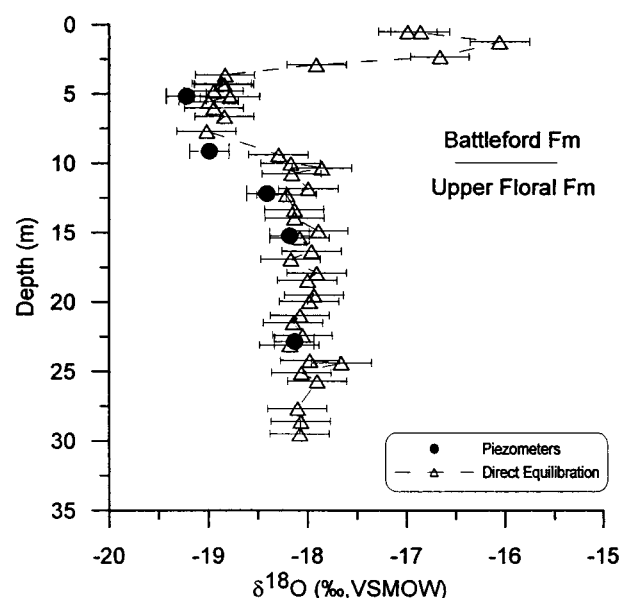


Figure 3.  $\delta^{18}\text{O}$  values of porewater determined by direct equilibration (triangles) versus depth from a single borehole near Lanigan, SK, Canada. For comparison, the  $\delta^{18}\text{O}$  values of water obtained from adjacent piezometers (circles) are shown. The Battleford Fm and Upper Floral Fm are composed of Late Pleistocene clay-rich glacial tills. Error bars denote the  $\pm\text{SD}$  for  $\delta^{18}\text{O}$ .

Table 3.  $\delta\text{D}$  and  $\delta^{18}\text{O}$  Repeatability of Direct H<sub>2</sub>– and CO<sub>2</sub>–Porewater Equilibration of Core Samples and Comparison of Results with Proximal Piezometer<sup>a</sup>

	$\delta\text{D}$ (‰)	$\delta^{18}\text{O}$ (‰)
<b>Core Equilibration</b>		
LC-21-a	–147	–18.1
LC-21-b	–145	–18.3
LC-21-c	–146	–17.9
LC-21-d	–146	nd <sup>b</sup>
mean ( $\pm\text{SD}$ )	$-146 \pm 1$	$-18.2 \pm 0.2$
<b>Piezometer Water</b>		
LC-23 m	$-145 \pm 1$	$-18.2 \pm 0.1$

<sup>a</sup> Core samples were taken within a 2-m depth interval laterally proximal to a piezometer at 23-m depth at the Lanigan field site. All results are reported relative to the VSMOW standard. <sup>b</sup> nd, not determined

equilibration on cores from Lanigan, we obtained accurate porewater  $\delta^{18}\text{O}$  results that provided equivalent information to 41 individual piezometers from a single borehole.

**Hydrogen Isotope Results.** The  $\delta\text{D}$  values of porewater determined by direct H<sub>2</sub>–porewater equilibration from field samples are presented in Table 3. An analysis of  $\delta\text{D}$  results from four individual Shelby cores taken over a 2-m depth interval centered at 21-m depth at the Lanigan site were compared with the proximal piezometer water at 23-m depth (Table 3). Here,  $\delta\text{D}$  results obtained from piezometer waters and those by direct equilibration were within the analytical error of direct H<sub>2</sub>–porewater equilibration ( $\pm 1\text{‰}$ ) and water equilibration ( $\pm 1\text{‰}$ ) techniques. Similarly, direct H<sub>2</sub>–porewater equilibration of 23 cores from the Colonsay site yielded  $\delta\text{D}$  values that were consistent with their  $\delta^{18}\text{O}$  values. Figure 4 shows the relationship between  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of porewater from Colonsay and Lanigan cores compared to the local meteoric water line (LMWL)

(28) Landon, M. K.; Delin, G. N.; Komor, S. C.; Regan, C. P. *J. Hydrol.* **1999**, *224*, 45–54.

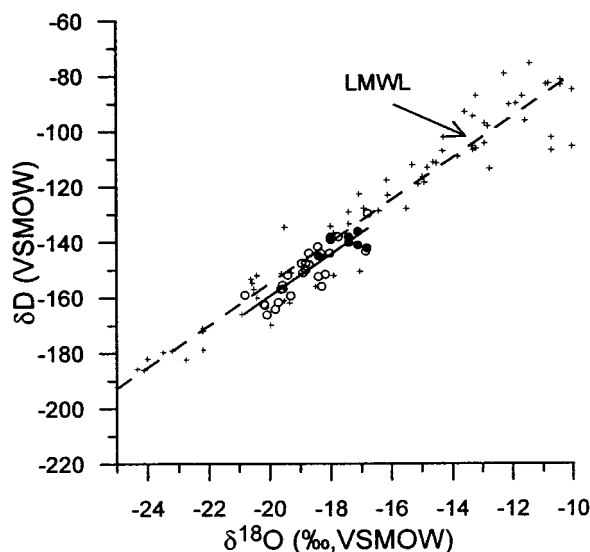


Figure 4.  $\delta D$  and  $\delta^{18}O$  values of porewater in cores from Lanigan (filled circles) and Colonsay (open circles) determined by direct equilibration versus precipitation (+) and the local meteoric water line (dashed line) for Saskatoon from 1991 to present (L. Wassenaar, Environment Canada, unpublished data). The short solid line denotes a least-squares regression of directly equilibrated sample results.

for Saskatoon, SK. A least-squares regression of porewater  $\delta D$  and  $\delta^{18}O$  values yielded a slope identical to the LMWL, indicating that the samples were not affected by potential handling effects such as evaporation. Moreover, the least-squares regression for direct equilibrated field samples (Figure 4) confirmed that  $\delta^{18}O$  results by direct equilibration were offset by  $\sim +0.5\text{‰}$ .

$\delta D$  porewater results for 23 core samples taken over a depth interval of 85 m near Colonsay are shown in Figure 5. The results yielded a detailed  $\delta D$  depth profile of groundwaters that were more depleted than present-day average precipitation ( $-136\text{‰}$ ), suggesting these waters were emplaced under cooler climatic conditions. Although interpretation of the depth profiles are currently hampered by a lack of information on hydrogeologic flow regimes and water ages in these geologic formations, the direct equilibration of porewaters demonstrated here represents a powerful new approach to obtaining accurate and high-resolution isotopic information in hydrogeologic and porewater studies.

## CONCLUSIONS

Direct equilibration of porewater in core samples of clay-rich geologic media with  $H_2$  and  $CO_2$  was used to accurately determine their  $\delta D$  and  $\delta^{18}O$  values. The precision ( $\pm 0.3$  and  $1\text{‰}$ , respectively) and accuracy of the direct equilibration method was comparable to most currently employed methods and considerably better than some. The direct equilibration technique was simple

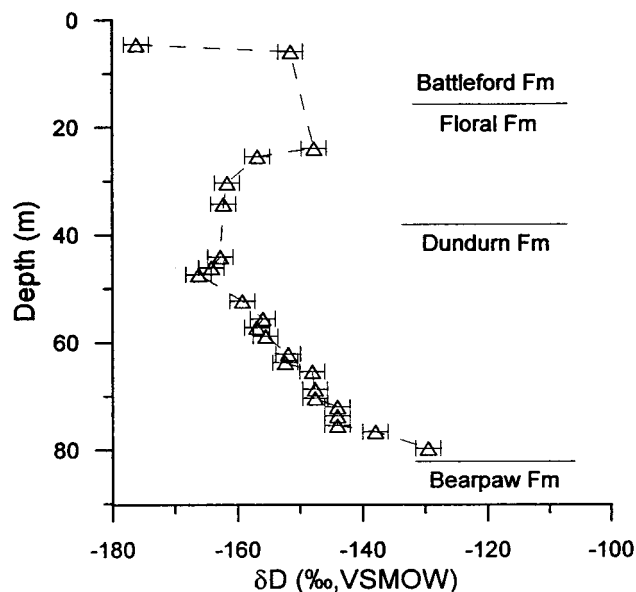


Figure 5. Depth profile of porewater  $\delta D$  values determined using cores from a single borehole at the Colonsay, SK. The Late Pleistocene Battleford Fm, Floral Fm, and Dundurn Fm are all composed of silty clay-rich glacial till. The underlying Cretaceous Bearpaw Formation is composed of shale. Error bars denote  $\pm SD$  for  $\delta D$ .

and fast compared to other conventional porewater extraction techniques. It was also easily automated using an equilibrator commonly used for  $\delta^{18}O$  measurements of water. Direct equilibration of saturated geologic media was used to obtain detailed  $\delta D$  and  $\delta^{18}O$  values through entire geologic sections with vertical resolution on the order of several tens of centimeters. With careful sample collection, a single drill hole is all that may be required to obtain detailed, high-resolution (cm scale) vertical isotopic depth profiles, thereby dramatically reducing the cost involved in obtaining detailed isotope studies of porewaters using piezometers or conventional porewater extraction methods. In addition, other problems such as flushing of wells and the uncertainty involved in contamination of wells by drilling fluids can be minimized or eliminated.

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