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Correcting for Methane Interferences on $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Measurements in Pore Water Using $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$ Equilibration Laser Spectroscopy

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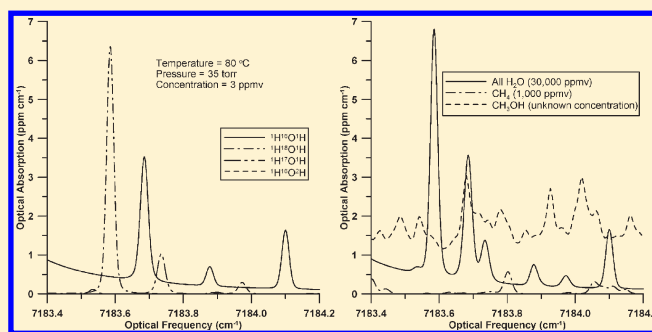
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S Supporting Information

ABSTRACT: Cavity ring-down spectroscopy (CRDS) is a new and evolving technology that shows great promise for isotopic $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses of pore water from equilibrated headspace H_2O vapor from environmental and geologic cores. We show that naturally occurring levels of CH_4 can seriously interfere with CRDS spectra, leading to erroneous $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results for water. We created a new CRDS correction algorithm to account for CH_4 concentrations typically observed in subsurface and anaerobic environments, such as ground waters or lake bottom sediments. We subsequently applied the correction method to a series of geologic cores that contain CH_4 . The correction overcomes the spectral interference and provides accurate pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values with acceptable precision levels as well as accurate concentrations of CH_4 .



Cavity ring-down spectroscopy (CRDS) is an optical linear absorption spectroscopy technique that, when combined with a precise wavelength measurement, can acquire extremely precise optical spectra from which high precision concentrations and isotopic ratios can be determined.^{1,2} For determining the hydrogen and oxygen stable isotopic composition of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), many manufacturers use a set of absorption peaks in the near-infrared wavelength range around 7184 wavenumbers (cm^{-1}) (Figure 1a).^{3,4} This set includes peaks corresponding to the common water isotopologue $\text{H}_2^{16}\text{O}^{18}\text{H}$ and each of the single-substitution rare isotopologues $\text{H}_2^{18}\text{O}^{16}\text{H}$, $\text{H}_2^{17}\text{O}^{16}\text{H}$, and $\text{H}_2^{16}\text{O}^{17}\text{H}$. The set of peaks can be scanned within a laser tuning range of less than 1 cm^{-1} , which typical telecom-grade distributed feedback (DFB) lasers can cover in a fraction of a second. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are determined indirectly from the concentrations of the $\text{H}_2^{18}\text{O}^{16}\text{H}$, $\text{H}_2^{17}\text{O}^{16}\text{H}$, and $\text{H}_2^{16}\text{O}^{17}\text{H}$ isotopologues by measuring the strengths of the corresponding absorption peaks and computing their ratios. The precision of this method allows accurate measurement of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of groundwater and surface water samples. CRDS methods have subsequently advanced to allow rapid and direct measurements of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of pore water from saturated and unsaturated geologic core samples by means of $\text{H}_2\text{O}_{(\text{liquid})}$ – $\text{H}_2\text{O}_{(\text{vapor})}$ equilibration in an air-filled headspace sampling device.^{5–7}

Most major (N_2 , O_2) and trace (CO_2 , NH_3 , N_2O) gases in air have no significant absorption features in the spectral region of interest for determining the isotopic ratios of water. However, a

few natural and anthropogenic organic compounds absorb in this region, especially the alcohols (as their hydroxyl groups are similar to those of water), HOOH , and methane (CH_4). Figure 1b illustrates the spectral interference of CH_4 and methanol (CH_3OH) with the water spectrum. The absorption features of these organic compounds, if present in sufficient amounts, can overlap with the absorption features of the water, leading to erroneous $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results. If spectroscopic analysis does not account for their presence, then the determination of the δ values will be systematically inaccurate.⁸ In addition, hydrocarbons such as ethane have weak, spectrally broad absorption, unlike the narrow absorption peaks of CH_4 . Their presence can also interfere with determination of δ values, but the lack of sharp absorption features makes them qualitatively less detrimental than CH_4 .

Measuring the H and O stable isotopic content of natural liquid water is generally straightforward with CRDS.⁹ However, CH_4 gas is ubiquitous in the subsurface, being found in both natural and contaminated (e.g., associated with landfill sites) soils as well as deep crustal settings and sedimentary basins (cf. ref 10). The small concentrations of CH_4 present in microliter quantities of natural liquid waters do not generally pose a problem for CRDS isotopic analyses and are easily purged out by shaking or

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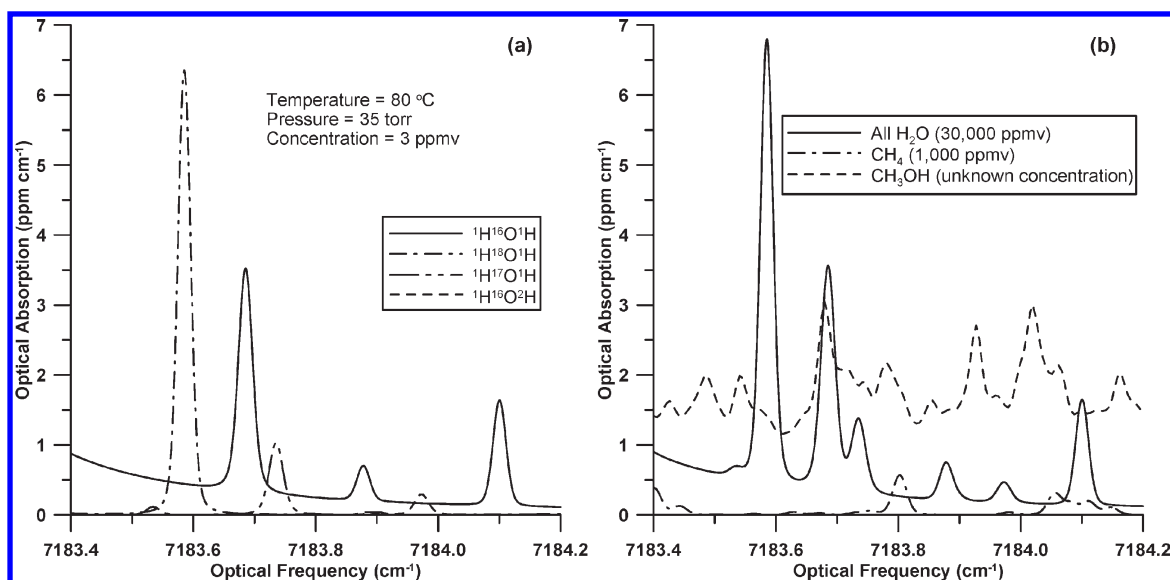


Figure 1. Water vapor absorption peaks in the near-infrared wavelength range around 7184 wavenumbers: (a) for each individual isotopologue of oxygen and hydrogen in water (natural abundances at 30 000 ppmv total concentration) and (b) methane (1000 ppmv concentration) spectrum compared with the total water vapor spectrum.

bubbling with N₂. However, because CH₄ is preferentially partitioned into the analyte headspace,¹¹ difficulties may arise with headspace analysis of water vapor obtained from saturated and unsaturated soil or core samples by H₂O_(liquid)–H₂O_(vapor) equilibration if CH₄ is present in sufficient concentrations to interfere with the CRDS liquid water spectra.

Here, we document the magnitude of the effect of CH₄ contamination on the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of headspace analyzed water vapor used for cores. We develop a correction algorithm to be applied to affected CRDS spectra, and verify and validate the correction on CH₄-rich, geologic core samples using the H₂O_(liquid)–H₂O_(vapor) equilibration technique. Our correction algorithm also yields CH₄ concentrations of the headspace. We conducted all development and testing of the correction algorithm on a Picarro L1102-*i* CRDS system.

EXPERIMENTAL SECTION

Calibration Using Water Vapor and Methane. Laboratory tests were conducted using the CRDS analyzer to determine the impact of varying the water vapor (of known isotopic composition) and CH₄ concentrations on the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of H₂O_(vapor). These data were used to develop a CH₄ correction algorithm for the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of H₂O_(vapor).

The experiment was conducted by bubbling dry nitrogen gas (N₂) through a 150 mL cylinder partially filled with liquid water of known isotopic composition to produce water vapor in equilibrium with the water, and then diluting the headspace with additional dry N₂ and CH₄ gas. CH₄ gas was obtained from Scott Specialty Gases (Air Liquide America Specialty Gases LLC) and was used at a concentration of 1 % by volume in N₂. The dilution and bubbler N₂ was ultrapure dry N₂ from Arc Gas (Aeris/Matheson TriGas). Mass flow controllers (MKS Instruments) programmed by computer were used to regulate the flow rates of the N₂ gas through the bubbler, the dilution by N₂, and the concentration of CH₄ in N₂. All gas tubing between the bubbler and the analyzer was 1/8 in. o.d. stainless steel (SS) with a

hydrophobic silica coating. A pair of bubblers was located inside an insulated cooler filled with pieces of steel to provide thermal mass stability and maintain a constant temperature of approximately 25 °C over the course of the experiment. The N₂ flow rate through the bubbler was low enough, at 200 standard cc per minute (sccm), that the water vapor exiting the bubbler was in isotopic equilibrium with the water and at 100 % relative humidity, which is approximately 30 000 ppmv at 25 °C. To ensure that any isotopic fractionation of the water vapor (e.g., as a result of evaporation) remained constant over the experiment, the N₂ flow rate through the bubbler was maintained at 200 sccm. The flow rates of the dilution N₂ and the CH₄ in N₂ were varied to obtain six different and nearly evenly spaced water vapor concentrations between 5000 and 25 000 ppmv H₂O, and six different and nearly evenly spaced CH₄ concentrations between 0 and 2000 ppmv CH₄ (Figure 2a). As only the lower CH₄ concentrations (0–1200 ppmv) were used with the lower water vapor concentrations (5000–9000 ppmv), the total number of H₂O–CH₄ concentration combinations was 30. The dwell time in the device for each concentration combination was 5 min. The CH₄ concentration was stepped quickly (every 5 min), and the water concentration was stepped after all CH₄ concentrations were complete for each water concentration (about every 35 min for water concentrations 13 000–25 000 ppmv and about every 25 min for water concentrations 5000–9000 ppmv). The dwell time in the device was doubled to 10 min for the first H₂O–CH₄ concentration combination with each new water vapor concentration to allow time for the gas delivery system to equilibrate to the new water vapor concentration. After all 30 combinations were completed, they were repeated in reverse order to provide diagnosis for drifts and hysteresis during the measurement. The flow of all gas concentration combinations was routed from the bubbler to the CRDS using approximately 1 m of SS tubing for isotopic measurement of $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

Testing with Core Samples. After the controlled laboratory H₂O_(vapor) experiment, the effects of CH₄ on $\delta^{18}\text{O}$ and $\delta^2\text{H}$

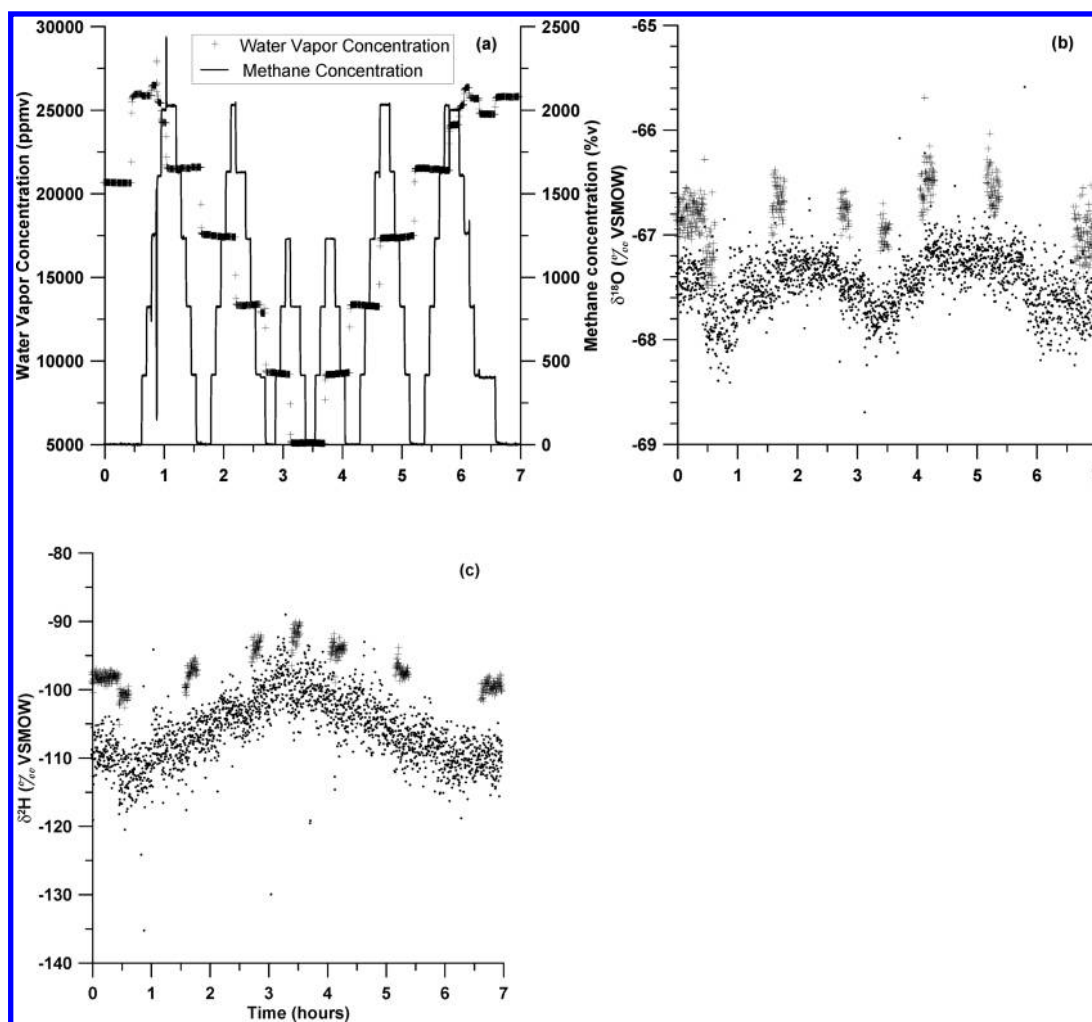


Figure 2. Impact of varying the vapor and CH_4 concentrations on the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of $\text{H}_2\text{O}_{(\text{vapor})}$: (a) concentrations of water vapor and methane throughout the test period; (b) $\delta^{18}\text{O}$ values of $\text{H}_2\text{O}_{(\text{vapor})}$; (c) $\delta^2\text{H}$ values of $\text{H}_2\text{O}_{(\text{vapor})}$. The continuous data in (b) and (c) are the C–H–H corrected $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, whereas the intermittent data (offset vertically for clarity) are the standard $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results when the methane concentration is zero.

measurements, as well as the new correction algorithm, were tested on $\text{H}_2\text{O}_{(\text{vapor})}$ equilibrated with $\text{H}_2\text{O}_{(\text{liquid})}$ in geological core samples. Ten core samples (64 mm diameter \times 89 mm long) of water saturated clay-rich glacial till of known isotopic composition (mean porosity = 0.46; SD = 2.6 %) containing no CH_4 were placed in medium sized (945 mL) double Ziploc polyethylene resealable bags and inflated with dry air. These inflated equilibration bags were then each placed in a larger sized (1 L) Ziploc polyethylene resealable bag. Excess air was squeezed from the larger bags and then they were sealed. The air and core samples were allowed to equilibrate for 3 days isothermally at 24 °C. The $\text{H}_2\text{O}_{(\text{vapor})}$ samples were run on the CRDS analyzer to obtain $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of $\text{H}_2\text{O}_{(\text{vapor})}$ and corrected to obtain the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of $\text{H}_2\text{O}_{(\text{liquid})}$ for each core sample. Details of the sampling methodology, equilibration, and analyses have been previously published.⁵

After the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were measured on the $\text{H}_2\text{O}_{(\text{vapor})}$ samples from “uncontaminated” cores, approximately 100 mL of 10 000 ppmv CH_4 was added to the remaining air in the bags (approximately 550 mL) in seven of the core samples, yielding a CH_4 concentration in the headspace of each bag of

about 2000 ppmv. After the addition of the CH_4 to the headspace, the samples were allowed to equilibrate for 1.5 h to ensure complete mixing of the added CH_4 and the water vapor. These samples were then reanalyzed on the CRDS analyzer to measure the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the CH_4 -contaminated $\text{H}_2\text{O}_{(\text{vapor})}$ samples. The three remaining samples were reanalyzed (without the addition of CH_4) with the remaining vapor in the bag to provide a check on the repeatability of the sample methodology.

All core analyses were conducted at 24 °C and the water vapor concentration in the bags was approximately 30 000 ppmv. In all cases, the vapor from each sample bag was directed to the CRDS analyzer for approximately 5 min using a stainless steel needle and valving system external to the analyzer. Dry air was routed into the analyzer for 3–5 min between sample pulses. As the analyzer measurement interval is ~ 12 s, 25 measurements were typically taken within each sample pulse. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for each sample were taken once the CRDS measurements from the headspace flow had stabilized. These values were later recalibrated on the basis of the calibration samples included in each sample set. The results and spectral data from the core

Table 1. Measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ (‰, VSMOW) Values of Pore Water in Core Samples before and after Spiking with CH_4 , with the Latter Corrected with the CH_4 Correction Algorithm as Well as the Measured CH_4 Concentration (ppmv) in the Headspace of Each Core Sample with the CRDS

sample	$\delta^2\text{H}$ before CH_4	$\delta^{18}\text{O}$ before CH_4	$\delta^2\text{H}$ after CH_4	$\delta^{18}\text{O}$ after CH_4	$\delta^2\text{H}$ after CH_4 correction	$\delta^{18}\text{O}$ after CH_4 correction	CH_4 conc (ppmv)
1	-168.1	-20.80	-629.0	16.33	-167.6	-20.65	1457
2	-167.4	-20.61	-683.8	20.52	-169.1	-20.66	1617
3	-167.7	-20.73	-669.8	19.97	-167.5	-20.82	1595
4	-168.0	-20.46	-625.3	17.15	-168.1	-20.64	1464
5	-170.8	-21.24	-674.1	19.16	-169.9	-20.92	1604
6	-169.8	-21.15	-597.3	13.15	-169.6	-20.86	1393
7	-168.2	-20.87	-671.6	21.44	-169.3	-20.93	1585
8	-168.7	-20.67	-169.2	-19.78	-168.7	-20.94	0
9	-168.2	-20.78	-169.6	-20.85	-169.9	-21.21	0
10	-170.7	-20.64	-170.0	-20.09	-169.1	-21.27	0

samples with CH_4 added were used to correct the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and, in so doing, test the accuracy of the previous lab-based $\text{CH}_4\text{--H}_2\text{O}_{(\text{liquid})}\text{--H}_2\text{O}_{(\text{vapor})}$ (C–H–H) algorithm. The spectra and correction algorithm were designed to provide the CH_4 concentrations for each sample for comparison to those estimated from mass balances presented above. A small additional correction to that found from the lab-based water vapor–methane calibration was determined from the computation of the delta values for this core experiment because the cores were run with the Picarro L1102-*i* optical cavity set at 80 °C, whereas the calibration using water vapor (in July 2010) was done at 60 °C. This additional temperature correction, which was also applied to the field verification data, amounted to approximately 0.1 ‰/1000 ppmv CH_4 for $\delta^{18}\text{O}$ and 1.5 ‰/1000 ppmv CH_4 for $\delta^2\text{H}$. These additions were comparable to the uncertainty of the measurement sets.

Field Verification. Verification of the C–H–H correction algorithm was conducted on fresh core samples (collected from 11 to 321 m below ground (BG) at 1 m intervals; $n = 290$) from a continuously cored borehole located near Esterhazy, Saskatchewan, Canada. The geology of the site consists of clay-rich Quaternary-aged glacial till (1–11 m BG) underlain by Late Cretaceous-aged shale (11–392 m BG) and the Mannville Formation (a regional aquifer consisting of sand and shale) (392–454 m BG). The Cretaceous-aged shale consists of the Pierre Formation (11–184 m BG) and the First (184–256 m BG) and Second Speckled shales (256–392 m BG). The water table at the site was located less than 1 m BG and the mean saturated porosity of the shale was 0.33 (SD = 0.04). A hydrocarbon smell was noted from the core samples collected from 245 to 300 m BG during drilling and was strongest in the speckled shales. The presence of hydrocarbons is common in these shales and their equivalents, which extend more than 2000 km from northwest New Mexico, USA, into Alberta and Saskatchewan, Canada.¹²

Coring was conducted in October 2009 using rotary drilling methods (water was used as the drill fluid) and a 3.04 m \times 75 mm core barrel. Core samples (\sim 75 mm long) were used for CH_4 gas and isotopic analyses. After retrieval, the outer 2–5 mm of each

sample was removed to minimize contamination from the drill mud. All samples were placed in medium sized Ziploc polyethylene resealable bags and the atmospheric air squeezed out of the bags prior to sealing. Bagged samples were then each placed inside a larger sized Ziploc polyethylene resealable bag, with the air again squeezed out prior to sealing. The bagged cores were placed in coolers and kept at ambient surface temperature (\sim 5–10 °C) until they could be transported to the University of Saskatchewan where they were kept in the coolers at \sim 15 °C and 100 % relative humidity until analysis.

Core samples of the shale were analyzed for the stable isotopes of water using $\text{H}_2\text{O}_{(\text{liquid})}\text{--H}_2\text{O}_{(\text{vapor})}$ equilibration. In the laboratory, the medium-sized Ziploc bags containing the samples were inflated with dry air and resealed. Each inflated bag was returned to the large Ziploc bag it came from, and the air from the large bag was removed before it was resealed. The samples were allowed to equilibrate isothermally at room temperature for 7 days, on the basis of prior experiments to determine optimum equilibration times for shale cores (data not presented). In all samples analyzed, the water content of the headspace ranged from 28 000 to 33 000 ppmv. Two water standards with known $\delta^{18}\text{O}$ and $\delta^2\text{H}$, which bracketed the core samples, were run alternately after every two samples to correct for possible instrumental drift. Details of the core sampling, sample preparation, and analytical methods have been previously published.⁵

Deuterium oxide (99 %) was added to the drilling fluid to determine which core samples were contaminated by the drill mud. Isotopic analyses (data not presented) show that very few ($n = 1$) of the core samples ($n = 290$) analyzed were contaminated with drill fluid. The one contaminated sample is not discussed further.

Twenty-one core samples, collected throughout the depth of the core hole, were used to assess CH_4 concentrations in sample headspace for comparison to the CH_4 concentrations calculated using the C–H–H algorithm. Each core sample was placed in a new 1 L Ziploc bag that was inflated to capacity (about 945 mL) with ultrapure N_2 gas. The cores were allowed to equilibrate with the headspace for 7 days, in keeping with $\text{H}_2\text{O}_{(\text{liquid})}\text{--H}_2\text{O}_{(\text{vapor})}$ equilibration testing. After equilibration, a 20 mL airtight syringe was flushed using extracted headspace from the sample bag. Twenty milliliters of headspace was then extracted from the bag and injected in two 10 mL increments into a Hewlett-Packard (HP) 5890 Series II Plus gas chromatograph (GC) fitted with an 8 ft. $1/8$ in. SS Haysep Q 80/100 mesh column and flame ionization detection (FID) for light hydrocarbon analysis. Run conditions for this GC column were set at 90 °C, and the carrier gas was helium (30 cc/min). Duplicate analyses were conducted on each sample. The HP GC was calibrated using a three-point calibration using ultrapure CH_4 Scotty gas standards of 15, 100, and 1000 ppmv. The calibration was verified after each 10–15 injections using the 100 ppmv CH_4 gas standard.

RESULTS AND DISCUSSION

Defining the Impact of CH_4 on the δ Values of Water Vapor. Methane absorption clearly interferes with a segment of baseline in the isotopic water spectrum (Figure 1b). The wings of the CH_4 peak at 7183.8 cm^{-1} also underlie the $^1\text{H}^{16}\text{O}^1\text{H}$ and $^1\text{H}^{16}\text{O}^2\text{H}$ peaks. These interferences affect the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values computed using the standard spectroscopic analysis (which assumes no directly interfering gas species). For example, in a 30 000 ppmv water vapor sample with 1000 ppmv of CH_4 ,

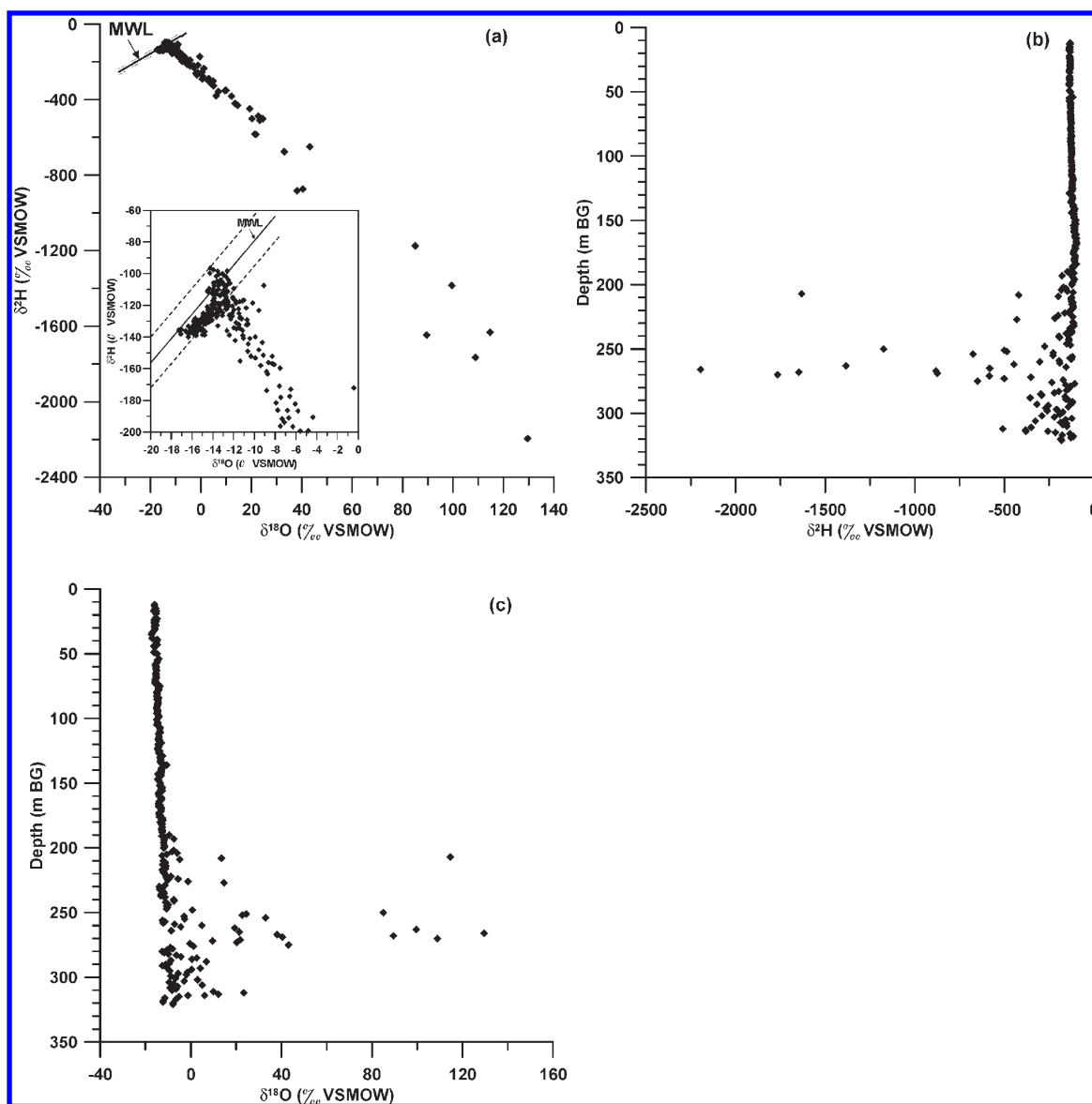


Figure 3. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of pore water from the core samples not corrected for the influence of CH_4 : (a) $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ values of pore water compared to the local meteoric water line (and 95 % confidence limit) for nearby Saskatoon, Canada (1990–2010; Environment Canada), and vertical depth profiles for (b) $\delta^{18}\text{O}$ and (c) $\delta^2\text{H}$ values.

the computed $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values from the standard analysis are in error by approximately +7 and –200 ‰, respectively, as determined from measurements of the same water vapor (same δ values) with and without added CH_4 . This error is expected to be linear up to a few 1000 ppmv CH_4 (in 30 000 ppmv water vapor), given the relative magnitudes of the absorption peak heights of the water vapor and CH_4 (Figure 1b).

Correcting the δ Values of Water Vapor for the Impact of CH_4 . The CRDS analyzer drew water vapor (in N_2 or dry air as carrier gas) into its main unit, and acquired optical absorption spectra of the water absorption peaks around 7184 cm^{-1} . The spectral analysis determines the heights and strengths (the integral area) of each of the various absorption peaks by fitting a mathematical model of the set of peaks to the acquired spectra using a nonlinear least-squares fit. The concentration of each water isotopologue species is proportional to the strength of its corresponding absorption peaks. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are

computed from the ratios of the water absorption peak heights (e.g., height of $^1\text{H}^{18}\text{O}^1\text{H}$ peak to height of $^1\text{H}^{16}\text{O}^1\text{H}$ peak) multiplied by a slope calibration factor and offset by an intercept calibration factor.

The spectral widths of the peaks (the “broadening”) depend on the absolute sample pressure (maintained constant at 35 Torr), the sample temperature, the carrier gas, the concentration of the water vapor itself (self-broadening), and other species present in the gas. In the absence of interfering species, the software that performs the least-squares fit originally sets the broadening parameter to a value that is a function of the water vapor concentration; the broadening parameter is not permitted to vary independently of the concentration. This dependence was enforced to optimize the precision of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value determination. As discussed below, we found that unidentified interfering species other than CH_4 also introduce errors to the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values through spectral broadening, and we

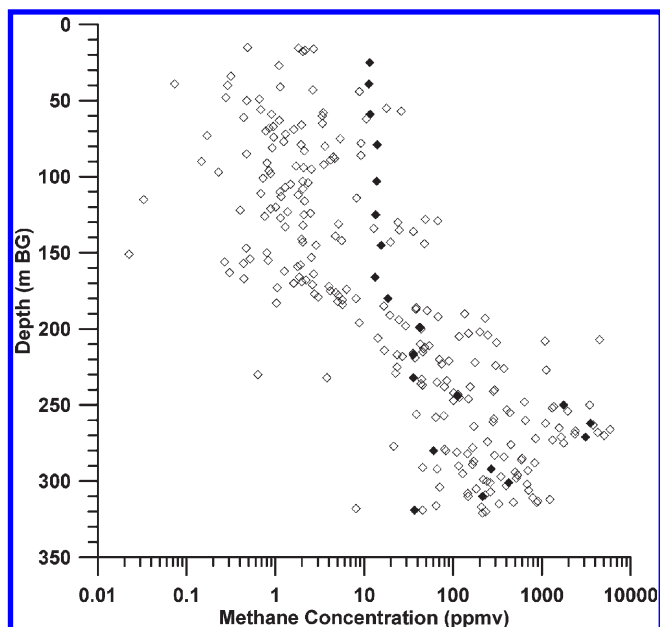


Figure 4. Methane concentrations determined on core samples using gas chromatography (solid diamond) and from the CRDS absorption peaks in the analyzer (open diamonds).

changed the standard spectral analysis to allow the broadening parameter to vary within the least-squares fit, regardless of the presence or absence of CH_4 .

As a first step in the incorporation of CH_4 into the spectroscopic analysis (C–H–H), we added the CH_4 absorption spectrum to the mathematical model used for the nonlinear least-squares fit. The output of this modified fit includes all parameters of the standard fit (such as the water absorption peak heights) as well as the CH_4 spectrum absorption strength. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are then computed from the ratios of the same peak heights and using the same calibration factors as for the standard fit results. In addition, the CH_4 concentration is computed from the CH_4 spectrum strength multiplied by a predetermined calibration factor. We applied the modified analysis to the spectra acquired during the water vapor– CH_4 calibration experiment. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values from the modified analysis at 25 000 ppmv water vapor concentration and 2000 ppmv CH_4 differ from the δ values with 25 000 ppmv water vapor and zero CH_4 by +1.5 and –25 %, respectively. These errors are significantly greater than the documented precision specifications of 0.2 and 1.0 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively, using the analyzer with pure water vapor (http://www.picarro.com/isotope_analyzers/h2o_isotopes_liquid_and_vapor). We believe these small errors remain because the acquired spectrum is not optimal given the presence of CH_4 . One specific problem is that a CH_4 peak disrupts the primary spectral baseline segment near the $^{16}\text{O}^{18}\text{O}^{2}\text{H}$ peak. Also, adding any free parameters to the nonlinear least-squares fit, such as those associated with the CH_4 spectrum, tends to introduce systematic changes in the fit results.

As a second step to incorporate the CH_4 correction into the C–H–H analysis, we determined an additional correction factor to “flatten” the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values versus CH_4 concentration based on the observed water vapor–methane calibration and experimental data. We performed multiple linear regressions using combinations of several simple functions of the CH_4

concentration and water concentration and found that simple linear corrections applied to the water peak heights proportional to the CH_4 concentration are adequate to flatten the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values versus CH_4 concentration (Figure 2). Using the correction, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are flat within each water vapor concentration step to within ~ 0.2 ‰ for $\delta^{18}\text{O}$ and ~ 1 ‰ for $\delta^2\text{H}$, except at the lowest concentration of 5000 ppmv H_2O . The δ values from the standard analysis for zero CH_4 are also shown for comparison (Figure 2; offset vertically for clarity). Notably, the apparent water vapor concentration dependence remains a separate issue from the CH_4 interference.

In addition, we incorporated into the C–H–H analysis a small correction to the CH_4 concentration proportional to the water concentration, amounting to approximately –100 ppmv CH_4 for 25 000 ppmv water. This CH_4 correction (Figure 2) does not affect the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values as the corrections are based on the raw CH_4 concentration output from the least-squares fit.

We also determined from the field core verification data (discussed below) that unspecified gaseous species other than CH_4 are present and also affect the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value computations. To mitigate the interference of these unknown interfering species, we freed the spectral broadening parameter in the least-squares fit, both for the CH_4 -modified analysis and for the standard analysis. These unknown gaseous species do not appear to have significant spectral absorption that interferes directly with the water absorption spectrum.

Because the CRDS spectroscopic analysis including CH_4 correction has several additional free parameters compared with the standard spectroscopic analysis without CH_4 correction, the precision (standard deviation) of the computed $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (in a continuous water vapor stream) is greater than pure water by a factor of ~ 1.1 for $\delta^{18}\text{O}$ and ~ 3 for $\delta^2\text{H}$. Thus, the standard analysis is preferred in the absence of CH_4 or other interfering species. To facilitate user selection of the most precise spectroscopic analysis to use for each sample measurement, a simple set of decision criteria were developed on the basis of the results of the analysis that included CH_4 and free broadening parameter. Postprocessing of the gas stream CRDS data (before averaging over each sample pulse) defined three key flags that could be used to decide which δ value results to use as well as provide an indication of confidence of their validity. One flag corresponds to diagnosis of the CH_4 concentration, one to diagnosis the $\delta^{18}\text{O}$ value, and one to diagnosis the $\delta^2\text{H}$ value. In general, if the flag is 0, then the standard analysis result should be used. If the flag is +1, then the C–H–H analysis result should be used. If the flag is –1, then both C–H–H and standard analysis results may be invalid because of unknown spectral interference. In this case, the C–H–H analysis may be more accurate than the standard analysis because CH_4 may still be present. All three flags are set to 0 if the water concentration is below a threshold value (default 1000 ppmv) or if the ratio of CH_4 concentration to water vapor concentration is below a threshold value (default $[30 \text{ ppmv methane}]/[30\,000 \text{ ppmv water vapor}]$). Additional details on these flags are presented in Supporting Information. These flags were used to select which analysis results to average for each sample pulse in the Field Verification section, as discussed below. Due to systematic differences between the standard and C–H–H corrected CRDS analyses, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value calibration must be performed for both analyses separately but can be done with the same measured spectra.

Methane Correction Applied to Saturated Core Samples. The results of the CH_4 control core equilibration experiment for

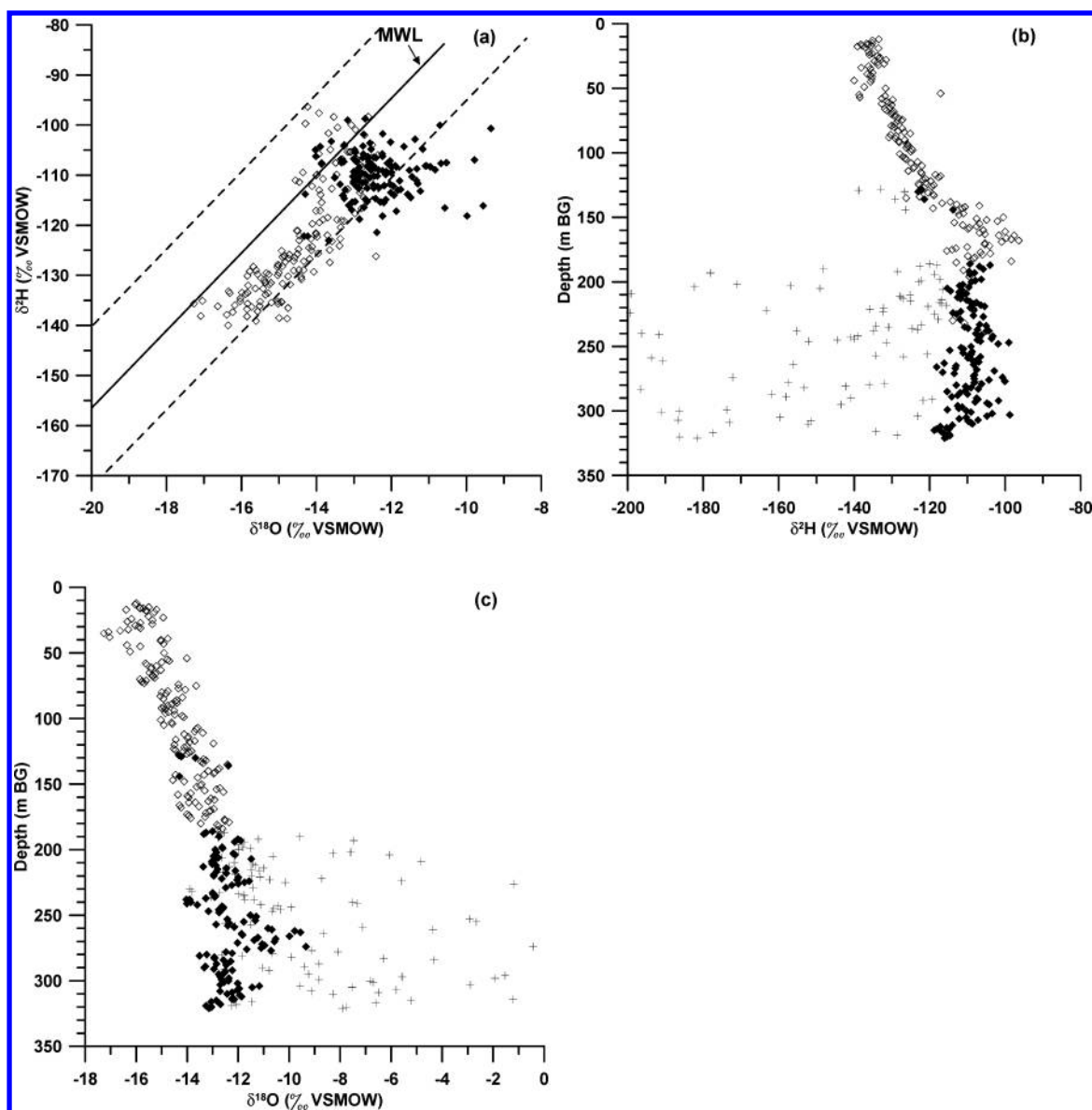


Figure 5. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of pore water from core samples before and after correction for the influence of CH_4 from the shale core samples: (a) $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ values of pore water compared to the local meteoric water line (MWL) (and 95 % confidence limit) for nearby Saskatoon, Canada (1990–2010; Environment Canada), and vertical depth profiles for (b) $\delta^{18}\text{O}$ and (c) $\delta^2\text{H}$ values. The standard (Flag 0; $\text{CH}_4 < 20$ ppmv) and corrected (Flag 1; $\text{CH}_4 \geq 20$ ppmv) values are represented by the open and closed diamonds, respectively. For comparison, samples with CH_4 concentrations ≥ 20 ppmv but not corrected (from Figure 3; those that plot within the $\delta^{18}\text{O}$ range) are presented as + symbols in (b) and (c).

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are presented in Table 1. The results of the three till samples replicated with no CH_4 addition confirm that the CRDS analyzer provides accurate and repeatable $\delta^2\text{H}$ and $\delta^{18}\text{O}$ pore water values (the difference in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values ranges from 0 to -1.7 ‰ and -2.7 to -0.63 ‰, respectively). The addition of CH_4 to the headspace of the seven core samples results in a large difference in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, in keeping with the findings of the water vapor experiment above. The $\delta^2\text{H}$ values decrease by approximately 480 ‰ and the $\delta^{18}\text{O}$ values increase by approximately 39 ‰ at a CH_4 concentration of approximately 1500 ppmv. The values differ in their amount of deviation due to the varying amounts of CH_4 added to the sample headspace, and perhaps also adsorption to the solid core samples. The corrected $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for the samples spiked with CH_4 closely approximate the values collected before spiking with

CH_4 (the difference in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values ranges from $+0.9$ to -1.7 ‰ and -0.18 to 0.32 ‰, respectively). These results show that the algorithm developed to correct the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of pore water measured on vapor samples in the presence of CH_4 with CRDS provides accurate and repeatable $\delta^2\text{H}$ and $\delta^{18}\text{O}$ pore water values.

Field Verification. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the pore water from the field core samples not corrected for any influence of CH_4 are presented in Figure 3. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the pore water for all core samples collected above 128 m BG plot on or near the local meteoric water line (LMWL) for Saskatoon, whereas many of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for pore water from the core samples collected from or below 266 m depth plot below the LMWL. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values that plot farthest below the LMWL are observed for the core collected at

266 m BG (+129.6 and −2195 ‰, respectively). The trend toward more negative $\delta^2\text{H}$ values and more positive $\delta^{18}\text{O}$ values (Figure 3a) is clearly shown in depth plots (Figure 3b,c). The obviously anomalous pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are associated with the First and Second Speckled shales (>184 m BG).

The anomalous pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are directly associated with the presence of the hydrocarbon odor detected in the core samples collected from 245 to 300 m BG and the presence of CH_4 as revealed by the depth plot of CH_4 concentrations measured in the headspace of the 21 core samples (Figure 4). The CH_4 data show a lack of CH_4 gas ($X = 13.7$ ppmv; $\text{SD} = 2.28$; $n = 9$) in the Pierre shale (11–184 m BG), higher concentrations in the First Speckled shale ($X = 397$ ppmv; $\text{SD} = 763$; $n = 5$) (184–256 m BG), and the greatest concentrations in the Second Speckled shale ($X = 1094$ ppmv; $\text{SD} = 1536$; $n = 7$) (256–321 m BG). The positive correlation between these gas data and the CRDS analyzer data suggests that the anomalous pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values measured below 136 m BG are likely associated with the CH_4 in the core samples. Acknowledging that the presence of CH_4 gas systematically alters the pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (see above), the C–H–H algorithm was applied to the raw analyzer data for all core samples to calculate the CH_4 concentrations in the vapor samples (Figure 4). The trend in this high-resolution core depth profile data set is in keeping with that determined using the GC, supporting the absorption spectroscopy correction method using CRDS. The analyzer data also show that CH_4 concentrations are low in the Pierre shale ($X = 3.6$ ppmv, $\text{SD} = 8.9$; $n = 159$), greater in the First Speckled shale ($X = 329$ ppmv, $\text{SD} = 755$; $n = 66$), and greatest in the Second Speckled shale ($X = 754$ ppmv, $\text{SD} = 1164$; $n = 65$).

These field data also provide additional details on the geologic profile resulting from the high-resolution nature of the coring. For example, the results of the algorithm yield CH_4 gas concentrations that generally range over 2 orders of magnitude over vertical distances of less than 1 m, as well as negative values that indicate an unidentified interfering species.

A cross-plot of $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ was created (Figure 5a), where for each $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value the standard analysis result was chosen if its flag was primarily 0 over the measurement pulse duration, and the C–H–H correction result was chosen if its flag was primarily 1. All data are within or slightly below the observed 95 % confidence limit for the LMWL. About 46 data points (16 % of values) plot below the 95 % confidence limit. These remaining data do not appear to correlate with the CH_4 concentration and so may be due to another unknown spectral interference.

The distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the standard analysis results and C–H–H corrected analysis results (Figure 5b,c) reflects the same well-defined depth trend for those samples that have negligible CH_4 . In contrast, no trend can be discerned from the standard results for the CH_4 rich vapor samples (Figure 5b,c).

CONCLUSIONS

CRDS is a relatively new and evolving technology that shows great promise for environmental isotopic $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses for liquid and vapor H_2O . Here, we verified that headspace H_2O isotopologue CRDS analyses are very cost-effective and useful for obtaining high-resolution isotopic data from geologic cores. However, gaseous species such as CH_4 and other possibly yet unidentified volatile organic compounds (VOCs), which are

common in natural subsurface and anaerobic environments (e.g., groundwater, lake bottom sediments) and contaminated subsurface environments, can seriously interfere with the spectra and lead to erroneous $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of pore water results. We provide the first CRDS correction algorithm to account for CH_4 concentrations. The correction method allows the user to screen samples for CH_4 spectral contamination, measure the CH_4 vapor concentrations, and decide the appropriate correction to apply to the measured values. The CH_4 correction algorithm overcomes the CH_4 spectral interference and provides pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values within acceptable precision.

ASSOCIATED CONTENT

S Supporting Information. Additional details on the three analytical flags. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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