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Key Points:
- Rhizon and squeeze samples from ocean sediments are compared
- Rhizon samples have offsets in concentration and isotopic values
- Rhizon samplers may diffusively fractionate isotopes and absorb water

Supporting Information:
- ReadMe
- Table S1

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Rhizon sampler alteration of deep ocean sediment interstitial water samples, as indicated by chloride concentration and oxygen and hydrogen isotopes

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Abstract Despite their potential to inform past ocean salinity, $\delta^{18}O$, and temperature, high-resolution depth profiles of interstitial water chloride concentration and hydrogen and oxygen isotopes exist in very few locations. One of the primary limitations to the recovery of these depth profiles is that traditional interstitial water sampling requires 5–10 cm whole rounds of the sediment core, which has the potential to interfere with stratigraphic continuity. The Rhizon sampler, a nondestructive tool developed for terrestrial sediment interstitial water extraction, has been proposed for efficient and nondestructive sampling of ocean sediment pore waters. However, there exists little documentation on the reliability and performance of Rhizon samplers in deep ocean sediments, particularly in regard to their effect on chloride concentration and oxygen and hydrogen isotopic measurements. We perform an intercomparison of chloride concentration and oxygen and hydrogen isotopic composition in samples taken using traditional squeezing versus those taken with Rhizon samplers. We find that samples taken with Rhizons have positive biases in both chloride concentration and stable isotopic ratios relative to those taken by squeezing water from sediments in a hydraulic press. The measured offsets between Rhizon and squeeze samples are consistent with a combination of absorption by and diffusive fractionation through the hydrophilic membrane of the Rhizon sampler. These results suggest caution is needed when using Rhizons for sampling interstitial waters in any research of processes that leave a small signal-to-noise ratio in dissolved concentrations or isotope ratios.

1. Introduction

The search for reliable proxies of past deep ocean temperature and salinity has proved difficult, thereby limiting our ability to understand the coupling of ocean circulation and climate over glacial-interglacial time scales. Depth profiles of chloride concentration and oxygen isotopes in ocean sediment interstitial (pore) water can be used to reconstruct past ocean salinity and $\delta^{18}O$, and, in combination with the $\delta^{18}O_c$ of benthic foraminifera, past temperature as well [*McDuff*, 1985; *Schrag and DePaolo*, 1993; *Schrag et al.*, 1996; *Adkins et al.*, 2002; *Schrag et al.*, 2002; *Adkins and Schrag*, 2003]. However, this method has been applied in few locations.

Obtaining high-depth-resolution pore fluid samples for chloride and oxygen isotope measurement is limited by the current interstitial water recovery method, which removes 5–10 cm sections of ocean sediment cores. In order to reconstruct the bottom water concentration history at a given location, we need a high-resolution depth profile of samples: at least one sample every 1.5 m of core depth down to at least 150 m below seafloor (mbsf). The traditional way to obtain these samples is to slice off a complete 5–10 cm piece of the sediment core, known as a "whole round," and squeeze the water out of the sediment in a hydraulic press. The pressure in the squeezer can reach as much as 300 MPa, which is well above the typical pressures reached at the seafloor or in the ocean sediments (6000 m of seawater is ~60 MPa), and the pressure is applied uniaxially. Squeezing the sediment in this way compresses and deforms the sediment, in some cases crushing foraminiferal tests, making sediment sampling (that is, subsampling) of this piece more challenging; therefore, the removal of a whole round has the potential to disrupt the chronology of the sediment core. In general, that is, independent of pore fluid sampling, multiple holes must be drilled at a given site to ensure full sediment recovery. Therefore, with careful attention during drilling, the potential

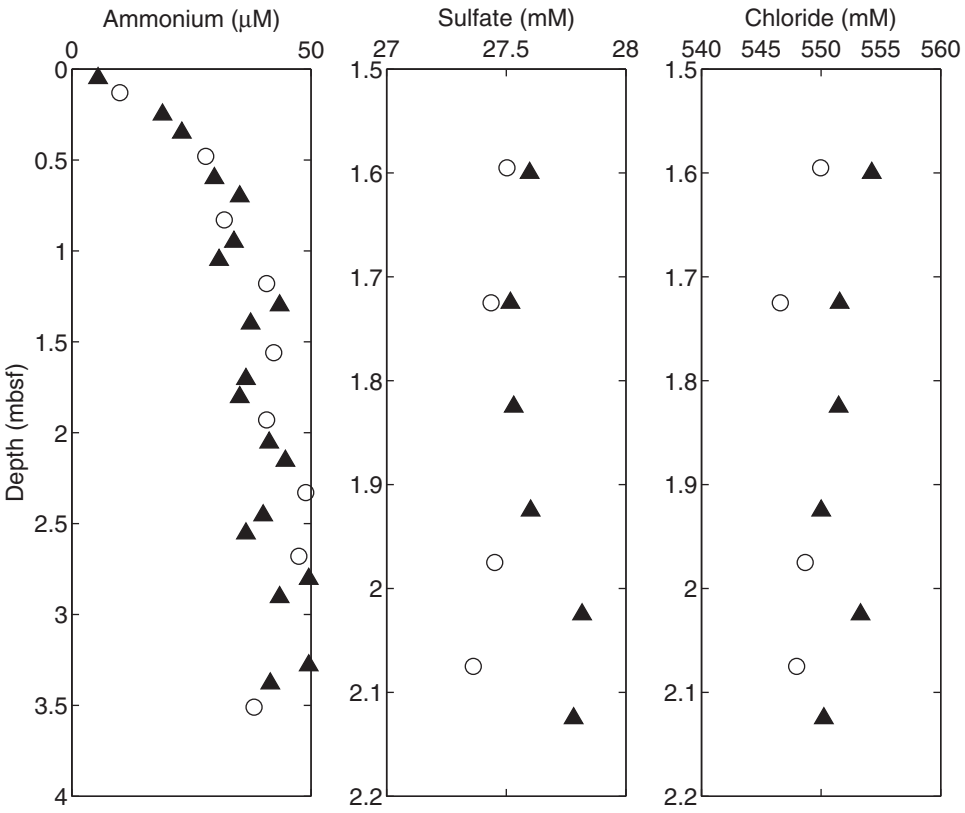

Figure 1. Intercomparison of measurements from Rhizon (black triangles) and squeeze (open circles) samples as reported in *Schrum et al.* [2012]. Note that the reported error bars are smaller than the plot symbols.

interference of pore fluid sampling with the chronology can be avoided. At the same time, deep core sediment samples are precious, as for many years the only scientific platform capable of recovering long sediment cores from the deep ocean has been the Integrated Ocean Drilling Program (IODP; formerly the Ocean Drilling Program and the Deep Sea Drilling Project). IODP expeditions are costly and logistically complicated, and many scientists with different goals must cooperate to optimize the ratio of time spent on site to sample recovery. For this reason, we desire a more efficient and nondestructive method than squeezing with which to sample pore fluids on IODP expeditions.

We tested whether Rhizon samplers (Rhizosphere Research Products) [*Seeberg-Elverfeldt et al*., 2005], a tool developed for terrestrial soil sampling, can recover water from deep ocean sediments at high depth resolution without compromising the water samples or the integrity of the sediment core. Rhizons have been used on several deep ocean drilling expeditions, but there is little documentation on how these samplers behave with respect to traditional squeezing methods, in regard to their effect on the concentration and isotopic content of the pore fluid. *Dickens et al*. [2007] compared the manganese and ammonium concentrations in samples recovered with Rhizons versus those recovered through squeezing, concluding that Rhizons had no deleterious effect on the samples, but their study only compared a few overlapping Rhizon and squeeze samples (six points). *Schrum et al*. [2012] made a more comprehensive study of alkalinity, dissolved inorganic carbon (DIC), ammonium, sulfate, and chloride. They found that the alkalinity and DIC in the Rhizon samples were compromised, presumably due to a loss of carbon dioxide and resultant precipitation of calcium carbonate, but concluded that ammonium, sulfate, and chloride were unaffected. However, visual inspection of their concentration plots (Figure 1) suggests that there may be a positive bias in their Rhizon sample concentration measurements, which are again difficult to compare to the squeeze sample measurements due to the small number of overlapping samples.

Previous intercomparisons suggest that Rhizon sampling can affect sample concentrations of dissolved species, both those sensitive to carbonate chemistry and those that are conservative. However, the available data are sparse, limiting our ability to quantify the Rhizon's effect on dissolved concentrations. Further,

there have not been tests on water stable isotopes. Here we perform a high-resolution (321 unique samples measured, with 59 overlapping points in chloride and 88 overlapping points in hydrogen and oxygen isotopes) intercomparison in order to better our understanding of the Rhizon sampling effect on dissolved concentration and to test for the first time whether Rhizon samplers affect sample isotopic composition. Our analysis demonstrates that both chloride concentration and stable isotopes in samples taken with Rhizons are significantly higher/heavier than in squeezed samples, most consistent with a combination of absorption and diffusive fractionation through the hydrophilic membrane.

2. Methods

2.1. Shipboard Sampling

We procured the samples for this work during IODP Expedition 339 (Mediterranean Outflow). The full details of the cruise track and our shipboard scientific results are reported in *Stow et al*. [2013]. Samples for the high-resolution intercomparison that follows were taken from IODP Site U1385B, which is located near the Western Iberian Margin at 37.6°N, 10.1°W and in a water depth of 2587 m.

2.1.1. Squeeze Samples

Following the established IODP protocol, interstitial waters were extracted from 5–15 cm-long sediment whole rounds at the bottom of every 9.5 m sediment core that were cut and capped immediately after core retrieval on deck. Standard whole rounds were 5 cm-long, but as porosity decreased down hole the size of the whole rounds was increased to enable extraction of ~30 mL total to split between shipboard and shore-based analyses. In the shipboard chemistry laboratory, whole round sediment samples were removed from the core liner, and the outside surfaces (~1 cm) of the sediment samples were carefully scraped off with spatulas to minimize potential contamination with drill fluids. The drill fluid was surface seawater, which is conservative in seawater and has a sulfate concentration of ~29 mM at salinity 35. Therefore, contamination of samples below the sulfate reduction zone was inferred when there were small deviations from zero in the shipboard sulfate measurement profile. None of the samples below the sulfate reduction zone at Site U1385B had detectable sulfate concentration.

To generate a high-resolution profile, we took interstitial water samples to be squeezed from the bottom of every ~1.5 m core section in addition to the routine samples. Small plugs of sediment ~10 cm^3 were taken from the bottom of each section, excluding the section from which the whole round came, using a 60 mL syringe. Each chopped syringe was equipped with a 0.25 mm diameter wire inserted through two holes drilled at the end. Once the syringe was inserted in the sediment, this attached wire facilitated separation of the sample from the core and a clean removal of the sediment. When the syringe was completely inserted into the core, and full of sediment, the syringe was rotated before removal to cut the sample cleanly from the section. This sampling technique was used to obtain high-resolution interstitial water samples while minimizing impact on the integrity of the composite section. Sediment plugs were taken on the catwalk, immediately after cores were sectioned. No acetone was used to seal the end caps of the cut cores until after all pore water had been extracted, because organic solvents can interfere with the spectroscopic analysis of water isotopes.

Sediment samples were then placed into a Manheim titanium squeezer and squeezed at ambient temperature with a Carver hydraulic press [*Manheim et al*., 1994], reaching pressures typically up to 150 MPa and as high as 300 MPa when needed. Interstitial water samples discharged from the squeezer were passed through 0.45 μm polyethersulfone membrane filters, collected in plastic syringes, and stored in plastic sample tubes for shipboard analyses or archived in flame-sealed glass ampules for shore-based analyses.

2.1.2. Rhizon Samples

At Site U1385B interstitial water was also sampled using Rhizon samplers, consisting of a hydrophilic porous polymer tube (5 cm porous part, Rhizosphere Research Products) [*Seeberg-Elverfeldt et al*., 2005]. The polymer composition is a blend of polyvinylpyrrolidine and polyethersulfone. Rhizon samplers were carefully inserted through holes drilled in the core liner such that the porous membrane was centered in the core. Syringes were attached to each Rhizon sampler with a Luer-lock, pulled to generate vacuum, and held open with wooden spacers. Samplers were left in place during the core temperature equilibration (~3 h). The Rhizon samplers were used in sets of three, spaced 3 cm apart, with the center Rhizon inserted at the center of each section (i.e., 75 cm from the section top for a standard 150 cm section). Water from all three samplers

was combined into one sample in a centrifuge tube and shaken to mix before splitting (samples were sent to two separate shore-based labs) and archiving. In the same manner as for the squeeze samples, Rhizon samples were archived in flame-sealed glass ampules for shore-based analyses.

In contrast to the methods on previous cruises, the Rhizon samplers were used dry in order to avoid sample contamination from pre-soaking. In qualitative tests, we found that flow rate through the Rhizons did not depend on pre-soaking. Further, stable water isotope measurements were sensitive to the isotopic values of the solution in which the Rhizons were pre-soaked even when the first few milliliters were discarded from the syringe during sampling. That is, the syringe was removed from the core, a few milliliters of water were discarded, then the syringe was reattached and a fresh sample was taken. This fresh sample's isotopic measurement was different than those of the sample taken with a dry Rhizon. Because of the low total water volume recovery, the pre-soaking fluid cannot be flushed completely from the Rhizon in order to recover an uncontaminated measurement.

2.2. $\delta^{18}O$ and δD Measurements

Oxygen and hydrogen isotope measurements of interstitial waters were made by cavity ringdown laser spectroscopy (CRDS). CRDS is a time-based measurement system that uses a laser to quantify spectral absorption lines unique to $H_2^{16}O$, $H_2^{18}O$, and $^2H^{16}O$ in an optical cavity [*Gupta et al*., 2009]. The equipment consisted of an L1102-i Picarro water isotope analyzer manufactured in July 2009 (Serial Number: 202-HBDS033; 200-CPVU-HBQ33), an A0211 high-precision vaporizer manufactured in August 2011 (SN: VAP 292), and a CTC HTC-Pal liquid autosampler (SN: 142552). The Picarro L1102-I measures $\delta^{18}O$, δD, and total H_2O concentration simultaneously.

For the present work, approximately 500 μL of filtered interstitial water was loaded in a 2 mL septa top glass vial and placed in the autosampler. Each water sample was injected nine times into the vaporizer. Memory effects from previous samples were avoided by rejecting the first three results and averaging the final six injections. An internal seawater standard (SPIT) was analyzed between each unknown sample to track instrumental drift. Analysis of each sample, consisting of nine injections, took 90 min. Three hours per sample is required if one includes the time needed to measure bracketing standards. The vaporizer septa were changed regularly after no more than 300 injections.

The analysis of seawater samples (particularly the initial sample evaporation step) generates considerable salt buildup in the Picarro's vaporizer, which compromises both the precision and drift of the measurements. To combat this problem we inserted a stainless steel mesh liner, recently designed and provided by Picarro, in the vaporizer injection port to capture the salt precipitate. The liner was changed with the same frequency as the vaporizer septa.

The instrument was calibrated using three working standards from the University of Cambridge with known values: Delta ($\delta^{18}O = -27.6‰$, $\delta D = -213.5‰$), Botty ($\delta^{18}O = -7.65‰$, $\delta D = -52.6‰$), and either VSMOW or SPIT ($\delta^{18}O = 0‰$, $\delta D = 0‰$). The $\delta^{18}O$ and δD of SPIT are indistinguishable analytically from VSMOW. Because the Picarro analyzer is extremely linear, it is only necessary to use three calibration standards. The calibration line was determined by linear regression of the Picarro output isotope values against the standards' known values. Measured $\delta^{18}O$ and δD were corrected to VSMOW in parts per mille (‰) by applying the linear calibration.

Because organic compounds can cause spectroscopic interference in CRDS and affect isotopic results, we processed the data using Picarro's ChemCorrect software that identifies irregularities caused by hydrocarbons. Despite significant amounts of methane in headspace samples, pore water samples were not flagged as being contaminated by the ChemCorrect software suggesting that methane gas is lost during the interstitial water sampling and squeezing process.

2.3. $[Cl^-]$ Measurements

The $[Cl^-]$ of each sample is measured by potentiometric titration against silver nitrate to form the precipitate silver chloride. Our titration apparatus is custom-built around a Gilmont Instruments precision micrometer buret (2.5 mL, discontinued parts), a National Instruments USB-6210 Data Acquisition module, and an Applied Motion STM-23 stepper motor and controller. In brief, the chloride concentration of the sample is determined by the equivalence point of the reaction, when an equivalent amount of silver nitrate reagent to the amount of chloride in solution has been added. The equivalence point is determined

potentiometrically by identifying the maximum $\frac{\Delta E}{\Delta V}$, where E is the potential difference between the reagent and solution and V is the volume of reagent that has been added to the sample. The addition of reagent to the solution is controlled by advancing the stepper motor coupled to the precision micrometer buret. The stepper motor and the voltage acquisition are driven through a LabVIEW program. After filling the buret with reagent and placing the tip of the buret in the sample beaker, the entire reaction is automated.

To determine the chloride concentration of an unknown sample, we weigh out a sample and titrate to the equivalence point. The concentration of an unknown sample is calculated from the sample's weight, the volumetric equivalence point, and the concentration of the silver nitrate reagent. Our typical sample sizes are $\sim$600 μL of pore fluid. The true size of the samples was determined through weighing on a precision balance. The silver nitrate reagent had a concentration of $\sim$0.23 M, which resulted in equivalence points at around 1.5 mL of reagent added. The approximate concentration of the silver nitrate is determined during its preparation, but to have a more accurate and precise knowledge of its concentration we calibrate the concentration by titrating against a known standard three to five times at the beginning of each measurement day. Our standard is the IAPSO P-Series Normal Standard Seawater (S = 35). Once we break the factory seal on a standard, we store it in its original bottle with parafilm around the top and inside a large glass jar that is $\sim$1/3 full of water. We use a standard for a maximum of two weeks. To check the continuing validity of this storage method, when we open a new standard we compare the old values to the new ones. We also validated the storage technique by measuring a consistency standard in triplicate every measurement day that was stored identically to the open IAPSO standards over the full period of all our measurements. Our consistency standard is low salinity, $\sim$33 g kg^{-1}, surface seawater from the North Pacific, in the vicinity of Hydrate Ridge. The stability of our consistency standard, that is, the absence of any trend in the measurements, confirmed that there is no evaporation of water stored in this way.

3. Results

We found that Rhizons were unable to be used in the very deepest, highly compacted ocean sediments. Near the Advanced Piston Core (APC) refusal depth, $\sim$150 mbsf at Site U1385, our attempts to insert Rhizons into the sediments without pre-drilling the sediment were typically unsuccessful. Even when pre-drilling the sediment, the sediment would quickly fill in, crushing the Rhizon and leading to minimal water extraction.

There are two major challenges in comparing our Rhizon and squeeze sample results. First, the depth profiles of chloride and stable isotopes at Site U1385B neither have a strong trend (increasing or decreasing) nor are they constant with depth, so our sedimentary signal-to-noise ratio is quite low. This issue exacerbates the second issue, which is that the Rhizon and squeeze samples by necessity were taken at different depths. These issues combined make it difficult to distinguish between offsets in the measurements due to either analytical or sedimentary noise versus those due to fractionation.

The problem with sediment signal-to-noise ratio is specific to this site, as most sites of interest show a strong depth dependent signal in both stable isotopes and chloride [e.g., *Adkins et al*., 2002]. We expected that the signal-to-noise ratio would be high enough to overcome the problem of comparing values at different depths, but unfortunately this was not the case.

One way around these problems is to consider the population of measurement offsets rather than the individual offsets. For this we interpolate linearly between squeeze measurements to find the hypothetical value that the Rhizon sample should record. We then subtract the interpolated squeeze value from the Rhizon sample value to find the offset. The majority of the following analyses rely on this technique. We note that if there were a strong second derivative of chloride or isotopic content with depth in the profile, this interpolation technique would be expected to give biased answers. However, the narrow range of our measured values makes interpolation suitable for our case.

Another possible issue is that there could be an offset between the reported depth and the actual depth the sample represents, as the samples span an average of 5–10 cm of sediment. For a straight line profile that increases with depth, the average value would be higher than the top depth's value and lower than the bottom depth's value. If the profile decreases with depth, the reverse would be true. We find however that adjusting for this few centimeter difference has no effect on the offset trend.

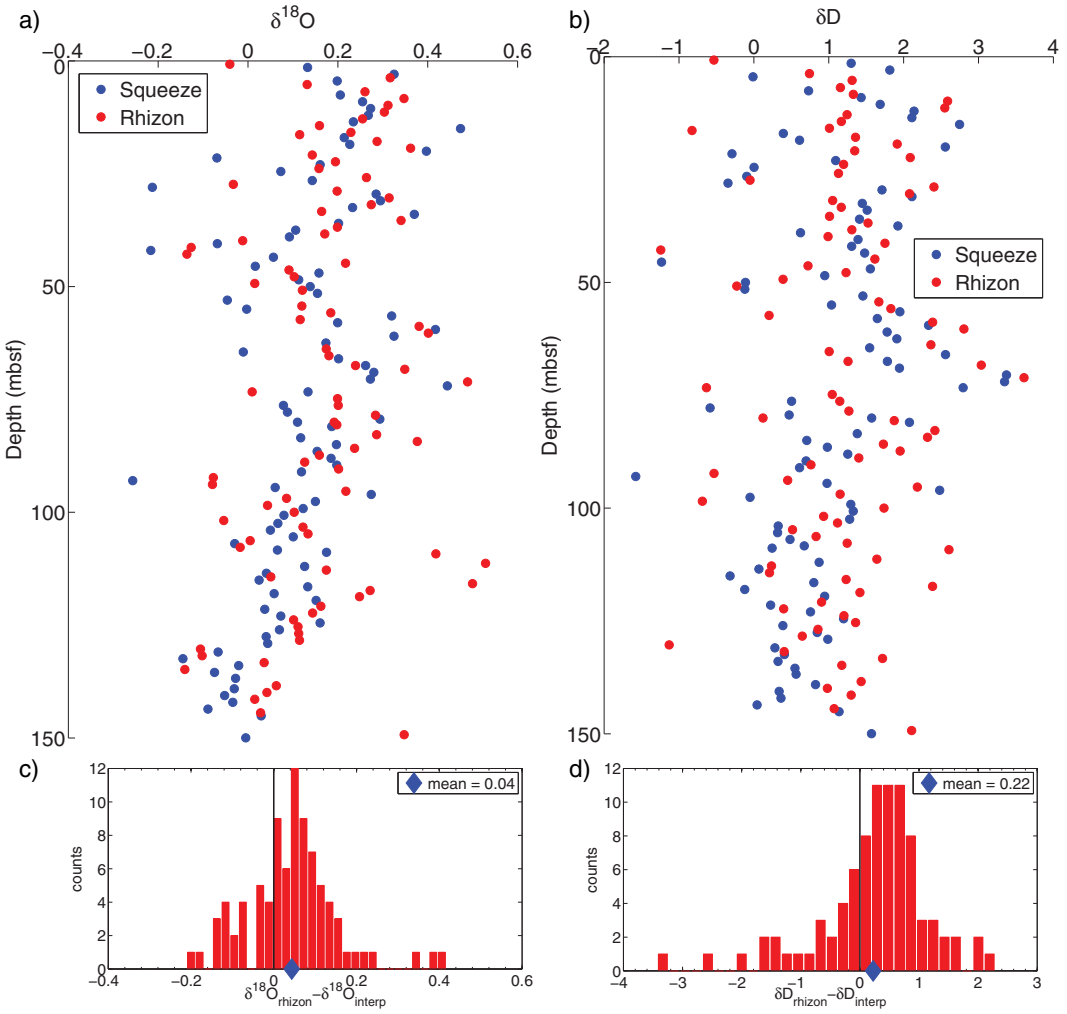

Figure 2. Depth profiles of (a) δ^{18}O and (b) δD measured in both squeeze and Rhizon samples and histograms of offset in (c) δ^{18}O and (d) δD between Rhizon and squeeze sample measurements interpolated to Rhizon sample depths. All δ values are in ‰ VSMOW.

3.1. Picarro Calibration and Drift

Calibrations were performed at the beginning of each ~24 h period of measurements, as the calibration shifts significantly over a few days. The slope of the δ^{18}O regression varied between 1.05 and 1.07 (average = 1.05), whereas the δD slope varied from 1.12 to 1.15 (average = 1.14). For a sample with a VSMOW value of 0.05‰, these different calibration curves would generate a range of VSMOW values between −0.33 and 0.53‰.

Even after re-calibrating on a daily basis, there is significant drift in the standard value over one day, as computed by applying the calibration curve to the measured output. Over the period of one day, the value of the standard drifts by 0.4–1‰ in δ^{18}O and 1–3‰ in δD, necessitating a drift correction. One complication is that the drift is not always unidirectional or linear over the course of a day. For this reason, we use a running drift correction. We drift-correct the measurements after they have been converted to ‰ using the calibration curve. For each pair of SPIT bracket measurements, we compute a time-local linear slope and intercept of the SPIT value from their nominal δ^{18}O and δD. We then subtract the appropriately time-weighted drift correction from the nominal computed values to obtain the drift-corrected values. This removes any trend from our SPIT standard replicates over the course of our measurements, and the mean and standard deviation of the SPIT standards are 0.09‰ and 0.05‰ in δ^{18}O and −0.14‰ and 0.41‰ in δD. The quoted precision of the instrument is ≤0.1‰ for δ^{18}O and ≤0.5‰ for δD and the quoted drift is ≤±0.3‰ for δ^{18}O and ≤±0.9‰ for δD. Picarro defines precision and drift as the standard deviation and range (max-min) of the

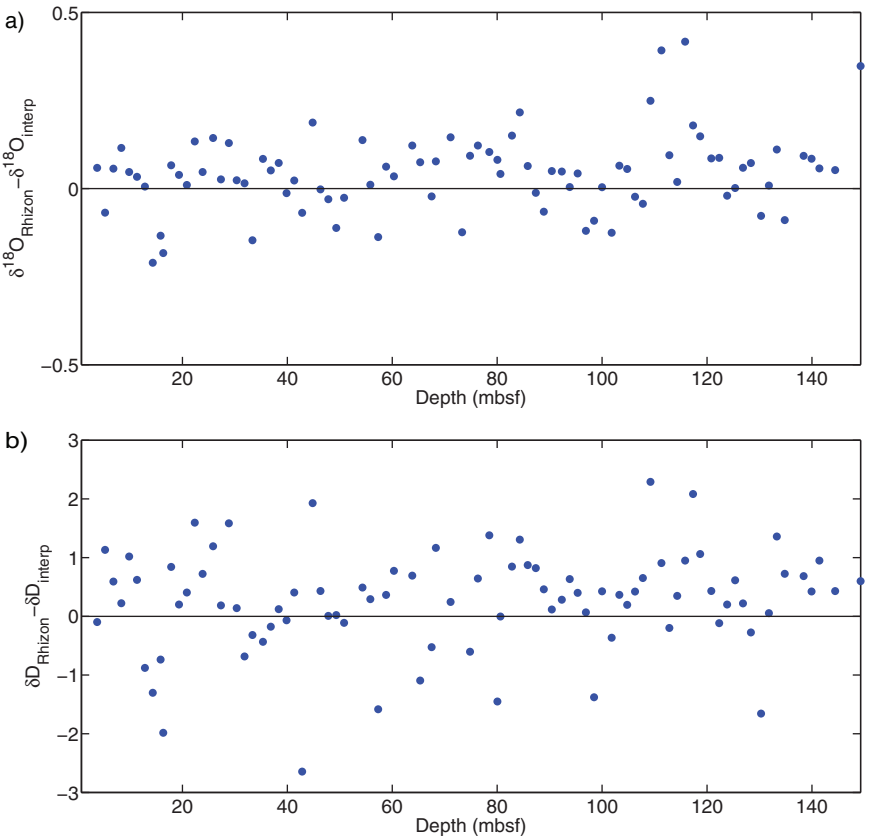

Figure 3. Offset between Rhizon sample measurements and squeeze sample measurements as a function of depth (mbsf). All δ values are in ‰ VSMOW. (a) δ^{18}Oand (b) δD.

average values for 12 injections of the same water sample (tap water) measured 12 times, which is equivalent to 144 injections averaged in blocks of 12.

3.2. Stable Isotopes

Visual inspection of the depth profiles of δ^{18}O and δD (Figures 2a and 2b), hints that many of the δD Rhizon measurements are heavier than the squeeze measurements, but the noise in the δ^{18}O profile obscures the relationship between Rhizon sample measurements and squeeze sample measurements. Figures 2c and 2d show histograms for the δ^{18}O and δD offsets. The mean and maximum likelihood are closely aligned, as can be seen by the location of the mean relative to the bin with the highest number of samples. The mean offset for δ^{18}O is 0.04‰ while the mean offset for δD is 0.23‰. The error in the determination of each of these means is equal to $\sqrt{\sigma^2/N}$, where σ is the precision of an individual measurement, assuming that the precision for each measurement is the same. With a reported precision of 0.1‰ in δ^{18}O, 0.5‰ in δD and 87 samples, the error in the mean offset for δ^{18}O is 0.02‰ while the error for the mean offset of δD is 0.08‰.

Neither the offsets in δ^{18}O nor those in δD show a clear trend with depth, as demonstrated in Figure 3. Instead, this view of the data confirms that of the histograms, which is that most of the Rhizon measurement values are greater than the squeeze measurement values.

3.3. Chloride

In contrast, in the [Cl^-] depth profile (Figure 4a), the Rhizon measurements lie clearly to the right of the squeeze measurements in the upper ~80 m, although below that point both profiles become noisier and the distinction between measurement techniques is less clear. The chloride offset histogram (Figure 4b) again has a closely aligned mean and maximum likelihood and the mean offset is 0.04 g kg^{-1}. Given an average precision of 0.013 g kg^{-1} based on standard replicate measurements, and 59 comparison points,

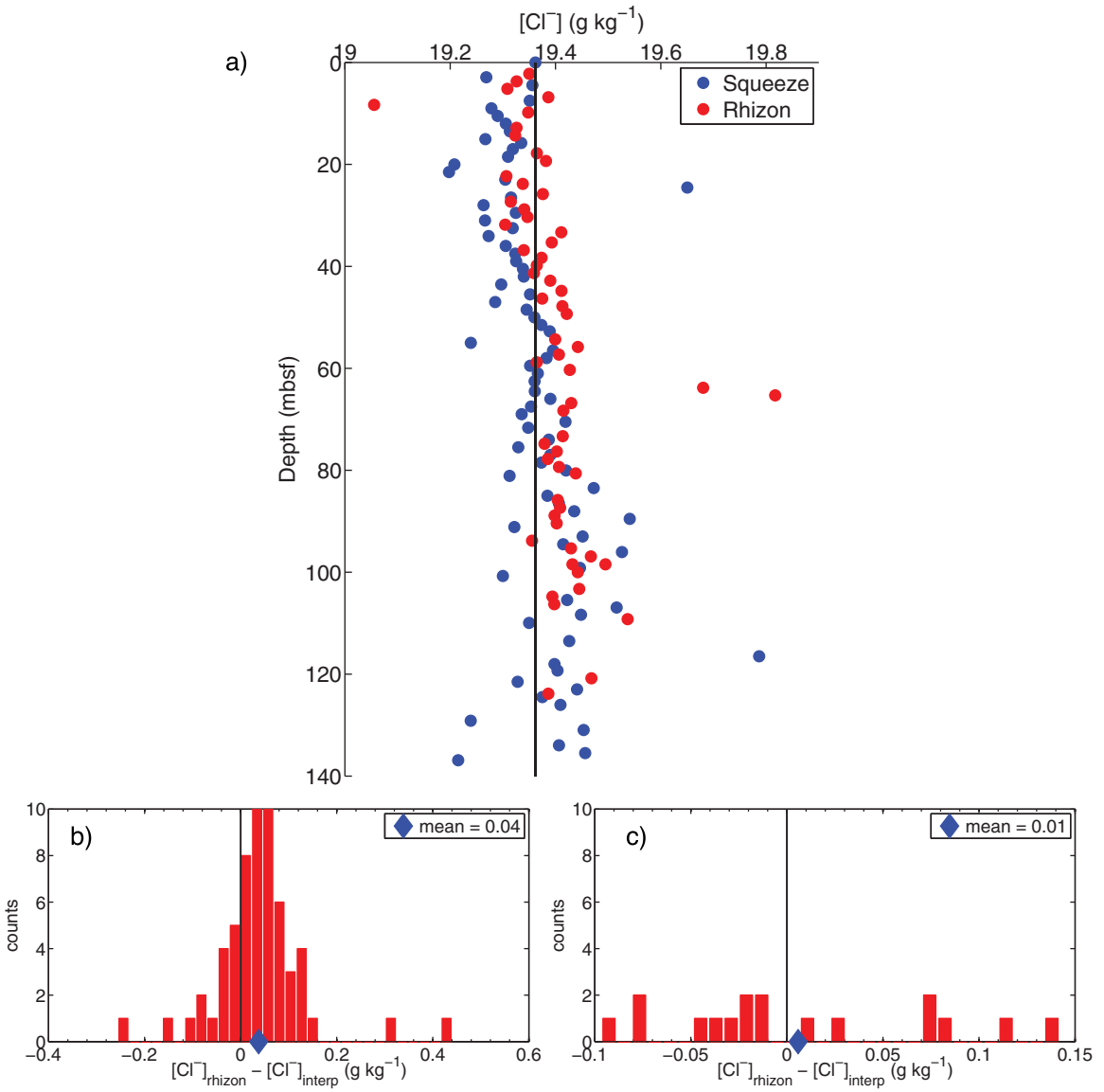

Figure 4. (a) Depth profiles of [Cl$^-$] measured in both squeeze and Rhizon samples at Site U1385 and (b and c) histograms of the [Cl$^-$] (g kg^{-1}) offset between Rhizon sample measurements and squeeze sample measurements interpolated to the depths of the Rhizon samples. Figure 4b shows all offset values, while Figure 4c shows only the values below 80 mbsf. Vertical black line in Figure 4a shows the bottom water value for reference, while vertical black lines in Figures 4b and 4c denote 0 g kg^{-1} offset.

the error in this mean offset is 0.0017 g kg^{-1}. Considering only the points below 80 m (Figure 4c), the offsets in chloride are almost indistinguishable from zero. However, considering the offset in chloride versus depth in Figure 5, there does not seem to be a significant trend below 80 m. Instead, it seems that perhaps the change is due to an inflection point in the depth profile. Or, below 80 m there is so much sedimentary noise that the interpolation technique is no longer valid. There is no relationship between the age of the IAPSO standard and the offset in chloride, as shown in Figure 6, confirming that the signal we see is real and not due to problematic storage of our standard.

4. Discussion

We find statistically significant offsets between measurements on Rhizon samples and squeezed samples in both stable isotopes and chloride. There are several possible reasons for these observed differences, which we discuss consecutively below.

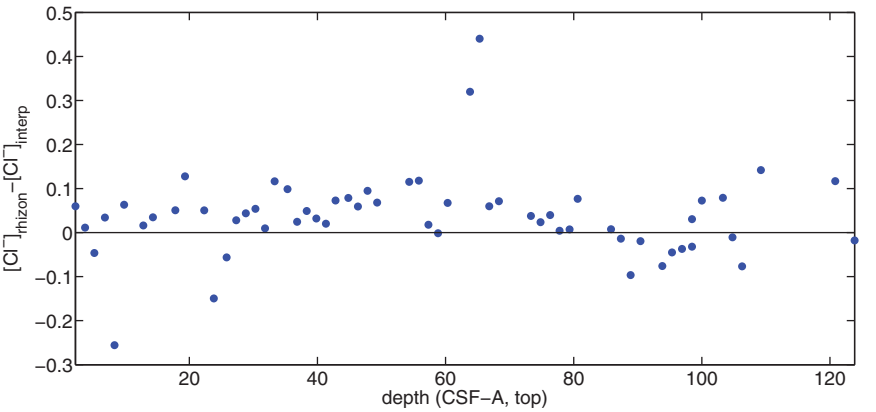

Figure 5. $[Cl^-]$ (g kg^{-1}) offset between Rhizon sample measurements and squeeze sample measurements as a function of depth.

4.1. Rhizon Absorption of Water or Diffusional Fractionation

The hydrophilic membrane of the sampler may have absorbed some of the water, creating higher measured chloride concentrations. However, we expect that absorption alone, that is, bulk volumetric uptake of water molecules, would not affect the oxygen and hydrogen isotope ratios. Instead, as there is an offset between Rhizon and squeeze samples in both isotopes and chloride concentration, these biases are more consistent with a combination of absorption and diffusional fractionation through the Rhizon membrane. Diffusional fractionation would preferentially affect the δD relative to δ^{18}O as the relative mass difference, and thus the difference in diffusivity, between hydrogen isotopes is greater than that between the oxygen isotopes. For this reason, diffusional fractionation produces a similar trend to evaporative fractionation (see section 4.4) in the relationship between hydrogen isotope ratios and oxygen isotope ratios.

4.2. Clay Ultrafiltration of Isotopes and Ions

Highly compacted fine-grained clays have the ability to exclude ions and fractionate isotopes of water passing through them [*Coplen and Hanshaw*, 1973; *Hanshaw and Coplen*, 1973]. This ultrafiltration effect would cause the squeeze samples' water to have lower chloride concentrations and lighter δ^{18}O and δD than the original water in the sediment, and hence the Rhizon samples. The sediment at Site U1385 is clay-rich, ranging from 25% to 30% carbonate, indicating potential for ultrafiltration. However, the only experiments (to our knowledge) studying this effect [*Coplen and Hanshaw*, 1973; *Hanshaw and Coplen*, 1973] maintained a hydraulic pressure gradient across the clay and a residual reservoir of

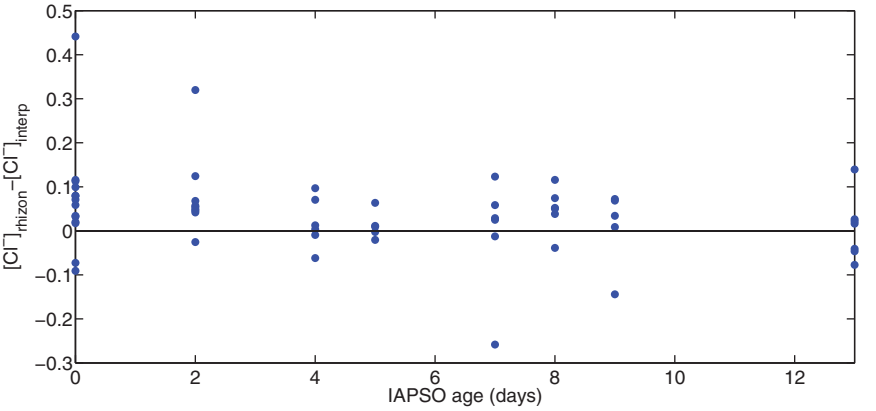

Figure 6. Offset between Rhizon and squeeze sample $[Cl^-]$ as a function of the age of the IAPSO standard (days) used to measure the Rhizon sample.

fluid on the input side of the clay filter. When we sample using a hydraulic press, the pressure in the sediment is evenly distributed and little water remains in the sediment whole round. More importantly, this clay ultrafiltration mechanism yields Rayleigh f values ~5, which is much larger than any f we compute (see section 4.4).

4.3. Contamination With Drill Fluid

Another possible source of the offset is drill fluid contamination. We inserted the porous membrane such that it was not in direct contact with drill fluid; however, in many cases we observed that the sediment in which we placed the samplers had pulled away from the liner by the time we removed the samplers. Such a thorough removal of water from the sections may mean that drill fluid was sucked into the sampler as well. The surface salinity generally exceeds ~19.9 g kg^{-1} [Cl^-] (36 psu), which is higher than almost all of our measurements by 0.5 g kg^{-1}. This could contribute to the offset we see, particularly in the less compacted sediments in the upper part of the hole, though it is difficult to quantify the expected effect. As mentioned in section 2.1.1, we did not detect any sulfate in the samples below the sulfate reduction zone, whether taken with Rhizons or by squeezing. We also did not observe a difference between shipboard sulfate profiles in Rhizon or squeeze samples, but our depth-resolution was lower and our instrumental error higher. For a 10 mL pore water sample with 19.4 g kg^{-1} chloride concentration that was contaminated by 19.9 g kg^{-1} drill fluid to have an offset of 0.04 g kg^{-1}, the equivalent contamination volume would be 0.8 mL. If the original sample contained no sulfate, the contamination would appear as a 2.3 mM concentration, within the shipboard detection capabilities.

4.4. Evaporation

Rhizon samples were taken over an ~3 h period during which water evaporation may have altered the isotopes and chloride concentration. While the sampling system is nominally closed, the syringes used to collect the samples did not have a perfect seal between plunger and barrel. We observed that in some cases the seal loosened with time, which would allow air exchange between the syringe and the surrounding environment. Syringes with imperfect seals are also used to collect samples from the squeezers, and the squeezing process can also take several hours. However, the squeezer sampling may be less sensitive to evaporation for three reasons: no vacuum is pulled on the squeezer syringes, so the headspace in the syringe is smaller; the total sample extracted using a squeezer is usually larger volume than that using a Rhizon sampler; and the time to extract a sample using the squeezer is often shorter. We were unable to carefully control for the sampling time, which may be one contributor to the noisiness in the data. Evaporative fractionation has been intensively studied, and there are good theoretical predictions for the relationship between $\delta^{18}O$ and δD undergoing evaporation. We can therefore compare the relationships between the oxygen and hydrogen isotopic ratios and the chloride concentrations to see if the measured Rhizon-squeeze offsets are consistent with evaporative fractionation.

Our case can be described best by open system Rayleigh fractionation. The ratio of heavy to light isotope, R (i.e., $\frac{^{18}O}{^{16}O}$ for oxygen or $\frac{D}{H}$ for hydrogen) in a pool of water with essentially infinite molecules and fixed conditions can be described by

$$R = R_0 \left(\frac{N}{N_0}\right)^{(\alpha-1)}. \quad (1)$$

R_0 is the initial isotope ratio, N is the total number of molecules remaining, N_0 is the original number of molecules, and α is the fractionation factor. At 20°C the evaporative fractionation factor for ^{18}O relative to ^{16}O is 1.0098 and for deuterium relative to protium is 1.084 [*Gat*, 1996].

Under evaporation the fraction of material left, $\frac{N}{N_0}$, is also known as f. f will be equal for both pairs of isotopes, such that there is a linear relationship between the natural logs of the element ratios, i.e.,

$$\frac{\alpha_H - 1}{\alpha_O - 1} \ln \frac{R^O}{R_0^O} = \ln \frac{R^H}{R_0^H}. \quad (2)$$

While the spectroscopic technique used in CRDS does not yield isotope ratios, the ratios can be computed simply from the δ values as follows:

$$\frac{\delta^{18}O}{1000}+1=\frac{R}{R_{std}}, \tag{3}$$

such that the relationship between δ^{18}O and δD under evaporation is

$$\frac{\alpha_H-1}{\alpha_O-1}\ln\left(\frac{\frac{\delta^{18}O_{final}}{1000}+1}{\frac{\delta^{18}O_{initial}}{1000}+1}\right)=\ln\left(\frac{\frac{\delta D_{final}}{1000}+1}{\frac{\delta D_{initial}}{1000}+1}\right). \tag{4}$$

Substituting in the α values, this is,

$$8.5714\ln\left(\frac{\frac{\delta^{18}O_{final}}{1000}+1}{\frac{\delta^{18}O_{initial}}{1000}+1}\right)=\ln\left(\frac{\frac{\delta D_{final}}{1000}+1}{\frac{\delta D_{initial}}{1000}+1}\right). \tag{5}$$

For our purpose, we assume the initial isotope ratio is that measured in the squeeze sample, interpolated to the depth of the Rhizon sample. The final isotope ratio is that measured in the Rhizon sample. The hypothesis we test with these choices is that the Rhizon values are fractionated relative to the squeeze values because they are left open to the atmosphere longer. It is important to note that in some cases the squeeze samples do sit for ~1 h in the squeezers; thus, we never have a perfect control on no evaporation.

The red line labeled evaporative fractionation in Figure 7 shows the expected relationship between the oxygen and hydrogen isotope ratios under evaporative fractionation. The average error (square root of the sum of square errors) of the data relative to the prediction, assuming all the error is in the hydrogen measurements, is 0.0082. The blue line is a linear fit to the logarithmic data, which has a slope of 4.992. The average error of the data relative to the fit is 0.0071. Propagating the precision of the hydrogen isotope measurements through the Rayleigh equation, the theoretical average error is ~0.2. Therefore, the difference between the evaporative fractionation line and the empirically calculated relationship between hydrogen and oxygen isotopes is indistinguishable.

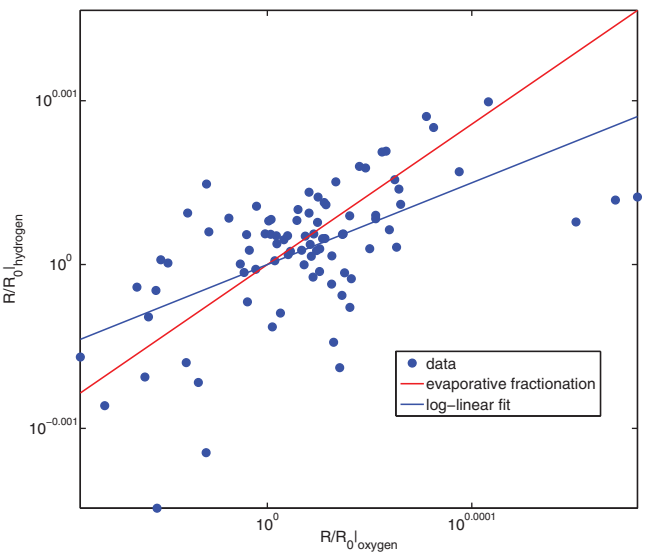

Figure 7. Hydrogen isotope ratios versus oxygen isotope ratios computed from measured δ values (blue circles and blue line), compared with the expected relationship between the isotope ratios (red line) under evaporative fractionation.

The evolution of concentrations with evaporations can be described analogously to Rayleigh fractionation, where $f=\frac{V_{final}}{V_{initial}}=\frac{[Cl^-]_{initial}}{[Cl^-]_{final}}$. Then the relationship between chloride concentrations and δ^{18}O (or analogously, δD) can be written

$$\frac{1}{\alpha-1}\ln\left(\frac{\frac{\delta^{18}O_{final}}{1000}+1}{\frac{\delta^{18}O_{initial}}{1000}+1}\right)=\ln\left(\frac{[Cl^-]_{initial}}{[Cl^-]_{final}}\right). \tag{6}$$

However, we find no correlation between the f calculated from the chloride concentrations and that calculated from the isotope ratios assuming evaporative fractionation, nor does the fractionation of the isotopes and [Cl$^-$], as shown in Figure 8, have any trend with depth.

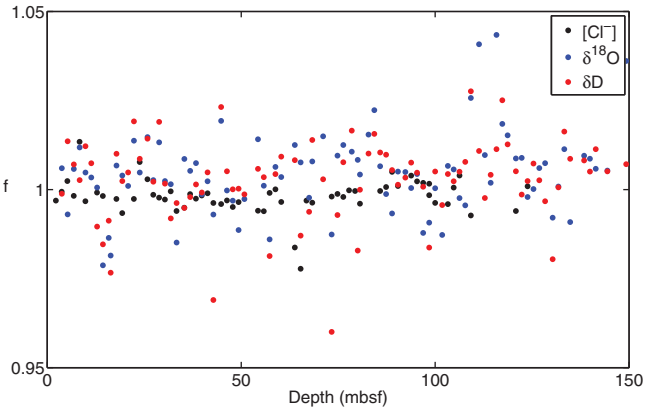

Figure 8. Rayleigh f versus depth computed from [Cl$^-$], δ^{18}O and δD, assuming that the difference in measurements in Rhizons and squeeze samples is due to evaporation of Rhizon samples.

Since the Rhizon bias measured in [Cl$^-$] is clearer than that in δ^{18}O and δD, we can consider whether the amount of fractionation, assuming it is evaporative, could be expected to be detectable by the Picarro. The most fractionated chloride measurement yields an f of 0.98. This would yield a ratio $\frac{R}{R_0}|_O$ of 0.9998. For a typical measured $\delta^{18}O_{final}$ equal to 0.2‰, the measured $\delta^{18}O_{initial}$ would be equal to 0.4‰ yielding a measured difference of 0.2‰ between Rhizon and squeeze samples. However, most of the [Cl$^-$] determined f values are greater than 0.995, equivalent to a ratio of $\frac{R}{R_0}|_O =$ 0.99995 which would yield a measured difference in δ^{18}O of less than 0.05‰, below the measurement precision of the Picarro. Because the relationship between isotope fractionation and chloride concentration due to evaporation is undetectable, we cannot rule out that the observed fractionation in our two sets of samples is at least in part evaporative. At the same time, we cannot conclusively point to evaporation as the culprit. Instead, the lack of correlation between f values computed using chloride concentration and those computed from isotope ratios suggests a different mechanism causes the offset in measurements between the two sampling techniques.

While there are multiple factors that may contribute to the measured offsets in chloride concentrations and stable isotope ratios in Rhizon versus squeeze samples, we maintain that the most likely cause is a combination of absorption and diffusional fractionation in the Rhizon hydrophilic membrane. Clay ultrafiltration should yield a much stronger signal in isotopic fractionation. Evaporation of water during the long process of Rhizon sampling cannot be ruled out; however, we expect a strong correlation between f_{conc} and $f_{isotope}$ if evaporation were indeed causing the offset, which we do not observe. A slight contamination of drill fluid is possible, but we did not detect any sulfate in the samples below the sulfate reduction zone, nor do we see an offset between shipboard Rhizon and squeeze sulfate profiles. Conclusive demonstration that Rhizon samplers absorb water and cause diffusive fractionation in samples will require controlled experiments designed to eliminate other potential factors.

The measured offsets in concentration and isotopic composition between Rhizon and squeeze samples were neither constant nor unidirectional. Further, the end-to-end spreads of the offset distributions were wide-close to 1 g kg^{-1} in [Cl$^-$], 1‰ in δ^{18}O, and 5‰ in δD. For these reasons, it is impossible to simply correct for this artifact post-sampling. It would be reasonable to ignore the bias entirely when measuring a signal several orders of magnitude larger, but it can be difficult to predict the signal in advance when choosing a sampling tool. Instead, we urge caution in interpreting concentration and isotopic measurements on samples taken with Rhizons and suggest that controlled experiments should be completed in order to better characterize the bias we observe.

5. Conclusions

Rhizon sampling alters the chloride concentration and oxygen and hydrogen isotopic composition in pore water samples relative to those measured in samples taken with traditional squeezing. Average Rhizon-squeeze offsets in chloride, δ^{18}O, and δD were, respectively, 0.04 g kg^{-1}, 0.04‰, and 0.22‰. As these biases were not constant or unidirectional across samples, it is impossible to correct for this artifact postsampling. For this reason, signals less than 0.5‰ in δ^{18}O, less than 0.5 g kg^{-1} in concentration and less than 2.5‰ in δD that are measured in samples taken by Rhizons must be considered unreliable. Our analysis indicates that the alteration of the samples' concentrations and isotopic values is most likely caused by a

combination of absorption by and diffusive fractionation through the Rhizon's hydrophilic membrane, but more conclusive evidence will require controlled experiments.

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References

Adkins, J., and D. P. Schrag (2003), Reconstructing Last Glacial Maximum bottom water salinities from deep-sea sediment pore fluid profiles, *Earth Planet. Res. Lett.*, *216*, 109–123, doi:10.1016/S0012–821X(03)00502-8.

Adkins, J. F., K. McIntyre, and D. P. Schrag (2002), The salinity, temperature and $\delta^{18}O$ of the glacial deep ocean, *Science*, *298*(5599), 1769–1773.

Coplen, T. B., and B. B. Hanshaw (1973), Ultrafiltration by a compacted clay membrane—I. Oxygen and hydrogen isotopic fractionation, *Geochim. Cosmochim. Acta*, *37*(10), 2295–2310.

Dickens, G. R., M. Koelling, D. C. Smith, and L. Schnieders (2007), Rhizon sampling of pore waters on scientific drilling expeditions: An example from the IODP Expedition 302, Arctic Coring Expedition (ACEX), *Sci. Drill.*, *4*, 22–25, doi:10.2204/iodp.sd.4.08.2007.

Gat, J. R. (1996), Oxygen and hydrogen isotopes in the hydrologic cycle, *Annu. Rev. Earth Planet. Sci.*, *24*(1), 225–262, doi:10.1146/annurev.earth.24.1.225.

Gupta, P., D. Noone, J. Galewsky, C. Sweeny, and B. H. Vaughn (2009), Demonstration of high-precision continuous measurements of water vapor isotopologues in laboratory and remote field deployments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) technology, *Rapid Commun. Mass Spectrom.*, *23*, 2534–2542, doi:10.1002/rcm.

Hanshaw, B. B., and T. B. Coplen (1973), Ultrafiltration by a compacted clay membrane—II. Sodium ion exclusion at various ionic strengths, *Geochim. Cosmochim. Acta*, *37*(10), 2311–2327.

Manheim, F. T., E. G. Brooks, and W. J. Winters (1994), Description of a hydraulic sediment squeezer, technical report, Dep. of the Inter., U.S. Geol. Surv., Woods Hole, Mass.

McDuff, R. E. (1985), The chemistry of interstitial waters, Deep Sea Drilling Project Leg 86, in *Initial Reports of the Deep Sea Drilling Project*, vol. 86, edited by G. R. Heath et al., chap. 31, pp. 675–687, U.S. Gov. Print. Off., Washington, D. C., doi:10.2973/dsdp.proc.86.131.1985.

Schrag, D., G. Hampt, and D. Murray (1996), Pore fluid constraints on the temperature and oxygen isotopic composition of the glacial ocean, *Science*, *272*(5270), 1930–1932.

Schrag, D., J. Adkins, K. McIntyre, J. Alexander, D. Hodell, C. Charles, and J. McManus (2002), The oxygen isotopic composition of seawater during the Last Glacial Maximum, *Quat. Sci. Rev.*, *21*, 331–342.

Schrag, D. P., and D. J. DePaolo (1993), Determination of $\delta^{18}O$ of seawater in the deep ocean during the Last Glacial Maximum, *Paleoceanography*, *8*(1), 1–6, doi:10.1029/92PA02796.

Schrum, H. N., R. W. Murray, and B. Gribsholt (2012), Comparison of Rhizon sampling and whole round squeezing for marine sediment porewater, *Sci. Drill.*, *13*, 47–50, doi:10.2204/iodp.sd.13.08.2011.

Seeberg-Elverfeldt, J., M. Schlüter, T. Feseker, and M. Kölling (2005), Rhizon sampling of porewaters near the sediment-water interface of aquatic systems, *Limnol. Oceanogr. Methods*, *3*, 361–371.

Stow, D., F. Hernández-Molina, C. Alvarez Zarikian, and the Expedition 339 Scientists (2013), *Proc. Integrated Ocean Drill. Program*, *339*, doi:10.2204/iodp.proc.339.2013.