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PORE WATER EXTRACTION FOR UNSATURATED ZONE ISOTOPE RESEARCH:
AN INVESTIGATION USING AN IMMISCIBLE DISPLACEMENT
FLUID AND A CENTRIFUGE

by

Caitlin Burnett Weaver

A THESIS

Presented to the Faculty of
The Graduate College at the University of Nebraska
In Partial Fulfillment of Requirements
For the Degree of Master of Science

Major: Earth and Atmospheric Sciences

Under the Supervision of Professor John B. Gates

Lincoln, Nebraska

May, 2014

PORE WATER EXTRACTION FOR UNSATURATED ZONE ISOTOPE RESEARCH:
AN INVESTIGATION USING AN IMMISCIBLE DISPLACEMENT
FLUID AND A CENTRIFUGE

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University of Nebraska, 2014

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Accurate and reliable pore water extraction techniques are important to an array of scientific fields including, but not limited to, hydrogeology, soil science, and paleoenvironmental research. The aim of the current project is to test the applicability of an immiscible displacement extraction technique for stable isotopes of water under a range of textural, hydrologic, and chemical conditions. In this study, laboratory experiments were conducted to establish the extent to which the proposed method 1) achieves sufficient yield for laboratory isotopic analyses, 2) results in isotopic exchange between water and the displacement fluid, 3) conserves initial isotopic compositions of spike test standards under a range of sediment conditions, and 4) is appropriate for natural stable isotope profile interpretation.

Overall, pore water extraction from the unsaturated zone using the immiscible displacement fluid, HFE-7100, and a centrifuge has proven to be a satisfactory method for stable isotopes of water under the test conditions considered in this project. HFE-7100 causes no isotopic discrimination with water exposure times up to 24 hours (maximum exposure time tested). Results suggest that yields are sufficient under a wide array of natural conditions including in water stressed regions (consistently with moisture

contents less than 6%). With few exceptions, the greatest percent yield resulted from high moisture contents, large grain sizes, and low clay contents. Persistent isotopic discriminations between spike test standards and extracts suggest that non-vaporization fractionation may be more common than is currently assumed under typical unsaturated zone conditions. The fact that pore water isotope fractionation was found in non-saline, unsaturated, highly permeable conditions suggests that the fractionation is most likely associated with water adsorption onto mineral surfaces. While fractionation-related uncertainty raises concerns about the validity of unsaturated zone isotopic profile interpretations, analysis of paired field cores suggests that fractionation-related uncertainty may be smaller than the temporal variability of meteoric water in many cases. In such instances, profiles may be interpreted reliably using standard conservative tracer assumptions.

ACKNOWLEDGMENTS

This research was made possible through funding provided by the University of Nebraska of Nebraska (UNL) Earth and Atmospheric Sciences Department. The teaching assistantship was a valuable learning experience.

I would first like to thank Dr. David Watkins for initially putting me into contact with Dr. John Gates. If he had not introduced us I may have never chosen hydrogeology as a discipline. Dr. Watkins has been an excellent Chair of the Earth and Sciences Department throughout my time at UNL. I would also like to thank my committee members, Dr. Sherilyn Fritz and Dr. Diego Riveros-Iregui for their valuable insights. Time and effort provided has been greatly appreciated.

I owe great thanks to my adviser, Dr. Gates. I am privileged to have had his support over the course of two research projects, first the UCARE project, and second, my master's research. His insight and guidance throughout my research has challenged me as a student and scientist. His continual enthusiasm for water science has been infectious. Also, a special thanks to Kate Boone for supplying the initial framework for the research project.

This degree would not have been possible without my amazing group of friends, Emily, Karma, Bradi, and Nicole (a.k.a. The Bros). Throughout our undergraduate and graduate degrees their continued passion for geology has inspired me. I have countless memories of silly moments that have taken place over years of study dates and field work.

Finally, I would like to thank my family who have given me unconditional love, support, and guidance throughout my life. They have been my greatest cheerleaders throughout my academic career. I am also grateful for the encouragement and patience from my partner, Taylor.

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Chapter 1.0

Introduction

Stable isotopes of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) can provide valuable insights into soil water processes, including evapotranspiration, drainage, and recharge, and can serve as indicators of paleoenvironmental conditions (Walker et al., 1994; Cook et al., 1992; Whelan and Barrow, 1980; Harvey, 2001; Harvey and Welker, 2000; Gat, 1996). Stable isotopes of water are excellent environmental tracers of the hydrological cycle, because they are naturally occurring, abundant, and have mass ratios that are affected in a predictable manner by hydrologic and meteorological processes. Because of these characteristics, stable isotopes of water are often referred to as the fingerprints of water (Clark and Fritz, 1997; Gat, 1996). The use of stable isotopes as hydrologic tracers is likely to continue to gain popularity as technological improvements make analyses more accessible and cost-effective.

A significant methodological challenge to the use of stable isotopes in unsaturated zone research is the difficulty of extracting pore water from sediments for laboratory analysis without altering its isotopic composition. The primary reason for this difficulty is that many of the most commonly used methods for extracting pore water from the unsaturated zone for isotopic analysis rely on phase changes (evaporation and condensation during distillation), which open the possibility for unintended fractionation (fractionation of isotopes are discussed in more detail in Section 1.2). For this reason, complete recovery of the pore water is required in order to achieve accurate $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions when using distillations (Revesz and Woods, 1990; Ingraham and Shadel,

1992; Walker et al., 1994; Araguàs-Araguàs et al., 1995). Extraction techniques that do not involve phase change are also available but also suffer from a range of methodological challenges (see Chapter 2). For this reason, there is no currently accepted “standard” method for pore water extraction for stable isotope analyses. Overall, a better understanding of the complexities and limitations associated with pore water extraction techniques is necessary in order to improve interpretations of resulting $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results.

The primary aim of this project is to assess the applicability of the centrifuge immiscible displacement method for investigation of unsaturated zone pore water isotopic compositions. The study aims to perform the investigation under a range of moisture, texture, and chemical conditions, in order to provide broad relevance to a range of natural environmental conditions. Particular attention is given to conditions of low moisture contents, which are characteristic of the water stressed areas where unsaturated isotopic methods are most commonly used and where most extraction methods are sub-optimal due to a combination of low yields and precision (Freeze and Cherry, 1979; Whelan and Barrow, 1980; Turner and Gailitis, 1988; Revesz and Woods, 1990). While uncommonly utilized to date, the centrifuge immiscible liquid extraction technique is potentially powerful as a simple inexpensive approach, with improved precision at low moisture contents.

The thesis is organized as follows. The remainder of Chapter 1 provides general context about unsaturated zone pore water, stable isotope dynamics, and the state of the literature on stable isotope applications in the unsaturated zone. Chapter 2 contains a literature review on the numerous pore water extraction and distillation techniques

currently in use (and Section 2.3.7 includes a comparison table of the pore water extraction techniques for a quick comparison of the key characteristics of each method). The laboratory pore water extraction methodology developed for this study is described in Chapter 3, including assessments of percent yield over an array of conditions (including grain size, moisture content, and clay abundance). Chapter 4 discusses $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of unsaturated zone pore water extractions (also analyzed in relation to grain size, moisture content, and clay abundance). Many $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of pore water extracts from isotope standard spike tests indicate fractionation relative to the isotope standards ($\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$). Because this is an important consideration for the primary aim of the thesis, and for the broader literature on stable isotopes in the unsaturated zone, this chapter also explores the issue of isotopic fractionation between free and adsorbed water using tests of adsorption onto sands and clays (Section 4.4.3), as well as chemical effects (Section 4.4.4). The immiscible displacement technique is also compared to a more widely used technique, azeotropic distillation, in order to provide comparison. Finally, in Chapter 5, the method is used on field unsaturated zone profiles.

1.1 Background on the Unsaturated Zone

The unsaturated zone, also known as the vadose zone or zone of aeration, is the area located below the earth's surface and above the water table. The water table and capillary fringe zone separates the saturated zone from the unsaturated zone. The pore spaces of the unsaturated zone are filled with varying percentages of water, water vapor, and air. When water infiltrates below the ground's surface, it must first travel through the pore spaces of the unsaturated zone before it reaches the saturated zone as recharge

(Freeze and Cherry, 1979; Fetter, 1994; Hornberger et al., 1998; Domenico and Schwartz, 1998; Healy, 2010).

Unsaturated zone moisture contents tend to be highly variable near the earth's surface, because of proximity to the atmosphere and plant root systems (Hornberger et al., 1998). The area of the unsaturated zone near the water table and capillary fringe tends to be saturated or near-saturated (Hornberger et al., 1998). In contrast, moisture contents can approach zero near the soil surface under dry climatic conditions; spatial and temporal gradients in moisture contents commonly result from wetting and drying trends at the surface. Common sources include precipitation, the addition of irrigation water, and losing streams. Primary sinks include evapotranspiration and advection (Domenico and Schwartz, 1998; Wang and Anderson, 1982). Rates and directions of water advection through the unsaturated zone are governed primarily by capillary and gravitational forces (Hornberger et al., 1998; Domenico and Schwartz, 1998; Fetter, 1994).

1.2 Unsaturated Zone Isotopic Systematics

Isotopes of an element are molecules of that element with differing numbers of neutrons. Isotopic compositions are typically reported as the ratio of a rare isotope to a common isotope, because relative isotopic abundances are easier to determine analytically. In Equation 1, m represents machine error (Clark and Fritz, 1997). The accepted international standard for reporting stable isotope measurements of water isotopes is permil difference from Vienna Standard Mean Ocean Water on the VSMOW-SLAP scale, where the delta values are expressed in permil (‰) rather than percent because of the small differences (Clark and Fritz, 1997).

$$\delta^{18}O_{sample} = \frac{m(^{18}O/^{16}O)_{sample} - m(^{18}O/^{16}O)_{standard}}{m(^{18}O/^{16}O)_{standard}} \quad (\text{Eq. 1})$$

$$\delta^{18}O_{sample} = \left(\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1 \right) * 1000\text{‰ VSMOW} \quad (\text{Eq. 2})$$

Craig (1961) determined that there is a linear relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in rain water on a global scale. This linear relationship is now referred to as the “global meteoric water line”. A prominent feature of global isotopic patterns in rainfall is that cold regions tend to receive more isotopically depleted precipitation than warm regions (Craig, 1961). This has been characterized as a Rayleigh distillation process, which describes the progressive separation of heavy isotopes from light isotopes over time (Clark and Fritz, 1997; Gat, 1996). The driving force behind Rayleigh distillation is fractionation. Fractionation of isotopes takes place during thermodynamic reactions that result in a disproportionate concentration of one isotope relative to the other (Clark and Fritz, 1997). The difference occurs because differing isotopes lead to differences in reaction rates (Clark and Fritz, 1997). The fractionation factor is expressed as α , and is defined below in Equations 3-5:

$$\alpha = \frac{R_{\text{reactant}}}{R_{\text{product}}} \quad (\text{Eq. 3})$$

$$\alpha^{18}O_{\text{water-vapor}} = \frac{(^{18}O/^{16}O)_{\text{water}}}{(^{18}O/^{16}O)_{\text{vapor}}} \quad (\text{Eq.4})$$

$$\alpha^2H_{\text{water-vapor}} = \frac{(^2H/^1H)_{\text{water}}}{(^2H/^1H)_{\text{vapor}}} \quad (\text{Eq.5})$$

Rayleigh distillation is described below in Equation 6 where R_0 is the initial isotopic ratio of the water and R is the ratio after a fraction of the original water (f) remains.

$$R = R_o f^{(\alpha-1)} \quad (\text{Eq. 6})$$

As the water vapor in an air mass moves from its source, a marine coastal region, into a continental interior, the air mass begins to rise and cool. As the air mass cools, relative humidity increases and precipitation occurs (Clark and Fritz, 1997). Heavy isotopes are preferentially precipitated out earlier than lighter isotopes, because of higher bonding energies. This is a process known as “rainout”. Therefore, rainout is the transition to depleted, colder precipitation (Clark and Fritz, 1997).

Because precipitation often infiltrates into the unsaturated zone, depending on location, the isotopic results reflected in the global meteoric water line often reflect the initial isotopic composition of the pore water (Clark and Fritz, 1997). Changes to the isotopic compositions of water in the unsaturated zone can take place in response to evaporation, the mixing of pore water with other water sources, and mineral interactions (Clark and Fritz, 1997). Evaporation of pore water from the unsaturated zone is also determined by Raleigh distillation. If significant amounts of soil water are evaporated, the isotopic composition of residual pore water may be deflected from the meteoric water line (Rozanski and Chmura, 2008; Clark and Fritz, 1997). An illustration of typical $\delta^{18}\text{O}$ and $\delta^2\text{H}$ relationships is seen in Figure 1.1. The Global Meteoric Water Line, as described by Craig (1961) has a slope of 8. Evaporation from surface water has a slope near 5. Slopes from sediments are lower than surface water due to kinetic effects.

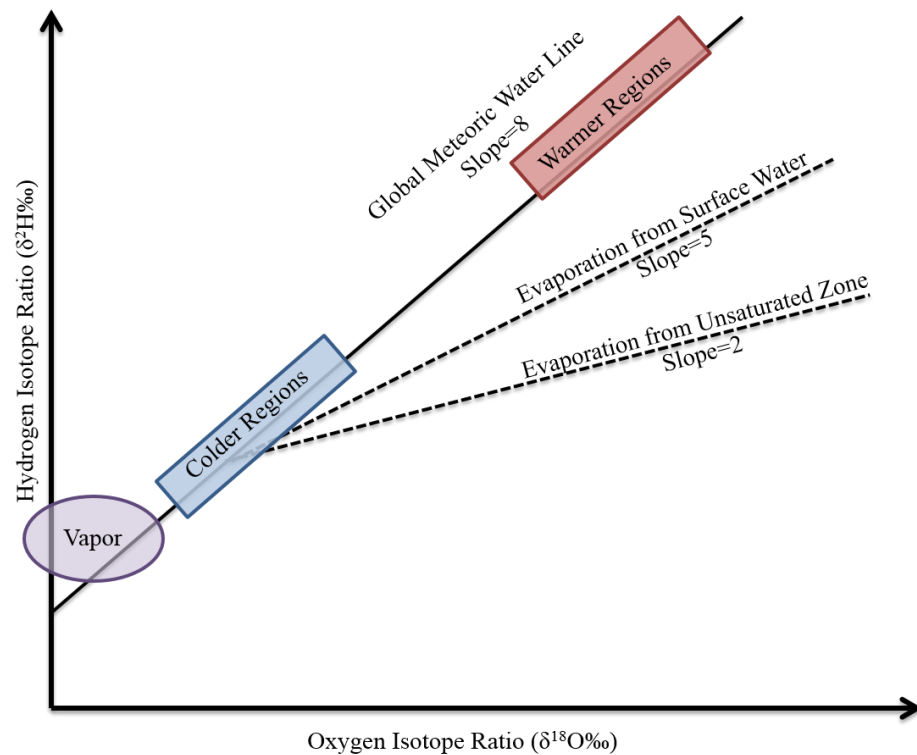


Figure 1.1: Typical $\delta^{18}\text{O}$ and $\delta^2\text{H}$ relationships and resulting slopes.

1.3 Overview of Unsaturated Zone Stable Isotope Research

Barnes and Allison (1983) were among the first to devise mathematical equations to interpret pore water stable isotope data quantitatively, developing a method to estimate a soil water evaporation rate from the enrichment of pore water isotope values.

Subsequently, stable isotopes collected from the unsaturated zone have found a broad array of applications, including the assessment of groundwater mixing, groundwater storage, preferential flowpaths, precipitation sources, evaporation, soil atmospheric CO_2 flux, transpiration, paleorecharge rates, and paleoclimates; they can be used to determine appropriate remediation techniques and have been used in ecological studies (Araguàs-Araguàs et al., 1995; Knowlton et al., 1989; Yang et al., 1996; Gvirtzman and Magaritz, 1986; Shurbaji et al., 1995; Lin and Wei, 2006; Newman et al., 1997; Wieczorek et al.,

2005; West et al., 2006; Izbicki et al., 2000; Izbicki et al., 2002; Scanlon, 2000; Gazis and Feng, 2004; Mathieu and Bariac, 1996; Nativ et al., 1995; Bauer et al., 2004; Cook et al., 1992; Edmunds and Tyler, 2002; Allison and Hughes, 1983; Darling and Bath, 1988; Hsieh et al., 1998; Hsieh et al., 1998 (2); Allison et al., 1983; Barnes and Allison, 1988; Kelln et al., 2007; Scrimgeour, 1995; Gillon and Yakir, 2000; Miller et al., 1999; Liu et al., 1995; Wassenaar, 1995; Rose et al., 2003; Yamanaka and Yonetani, 1999). In addition to $\delta^{18}\text{O}$ and $\delta^2\text{H}$, tritium ($\delta^3\text{H}$) has been used extensively to make inferences about pore water (Gvirtzman and Magaritz, 1986; Cook et al., 1994; Hendry, 1982; Lin and Wei, 2006; Yang et al., 1996). More recently, $\delta^{17}\text{O}$ is gaining popularity as a potential hydrology tracer (Landais et al., 2012; Luz and Barkan, 2010; Uemura et al., 2010).

Stable isotopes of water are not only useful for interpreting local physical, chemical, and biological patterns, but also those on a regional and global scale. Isotopic patterns associated with stable isotopes of water have been used across a variety of fields to predict environmental changes across space and time, also known as isoscapes (Bowen, 2010). Similarly to the global precipitation pattern described by Craig (1961), stable isotopes of water can be used to predict surface and groundwater isoscapes across the continental United States (Bowen, 2010). Isoscapes allow researchers to make interpretations across large areas of space and time, in areas which may not have observational data (Bowen, 2010). Soil moisture on a global scale is an important component in current weather forecast models (Robock et al., 2000). Field measurements, along with isoscapes, of soil moisture have been used to improve climate and meteorological modeling across the world (Robock et al., 2000; Kerr et al., 2010).

Stable isotopes can be used to estimate water budgets of unsaturated zones which can be very beneficial information in agricultural settings. Water budgets, which predict recharge rates and residence times, help estimate how much water may be available for plants, and how much water will recharge the aquifer (which may be used as an irrigation source; Fisher and Healy, 2008). Additionally, Fisher and Healy (2008) have identified the importance water budgets may play in estimating contamination risks to groundwater, which may be a result of pesticides and fertilizers used in agricultural settings.

Moisture dynamics in desert locations with thick unsaturated zones have been a major area of unsaturated zone stable isotope applications (Izbicki et al., 2000; Izbicki et al., 2002; Scanlon, 2000; Yang et al., 1996). Evaporation can remove pore water once it enters the unsaturated zone, and this can be inferred using $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water. Barnes and Allison (1983) also noted that isotopic compositions decrease quickly towards the surface due to diffusion of water vapor into the regions pore water was evaporated from (Allison and Hughes, 1983; Darling and Bath, 1988; Hsieh et al., 1998; Gazis and Feng, 2004). Barnes and Allison (1983) noted that near the surface, where significant amounts of evaporation occurs, a soil profile can be divided into two distinct water movement sections. In the top section water moves by vapor diffusion, and water in the bottom section moves according to the liquid phase (similar to water movement in the saturated zone). Barnes and Allison (1988) noted that the stable isotopes of water are extremely useful in determining where evaporation occurs in the unsaturated zone.

Nativ et al. (1995) determined $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of pore water from fractured chalk under desert conditions. The isotopic information gained, coupled with tritium, chloride, and bromide profiles, helped determine a conceptual model for drainage

through a fractured chalk (Nativ et al., 1995). Gazis and Feng (2004) noted that a comparison of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from precipitation and pore water indicates that pore water varies locally based on soil texture and drainage processes. They noted that deep pore water, or pore water residing deeper than 50 cm, is only replaced when there is a large surge of rainwater and snowmelt allowing for an average residence time of 4.5 months. Also, small surges of rainwater can become recharge when traveling along preferential flowpaths (Gazis and Feng, 2004). Mathieu and Bariac (1996) also noted fast recharge in areas where macropores and fissures are present, even in clayey soils.

Semiarid regions tend to be the most favorable location for recording long-term climatic oscillations due to deep unsaturated zones. Cook et al. (1992) compared isotopic profiles from the unsaturated zone to variations in lake levels in Cyprus and Senegal. They found the unsaturated zone to be a very reliable archive for recording paleorecharge rates and paleoclimate conditions. Accuracy declines when the unsaturated zone profile is subject to preferential flowpaths, land use changes, and groundwater level fluctuations (Cook et al., 1992). Advances in this field indicate the possibility of recording paleoclimates and paleorecharge ranging from 20-120,000 years (Edmunds and Tyler, 2002).

Chapter 2.0

Previous Research on Pore Water Extraction

2.1 Introduction

This chapter provides a review of pore water extraction methods for unsaturated zone stable isotope applications. Extraction of moisture from unsaturated zone sediments without isotopically altering the pore water can be difficult. Extracting pore water from the unsaturated zone requires overcoming surface tension between water and sediment, and numerous methods have been developed to do so. The following sections provide an overview of the most widely used pore water extraction methods, technicalities involved with each method, examples of studies that have used each method, and a critical discussion of previous multi-method inter-comparisons. Although the following methods are collectively referred to as extraction techniques, it is important to note that not all of the techniques require removal of pore water (e.g. direct equilibrations with CO_2/H_2 and zinc reduction only require isotopic equilibrium with pore water). Pore water extraction techniques can be divided into two broad categories: 1) quantitative, meaning they require a phase change and therefore complete recovery of the pore water, and 2) non-quantitative, which do not require a phase change and therefore do not require full moisture recovery.

2.2 Pore Water Extraction Techniques

2.2.1 Azeotropic Distillation

Azeotropic distillation was first applied to unsaturated zone stable isotope research by R.M. Brown and G.B. Allison in the 1970's and has remained a widely-used

method (Revesz and Woods, 1990). Azeotropic distillation involves using an organic solvent, which forms an azeotropic mixture with water at elevated temperatures but is water-immiscible at room temperature. An unsaturated soil sample is added to a flask and is placed atop a heating device. A volume of organic solvent, enough to cover the soil throughout the distillation process, is added to a flask, which is then connected to a receiving funnel and straight condenser. Examples of organic solvents that have been used include toluene and kerosene (Revesz and Woods, 1990). The soil/water/solvent mixture is heated to the temperature at which the solvent and water form an azeotropic mixture. The evaporation process continues until all the water is evaporated from the sediment. The azeotropic mixture then travels across the receiving funnel and is condensed out in the straight condenser into a sampling bottle. Once the azeotropic mixture is condensed into liquids, the toluene can be removed from the water. Revesz and Woods (1990) utilized paraffin wax to separate the toluene from the water. Wax and the toluene-water mixture are added to a closed bottle, and the bottle is heated until the wax melts. The bottle is turned upside down, allowing the wax to solidify at the top of the bottle, and the water can then be decanted off.

The evaporation that takes place during the distillation follows a Rayleigh distillation in which there is progressive separation of heavy and light isotopes (Clark and Fritz, 1997). When heating first begins, the isotopically lightest water is evaporated first from the sediment. Complete recovery is essential with this method, because there is preferential separation of water molecules based on their isotopic weight when evaporating and condensing. For instance, if only half of the pore water were evaporated

from the sediment, the isotopic ratio of the pore water would be extremely enriched, because not all of the isotopically heavy water is included.

Revesz and Woods (1990) used this technique to test the method under numerous conditions including different soil types, grain sizes, water contents, and two solvents (toluene and kerosene). Their results indicated that azeotropic distillation with toluene had an accuracy of $\pm 2\%$ $\delta^2\text{H}$ and $\pm 0.2\%$ $\delta^{18}\text{O}$, and that toluene had no isotopic discrimination effect. Revesz and Woods (1990) did, however, record an effect of soil type. For instance they concluded that this method is applicable to a wide range of natural sediment types, including sand, clay, shale, and till, but is problematic for soils that contain a mineral with water of crystallization (in this case, gypsum); such minerals can lose hydration water at elevated temperatures (Revesz and Woods, 1990). Isotopic discrimination associated with soils that contain a mineral with water of crystallization is magnified with lower moisture contents, because there is less water present; therefore the isotopic discrimination is larger. Like many other pore water extraction techniques, Revesz and Woods (1990) noted that accuracy declined with low water contents (3% and lower), because soil water strongly adsorbs to soil particles, making 100% yield difficult to achieve. Additional sources determined that for wet samples, 100 grams of sediment was needed and for dryer samples, 300 grams of sediment was needed. Cook et al. (1994) found that when using large sediment samples, distillation time needed to be increased from a few minutes up to 2-3 hours. Izbicki et al. (2000) found that the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ compositions from the same core line, determined through azeotropic distillation, agreed within $\pm 1.9\%$ and $\pm 0.2\%$, respectively.

Azeotropic distillation has been widely employed to determine $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of pore water. Azeotropic distillation has been used to study groundwater movement through fractured chalks, clays, glacial till, and desert environments; estimate evapotranspiration, recharge, and runoff; and assess plant water uptake (Nativ et al., 1995; Izbicki et al., 2000; Izbicki et al., 2002; Bauer et al., 2004; Leaney et al., 1992; Hendry, 1982; Cook et al., 1994; Thorburn et al., 1993). The technique has also been used to determine tritium concentrations (Cook et al., 1994; Hendry, 1982). Despite its wide range of applications, the possibility for introducing isotope fractionation requires extreme caution (Leaney et al., 1993). For example, Leaney et al. (1993) used azeotropic distillation with kerosene at a temperature of 185°C and noted a depletion of 4-6‰ $\delta^2\text{H}$ (Leaney et al., 1993; Araguàs-Araguàs et al., 1995).

2.2.2 *Vacuum Distillation*

Vacuum distillation requires that the moist sediments be frozen, placed in a glass flask, and then the headspace is evacuated under vacuum (Knowlton et al., 1989). The flask is connected to a distillation line, and a heating element is then applied to the sample in order to evaporate all the pore water. The moisture is then condensed into a collection flask using liquid nitrogen or other coolant (Knowlton et al., 1989). This process is repeated until all pore water has been condensed into the collection flask. For example, Araguàs-Araguàs et al. (1995) used extraction times from 0.5 to 7 hours and extraction temperatures from 60 to 160°C (all tests involved gravimetric moisture contents of 10% or higher.) Finally, the collection flask is flooded with gaseous nitrogen, to prevent contamination by atmospheric gases (Knowlton, 1989). Azeotropic distillation and vacuum distillation differ, because azeotropic distillation does not require the sample

to be frozen. However, both azeotropic and vacuum distillation require complete recovery of the original pore water in order to achieve accurate isotopic results.

Araguàs-Araguàs' et al. (1995) dried 5 kg of sandy sediments and spiked with water of known isotopic composition. Their results indicated that vacuum distillation yields acceptable results for sandy sediments with high moisture contents, as long as at least 98% of original pore water is recovered. They noted a standard deviation for replicates of 0.14‰ and 1.3‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively, which was only slightly outside analytical error of the mass spectrometer ($\pm 0.1\text{‰}$ and $\pm 1.0\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively; Araguàs-Araguàs et al., 1995). If 98% recovery was achieved, then the isotopic composition of the pore water was considered identical to the original pore water, because it was within experimental error. However, when the recovery was only 50%, the isotopic composition of the extracted water was depleted by as much as 7‰ $\delta^{18}\text{O}$ and 45‰ $\delta^2\text{H}$ (Araguàs-Araguàs et al., 1995). This outcome indicates the large effect fractionation can have on results. They did, however, conclude that there was no isotope effect resulting from the transport of the water vapor through the vacuum line or from the condensation in the cooling trap, and because of this, the extraction process should be considered a Rayleigh distillation process (Araguàs-Araguàs et al., 1995).

Araguàs-Araguàs et al. (1995) also tested their vacuum distillation technique on two clayey sediments ranging in clay content from 50-80% with water contents ranging from 34-44%. In this experiment, they noted isotopic fractionation that was attributed to the uptake of the spike water onto the dry clays as the wetting front percolates through the column (Araguàs-Araguàs et al., 1995). The yielded pore water deviated from the original isotopic composition by 5.2-9.6‰ $\delta^{18}\text{O}$ and 0.36-0.47‰ $\delta^2\text{H}$ (Araguàs-Araguàs

et al., 1995). They calculated a best fit line with a fractionation factor due to water uptake onto clay (ϵ_D/ϵ_{18}) to be 4.1. They also noted that vacuum extraction sequences involving high temperatures (350°C or higher) caused the isotope compositions to be skewed. The authors attributed the pattern to vaporization of weakly bound water attached to the sediment particles. The weakly bound water in sediments containing clay has a greater isotopic difference than in sandy soils not containing clay (Araguàs-Araguàs et al., 1995). Because of this, Araguàs-Araguàs et al. (1995) noted the importance of temperatures used during vacuum distillation, especially with soils containing large percentages of clay. They noted that if the mobile water is the water of interest, then the extraction temperatures should be kept as low as possible in order to extract as little of the weakly bound water as possible.

Shurbaji et al. (1995) used a technique very similar to Knowlton et al. (1989) in which they heated their sediments from 100-120°C for a period of 100-250 minutes depending on the initial moisture content and the soil texture (Shurbaji et al., 1995). Some studies have also used lower temperatures and longer distillation times (Lin and Wei, 2005). For instance, Lin and Wei (2005) heated their 120 gram sample for 5 hours at 70°C. A methodological difference from other distillation techniques described is they used a heat gun in order to vaporize any water that may not have reached the collection flask (Shurbaji et al., 1995). When no more condensation was observed, Shurbaji et al. (1995) heated the sample for an additional 20 minutes as a precautionary measure.

Newman et al. (1997) utilized the vacuum distillation technique following the methods of Shurbaji et al. (1995) to monitor water movement in the unsaturated zone. However, the isotopic results for the pore water were much lighter than the rainfall in the

region (a difference of 1‰ and 20‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively). They concluded that this difference in isotopic compositions was due to an error with the distillation process most likely due to incomplete extraction (Newman et al., 1997). However, when West et al. (2006) used vacuum distillation to extract water samples from plant matter (stems and leaves), they achieved results similar to Araguàs-Araguàs et al. (1995) even without complete recovery of the original water. They then concluded that complete recovery was not necessary to achieve unfractionated results, although percentages were not included to validate this claim (West et al., 2006).

Some researchers have found that the vacuum distillation technique leads to isotope fractionation, and others have found that azeotropic distillation leads to fractionation (Knowlton et al., 1989; Allison and Hughes, 1983; Leaney et al., 1993; Walker et al., 1994; Ingraham and Shadel, 1992; Newman et al. 1997; Yang et al., 1996; West et al., 2006). Knowlton et al. (1989) initially attempted to use azeotropic distillation as their pore water extraction technique. They utilized paraffin wax to adsorb any toluene that may be present in the pore water. In repeated experiments, they found that the paraffin was insufficient in removing the toluene from the pore water, and the toluene caused contamination for their mass spectrometer (Knowlton et al., 1989). Yang et al. (1996) used vacuum distillation to determine flow mechanisms taking place in the unsaturated zone near Yucca Mountain. They determined that precision for stable isotope compositions were $\pm 0.2\text{‰}$ and $\pm 1.0\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively (Yang et al., 1996). However, to the contrary, Allison and Hughes (1983) initially attempted to determine stable isotopes compositions through vacuum distillation at 200°C , but their results were determined to be unreliable and discarded for reasons not explained (Allison and Hughes,

1983). Azeotropic distillation with toluene was then used, with no fractionation recorded (Allison and Hughes, 1983).

2.2.3 Direct Equilibration with CO₂ and H₂

Direct equilibration with CO₂ does not require extraction of the pore water. It involves direct equilibration of CO₂ with the pore water in the sediments and therefore eliminates the problem associated with incomplete extraction (Hsieh et al., 1998). Direct equilibration with CO₂ involves a sample being placed in a glass vessel attached to a vacuum line. The sample is frozen using ethanol-dry ice. Once frozen, the vacuum line is opened and the air space is evacuated (Hsieh et al., 1998). The sample is then allowed to thaw, and any trapped gasses are released into the headspace of the vessel. If necessary, the freezing and thawing step is repeated until all gases are released from the sediment samples. CO₂ from a tank is then pumped into the vessel and allowed to equilibrate with the pore water. Equilibration was determined by sampling the CO₂ with a syringe every few hours and analyzing the sample with a mass spectrometer. In the case of Hsieh et al. (1998), the CO₂ was considered equilibrated with the soil water once the $\delta^{18}\text{O}$ of the CO₂ did not vary more than 0.5‰ over the course of several days. Hsieh et al. (1998) noted the lower the moisture contents and the finer the grain type, the slower the equilibration times. A syringe was used to remove a headspace CO₂ sample, which was then analyzed for $\delta^{18}\text{O}$ of CO₂ using a mass spectrometer (Hsieh et al., 1998). Once analyzed using the mass spectrometer, the initial $\delta^{18}\text{O}$ of the pore water is back calculated using the results of the mass spectrometer, mass balance equations, and fractionation factors. Variables needed in mass balance equations include weight of sample, density of sample, volume of

sample and equilibration flask, absolute temperature, water content, pressure of CO₂, gas constant, and ideal gas law (Hsieh et al., 1998).

Direct equilibration with H₂ can be used to analyze $\delta^2\text{H}$. It is very similar in method to direct equilibration with CO₂, with the difference that once the freezing and thawing has taken place, and all the gases are released from the sediments, H₂ is pumped into the vessel to equilibrate with the pore water. A small difference in procedure for direct equilibration with H₂ is the addition of a Pt catalyst referred to as “Hokko beads”, which enhance the exchange between H₂ and $\delta^2\text{H}$ (Horita and Kendall, 2004; Koehler et al., 2000). Additionally, because of the lower signal per unit volume compared to CO₂, the sample flask needed to be refilled with H₂ after each equilibration (Koehler et al., 2000).

Hsieh et al. (1998) tested the accuracy of direct equilibration with CO₂ using three varying sediment types including a clay loam, silt loam, and a coarse sandy loam. The sediments were dried and spiked with water of a known $\delta^{18}\text{O}$ value. The samples were processed using the previously described method. Hsieh et al. (1998) noted a reproducibility of 0.3-0.4‰ for direct equilibration with CO₂ and an increase in $\delta^{18}\text{O}$ with increasing moisture content. This was attributed to water partitioning itself within the sediments. For instance, water bonded to sediment grains had a different isotopic composition than water not bonded. Miller et al. (1999) concluded the direct equilibration technique has an accuracy of $\pm 0.2\text{‰}$ $\delta^{18}\text{O}$ and precision of $\pm 0.3\text{‰}$ $\delta^{18}\text{O}$. Hsieh et al. (1998 (2)) referenced their companion paper (Hsieh et al., 1998) in regard to the methods associated with the equilibration process for direct equilibration with CO₂ and reported a

reproducibility of $\pm 0.3\text{‰}$ $\delta^{18}\text{O}$. Additionally, Kelln et al. (2007) reported a precision of $\pm 0.2\text{‰}$ $\delta^{18}\text{O}$ and $\pm 2.0\text{‰}$ $\delta^2\text{H}$.

Koehler et al. (2000) tested direct equilibration with CO_2 and H_2 on three sediments that were oven dried and spiked with water of known isotopic compositions. The first two were clay-rich sediments, which were spiked to gravimetric moisture contents of 24 and 8.5%. The third sediment was 100% fine-grained silica sand saturated to a moisture content of 24%. Koehler et al. (2000) noted an increase of about 0.5‰ $\delta^{18}\text{O}$ for all three sediments. Koehler et al. (2000) concluded that isotopic values were influenced by contact time with atmosphere, grain size, distillation temperature (partially extracting bound water and not all free water), and yield of extraction. Koehler et al. (2000) recorded precision values of $\pm 1.0\text{‰}$ and $\pm 0.3\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively, leading them to conclude direct equilibration is a sufficiently accurate technique for determining the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of pore water from clay rich sediments.

Direct equilibration has also been used on plant water samples. Scrimgeour (1995) and Gillon and Yakir (2000) used direct equilibration to analyze water contained in plant samples. Scrimgeour (1995) noted that direct equilibration with CO_2 yielded an accuracy of 0.5‰ $\delta^{18}\text{O}$ with adequate water content, which is comparable to results from azeotropic distillation. Results from direct equilibration using H_2 were not nearly as accurate ($\pm 15\text{‰}$ $\delta^2\text{H}$), leading Scrimgeour (1995) to conclude that his method was not accurate enough to be used in natural abundance measurements, but can still be used in field tracer experiments.

2.2.4 Zinc Reduction

Direct equilibration and zinc reduction are both common methods for the analysis of free water, and pore water (Turner and Gailitis, 1988; Coleman et al., 1982; Vennemann and O'Neil, 1993). Zinc reduction for analysis of $\delta^2\text{H}$ is an alternative method adapted from a technique using a uranium reagent (Vennemann and O'Neil, 1993; Demény, 1995). In this technique, a reaction tube is connected to a vacuum line. In the case of free water, the water sample is pipetted onto the zinc, and the mixture is frozen with dry nitrogen (Turner and Gailitis, 1988). In the case of pore water, a sediment sample is removed from the bulk sample with the aid of a coring tube. The damp sediment and zinc shot are added to the reaction tube, and the tube is evacuated of any atmospheric gasses by freezing with the use of liquid nitrogen and pumping out any gasses. The tube is then heated to 450°C , and microdistillation between the water and zinc takes place (Turner and Gailitis, 1988; Coleman et al., 1982). During the microdistillation process, a reaction between zinc and the water takes place in which ZnO is produced and a measurable yield of H_2 (Vennemann and O'Neil, 1993). The reaction tube can then be directly attached to the mass spectrometer, where isotopic analysis takes place (Coleman et al., 1982). With free water, reaction times typically take place within 30-40 minutes, however, with damp sediments, the reaction times are longer. The reaction times also increase with finer grain sizes and lower moisture contents (Turner and Gailitis, 1988). For instance, Turner and Gailitis (1988) noted that when using 150 mg of a fine-grained porous medium with low moisture contents (less than 20%), the reaction time increased to 2.5 hours.

In their experimentation, Turner and Gailitis (1988) tested this technique with three porous media types, including fine-grained quartz sand, sandy clay, and kaolinite clay. Each sample was dried for 8 hours at 105°C before being spiked with water of known isotopic composition. Turner and Gailitis (1988) found that short reaction times paired with large water samples leads to isotopic fractionation. This is due to incomplete distillation, in that there is too much water for the reaction to take place in a short amount of time (Turner and Gailitis, 1988). Coleman et al. (1982) reported a reproducibility of 0.2-0.4‰ $\delta^2\text{H}$ when using quartz samples. Coleman et al. (1982) concluded that an important aspect of this technique is the choice of grain size of the zinc shot. They noted that a coarser shot lead to an incomplete reaction and a very fine shot could be difficult to manage (Coleman et al., 1982). Multiple sources have emphasized the importance of choice of zinc due to a hydrogen contaminant contained in certain zincs or the risk of dissolution of hydrogen in zinc (Demény, 1995; Kendall and Coplen, 1985; Coleman et al., 1982). Demény (1995) noted that hydrogen can be adsorbed by zinc at low temperatures, resulting in isotope fractionation. Because zinc reduction is used to determine the $\delta^2\text{H}$ of a sample, it is often paired with an additional pore water extraction method in order to determine $\delta^{18}\text{O}$ (Liu et al., 1995; Rose et al., 2003; Wassenaar, 1995; Yamanaka and Yonetani, 1999).

2.2.5 Centrifugation

The centrifugation procedure utilized by Edmunds and Bath (1976) involved a centrifuge tube, which allows dispersed water samples to drain through Whatman 41 filter papers (20µm pore space) and collect at the bottom of the centrifuge tube. Edmunds and Bath (1976) tested their equipment on a series of samples from the Upper and Lower

Cretaceous Chalk from England and the Bunter Sandstone. They noted that with centrifugation, only a fraction of the total pore water volume is extracted due to properties of sediments and the centrifuge. In the case of chalk, 5-15% of the total pore water remained in the sediment post centrifugation. Davies and Davies (1963) noted similar conclusions in their experiments involving loams and silty loams with moisture contents ranging from 30-47%. After 120 minutes of centrifugation at speeds of 4,000 and 3,000 rpm, the volume of pore water extracted begins to level off indicating a maximum centrifugation time (Davies and Davies, 1963). Centrifugation has been utilized as a technique in recharge studies, profiling unsaturated zones in water stressed areas and chalks; and studying movement of pollutants (Wood and Petraitis, 1984; Wellings and Bell, 1980; Geake and Foster, 1989; Nimmo et al., 1994; Whelan and Barrow, 1980; Edmunds and Bath, 1976; Kinniburgh and Miles, 1983).

Pore water displacement with centrifugation can be greatly increased with the use of an immiscible displacement fluid (Batley and Giles, 1979). This process involves using a liquid whose density is higher than that of water. This density of the immiscible liquid overcomes the capillary pressure of water and displaces pore water to the top of the centrifuge tube during centrifugation. The pore water can then be separated from the immiscible liquid by pipette or by being poured through filter paper. Mubarak and Olsen's (1975) experiment involved adding 10 g of a moist soil (clay soil or fine sandy loam with 25% moisture content) to a 50-ml centrifuge tube. 10 ml of immiscible liquid, in their case carbon tetrachloride, was then added atop the soil. The centrifuge tube was shaken for one minute to encourage mixing and then centrifuged for varying time periods at 48,300 g. Mubarak and Olsen (1976) noted that half of the total pore water was

displaced after 2 hours of centrifugation, and as Davies and Davies (1963) noted, 2 hours in the centrifuge yielded as much pore water as 3 hours. Mubarak and Olsen (1976) also found that it is easier to remove a greater percentage of pore water from sediments with greater moisture contents, than those with low moisture contents.

Whelan and Barrow (1980) tested three different immiscible fluids (carbon tetrachloride, 1, 1, 1-trichloroethane, and tetrachloroethylene) on 6 different sediment types ranging from clay to coarse sand. They varied centrifuge time, speed, and moisture content. Centrifuge speed had little effect on the volume of pore water displaced for sandy soils, but for clays, Whelan and Barrow (1980) noted an increasing relationship between yield and centrifuge speed. They noted 10 min of centrifugation was enough time for sandy soils, however, the yield associated with centrifuge time for clays increased for up to 2 hours. They also found that shaking sediments before centrifuging had no effect on the volume of pore water extracted. In the case of clay soils, Kinniburgh and Miles (1983) saw evidence of fractionation, however they concluded that additional research must be done to determine the dominant processes controlling concentrations.

Many of the immiscible displacement fluids utilized exhibit harmful environmental effects. The Montreal Protocol on Substances that Deplete the Ozone Layer was a collaborative treaty between nations across the world that established controls on chemicals found harmful to the stratosphere (Benedick, 1990). Prior to the Montreal Protocol in 1987, the immiscible displacement liquid with the aid of a centrifuge was an emerging technique to quickly and easily extract pore water for chemical analysis. The Montreal Protocol banned this technique, because research indicated the immiscible displacement liquids being used contained chlorofluorocarbons,

which contributed to the deterioration of the ozone layer. Therefore, since the mid 1980's this technique has largely been unused.

However, in recent years, Jin and Edmunds (2010) proposed a replacement immiscible displacement fluid by the name of HFE-7100. This differs from the immiscible displacement liquids of the past, because this particular liquid produces no harmful environmental effects (Jin and Edmunds, 2010). Therefore, this technique and subsequent areas of research have been reopened. Jin and Edmunds (2010) compared major ion results (no isotopes) using the new immiscible displacement fluid (HFE-7100) to one used in past research by the trade name of Arklone. They found strong similarities between water extracted by the different immiscible displacement fluids, with R^2 values greater than 0.90. They then concluded that HFE-7100 can be used as a replacement for Arklone for major ion studies (Jin and Edmunds, 2010).

2.2.6 Radial Diffusion and Diffusive Exchange

Radial diffusion cells consist of a cylindrical tube packed with a porous medium. The cylindrical tube is encased within an impermeable casing, which is sealed along the top and the bottom of the casing (van der Kamp et al., 1996). The impermeable casing prevents any swelling of the sample and water loss through evaporation. A cylindrical hole is drilled into the porous medium to create a reservoir. Deionized water containing specific tracers (isotopes or solutes) is added to the reservoir, and any changes in composition are recorded. The equilibration of the tracer compositions takes place by molecular diffusion (van der Kamp et al., 1996). Novakowski and van der Kamp (1996) noted that equilibration times are much longer for small porosities than large porosities. Radial diffusion requires the precise measurements of several physical and isotopic

parameters including porosity, moisture content, cell geometry, and initial $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions. These parameters are then used in a series of mass balance equations.

Mass balances are used to determine the original chemistry and effective porosity of the pore water (van der Kamp et al., 1996). Van der Kamp et al. (1996) tested this technique on clay-rich tills from Saskatchewan. In order to test the accuracy of the radial diffusion cell, they collected groundwater samples from three nearby piezometers and used a standard zinc reduction technique to determine $\delta^2\text{H}$ for the pore water. The results from the piezometer were then compared to those generated from the radial diffusion method. They noted that the $\delta^2\text{H}$ values determined by radial diffusion agreed closely to those collected from the piezometers, with reproducibility greater than 2‰ (van der Kamp et al., 1996).

Radial diffusion has been used to determine not only the isotopic composition, chemical makeup, and effective porosities of groundwater but also the diffusion coefficients and porosities of clays, consolidated argillaceous rocks, and other geologic medium (Savoye et al., 2006; Remenda et al., 1996; van der Kamp et al., 1996; Novakowski and van der Kamp, 1996; Rübel et al., 2002). Rübel et al. (2002) noted that the equilibration time between the porous medium and the water containing the isotopic tracers (which they refer to as test water) is about 2.5 days for clay material. In addition to radial diffusion, Rübel et al. (2002) used the vacuum distillation method to determine the isotopic composition of pore water. They noted that the isotope values yielded through radial diffusion were 9‰ $\delta^2\text{H}$ and 2‰ $\delta^{18}\text{O}$ greater than the results from the vacuum distillation method. Because the vacuum distillation results all plotted to the left of the meteoric water line, they determined the discrepancy to be a result of incomplete

extraction during the distillation process (Rübel et al., 2002). They found that the most accurate isotopic values resulted when the test water were close in isotopic composition to the pore water (Rübel et al., 2002).

Savoye et al. (2006) used the diffusive exchange method on the claystone of Tournemire. Radial diffusion and diffusive exchange are very similar methods, with the exception that radial diffusion requires diffusion in the liquid stage and diffusive exchange requires diffusion in the vapor stage. In their case, three mass balance equations were used: one relative to mass of tracer, one to the mass of the fluid, and a total mass that included rock and fluid. Savoye's et al. (2006) results indicated the diffusive exchange method yielded stable isotope values of pore water that were in close agreement with pore water taken from nearby fractures. This led them to the conclusion that diffusive exchange is a valid pore water extraction method. Savoye et al. (2006) also tested the vacuum distillation technique and found similar results to Rübel et al. (2002): the isotope values yielded through radial diffusion were 20‰ $\delta^2\text{H}$ and 3‰ $\delta^{18}\text{O}$ greater than the results from the vacuum distillation method, which they also attributed to incomplete extraction in the distillation method (Savoye et al., 2006).

2.2.7 Sediment Squeezer

Sediment squeezers allow for pore water to be extracted with little or no contact with the atmosphere. They have been used to extract water from marine sediments, as well as unsaturated zone settings (Jahnke, 1988; Kalil and Goldhaber, 1973; Hoek and Franklin, 1968; Yang et al., 1988; Reeburgh, 1967; Siever, 1961; Moncur et al., 2013). Low-pressure sediment squeezers, like the ones used by Jahnke (1988) and Kalil and Goldhaber (1973), simply involve a subsurface core to be gently pressurized at a constant

temperature. Pore water is excluded through sampling ports at specific depths in the core. The low-pressure sediment squeezer is appropriate for use on ocean sediments and can be used aboard a ship (Jahnke, 1988; Kalil and Goldhaber, 1973).

Hoek and Franklin (1968) used a triaxial cell squeezer, which utilizes a steel cell body able to withstand internal pressures of ~ 70 MPa. Inside the steel cell is a rubber sleeve with seals on either end. The cavity space between the steel cell and rubber sleeve is filled with oil, which acts as the hydraulic liquid (Hoek and Franklin, 1968). The sediment sample is fed into the cell, tested, and removed without breaking the seal and exposing the sample to the atmosphere. The triaxial cell enables the user to take in situ geologic observations, cutting down on inaccuracies that may result from travel of the sample (Hoek and Franklin, 1968). However, Batley and Giles (1979) noted gas breakthrough is a possibility, resulting in evaporation, and thus fractionation of samples.

In addition to ocean sediments, sediment squeezing has been used in unsaturated zone studies. A Water-Resources Investigations Report from the U.S. Geological Survey used sediment squeezing to aid risk assessments at the proposed Yucca Mountain radioactive water storage site (Yang et al., 1988). The scope of their project focused on estimating the residence time, recharge amount and location, and chemical reactions taking place in the volcanic tuff (which makes up the unsaturated zone in the area), through the chemical analysis of the pore water. Yang et al. (1988) used a modified triaxial cell method (for example, using Teflon instead of rubber, and adjusting so samples can be taken from either end of the cell) to extract pore water from the volcanic tuff. Yang et al. (1988) noted the importance of using the smallest pressures (axial pressures less than 152 MPa) and durations required to achieve adequate yield, because

higher pressures may remove water that was adsorbed onto the tuff minerals (in their study they were only interested in free water). They noted the chemical composition of the pore water changed with increasing pressures. For example, sulfate and chloride concentrations increased with axial pressures greater than 140 MPa. Pore water was only extracted from samples with moisture contents greater than 13% (Yang et al., 1988).

Moncur et al. (2013) combined the use of a sediment squeezer with an immiscible displacement fluid. Their squeezer utilized a piston core-barrel method, which allows can be used on a range of sediment sizes from clay to sand. It also does not any drilling fluids, which may act to contaminate the pore water sample (Moncur et al., 2013). They found the technique was applicable to sediments sediment types ranging from silt to clay, and moisture contents as low as 6% (Moncur et al., 2013).

2.3 Pore Water Extraction Method Comparison

Contradictory results exist in the literature for respective methods; meaning some find a certain technique yields accurate and precise results, while others do not (Walker et al., 1994; Araguàs-Araguàs et al., 1994; Altinier et al., 2007; Adams et al., 1980; Ingraham and Shadel, 1992; Revesz and Woods, 1990; Knowlton et al., 1989; Allison and Hughes, 1982; Leaney et al., 1993; Newman et al. 1997; Yang et al., 1996; West et al., 2006; Turner and Gialitis, 1988). Each of the following sections summaries a study involving direct comparison between different pore water extraction techniques.

2.3.1 Interlaboratory Comparison: Azeotropic Distillation, Vacuum Distillation, Zinc Reduction, and Centrifugation

Walker et al. (1994) noted that it is uncommon for more than one laboratory to utilize the same methods for a given pore water extraction technique. Therefore, they

bring to light the importance of comparing results across laboratories for a given technique. In their research, Walker et al. (1994) sent four sediment types (sand, gypseous sand, clay at high moisture content, and clay at low moisture content), which were spiked with water of a known isotopic composition, to fourteen different laboratories. A standard pore water was then extracted according to the technique of the laboratory. The different techniques included azeotropic distillation, vacuum distillation, zinc reduction, and centrifugation.

Isotopic results varied between laboratories up to 30‰ $\delta^2\text{H}$ and 3.4‰ $\delta^{18}\text{O}$. Walker et al. (1994) noted that for distillation methods, the variation was greater for clays than sands, and also increased as the moisture content of the sediment decreased. They attributed this isotopic variation to incomplete extraction of pore water. The laboratory that utilized centrifugation used Arklone as the immiscible displacement fluid. They only achieved accurate results for the gypseous sand, which had the highest moisture content. Walker et al. (1994) also stated that inaccuracies may have resulted from the spiking of sediments. In this case, when vacuum drying sediments, not all of the original pore water was removed, therefore water extracted for isotopic analysis was a mixture of original pore water and standard water. This paper identifies the necessity of standard protocols across laboratories (Walker et al., 1994).

2.3.2 Comparison of Column-Displacement and Centrifugation

Adams et al. (1980) compared the results of three different pore water extraction methods; column-displacement, simple centrifugation, and centrifugation with the aid of an immiscible displacement fluid. Their technique involved four soils types ranging in grain size from clay to loamy sand. These sediments were fertilized with dry salts of

known amounts, wet to field capacity, and allowed to equilibrate for seven days. In the case of the column-displacement samples, the moist soil was added to a glass column, and compacted using a rubber-stopper. Adams et al. (1980) noted that a great deal of experience is required to achieve the correct degree of compaction. The saturated solution, CaSO_4 with 4% KCNS was added to the top of the glass column and allowed to equilibrate throughout the column. Leachates from various increments within the column were collected to be tested. Total time required to collect enough pore water ranges from three to eight hours.

In the simple centrifugation case, Whatman no. 42 filter paper (2.5 μm particle retention) were placed in the centrifuge tubes. The moist soil was then packed atop, and the tubes were centrifuged for two hours at 1,070 g. Centrifugation with the aid of an immiscible displacement fluid utilized CCl_4 . Moist soil was packed into centrifuge tubes, which were then centrifuged for one hour at 22,000 g. The two cases were adapted from previous studies, which is the reason for the different centrifugation times and speeds.

Results indicated that column-displacement yielded more pore water per gram of soil than the centrifugation methods for all sediment types except loamy sand, which the authors hypothesized could not be packed tight enough to prevent early breakthrough of the solution. Both centrifugation methods yielded enough pore water for the loamy sand, but not for the finer grained sediments. Adams et al. (1980) noted that all three methods recovered pore water within experimental error, although this number was not reported. The difference in preference for the three methods, therefore, is not based on accuracy of results, but rather on sediment type, skill level, and time available. Centrifugation methods do not require any degree of special skill, whereas column-displacement does

require a degree of skill. Centrifugation methods work especially well for coarse grained sediments, whereas column-displacement works for all sediment types with the exception of loamy sand (Adams et al., 1980).

2.3.3 Comparison of Vacuum Distillation, Radial Diffusion and Diffusive Exchange

Altinier et al. (2007) tested four different pore water extraction techniques (two based on vacuum distillation and two based on equilibration) on clay-rich sediment. The first vacuum distillation technique involved a sediment sample being heated at 50°C under pressure for 20 hours. The second vacuum distillation technique was developed to prevent water loss by evaporation. The sediment sample was placed in an airtight compartment, which was connected to the extraction tube. Pore water was extracted by vaporization at two temperatures, 105°C and 150°C, under pressure for 20 hours. The equilibration techniques involved one by diffusion in the liquid phase (radial diffusion) and one in the vapor stage (diffusive exchange).

In terms of determination of moisture content, vapor equilibration resulted in overestimations, whereas vacuum distillation at 105°C and 150°C and radial diffusion were in agreement with each other. For isotopes of water, vacuum distillation yielded results that were depleted of the heavy isotope. They conclude that this is due to incomplete extraction of pore water. Altinier et al. (2007) concluded that if one wished to determine both isotopes of pore water and moisture content, equilibration by radial diffusion would be the best technique to use.

2.3.4 Comparison of Azeotropic and Vacuum Distillation

Ingraham and Shadel's (1992) research compared the precision and accuracy of azeotropic distillation with toluene and simple vacuum distillation. Loam was used in

both experiments. The loam was oven dried overnight at a temperature of 105°C before being spiked with water of known isotopic composition to moisture contents of 8 and 4%. They concluded that fractionation in the vacuum distillation process was more than the fractionation resulting from the azeotropic process and also occurred over a larger range of temperatures. Ingraham and Shadel (1992) concluded that neither method was sufficiently accurate: their results indicated that the isotopic composition of the extracted water varies up to 1.4‰ $\delta^2\text{H}$ and 4.2‰ $\delta^{18}\text{O}$ for azeotropic distillation using toluene and 11‰ $\delta^2\text{H}$ and 1.8‰ $\delta^{18}\text{O}$ for vacuum distillation.

2.3.5 Comparison of Direct Equilibration with CO₂, Azeotropic Distillation, and Vacuum Distillation

Hsieh et al. (1998) tested the accuracy and precision of direct equilibration technique with CO₂ on three varying sediment types including a clay loam, silt loam, and a coarse sandy loam and a range of moisture contents (the results are seen in Section 2.2.3). Additionally, Hsieh et al. (1998) also sent prepared sample to other laboratories to be analyzed using azeotropic and vacuum distillation in order to compare the results of direct equilibration with two well-studied and widely used techniques. The results yielded systematic differences between the three methods, including an overall difference of 8.9‰ $\delta^{18}\text{O}$ for azeotropic distillation compared to direct equilibration results and an overall difference of 3.9‰ $\delta^{18}\text{O}$ for vacuum distillation compared to results from direct equilibration (Hsieh et al., 1998). No pattern associated with moisture content or sediment type was recorded (Hsieh et al., 1998). These results could indicate a problem with the distillation methods, the direct equilibration method, or all three methods.

2.3.6 Comparison of Direct Equilibration and Centrifugation

McConville et al. (1999) compared the method of direct equilibration with CO₂ to centrifugation. Sediment used included well-graded medium sand, which was spiked with water of a known $\delta^{18}\text{O}$ value to varying moisture contents ranging from 1-15%. In the case of direct equilibration, the soil samples were allowed to equilibrate with the CO₂ for a period of 4 hours, while being at 40°C (McConville et al., 1999). Results indicated excellent agreement between the two. Direct equilibration yielded an average $\delta^{18}\text{O}$ value that was enriched by 0.10‰ compared to the spike value, and centrifugation had an average $\delta^{18}\text{O}$ value that was enriched by 0.08‰ (McConville et al., 1999). They also noted, however, that temperature of equilibration can affect the results. They concluded a correction factor would be needed for moisture contents less than 10% (McConville et al., 1999).

2.3.7 Pore water Extraction Comparison Chart

The previous discussion illustrates that there are numerous pore water extraction methods that can be employed, depending on soil conditions, including texture, moisture content, and chemistry. Additionally, needs vary in terms of time allotted, experience, and funds. Because of this, there is no single pore water extraction method suitable for all conditions (Litaor, 1988). Table 2.1 can be used as a method comparison chart. This table highlights the representative references, strengths and weaknesses, as well as key characteristics for each method. It can be used as a quick reference in choosing a suitable pore water extraction method.

Table 2.1: Pore water extraction comparison chart.

<i>Method</i>	<i>Representative Reference Samples</i>	<i>Strengths</i>	<i>Weaknesses</i>	<i>Is Quantitative Recovery Necessary?</i>
Azeotropic Distillation	Revesz and Woods (1990) Ingraham and Shadel (1992) Walker et al. (1994) Izbicki et al. (2000) Bauer et al. (2004)	Extensively used; can be used on a wide variety of sediment types	Requires the use of toxic solvents; organic solvent can sometimes interfere with mass spectrometer; difficult to achieve complete recovery with low moisture contents; accuracy is a function of extraction temperature; cannot be used on waters containing gypsum.	Yes
Vacuum Distillation	Ingraham and Shadel (1992) Araguàs-Araguàs et al. (1995) Shurbaji et al. (1995) Newman et al. (1997) Knowlton (1989)	Does not require the use of toxic solvents; pore water can be easily measured to determine completeness	Can be contaminated by the presence of weakly bound pore water; difficult to achieve complete recovery with low moisture contents; requires longer distillation times than azeotropic distillation.	Yes
Direct Equilibration	Scrimgeour (1995) Hsieh et al. (1998) Koehler et al. (2000) McConville et al. (1999) Kelln et al. (2007)	Quicker than azeotropic and vacuum distillation; Eliminates extraction step to remove pore water from sediments; minimal handling; no toxic chemicals used	Accuracy is a function of equilibration temperature; Decreased accuracy requiring corrections for moisture contents less than 10%	No

<i>Method</i>	<i>Representative Reference Samples</i>	<i>Strengths</i>	<i>Weaknesses</i>	<i>Is Quantitative Recovery Necessary?</i>
Zinc Reduction	Coleman et al. (1982) Turner and Galitis (1988) Vennemann and O'Neil (1993)	Enables rapid measurement; requires only 100-300 mg of sample depending on moisture content	Only used for $\delta^2\text{H}$	No
Centrifugation	Davies and Davies (1963) Mubarak and Olsen (1976) Edmunds and Bath (1976) Whelan and Barrow (1980) Kinniburgh and Miles (1983) Jin and Edmunds (2010)	User friendly; No complicated equipment required	Low yields for clays and fine grained sediments; Difficult to achieve adequate yield with low moisture contents	No
Radial Diffusion/Diffusive Exchange	van de Kamp et al. (1996) Koehler et al. (2000) Savoye et al. (2006) Altinier et al. (2007)	Overcomes limitations associated with determining isotopic composition of pore water from low permeability and clay rich sediments; limits effects due to swelling of clay material	Requires the precise measurements of several physical and isotopic parameters; requires use of mass balance equations; requires 40-60 days to complete one sample	No
Sediment Squeezing	Hoek and Franklin (1968) Kalil and Goldhaber (1973) Jahnke (1988) Yang et al. (1988)	In situ observations; can be conducted aboard ships; little or no contact with atmosphere	Accuracy is a function of axial pressure	No

2.4 Conclusion

This chapter has provided a review of the most widely used pore water extraction techniques. Isotopic information resulting from pore water extraction has numerous applications. Despite much research on each technique, inconsistencies regarding accuracy and precision persist in the literature. One commonality across all methods is the increased difficulty in achieving accurate results with low gravimetric moisture contents. This difficulty also increases with fine-grained sediment types such as clays, because of the small pore spaces and tendency for adsorption. Many studies have also reported apparent fractionation patterns, but have typically only been able to speculate about the mechanisms giving rise to the fractionation. This topic is revisited in Chapter 4.

Chapter 3.0

Feasibility of HFE-7100 as an Immiscible Displacement

Fluid: Yield and Isotopic Exchange Considerations

3.1 Introduction

This chapter described the systematic testing of a centrifuge immiscible displacement method for extraction of unsaturated zone pore water for stable isotope analyses. As described in Section 2.2.5, the engineered fluid with trade name HFE-7100 (or Novec) has been determined to be an acceptable immiscible displacement fluid for major ion studies (Jin and Edmunds, 2010). However, it remains to be seen whether HFE-7100 can be used in stable isotope studies. There are two major concerns for using HFE-7100 as an immiscible displacement fluid with the aid of a centrifuge. The first concern pertains to sufficient yield with low moisture contents (Whelan and Barrow, 1980; Turner and Gailitis, 1988; Revesz and Woods, 1989). The second concern is whether HFE-7100 could alter the isotopic concentration of pore water. This is a concern, because HFE-7100's chemical composition contains both oxygen and hydrogen (Jin and Edmunds, 2010; 3M, 2005).

Preliminary methods explore a washing technique used to remove clay coatings from sediment grains and a pipette precision test in which pore water is extracted from the centrifuge tube after centrifugation. Yield tests are conducted on three different sediment types, varying moisture content, grain size, and clay content. The sediments used include a laboratory-sorted commercially purchased sand, a well-sorted eolian sand,

and a poorly sorted glacial till. The sediment grain size ranges in diameter from 63 μm to 710 μm . The gravimetric moisture contents range from 1.5% to 20%. An isotopic exchange test was also conducted to determine if contact with HFE-7100 can skew isotopic results of displaced pore water.

3.2 Materials and Methods

3.2.1 Overview of Immiscible Displacement Centrifuge Approach

The immiscible displacement fluid used in this study is referred to by the trade name HFE-7100 (or Novec, produced by 3M). HFE-7100 is colorless and odorless and has been used as a replacement for ozone-depleting substances, because of the fact that HFE-7100 has 0 ODP (ozone depletion potential). The chemical composition of HFE-7100 is $\text{C}_4\text{F}_9\text{OCH}_3$ (methoxy-nonafluorobutane; 3M, 2005). The density of HFE-7100 is 1.5 g/ml, compared with 1.0 g/ml for deionized water. Its solubility in water is less than 12 ppm (3M, 2005). In order to test the reliability of HFE-7100 as an immiscible displacement fluid with the aid of a centrifuge to analyze isotopes of water, the following method was developed. Room-temperature oven-dried sediments are placed in a 50-ml polypropylene centrifuge tube, and then water of known isotopic ratios is added until the target gravimetric moisture content is achieved. This water will be referred to as “spike water”. In order to homogenize the sample, a metal spatula is used to manually agitate the sand and water mixture. The water-sediment mixture is considered homogenized when a visual inspection indicates the spike water has evenly wet the sediment grains (this assumption was verified using replicate tests; see Section 4.3.2). Next, the immiscible displacement fluid is added to the centrifuge tubes. An excess of HFE-7100 is added to each of the centrifuge tubes to ensure there is enough immiscible displacement fluid to

saturate the sediments and still leave a considerable head of HFE-7100 atop the sediments. The centrifuge tubes are then centrifuged at about 15,000 rpm for one hour (in the case of results seen in Figure 3.3, the sediments were centrifuged for three hours. This is the only case in which longer centrifugation times were used). The ratio of sediment weight to immiscible liquid weight in each centrifuge tube ranged from 1/2 to 1/5.

Due to the higher density than water, centrifugation forces the HFE-7100 into the soil pore spaces (as illustrated in Figure 3.1) and displaces the pore water to the top of the centrifuge tube. After centrifugation, the displaced pore water floats atop the immiscible displacement fluid as a bubble. The pore water is then extracted by pipette and transferred into a 2 ml (or 0.2 ml with conical insert) autosampler vial for analysis with a Cavity Ring-Down Spectroscopy (CRDS) analytical system. Analytical methods are described in more detail in Section 4.3.4. The isotopic results obtained by the CRD instrument are compared to the isotopic ratios of the spike water.

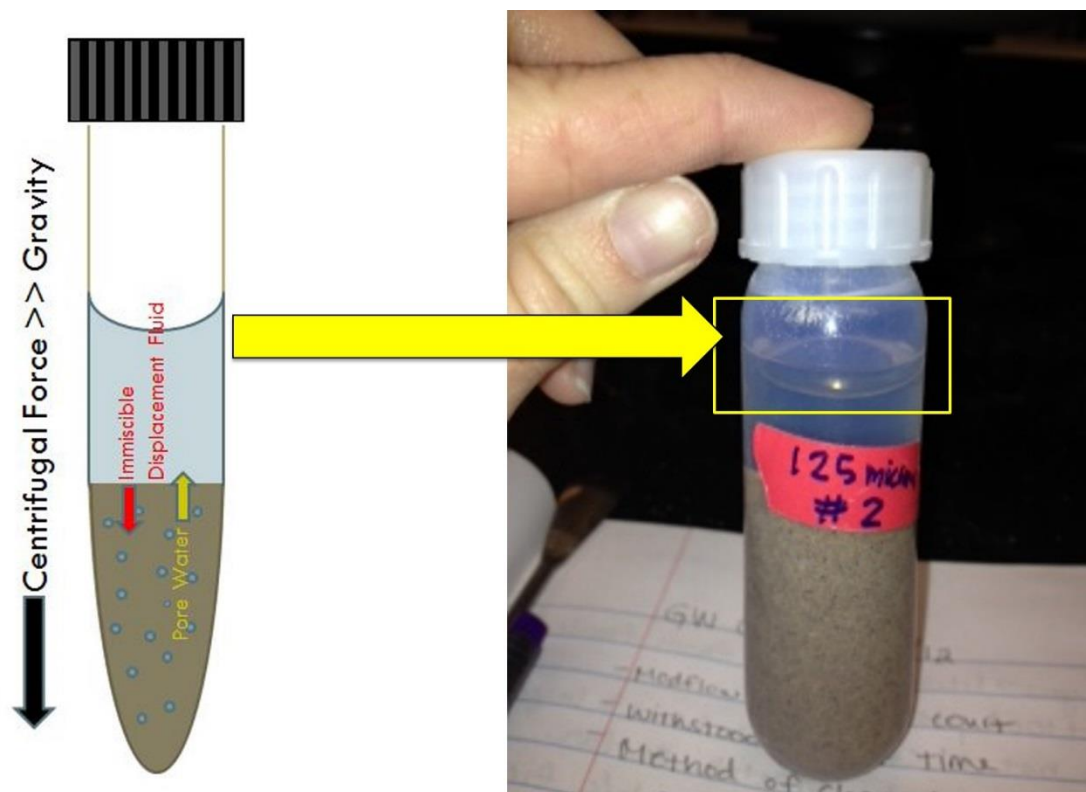


Figure 3.1: The spiked sediments sit in the bottom of the centrifuge tube. The HFE-7100 is then added to the tube. Once run in the centrifuge, centrifugal force pushed the HFE-7100 into the pore spaces of the sediment and the pore water is displaced to the top of the tube. The bubble of displaced pore water is outlined with the yellow box.

3.2.2 Preparation of Sediments and Standards

Three different sediment types were used in the following experiments: a washed sand purchased from a local hardware store referred to as “laboratory sand”, and two natural field samples referred to as Gudmundsen sediments and Lewis and Clark sediments. The laboratory sand ranges in grain size from very fine to gravel size. The laboratory sands have very low clay content coating the sand grains, because of the prewashing. The Gudmundsen field samples, referred to as GUD01 and GUD02, were retrieved from the Nebraska Sandhills. The Nebraska Sandhills are a dune field stabilized by grasses and other prairie vegetation (Loope and Swinehart, 2000; Ahlbrandt and Fryberger, 1980). The cores collected from the area consist of well-sorted eolian sands

(Loope and Swinehart, 2000; Ahlbrandt and Fryberger, 1980). Lewis and Clark field samples were collected from northeastern Nebraska; they consist of glacial till and are poorly sorted. Selected cores from each of the field locations, GUD01, GUD02, and Lewis and Clark, were dried overnight at 85°C and sieved into varying grain sizes in order to record grain-size distributions for the cores. The grain-type distributions from all three locations are shown in Tables 3.3 and 3.4.

Six laboratory working standards, or waters of known isotopic concentrations, were created by distillation: 1) SEA was created by full distillation of ocean water (collected near Melbourne Beach, FL) and serves as the isotopically heavy standard (-3.31‰ and -0.64‰ $\delta^{18}\text{O}$ and -15.50‰ and 2.0‰ $\delta^2\text{H}$), 2) LTW is Lincoln tap water and has moderate isotopic concentrations (-7.54‰ and -8.51‰ $\delta^{18}\text{O}$ and -56.20‰ and -65.8‰ $\delta^2\text{H}$), and 3) LOW is Lincoln tap water that has been partially distilled in order to create an isotopically depleted standard (-13.99‰ and -13.49‰ $\delta^{18}\text{O}$ and -92.96‰ and -91.2‰ $\delta^2\text{H}$). Part way through experimentation, standards were used up and new standards had to be created through distillation. This is why there are two replicates for each standard. All laboratory working standards were calibrated on the VSMOW-SLAP scale and then included in every analytical sequence throughout the project.

Prior to experimentation, all sediments were dried overnight at 85°C in order to evaporate all original pore water. Clays have been identified as a possible cause for fractionation. For this reason, some sediments were washed in order to remove adsorbed clays before being dried and spiked. The washing technique was developed in an effort to investigate the effects clays may have on isotopic concentrations of pore water. The washing technique involved rinsing sediments with deionized (DI) water, then slurring

with a Calgon detergent solution (the main active ingredient in Calgon is sodium hexametaphosphate, which acts to remove clays that may be coating the sand grains.) Sediments were repeatedly rinsed with DI water until the leachate was visibly clear and then rinsed three additional times to ensure no Calgon remained. The sands were then dried in an oven over-night at a temperature of 85°C. In order to test the impact of the wash procedure on leachable solutes in the sediment matrix (see Sections 4.2 and 4.4.4 for indication of importance), two washed sand samples of differing grain sizes (1.18 mm and 250 μm) were elutriated with deionized water and shaken for two hours. After the shaking, DI water was decanted and tested for electrical conductivity (using a portable electrochemical meter) and major cations (using ion chromatography). The results of the test are shown in Tables 3.5 and 3.6

3.2.3 Pipette Precision Test

In the methodology described in Section 3.2.1, the accuracy of the yield estimate depends upon the user's ability to remove all displaced water from the centrifuge tube with a pipette, without including any HFE-7100. Any extracted water not obtained by pipette or any HFE-7100 included in the pipette extraction will result in yield estimate error. In order to assess the range of yield estimate error caused by this process, a precision test was conducted involving repeated extraction of known water volumes within a centrifuge tube containing both water and HFE-7100. The experiment involved adding about 40 grams of HFE-7100 to a centrifuge tube, and then adding varying amounts of DI water. Weights of liquid retrieved using the pipette were recorded for each replicate and percent error was then calculated for each pipette (results are shown in Table 3.2).

3.2.5 Yield Tests

Preliminary research involved using the immiscible displacement technique with laboratory sands. Yield tests involved processing the laboratory sands using the immiscible displacement method described above, and recording what percentage of the original water added was yielded after centrifugation. The laboratory sands were separated into varying grain size diameters by sieving. The grain sizes included 710 μm , 500 μm , and 250 μm . After the sands were sieved into different grain sizes, spike water was added. Gravimetric moisture contents of the sands were varied to determine the effect on yield. With the exception of grain size and moisture content, all other variables were held constant: about 37 g of sediment and 34 g immiscible displacement fluid were used, and the samples were centrifuged for one hour at 15,000 rpm. The results of the yield test using laboratory sands are shown in Figure 3.2. Resulting percent yield curves throughout experimentation are both method and centrifuge specific.

After results were recorded for the laboratory sands, natural field samples were tested. Using the experimental methods described above, an unsieved section of GUD01 was dried, spiked at varying moisture contents, and centrifuged. The results of this test are shown in Figure 3.3. Figure 3.4 shows the results from two unsieved cores from Lewis and Clark. One core consists of coarse-grained sediments (354-710 μm), half of which were washed; the other core consists of fine-grained sediments (75-200 μm), half of which were washed. Washed and unwashed sediments from each profile were spiked to varying gravimetric moisture contents, ranging from 1.5-20.0%. Figure 3.5 shows the resulting yields from washed and unwashed GUD01 and GUD02 samples of varying grain sizes. Figure 3.6 shows the same for Lewis and Clark sediments.

3.2.6 Isotopic Exchange Tests

Because HFE-7100 contains both oxygen and hydrogen, and has a solubility of water in the solvent of 95 ppmw, there is the potential for isotopic exchange with displaced pore water (Jin and Edmunds, 2010; 3M, 2005). In order to test for isotopic effects of contact with HFE-7100 on extracted pore water, 25 centrifuge tubes were filled with a mixture of isotopic standard water and HFE-7100 (~3 g each). The centrifuge tubes were placed on a shaker, and vigorously shaken. After 2 hours, 10 centrifuge tubes were taken off the shaker and the water was sampled. (The time interval of 2 hours was selected, because that was determined to be the maximum amount of time pore water was exposed to HFE-7100 in all previous experiments.) 5 centrifuge tubes were then taken off the shaker after 6.5 hours, and the remaining ten centrifuge tubes after 24 hours.

3.3 Results

Table 3.1 outlines the number of yield tests that were conducted for each moisture content and grain size throughout experimentation.

Table 3.1: Number of yield tests: ranging moisture content and grain size.

Moisture Content	710 μm	500 μm	354 μm	250 μm	200 μm	150 μm	75 μm	63 μm
1.5	2	1	0	2	0	0	0	0
2	2	1	0	2	0	0	0	0
3	4	1	2	4	2	4	2	0
4	4	1	2	4	2	4	2	0
5	2	0	2	3	2	5	3	1
6	2	0	2	2	2	4	2	0
8	0	0	0	2	0	4	2	0
9	0	0	0	1	0	0	0	0
10	0	0	0	2	0	2	2	0
15	0	0	0	2	0	2	2	0
20	0	0	0	2	0	2	2	0

3.3.1 Pipette Precision Test

Table 3.2 shows the results of the pipette precision test. The percent error ranges from 0.00% to 8.47%, with the majority of errors less than 2%. Table 3.2 indicates that the smaller the amount of pore water available to retrieve, the higher the likelihood of extracting HFE-7100 with the pore water. However, in general this issue is easily resolved by removing the HFE-7100 bubble with a needle and syringe. For most replicates, gravimetric results suggest that more water was retrieved than added to the tube (replicates with negative numbers listed for the ΔDI column). In Precision Tests 7 and 8, the discrepancy could be due to the fact that HFE-7100 was present. In other cases, this may be an indication that there was a small volume of HFE-7100 present that was not apparent visually. Although unlikely, another possibility is that some of the negative numbers could be associated with errors in the precision balance measurements.

Table 3.2: Pipette precision test. “DI Amount” is the amount of water added to the centrifuge tube, and “DI Retrieved” is the amount of water pipetted from the centrifuge tube. “ Δ DI” indicates the DI amount minus DI retrieved. If HFE-7100 is detected with the pipetted water, it is indicated as so in the “HFE-7100 Present” column. Percent error was then calculated for each pipette precision test.

Precision Test	DI Amount (g)	DI Retrieved (g)	Δ DI (g)	HFE-7100 Present	Percent Error
1	2.1550	2.1134	0.0416	No	1.93
2	1.6927	1.7139	-0.0212	No	1.25
3	1.6046	1.6171	-0.0125	No	0.78
4	1.4200	1.4200	0.0000	No	0.00
5	0.8240	0.8280	-0.0040	No	0.49
6	0.6087	0.6337	-0.0250	No	4.11
7	0.4130	0.4480	-0.0350	Yes	8.47
8	0.3233	0.3241	-0.0008	Yes	0.25

3.3.2 Yield Tests

Table 3.3 shows the grain size distribution for cores GUD01 and GUD02. These cores have very similar grain size distributions, because they are from neighboring locations on a relatively homogeneous sand dune. The predominant sediment grain size for both cores was 150 μm (>50% by volume in both cases). Table 3.4 shows the grain size distribution for the Lewis and Clark core LC02. Because this core represents glacial till, there is a greater variation in the grain types, ranging from less than 63 μm to greater than 710 μm . The major sediment grain size for the Lewis and Clark core was 150-200 μm representing about half of the sediment grain type.

Table 3.3: GUD01 and GUD02 4'-8' core grain type distribution.

Grain Type	Percentage: GUD01	Percentage: GUD02
$\geq 250 \mu\text{m}$	5.35	8.73
150 μm	63.9	71.07
75 μm	29.51	19.52
$\leq 63 \mu\text{m}$	1.24	0.67

Table 3.4: Lewis and Clark 6'-8' core grain type distribution.

Grain Type	Percentage
$\geq 710 \mu\text{m}$	17
500 μm	10.56
354 μm	17.4
200 μm	23.7
150 μm	25.5
75 μm	0.5
$\leq 63 \mu\text{m}$	0.5

In Figure 3.2, three different grain sizes of laboratory sands (250, 500, and 710 μm) were spiked to different moisture contents. Figure 3.2 indicates that there is a positive relationship between moisture content and percent yield. Percent yield also tends to increase with increasing grain size. For example, the highest yield percentages were found for 710 μm with gravimetric moisture content of 4%. This yield approaches 90% of the total initial pore water. The smallest percent yield is associated with the 250 μm grain and 1.5% gravimetric moisture content. The percent yield associated with this case is near 20%.

Figure 3.3 shows the percent yield associated with differing moisture contents for the unsieved GUD01 core. As indicated in the methods, these samples were centrifuged for 3 hours, as opposed to the typical 1 hour. Despite the longer centrifugation time, no

pore water was yielded for the lowest moisture contents of 1.5 and 2%. Additionally, only a very small percentage of pore water, about 1.3%, was yielded for the highest moisture content of 4%.

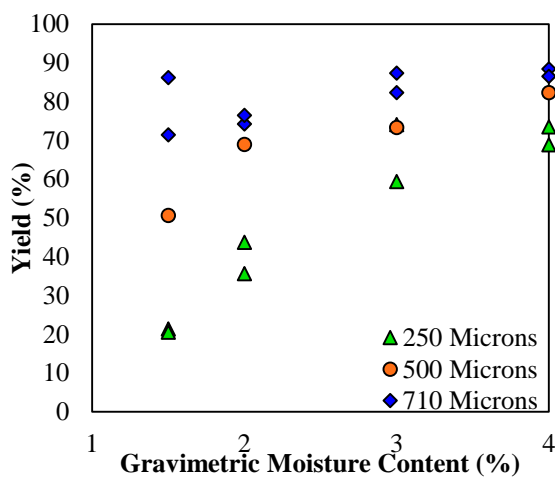


Figure 3.2: Yield test for laboratory sands with varying gravimetric moisture contents and grain sizes.

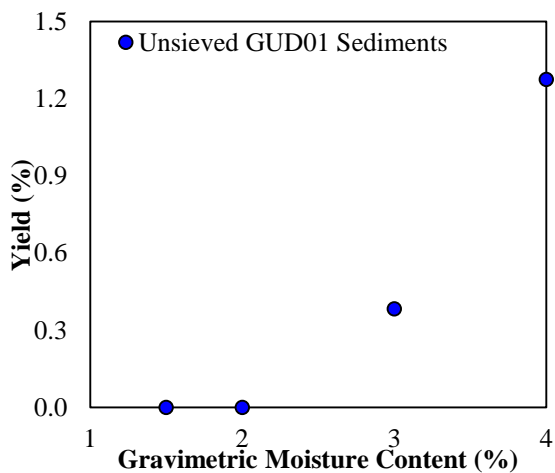


Figure 3.3: Yield test for unwashed, unsieved GUD01 sediments with varying gravimetric moisture contents.

Figure 3.4 shows the yield results for two Lewis and Clark cores from the same profile. These cores are from depths of 8'-10' and 26'-28'. The 8'-10' core is a predominantly fine-grained sample, and 26'-28' is a predominantly coarse-grained sample. Half of each of these cores were washed according to the previously described

washing technique to compare yield results from washed and unwashed sediments.

Figure 3.4 shows that, for the unsieved Lewis and Clark cores, the unwashed fine-grained sample (8'-10') had greater percent yield than the washed fine-grained sample. The washed coarse-grained core, however, had much greater percent yield than the unwashed core. The difference in yield between the washed and unwashed fine-grained samples is quite small in comparison to the difference between the washed and unwashed coarse-grained samples.

Figure 3.5 is a comparison of gravimetric moisture content and percent yield for GUD01 and GUD02 for grain sizes ranging from 75-250 μm . Figure 3.5 indicates that percent yield increases with moisture content and with grain size. Yield is also higher for the washed sediments than it is for the unwashed sediments.

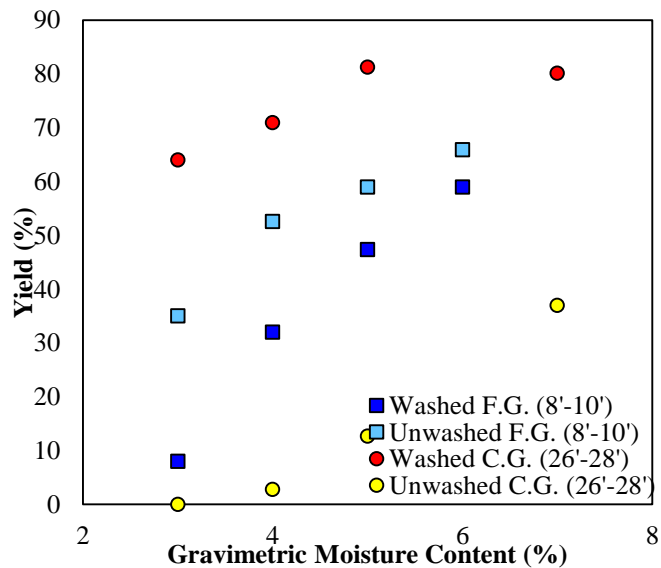


Figure 3.4: Yield test for two Lewis and Clark Cores, one fine-grained (8'-10') and one coarse-grained (26'-28') based on varying gravimetric moisture contents and washed versus unwashed.

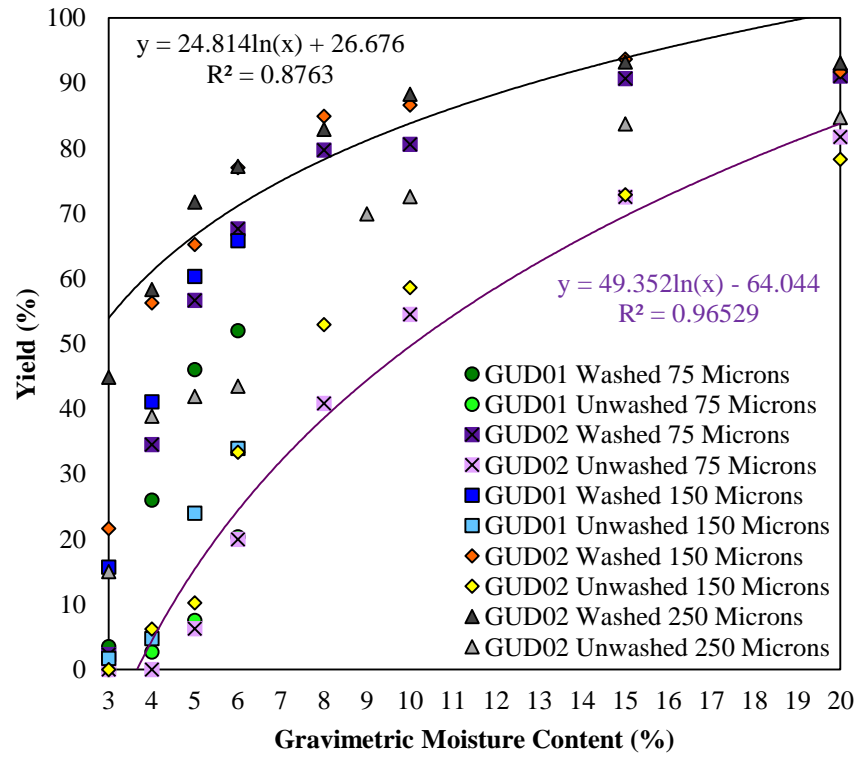


Figure 3.5: Yield test for washed/unwashed GUD samples with varying grain sizes.

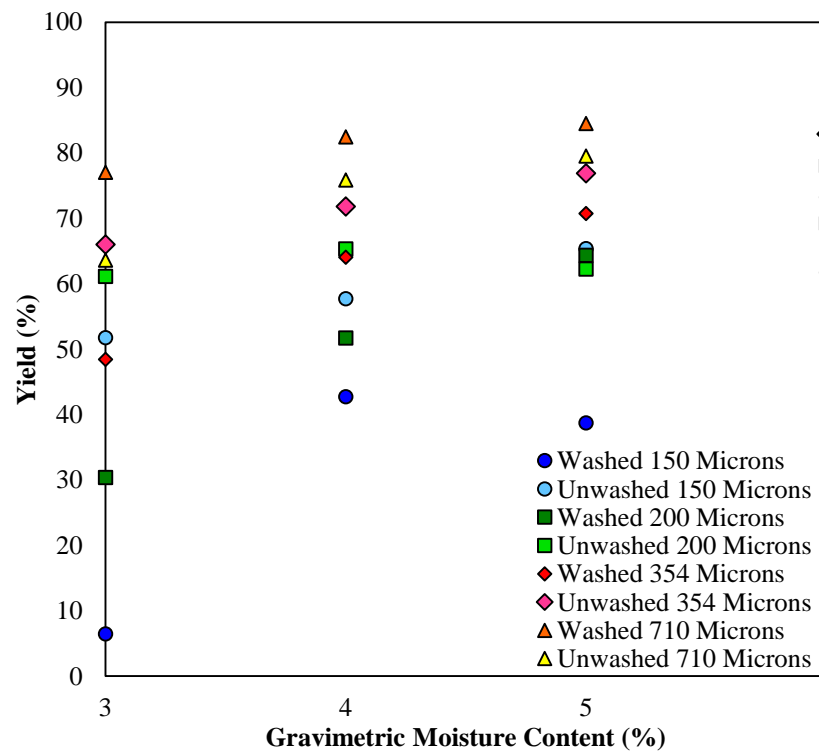


Figure 3.6: Yield test for washed/unwashed Lewis and Clark samples with varying grain size.

Figure 3.6 is a comparison of gravimetric moisture content and percent yield for Lewis and Clark cores for grain sizes ranging from 150-710 μm . With the exception of two discrepancies (washed 150 μm and unwashed 200 μm at 5% gravimetric moisture content), the percent yield for the Lewis and Clark sediments increases with moisture content. For the coarse grained sand (710 μm), the percent yield is higher for the washed sediments than the unwashed. However, for the finer grained sands (150, 200, 354 μm), the unwashed sediments have a higher percent yield than the washed yield. These results are comparable to those seen in Figure 3.4.

3.3.3 Isotopic Exchange Tests

Figure 3.7 shows the results of the isotopic exchange tests. The isotopic composition of the spike water is shown with experimental errors calculated from analytical repeats of standards and unknowns (2 standard deviations equal to $\pm 0.16 \delta^{18}\text{O}$ and $\pm 0.82 \delta^2\text{H}$). All samples with all exposure times are within experimental error, and there is no clear grouping with exposure time. Even after 24 hours, there is no apparent isotope effect caused by pore waters' contact with HFE-7100.

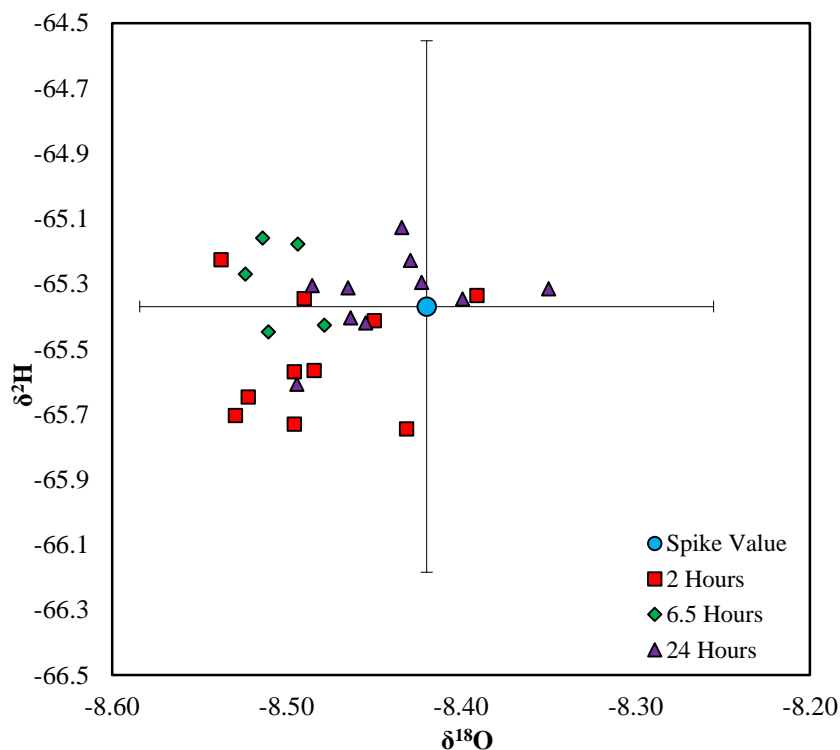


Figure 3.7: Mixing of spike water and HFE-7100 for varying times.

3.4 Discussion

The pipette precision test showed that the error in the yield estimates should be very minor in most cases. The average error from the 8 replicates was 2.16% (expressed as the difference between input and output divided by input). It is concluded that pipetting is a reasonable approach for both yield estimations and extract transfer for analysis. Therefore, the yield estimates discussed below are considered to be estimates of adequate precision for interpretation of relationships with variables, such as moisture content and grain size. Pipetting also has advantages over alternatives such as filter paper, because it can better avoid pore water exposure to the atmosphere and adsorption to filter paper (Mubarak and Olsen, 1976).

Percent yield was found to increase with gravimetric moisture content, and this is consistent with previous studies (Mubarak and Olsen, 1976; Whelan and Barrow, 1980). This pattern is presumably due to the fact that moisture content has a strong positive correlation to matric potential (a measure of the bond between water and sediment); at higher matric potentials, a higher percentage of water can be displaced by centrifugal force. Additionally, the yield increases with sediment grain size. This is most likely due to the larger pore spaces associated with the larger grain sizes.

The GUD samples (Fig 3.3) contain a small percentage of clay based on previous analyses from the area (determined in the laboratory; likely no greater than 4%). These samples required an extended centrifuge time in order to produce extract yields (3 hours versus 1 hour for all other samples). Even then, pore water was only yielded for the higher moisture contents. It is inferred from this result that the low yields are mostly likely associated with clay coatings adsorbing water more strongly than sand grains. Clays have the capacity to adsorb liquid, determined by an overall increase in volume (Baeshad, 1955). This is supported by the fact that washed GUD01 and GUD02 sediments all had higher yields than the corresponding unwashed sediments. The washing effect was also found for the laboratory sand.

In contrast to all other samples, the unwashed fine-grained Lewis and Clark sediments had greater yields than the corresponding washed sediments. It was assumed that the washing technique removes clays that act to adsorb water, and therefore higher yields on washed sediments were expected for all cases. However, this assumption cannot be confirmed, because clay contents of washed sediments were not measured. The reason for the unwashed fine-grained sample having higher yields than the washed fine-

grained sample is not clear. One hypothesis is that unmeasured differences in sediment chemistry may play a role. To explore this possibility further, water extracts from washed and unwashed sediment slurries were analyzed for major cations and conductivity. This is discussed more fully in Sections 4.2 and 4.4.4.

The results in Table 3.5 indicate the washed sands have an electrical conductivity nearly double that of the unwashed samples. Additionally, after the second elutriation, the electrical conductivities decreased somewhat, but remain greater than deionized water. As indicated in Table 3.6, in the unwashed sediment, the cations present are small amounts of Na^+ , Ca^{2+} , K^+ , and Mg^{2+} . In the washed sediment, all cations are near zero with the exception of sodium, which has increased.

Table 3.5: Washed lab sand electrical conductivity test.

Sand Type	First Electrical Conductivity Test ($\mu\text{S}/\text{cm}$)	Second Electrical Conductivity Test ($\mu\text{S}/\text{cm}$)
Washed 250 μm	71.5	24.7
Unwashed 250 μm	43.5	17.5
Washed 1.18 mm	39.1	15.6
Unwashed 1.18 mm	23.8	10.1

Table 3.6: Cations present in washed and unwashed sediments.

Sample	$\text{Na}^+(\text{ppm})$	$\text{Ca}^{2+}(\text{ppm})$	$\text{K}^+(\text{ppm})$	$\text{Mg}^{2+}(\text{ppm})$
Unwashed Sediment	2.5	1.4	1.7	0.2
Washed Sediment	8.9	0.6	0.4	0.0

One possible explanation for the increased electrical conductivity and observed change in cation distributions is that the washing process removed most cations but partially desorbed Na^+ ions that were adsorbed onto sand grains without removing them entirely.

If so, when the samples were elutriated, some of the remaining ions may have leached into solution. Sample contamination with Na^+ derived from the detergent used in the washing procedure is another possibility. In any case, the extract chemistry provides no strong insights about why Lewis and Clark fine sediments diverge from the overall pattern of higher yields after washing. Neither washed nor unwashed sediments had salinities of a sufficient concentration for osmotic potential to play a role. Further investigation is necessary in order to explain this counterexample.

There is no measurable discrimination between the fluid and displaced pore water, even after exposure times of 24 hours. Because of the rapid nature of centrifuge tests, it is not likely for pore water to be in contact with HFE-7100 for more than a few hours. HFE-7100 should be considered a sufficient immiscible displacement fluid for research including stable isotopes of water.

3.5 Conclusions

Results of this study suggest that immiscible liquid centrifugation using HFE-7100 is a suitable pore water extraction technique for unsaturated zone stable isotopic investigations under a broad range of environmental unsaturated zone conditions. In most conditions tested in this study, adequate yields (defined as any percent yield above 0.2 ml) were achieved after one hour of centrifugation using a standard benchtop centrifuge. Adequate yields were achieved with low moisture contents, as low as 1.5% in some cases, with coarse sandy sediments, suggesting that the method may be applicable in the context of arid zone research. The approach was also successful across a range of sediment grain sizes from 75 μm to 710 μm , although problems with insufficient yields may be expected with clay-rich sediments. With few exceptions, the greatest percent

yield resulted from high moisture contents ($> 6\%$), large grain sizes, and 0% clay contents. Critically, it can be concluded that exposure times between water of HFE-7100 of up to 24 hours do not result in measureable amounts of isotopic exchange (under laboratory conditions of $\sim 20^{\circ}\text{C}$ and 1 bar atmospheric pressure). Therefore, typical exposure times for sample processing need not be a concern. Overall, the technique is likely to be an approachable and low-cost alternative to distillation and other methods and is suitable to diverse experimental settings.

Chapter 4.0

Unsaturated Zone Sediment Factors Affecting Isotopic Ratios of Extracted Pore Water: Evidence from Immiscible Displacement Fluid Centrifuge Extraction and Cavity Ring-Down Spectroscopy

4.1 Introduction

This chapter describes experiments that were undertaken to characterize the effects of sediment characteristics on pore water $\delta^{18}\text{O}$ and $\delta^2\text{H}$. A large body of literature has treated stable isotopes of water as conservative tracers of evaporation, transpiration, and drainage in the unsaturated zone, implicitly assuming that no significant isotopic discrimination occurs within the sediment matrix other than fractionation caused by vaporization. However, pore water isotope fractionation associated with water adsorption onto mineral surfaces has been shown experimentally and theoretically in the case of pressurized saturated flow through dense clay. The question as to whether adsorption-related fractionation may be more common than is currently assumed under common unsaturated zone conditions (low-pressure, permeable, non-saline) remains unclear. This chapter aims to fill this gap using systematic experimentation in an effort to better understand influences and magnitudes of fractionation. The experiments explore several factors including grain size, moisture content, clay content, chemistry of pore water, and chemistry of sediments.

4.2 Background and Previous Research

Traditionally, soil water isotope studies have only considered fractionation due to phase changes (e.g. evaporation, condensation). Early soil water isotopic studies largely dismissed the possibility of fractionation due to adsorption (Stewart, 1972). However, there has been much experimental evidence to the contrary (Washburn and Smith, 1933; Coplen and Hanshaw, 1973; Hayden and Graf, 1986; Phillips and Bentley, 1987; Sacchi et al., 2001). Water molecules are attracted to the surfaces of clay particles because of differing electrical charges, and this attraction may lead to differences in energy states between adsorbed and free water (Sacchi et al., 2001; Stewart, 1972). Theoretically, this may cause isotopic fractionation, because desorption requires sufficient energy to break the bonds between the clay surfaces and the water molecules. Laboratory experiments have shown that when forcing water through a compressed clay layer, ionic solutes can be filtered out (Hanshaw and Coplen, 1973; Phillips and Bentley, 1987). Additionally, some have noted that along with the ion solutes being filtered out, as water adsorbs onto clay surfaces, there is the possibility for that water to fractionate (Coplen and Hanshaw, 1973; Hayden and Graf, 1986; Phillips and Bentley, 1987; Washburn and Smith, 1933). Coplen and Hanshaw (1973) found that by forcing water through a montmorillonite disk, fractionation occurred. They believe that adsorption is the major cause of fractionation, and that salt filtering is not a cause, because of the lack of fractionation observed during an experiment using NaCl concentrations up to 0.01 N (Coplen and Hanshaw, 1973). They therefore concluded that because of the fractionation observed after passing water through 100% montmorillonite clay, fractionation in clayey sediments should be assumed. This does not, however, answer the question as to whether only slightly clayey

sediments, silty sediments, and flow in non-pressured conditions can also cause fractionation.

In addition to the presence of clay, the effect of pore water and adsorbed ion chemistry has also been suggested as a cause of water isotopic fractionation. Phillips and Bentley (1986) concluded that ion filtration may cause water isotope fractionation under some conditions. Ion filtration occurs when some water molecules become bonded to ion surfaces, based on molecular weight. The molecules bonded are not included in water extracted and can lead to fractionation. Feder and Taube (1952) also suggested that fractionation of the oxygen isotope can occur due to ions present in pore water. Sofer and Gat (1972) and Stewart and Friedman (1975) found there to be a linear relationship between the fractionation of deuterium samples and the salt concentration. Sofer and Gat (1972) also noted fractionation in opposite directions of the spike value with solutions saturated with respect to potassium.

Molecular diffusion may also be a cause of isotopic fractionation in porous media (Phillips and Bentley, 1986). Molecular diffusion is a process in which the mass differences of water molecules of different ionic species diffuse through solutions at different rates (Phillips and Bentley, 1986). However, Coplen and Hanshaw (1973) noted that if molecular diffusion is the sole cause of isotopic fractionation, then the slope of the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ graph would be equal to 0.5, and there is little or no experimental evidence consistent with this finding.

An additional cause of isotopic fractionation could be due to the hydration sphere (Feder and Taube, 1952; Phillips and Bentley, 1987; Sofer and Gat, 1972; Stewart and Friedman, 1975). This takes place due to the high cation exchange capacity of clays

(Phillips and Bentley, 1987). The activity of the water passing through the clay layers will change activity. This change in activity then causes differences in transport rates of the isotopic species, leading to fractionation (Phillips and Bentley, 1987).

Several studies on pore water extraction techniques have indicated apparent fractionation between input and extracted water (discussed in Chapter 2). The purported mechanisms have varied widely but have often been poorly constrained by available data. Hsieh et al. (1998) suggested that observed differences between input and extracted water at low moisture contents were due to either adsorption onto mineral grains or isotopic differences between free water and “coordination spheres” around solute ions.

Koehler et al. (2000) attributed $\delta^{18}\text{O}$ enrichments in tests of direct equilibration with CO_2 on three different soil types (two clay rich sediments with moisture contents of 24% and 8.5% and a fine grained silica sand with a moisture content of 24%) to either incomplete equilibration or to a partitioning of water molecules between adsorbed and free water. However, the authors suggested that the latter could only explain the isotopic enrichment associated with the clay-rich sediments and not the silica-rich sands.

Ingraham and Shadel (1992) hypothesized that reasons for differences between azeotropic distillation and vacuum distillation results were because some introduced water became weakly bound onto the soil, and that the weakly bound water was only released from the soil when extraction temperatures exceeded 110°C. There was also greater isotopic difference in the case of the 4% moisture content than the 8% moisture content. They concluded that this was because in the case of the 8% moisture content, the weakly bound water made up a smaller percentage of the total water, leading to a lessened effect on the isotopic compositions.

4.3 Materials and Methods

4.3.1 Overview of Experimental Design

In order to test the hypothesis that minor clay contents can cause fractionation, a series of experiments were conducted in which clay contents were varied systematically in order to assess whether isotopic results indicate depletion with increased clay content. Gravimetric moisture contents were kept to 15% or lower (similar to Chapter 3) in order to focus on representative natural unsaturated zone conditions. Clay contents were restricted to 3% and lower in order to maintain sufficient yields using the methods developed in Chapter 3. Experimentation also included tests of varying pore water chemistry and adsorbed ion chemistry.

4.3.2 Preparation of Sediment and Water Matrices

Spike tests for this study used mixtures of sand and sodium montmorillonite clay powder. Sodium montmorillonite clay powder was obtained from a commercial scientific supplier. Sands were sieved into grain-size categories and washed according to the methods described in Chapter 3. Desired weights of sand and sodium montmorillonite were manually mixed inside a 3.8 L plastic Ziploc[®] bag until homogenized (~180 g sand on average). A subset of the sand/clay mixtures were treated with salt solutions in order to replace adsorbed sodium with other cations for the adsorbed cation tests. For these tests, dry sediment was added to three separate glass bottles, to which potassium bromide or magnesium chloride salts were added. 125 mL of deionized water (DI) was then added to each jar, along with enough salts in order to reach 3 Mol/L. A magnetic stirrer was added to each bottle, and solutions were stirred until the salts dissolved. Once dissolved, the bottles were put on a shaker and agitated for 24 hours. The resulting salt solutions

were decanted off, and an additional 125 mL of DI water was added and elutriated for 20 minutes. This process was repeated two additional times. The sediments were then oven dried at 90°C and dried for 24 hours and then manually remixed to ensure textural homogenization.

Water was added by pipette to dry sediment matrices to achieve the desired gravimetric moisture content. Each bag containing the sand/clay/water mixture was sealed and then manually agitated until the sample appeared uniformly moistened. In order to test whether this approach yielded suitable homogenization with respect to moisture content, three samples were taken from various locations in a sample bag after manual agitation. These samples were weighed, dried in the oven overnight at 95°C, and re-weighed to determine moisture content. The results of this test are seen in Table 4.1. All three samples indicate gravimetric moisture content of ~10%, which was well within in the range of the initial moisture content (maximum error 0.23%). As a result, this technique is concluded to be an adequate method of moisture homogenization.

Table 4.1: Bag homogenization technique.

Sample Number	Wet Weight (g)	Dry Weight (g)	Gravimetric Moisture Content (%)
1	14.9644	13.5957	10.07
2	12.9393	11.7399	10.23
3	11.7801	10.7005	10.09

Three different water sources were used for spike tests. Most tests used the laboratory standard LTW (See Section 3.2.2). LTW is a deionized water of moderate isotope composition. For some tests of pore water chemistry, either a MgCl standard (with Mg²⁺ of 1000 mg/L) or a KCl standard (with K⁺ of 1000 mg/L) was used instead.

4.3.3 Extraction Methods

Pore water extractions primarily used the immiscible displacement method described in section 3.2.1. In addition, this technique was compared to results from azeotropic distillation with toluene for some of the experiments. Ten replicates using 500 μm sand and gravimetric moisture contents of 10% were tested according to the method of Revesz and Woods (1990). The moist sediment samples were distilled using a standard distillation apparatus made of borosilicate glass. A plastic spatula was used to push any adsorbed water droplets from the distillation arm into the collection flask after distillation was complete. Paraffin wax was used to remove any remaining toluene from pore water extracts.

4.3.4 Isotopic Analysis

The stable oxygen and hydrogen ratios of water were measured using a Cavity Ring-Down Spectroscopy (CRDS) system manufactured by Picarro Inc. Picarro CRDS machine utilizes a laser, optical cavity with multiple mirrors and a photo-detector (Crosson, 2008). The autosampler utilizes a needle, which first cleans itself to eliminate memory effect. The needle then collects 2 μL of the water sample and injects the sample into an evaporator. The sample is vaporized and mixed with a dry N_2 carrier gas (this allows the transport of the sample with limited adsorption; Gupta et al., 2009). The sample is then injected into the optical cavity. The laser introduces light into the cavity through one mirror. The intensity of the light increases over time and is censored by another mirror within the cavity and a photodetector. After the laser is turned off, the light bounces within the cavity; the path length of the light can be tens of kilometers long (this is what gives a CRDS machine its sensitivity). Ring-down is determined by

measuring exponential loss of light censored within the mirrored cavity, which contains the gas sample (Crosson, 2008; Gupta et al., 2009). Decay time constant is defined as:

$$\tau = \frac{1}{c(L + A)} \quad (\text{Eq. 7})$$

Where τ is the light decay constant, c is light speed, L is loss in cavity, and A is adsorption loss due to gas species (Gupta et al., 2009).

Because pressure and temperature measurements must be precise, Picarro uses equipment, such as the high-linearity pressure transducer, to measure pressure in the cavity, and thermal insulating layers to maintain temperature in the cavity (Picarro, 2014). CRDS machines tend to have very low instrumental drift compared to other technologies such as non-dispersive infra-red spectroscopy and isotope ratio mass spectrometry (Crosson, 2008; Gupta et al., 2009). The estimated 2σ analytical uncertainty, calculated from repeats, for the CRDS machine used in the following experiments is $\pm 0.16\text{‰}$ $\delta^{18}\text{O}$ and $\pm 0.82\text{‰}$ $\delta^2\text{H}$. The Picarro CRDS is relatively quick and easy to use in comparison to traditional IR-MS; it also has the capacity to be used in the field, as well as the laboratory (Crosson et al., 2008; Tremoy et al., 2011; Gupta et al., 2009; Johnson et al., 2011).

4.4 Results and Discussion

4.4.1 Grain Size and Moisture Effects

Results of tests where more than one isotopic standard was used for spike water are expressed as permil deviation of extract water isotope value from spike water isotope value, denoted “ $\Delta\delta$ ”. The majority of results tend to fall along the regression line $\Delta\delta^2\text{H} = 4.69 \Delta\delta^{18}\text{O} + 0.12$ ($r^2 = 0.88$ for $n = 72$ with one outlier removed). Individual values

ranged from -0.83 to $+2.02$ $\Delta\delta^{18}\text{O}$ and -4.79 to $+4.26$ $\Delta\delta^2\text{H}$, illustrating that both positive and negative isotope discrimination between the input water and extracts. 73.6% of all extract values were significantly different from the input standard based on the estimated 2σ analytical uncertainty. Figure 4.1 shows experimental results categorized according to moisture contents and scaled according to deviation from the isotopic value of the standard used in the spike tests. Results generally suggest that gravimetric moisture content was not an influential factor affecting $\Delta\delta^2\text{H}$ or $\Delta\delta^{18}\text{O}$ values. Whereas the two most enriched samples had low moisture contents (3.0%), the results of the test with the lowest moisture contents (1.5% to 2.0%) cluster nearer to the input standard. Similarly, the most depleted results do not correspond to high moisture contents. Figure 4.2 shows the same extracts dataset categorized by grain size of the sediment matrix. Similar to moisture content, there is significant scatter among the relationships between grain size $\Delta\delta^2\text{H}$ or $\Delta\delta^{18}\text{O}$ values, with both positive and negative discriminations between the input water and extracts (Fig 4.2). However, the majority of the scatter is associated with 75 μm and 150 μm textural classes (Fig 4.3). In contrast, Figure 4.4 shows that little or no fractionation is associated with the three coarsest grain sizes (354-710 μm), in contrast to grain sizes 75-250 μm .

Figure 4.1 indicates that moisture content does not affect the amount or direction of fractionation: approximately equal scatter results in both directions for high and low gravimetric moisture contents. The results in Figures 4.3 and 4.4 indicate that the coarse grained sediments, with the larger pore spaces, allow the transfer of water much more readily. The fine grained sediments have much smaller pore spaces, therefore, when the samples are centrifuged, the bond between the water and the grains is much higher for the

fine grained sediments, which causes a preferential separation of the light and heavy isotopes. Sediment size could have an effect on fractionation direction: fine grained sediments are both enriched and depleted relative to the spike value, but coarse grained sediments are only enriched relative to the spike value (see Figures 4.8 and 4.9). Coarse grained sediments, on average, have smaller fractionation amounts: -0.07 to $+0.51$ $\Delta\delta^{18}\text{O}$ and $+0.24$ to $+1.88$ $\Delta\delta^2\text{H}$ for coarse grained sediments and -0.83 to $+2.02$ $\Delta\delta^{18}\text{O}$ and -4.79 to $+4.26$ $\Delta\delta^2\text{H}$ for fine grained sediments.

When soils are damper, movement of water is controlled by capillary processes. When soils have low gravimetric moisture contents, water movement is controlled by van der Waals absorptive processes, which results in a thin film of water forming around the sediment grain (Tuller and Or, 2005). The amount of water adsorbed onto sediment grains is directly correlated to the soil specific surface area (Tuller and Or, 2005). Results of Tuller and Or's (2005) experimentation indicated that the finer the sediment grains, the larger the soil specific surface area, thus leading to a greater percentage of total pore water retained by adsorption as thin films around sediment grains. Lebeau and Konrad (2010) noted that wetter sediments may have thicker films, but they also have water contained within pore spaces allowing liquid water movement. Dry sediments, on the other hand, allow liquid water movement only through the thin film surrounding sediment grains (Lebeau and Konrad, 2010). These results, coupled with greater fractionation associated with finer-grained sediments, indicates that the greater adsorptive forces associated with the finer-grained sediments is resulting in a preferential separation of heavy and light isotopes. Phillips and Bentley (1987) hypothesized hydration-sphere mechanisms controlled isotopic fractionation in certain cases. They concluded that the

thin film of adsorbed water surrounding the sediment grain consisted of water molecules of lighter molecular weight, and free water consisted of water molecules of heavier molecular weight (Phillips and Bentley, 1987). Thus centrifugation forces are not enough to overcome the adsorptive forces influenced by sediment specific surface area, which results in displaced pore water being depleted of water molecules of lighter molecular weight, leading to fractionation. This could explain the greater fractionation values associated with finer-grained sediments.

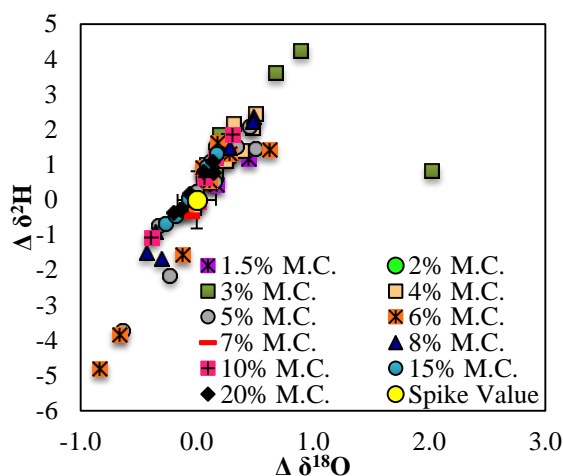
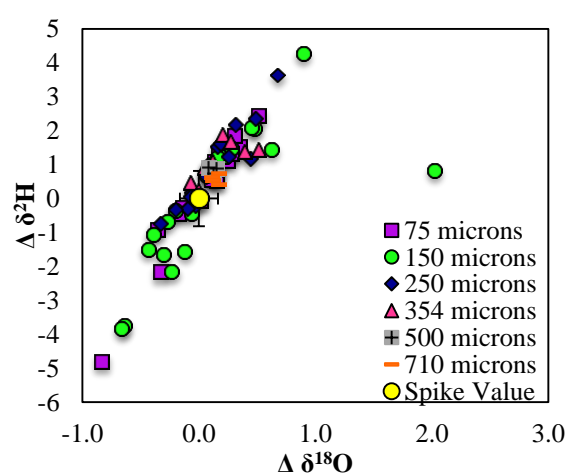
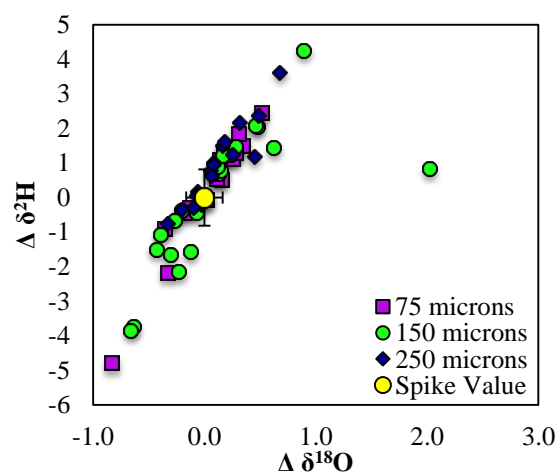
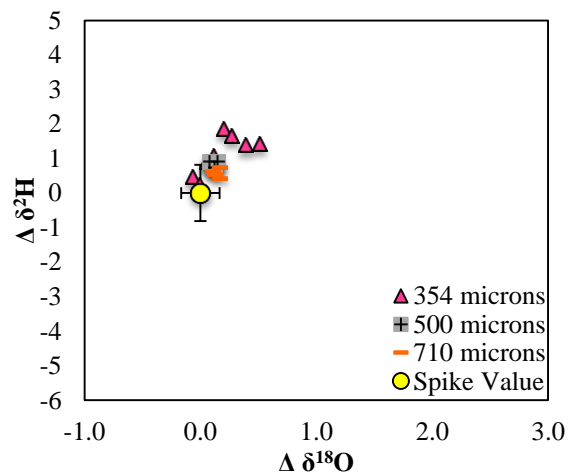
Figure 4.1**Figure 4.2****Figure 4.3****Figure 4.4**

Figure 4.1: Isotopic differences from the spike value with varying gravimetric moisture contents ranging from 1.5% to 20%. Note that results in Figures 4.1-4.5 are the same data only categorized to emphasis different sediment characteristics.

Figure 4.2: Isotopic differences from the spike value with varying grain size diameter ranging from 75 microns to 710 microns.

Figure 4.3: Isotopic differences from the spike value with varying grain size diameters for only the fine grained sediments.

Figure 4.4: Isotopic differences from the spike value with varying grain size diameters for only the coarse grained sediments.

4.4.2 Washed and Unwashed Sediments

Figure 5 shows experimental results categorized according to sediment source and preparation method (washed versus unwashed). In contrast to categorizations by texture and moisture content, there are close associations between sediment source and deviation from the standard used in the spike tests. In particular, the only samples to be depleted relative to the spike value are the unwashed Gudmundsen samples (both GUD 10-01 and GUD 10-02 cores).

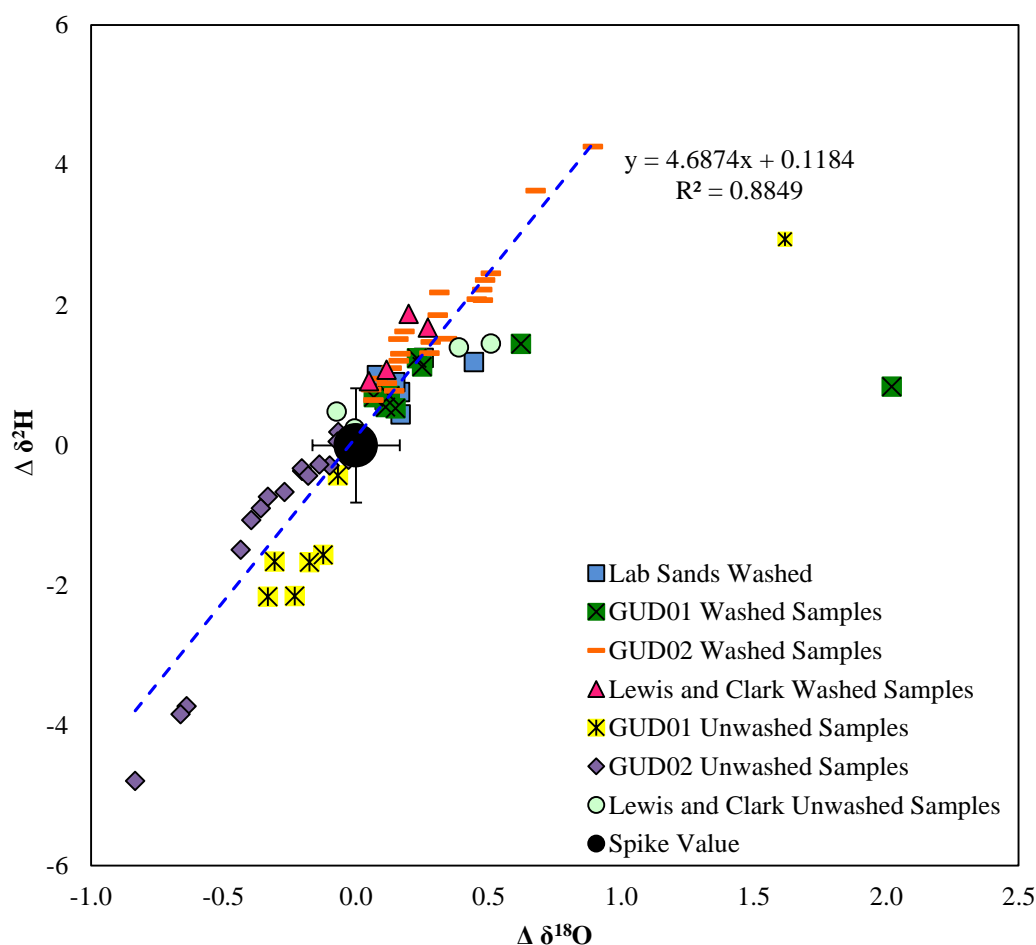


Figure 4.5: Isotopic differences from spike value for all washed versus unwashed sediments. The sediments used are from laboratory sands, Gudmundsen cores, and Lewis and Clark cores. Regression line does not include the two outliers (1.6, 2.9; 2.0, 0.8). Point (1.6, 2.9) is not included in Figures 4.1-4.4 because moisture content and grain size were not recorded.

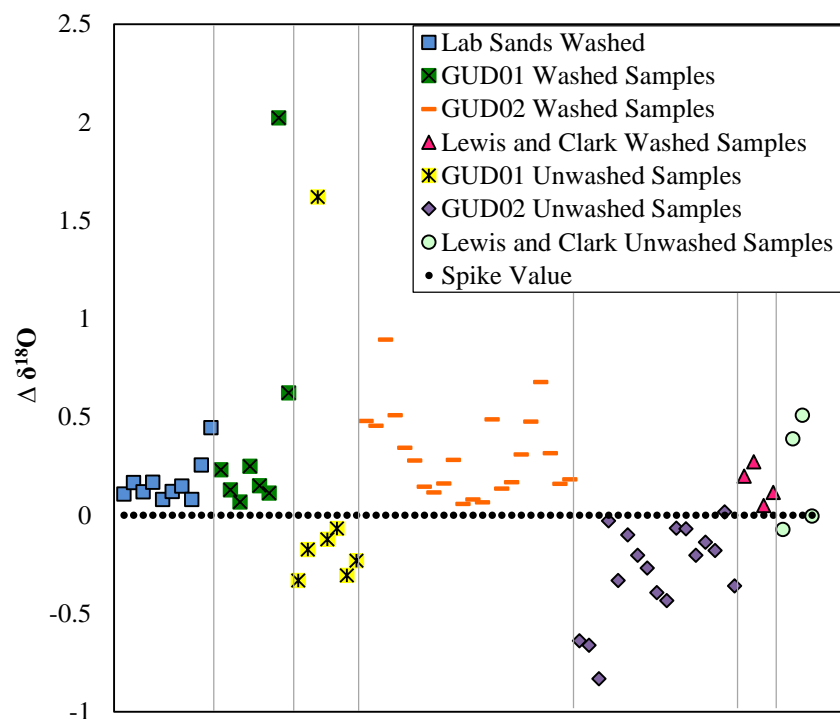


Figure 4.6: $\delta^{18}\text{O}$ comparison of washed versus unwashed sediments for Gudmundsen cores, Lewis and Clark cores and laboratory sands.

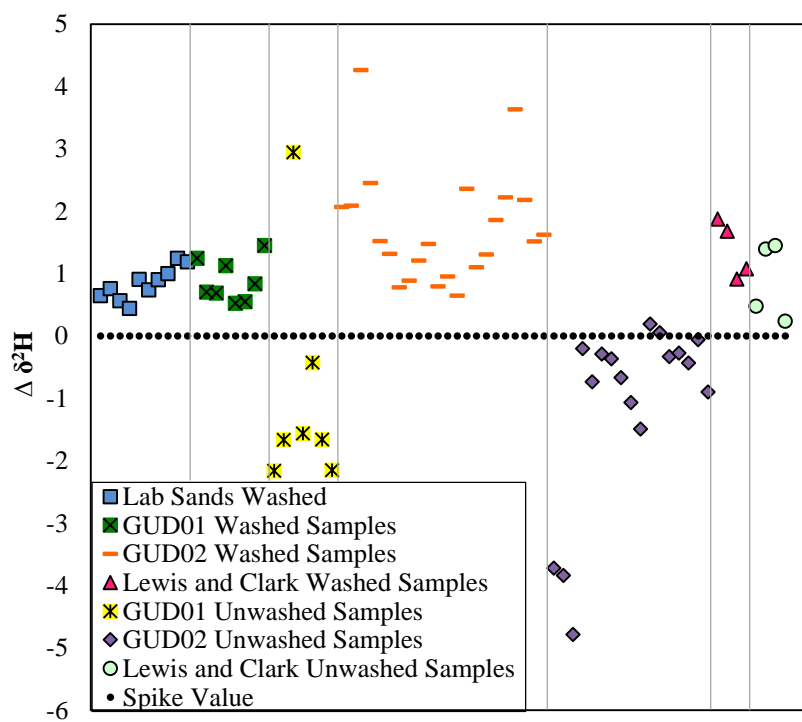


Figure 4.7: $\delta^2\text{H}$ comparison of washed versus unwashed sediments for Gudmundsen cores, Lewis and Clark cores and laboratory sands.

All other sediments, including the washed Gudmundsen sediments, washed and unwashed Lewis and Clark, and washed laboratory sands, are enriched relative to the spike water value (also see Figures 4.6 and 4.7 for an illustration of isotope variations according to sediment group). The opposite fractionation direction of the unwashed Gudmundsen samples could be the result of one of three factors: 1) clay content, 2) chemistry of the sediment, or 3) chemistry of sediments and clays; the results in sections 4.4.3 and 4.4.4 aim to determine which of these possibilities is most likely.

Figures 4.8 and 4.9 show the same data categorized according to sediment source and grain size. Figure 4.8 includes sediment sources laboratory sands, Gudmundsen washed, and Gudmundsen unwashed with grain sizes 75, 150, and 250 μm . Figure 4.9 includes sediment sources laboratory sands and Lewis and Clark washed and unwashed with grain sizes 354, 500, and 710 μm . Again, the majority of the scatter is associated with 75 μm and 150 μm textural classes (Fig 4.8). In contrast, Figure 4.9 shows that little or no fractionation is associated with the three coarsest grain sizes (354-710 μm). Results in Figures 4.8 and 4.9 indicate that fractionation amount is partially influenced both by sediment source and grain size. Fractionation direction is most likely solely associated with sediment source, though there is not enough data to determine this. Outliers present in Figures 4.1-4.7 (1.6, 2.9; 2.0, 0.8) are most likely a result of contamination during sample preparation or isotopic analysis by the CRDS machine. The fact that only two sample points throughout experimentation did not fall along trend increases reliability.

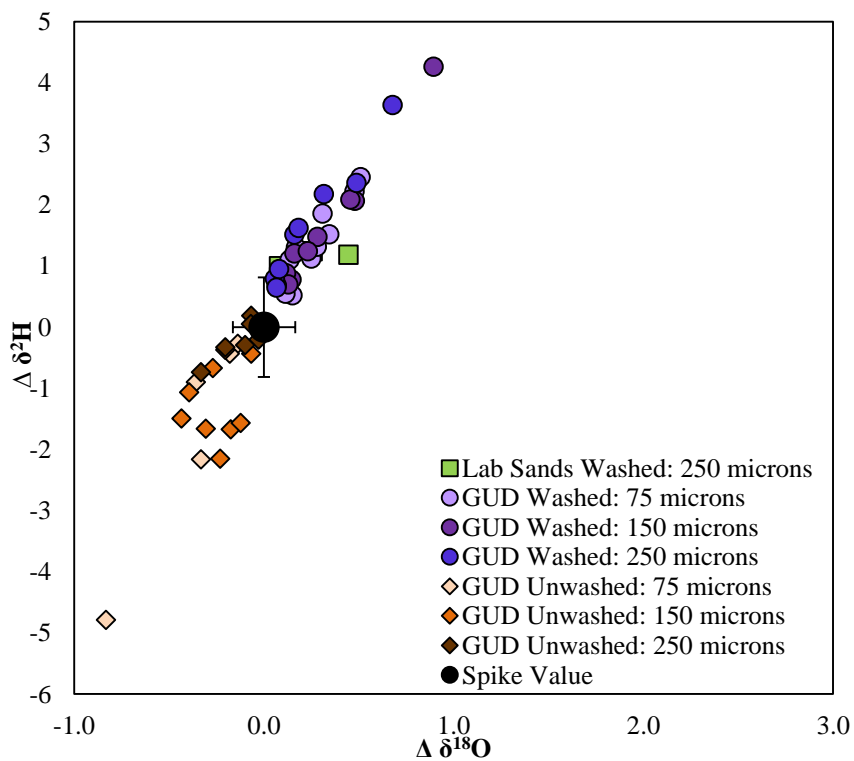


Figure 4.8: Isotopic differences from the spike value with different sediment sources and varying grain size diameters for only the fine grained sediments.

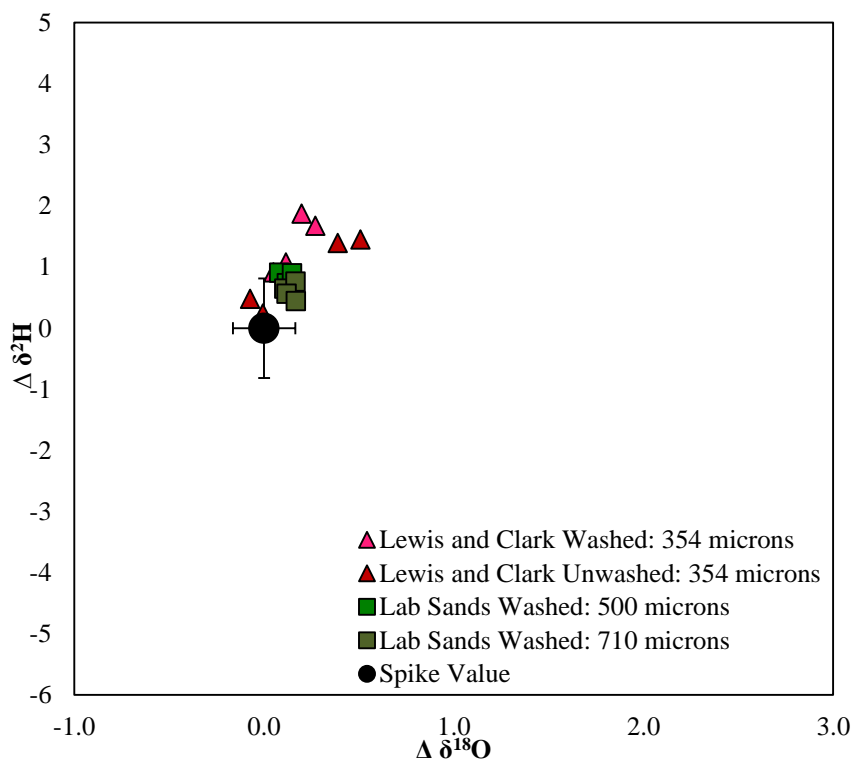


Figure 4.9: Isotopic differences from the spike value with different sediment sources and varying grain size diameters for only the coarse grained sediments.

4.4.3. Clay Content Effects

Figure 4.10 shows the effects of varying clay contents when combined with 150 μm sand and 10% gravimetric moisture content of isotopically spiked water. The majority of samples were within experimental error of the spike water (three of four samples with 0.5% clay content, all samples with 1.0% clay content, and one of four samples with 2% clay content). All samples follow the regression line $\delta^2\text{H}=3.63 \delta^{18}\text{O}-34.21$ ($r^2=0.86$ for $n=12$). Figure 4.11 shows the effects of varying clay contents when combined with 500 μm sand and 10% gravimetric moisture content of isotopically spiked water. In this set of tests, most of the 0.5% and 1% clay content repetitions were within experimental error, as was the case with the 150 μm sand tests. But in contrast to the 150 μm sand tests, all 2% clay content results were enriched greater than experimental error. The regression line for this data was similar to Figure 4.10: $\delta^2\text{H}=3.92 \delta^{18}\text{O}-32.16$ ($r^2=0.92$ for $n=12$). Figure 4.12 shows the results of tests that used 150 μm sand (same as Fig 4.8) and 15% gravimetric moisture contents (higher than other clay tests). The clay contents range from 0.5-3.0%. The majority of these extracts were within experimental error of the

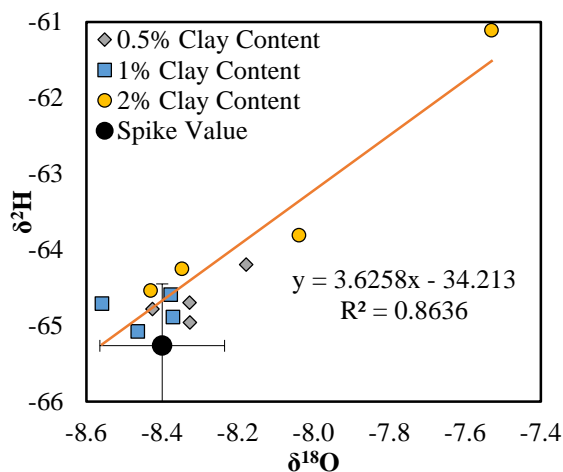
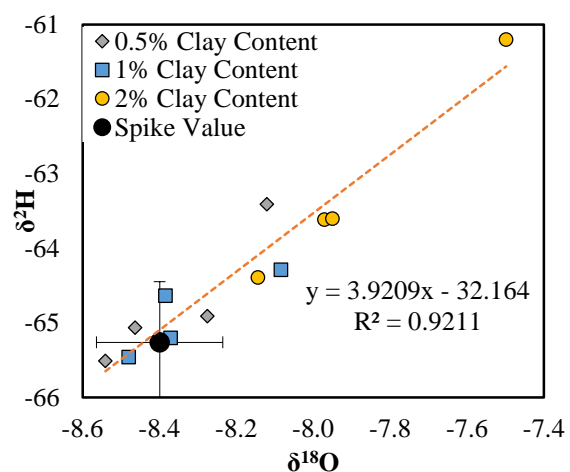
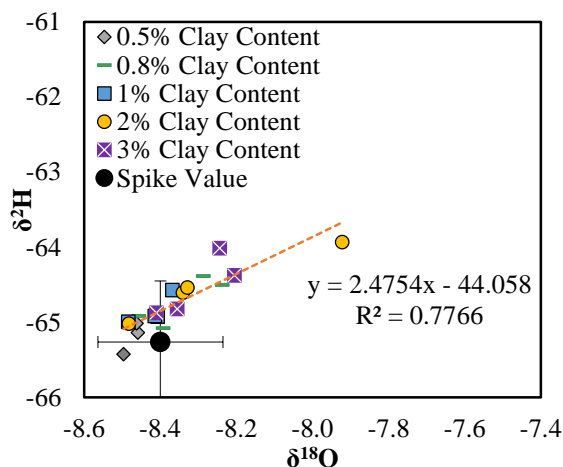
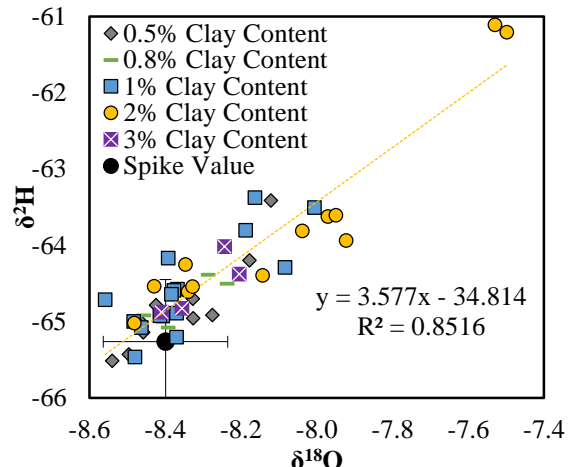
Figure 4.10**Figure 4.11****Figure 4.12****Figure 4.13**

Figure 4.10: Effects of varying clay contents on clean sand. 150 μm sand, 10% gravimetric moisture content.

Figure 4.11: Effects of varying clay contents on clean sand. 500 μm sand, 10% gravimetric moisture content.

Figure 4.12: Effects of varying clay contents on clean sand. 150 μm Sand, 15% gravimetric moisture content.

Figure 4.13: Summary of the effects of clay content. Varying gravimetric moisture content and grain size.

spike water (5 of 16 outside experimental error: zero of the three samples with 0.5% clay content, two of the four samples with 0.8% clay content, zero of the four samples with 1% clay content, one of the four samples with 2% clay content, and two of the four samples with 3% clay content). The regression line for Figure 4.12 has a lower slope and r^2 value than the other figures: $\delta^2\text{H}=2.48$ $\delta^{18}\text{O}-44.06$ ($r^2=0.78$ for $n=19$) The Figure 4.13 is a summary of the effects of clay content on fractionation, including the results of all previously listed tests. The regression line of the summarized data is as follows: $\delta^2\text{H}=3.58$ $\delta^{18}\text{O}-34.81$ ($r^2=0.85$ for $n=47$). Individual values ranged from -8.56 to -7.49 $\delta^{18}\text{O}$ and -65.5 to -61.1 $\delta^2\text{H}$. This figure illustrates, on average, greater fractionation values for samples with 1- 2% clay content than with 3% clay content. Due to the variability in fractionation values in relation to clay content, small percentages of clay (3% or less) are not the driving force behind isotopic fractionation amount. Coplen and Hanshaw (1973) determined an average slope of 3.1 to be consistent with adsorption mechanisms. This was determined by passing water through clay disks at high pressures. The fact that their slope is similar to those seen in this experiment indicate porous sediments with low clay contents under no hydrostatic pressure can also experience adsorption-related fractionation.

4.4.4 Sediment and Pore Water Chemistry Effects

Figure 4.14 shows the results of an experiment in which the chemistry of the spike water was altered using a potassium standard and a magnesium standard. Figure 4.15 shows the results from the experiment where the chemistry of the sands and sands with clays are changed. Because of the results seen in Sofer and Gat (1975), it was expected that the samples plot on opposite sides of the standard (magnesium chloride to

the right, and potassium bromide to the left). The results show that the sands saturated with the magnesium standard and the potassium standard plot are both enriched relative to the spike value. However, the sand and clay mixture saturated with potassium bromide was depleted relative to the spike value. Tuller and Or (2005) noted that the larger, less hydrated cations, such as potassium, adsorb less water than smaller cations, such as sodium and magnesium. This could explain why the results of the potassium saturated clay test are within experimental error.

The natural pore waters contained in Gudmundsen field samples contain potassium. Figures 4.16 and 4.17 show the concentrations of K^+ in Gudmundsen samples correlated to isotopic concentrations (Boone, K. unpublished data). These figures indicate that with increasing amount in potassium, samples become more isotopically depleted. Therefore, the reason unwashed Gudmundsen samples were depleted relative to the spike value in Figure 4.5 was due to the potassium saturated clays. Sofer and Gat (1975) identified the salt effect, different ions plotting in different direction of the spike value, with extremely salty concentration (those seen in brines). The Gudmundsen sediments are not nearly as salty as brines, yet the same salt effect is seen. This indicates that salt effect can control isotopic fractionation in non-saline sediments. (Clay content for Gudmundsen samples was calculated to be no more than 4%). Mechanisms controlling the salt effect, resulting in opposite fractionation direction depending on the ion, have not yet been identified. Figure 4.18 is a summary of the results from Figures 4.14 and 4.15 and indicates chemistry of sediment, clay, and pore water do not effect fractionation amount.

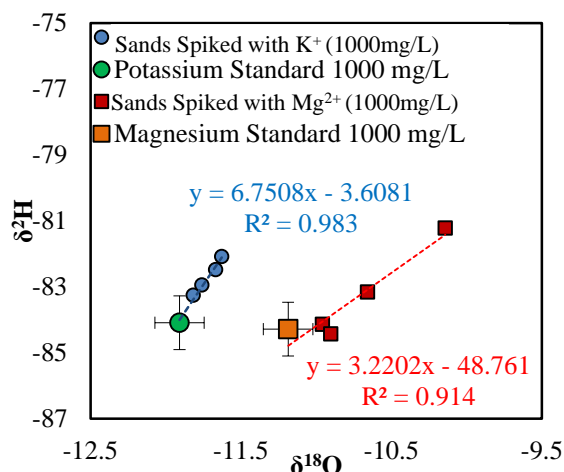
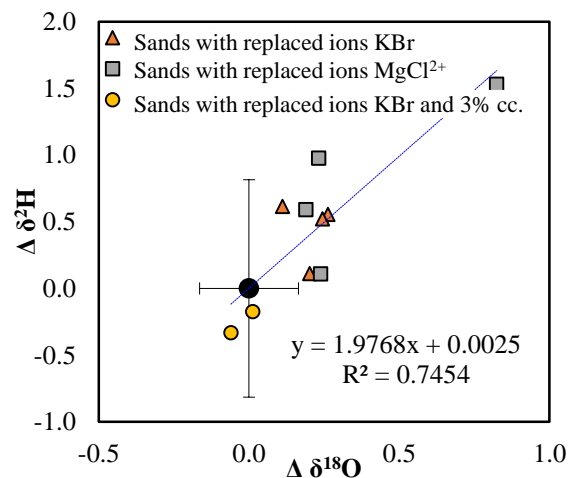
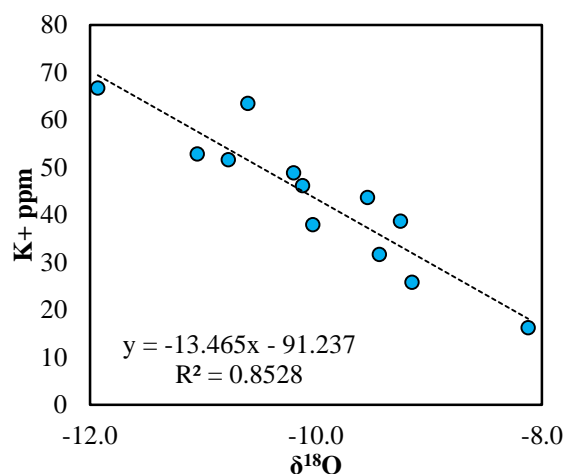
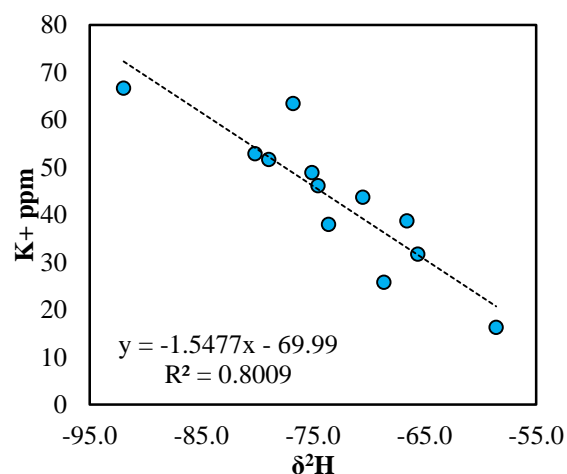
Figure 4.14**Figure 4.15****Figure 4.16****Figure 4.17**

Figure 4.14: Sands spiked with ion chromatography standards. 500 μm sand, 10% moisture content, and 1% clay content.

Figure 4.15: Sands saturated with 3M potassium bromide or magnesium chloride (then rinsed to reduce concentration). 500 μm sand, 10% moisture content, and 0 or 3% clay content.

Figure 4.16: Potassium amounts correlated to $\delta^{18}\text{O}$ concentration for Gudmundsen sediments (Boone, K. unpublished data).

Figure 4.17: Potassium amounts correlated to $\delta^2\text{H}$ concentration for Gudmundsen sediments (Boone, K. unpublished data).

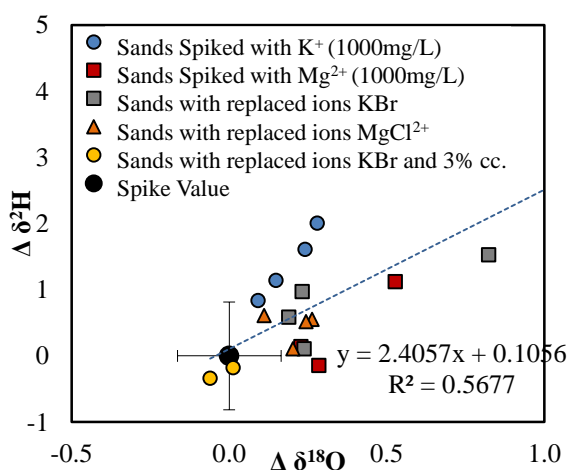


Figure 4.18: Summary of chemistry effects.

4.4.5 Sampling Times and Evaporation Effects

Slope values for the majority of the figures are near 4. Slope values less than 5 have been associated with evaporation from sediments (Clark and Fritz, 1997). Throughout the laboratory procedures described above, moist sediments do have small exposure times with the atmosphere. Because of this, and the similar slope values, evaporation must be explored as a possible methodological limitation imparting isotopic fractionation. Samples in Figures 4.19 and 4.20 were prepared according to the methods described in section 4.3.2. However, instead of being centrifuged immediately, the moist sediments were stored in a plastic bag within a plastic jar (Fig 4.19) and glass jar (Fig 4.20) for 24 and 48 hours. Figure 4.21 shows the results of two evaporation tests in which sediments were spiked with water of known isotopic compositions and left uncovered (open to the atmosphere) in the laboratory for varying times. The regression line of Figure 4.19 was: $\delta^2\text{H} = 3.32 \delta^{18}\text{O} - 36.76$ ($r^2 = 0.68$ for $n = 8$), the regression line of Figure 4.20 was: $\delta^2\text{H} = 4.27 \delta^{18}\text{O} - 37.21$ ($r^2 = 0.52$ for $n = 11$); both slopes are near 4. The regression

lines of the evaporation tests in Figure 4.21 were: $\delta^2\text{H}=2.52 \delta^{18}\text{O}-41.95$ ($r^2=1$ for $n=9$) and $\delta^2\text{H}=2.79 \delta^{18}\text{O}-41.91$ ($r^2=1$ for $n=8$). In the case of Figure 4.21, samples become more isotopically enriched with time. This makes sense conceptually, because the longer the samples are exposed to the atmosphere, the greater the evaporation, leading to greater fractionation. In Figure 4.20, however, the zero hour samples have roughly the same fractionating amount as the 24 and 48 hour samples, as opposed to gradual enrichment. Additionally, the slopes for the evaporation tests are consistent with evaporation from the unsaturated zone under moderate humidity (Clark and Fritz, 1997), but the slopes for Figures 4.19 and 4.20 are about double that. Water samples used in experimentation were extracted within two hours of preparation. This indicates that evaporation is not the driving force of fractionation amount associated with the immiscible displacement fluid technique with the aid of a centrifuge.

Figure 4.19

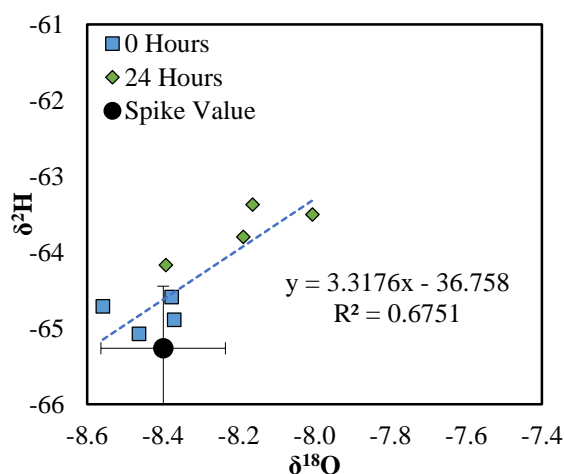


Figure 4.20

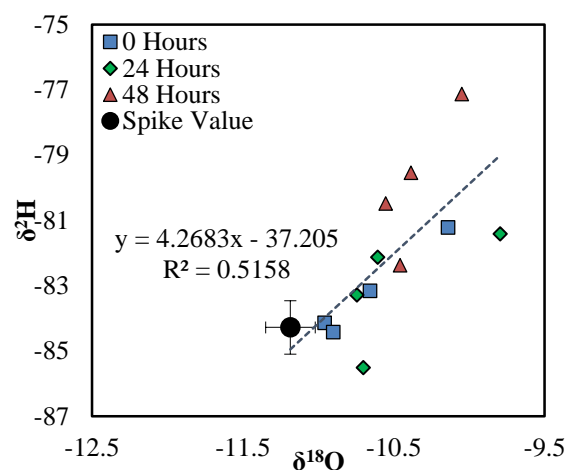


Figure 4.19: Sampling time effect: 0 and 24 hours. Stored in plastic jar.

Figure 4.20: Sampling time effect: 0, 24, and 48 hours. Stored in glass jar.

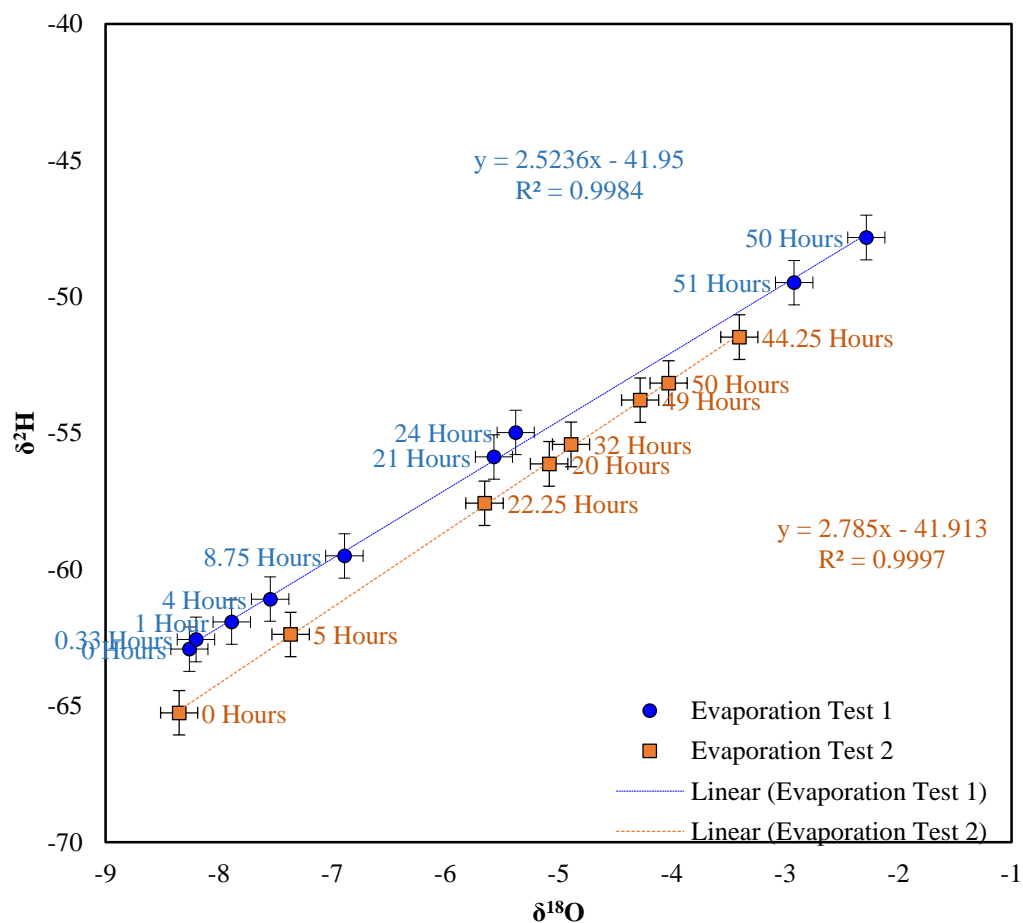


Figure 4.21: Results of two evaporation tests.

4.4.6 Effects of Extraction Method

Figure 4.22 is a comparison between the centrifuge method and the more widely used azeotropic distillation method with toluene. Results for both methods are outside analytical error of the spike value. The samples yielded by centrifuge, however, are more precise than those from the distillation method. Fractionation associated with the azeotropic distillation technique can be attributed to incomplete extraction. Fractionation associated with the centrifuge method can assumedly be attributed to adsorption effects. This indicates that centrifugation with the aid of an immiscible displacement fluid should be considered a viable replacement for azeotropic distillation.

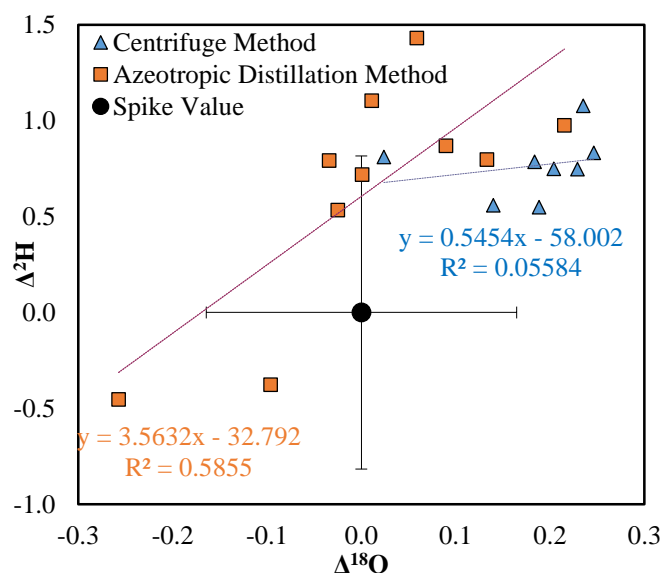


Figure 4.22: Pore water extraction method comparison: azeotropic distillation with toluene to centrifuge method with immiscible displacement fluid.

4.5 Conclusion

Evidence suggests fractionation amount is not controlled by clay content, moisture content, or sediment chemistry; however it may be partially controlled by grain

size. Additional research must be conducted in order to validate this hypothesis.

Fractionation direction is most likely controlled by the salt effect: clays containing potassium will have a negative discrimination relative to the spike value. Experimental evidence indicates this holds true for non-saline conditions. The immiscible displacement fluid technique involves small exposure times of the moist sediment with the atmosphere, however this exposure time is not enough to evoke an evaporation effect. The comparison of the centrifuge technique to the more widely used azeotropic distillation technique indicated that both techniques evoke fractionation: due to incomplete extraction for azeotropic distillation and adsorption effects for the centrifuge method. The standard deviation of fractionation associated with experimentation is calculated to be $\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$. Fractionation outside analytical error resulted from all experimental cases, even those under non-saline, non-pressurized, and highly permeable conditions. This indicates adsorption-related fractionation may be more common than is typically assumed by researchers using stable isotopes of water as conservative tracers in the unsaturated zone.

Chapter 5.0

Field Profile Interpretation

5.1 Introduction

This chapter presents the results of isotopic measurements from five unsaturated zone cores collected from three field locations in Nebraska with differing texture and moisture conditions. Its main contribution to the thesis is to assess the magnitude of natural isotopic variability in natural unsaturated zone profiles relative to the magnitude of uncertainty in tracer interpretation, based on quantitative estimates of a) analytical uncertainty and b) potential for adsorption-related fractionation in the profile, which were developed in Chapters 3 and 4. Another focus of this chapter is the probable drivers of vertical variability in pore water isotopes. The samples used for this assessment were selected based on a combination of availability of archived core material and diversity of sediment textures.

5.2 Study Areas

Field sediment cores for this study were collected from sites in Nebraska that have been subject to previous or concurrent unsaturated zone investigations (Fig 5.1). Profiles (GUD01 and GUD02) were collected from a dune ridge setting within the Gudmundsen Sandhills Laboratory of the University of Nebraska, in the Sandhills region near Mullen, NE (which is located in Hooker County; 42.07°N, 101.44°W). Prior to the Tertiary, Hooker County was covered multiple times by ocean waters, leading to the deposition of sedimentary rocks such as shale, sandstone, and limestone (Plantz and Merkel, 1964). During the Tertiary, outwash from the Rocky Mountains deposited

several feet of stratified sands, which are now the Ogallala Formation (Plantz and Merkel, 1964). In this area, the Ogallala Formation is overlain by an extensive eolian sand dune known as the Sandhills, which are stabilized by prairie vegetation used as rangeland (Loope and Swinehart, 2000). Due to the high hydraulic conductivity of the Sandhills, runoff is uncommon (Plantz and Merkel, 1964). Average total annual precipitation for Mullen, NE from 1971 to 2000 is 559 mm. Monthly mean temperatures ranged from approximately -3.2°C in winter months to 22.2°C in summer months (station records 1971-2000; HPRCC, 2014).

Lewis and Clark Profiles, LC01 and LC02, were collected in Cedar County, located in northeastern NE (42.75°N, 97.35°W). Bedrock geology in Cedar County consists of Carlile Shale, Niobrara Formation, Pierre Shale (Cretaceous), and Ogallala (Tertiary; Milliron, 1985). During the Pleistocene, Cedar County was glaciated (Milliron, 1985). Sediments remaining from the glaciation are heterogeneous including loess and glacial till consisting of silty-clay intermittent with gravel layers ranging in size from pebble to boulder (Milliron, 1985). Primary vegetation of the area includes prairie and introduced grasses used for grazing and scattered trees focusing near major stream (Milliron, 1985). Average total annual precipitation near Cedar County from 1971 to 2000 is 670 mm (taken from HPRCC station in Harrington, NE). Monthly mean temperatures ranged from approximately -5.2°C in winter months to 22.7°C in summer months (station records 1971-2000; HPRCC, 2014).

Profile H01 was collected from an irrigated agricultural site near Holdrege, NE (40.35°N, 99.32°W). Holdrege, NE is a loess plain; the most common soil type in the area is Holdrege silt-loam which is dark brown in color and generally extends 0.5 m deep

(Tillman, 1919). The Holdrege silt-loam is underlain by an additional silt loam, which tends to be less consolidated and yellow in color (Tillman, 1919). Bedrock in the area consists of sedimentary rocks: shale, sandstone, and limestone (Cretaceous and Tertiary; Tillman, 1919). Agriculture in the area is common, with corn and soybean rotations and center pivot irrigation. Average total annual precipitation for Holdrege, NE from 1971 to 2000 is 662 mm. Monthly mean temperatures ranged from approximately -2.3°C in winter months to 23.6°C in summer months (station records 1971-2000; HPRCC, 2014).

5.3 Methods

Sediments used for this investigation were collected as part of previous investigations using direct-push sampling (Geoprobe dual-tube system). Cores sections were collected in ~2 m intervals and were cut to ~50 cm lengths in the field in order to prevent moisture redistribution during storage. All cores had been sealed and refrigerated at all times between field sampling and pore water extraction. In this study, pore waters were extracted using the methods described in Chapters 3 and 4. All reported analyses followed previously described methods (Chapters 3 and 4).

5.4 Results and Discussion

5.4.1 Gudmundsen Profiles

The isotopic profiles for $\delta^{18}\text{O}$ versus depth and $\delta^2\text{H}$ versus depth are fairly similar at the two neighboring locations, GUD01 (Figure 5.1a and Figure 5.1b) and GUD02 (Figure 5.2a and Figure 5.2b). The $\delta^{18}\text{O}$ values for GUD01 and GUD02 range from -8‰ to -12‰ with most values from -8.5‰ to -10.5‰. The $\delta^2\text{H}$ values range from -60‰ to -95‰ with most values from -65‰ to -80‰ for GUD01 and -60‰ to -75‰ for GUD02. The least squared regression slope for $\delta^{18}\text{O}/\delta^2\text{H}$ is 8.2 in GUD01 and 7.9 in GUD02. The

slopes are very close to the global meteoric average of 8.0. The moisture contents for GUD01 in the first few feet of the profile are very low, indicating evaporation. The moisture contents for the rest of the profile range from 5% to 10%. There are insufficient data points to make inferences about moisture content from the GUD02 profile.

Both Gudmundsen profiles indicate isotopic maximum just below the surface, around 2-3 meters. The isotopic concentrations then decrease rapidly toward the surface. The isotopic maximum most likely represents evaporation from the sediment profile. The isotopic depletion above the location of evaporation could be due to diffusion of water vapor from the evaporation site (Barnes and Allison, 1988). In the case of the GUD01 profile, vapor diffusion could also be taking place below the isotopic maximum (Barnes and Allison, 1988). The gradual depletion in both profiles after the maximum could be due to the effect of a temperature gradient. Although unlikely, because of the homogeneous nature of the sediments, the small enrichment point at 6 meters could be due to a layer of finer-grained sediments, or clays.

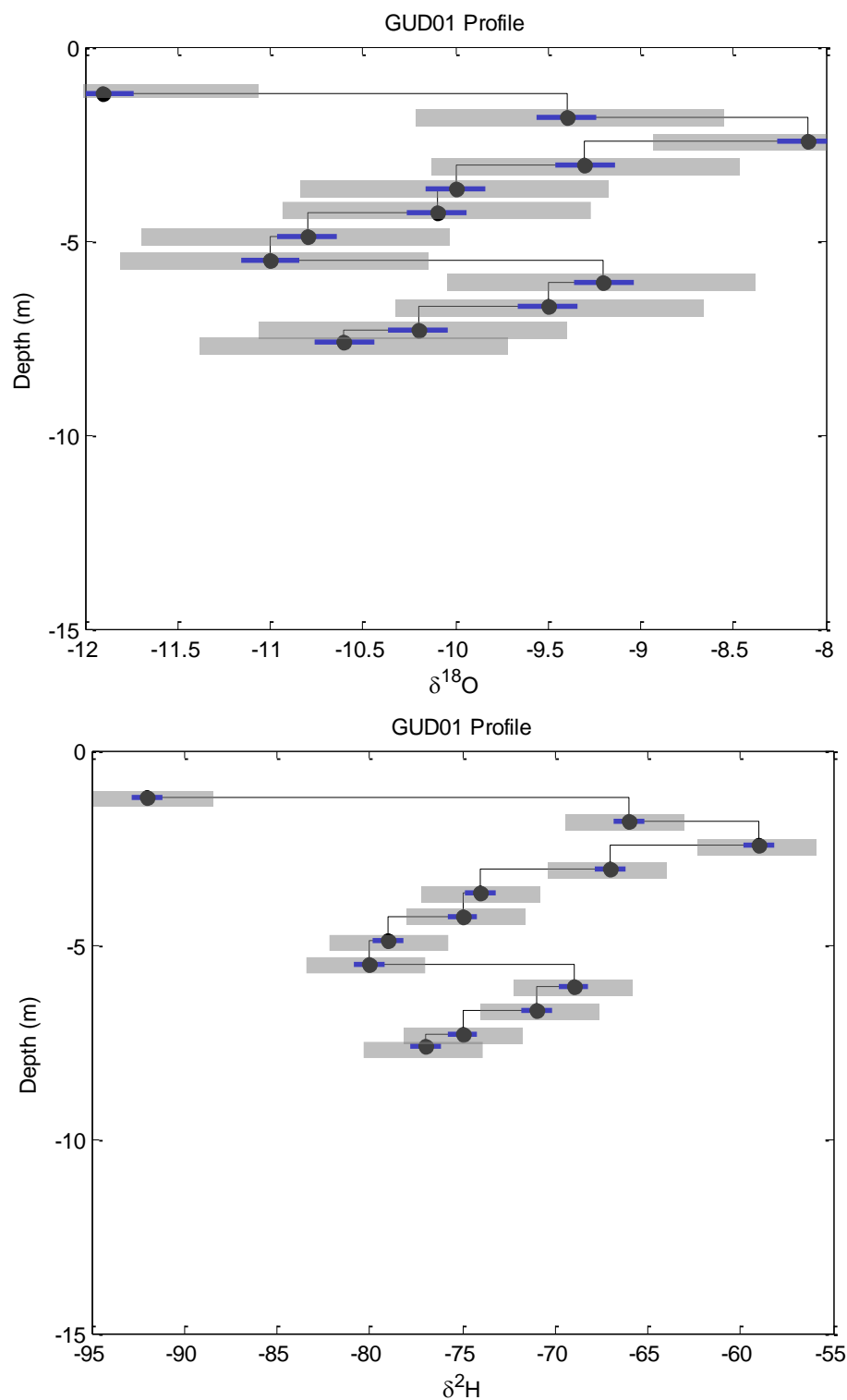


Figure 5.1a: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ versus depth for GUD01. Blue bars indicate analytical uncertainty ($\pm 0.16\text{‰}$ $\delta^{18}\text{O}$ and $\pm 0.82\text{‰}$ $\delta^2\text{H}$). Grey bars indicate adsorption based uncertainty ($\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$).

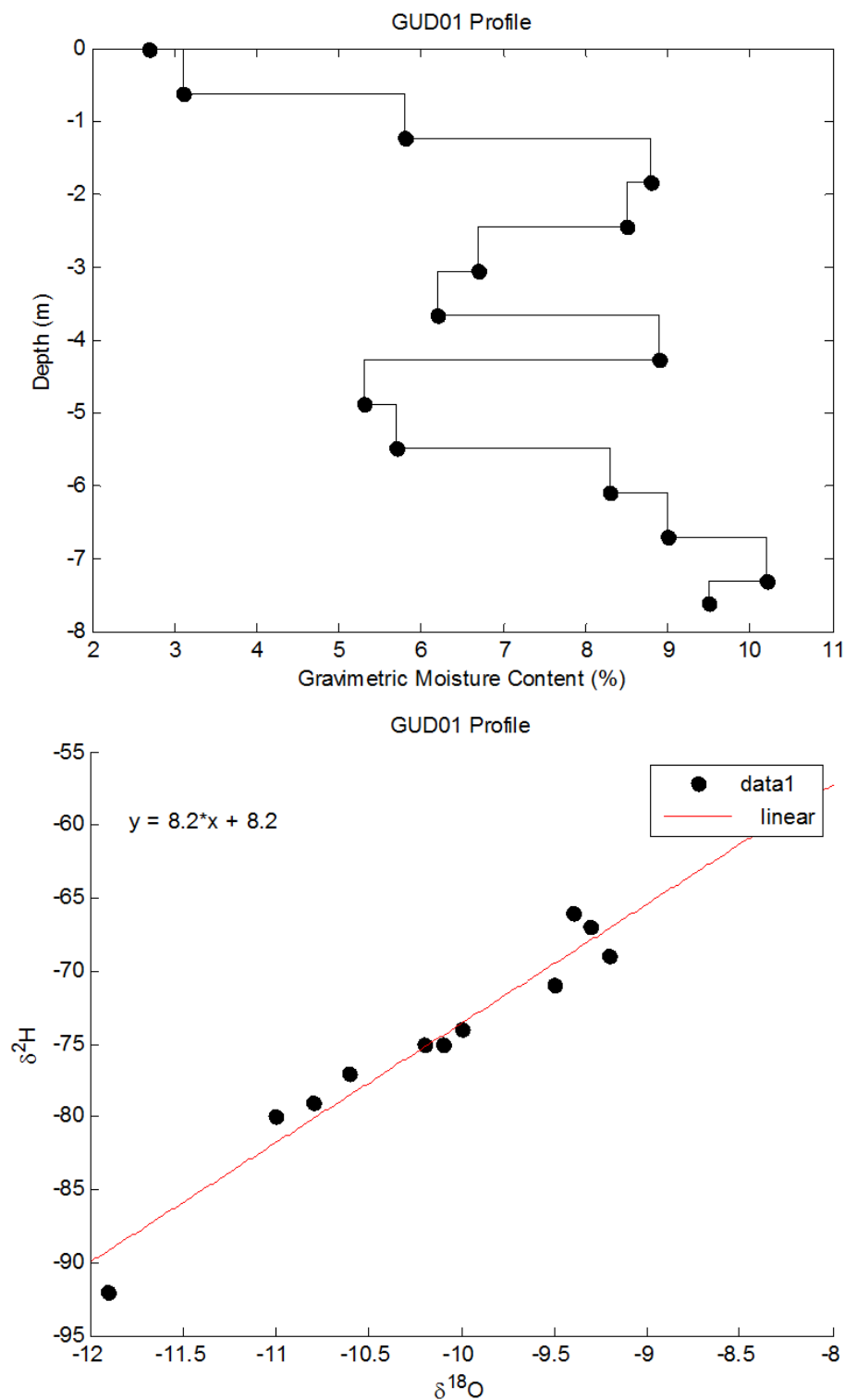


Figure 5.1b: Moisture content with depth and $\delta^{18}\text{O}/\delta^2\text{H}$ comparison for GUD01.

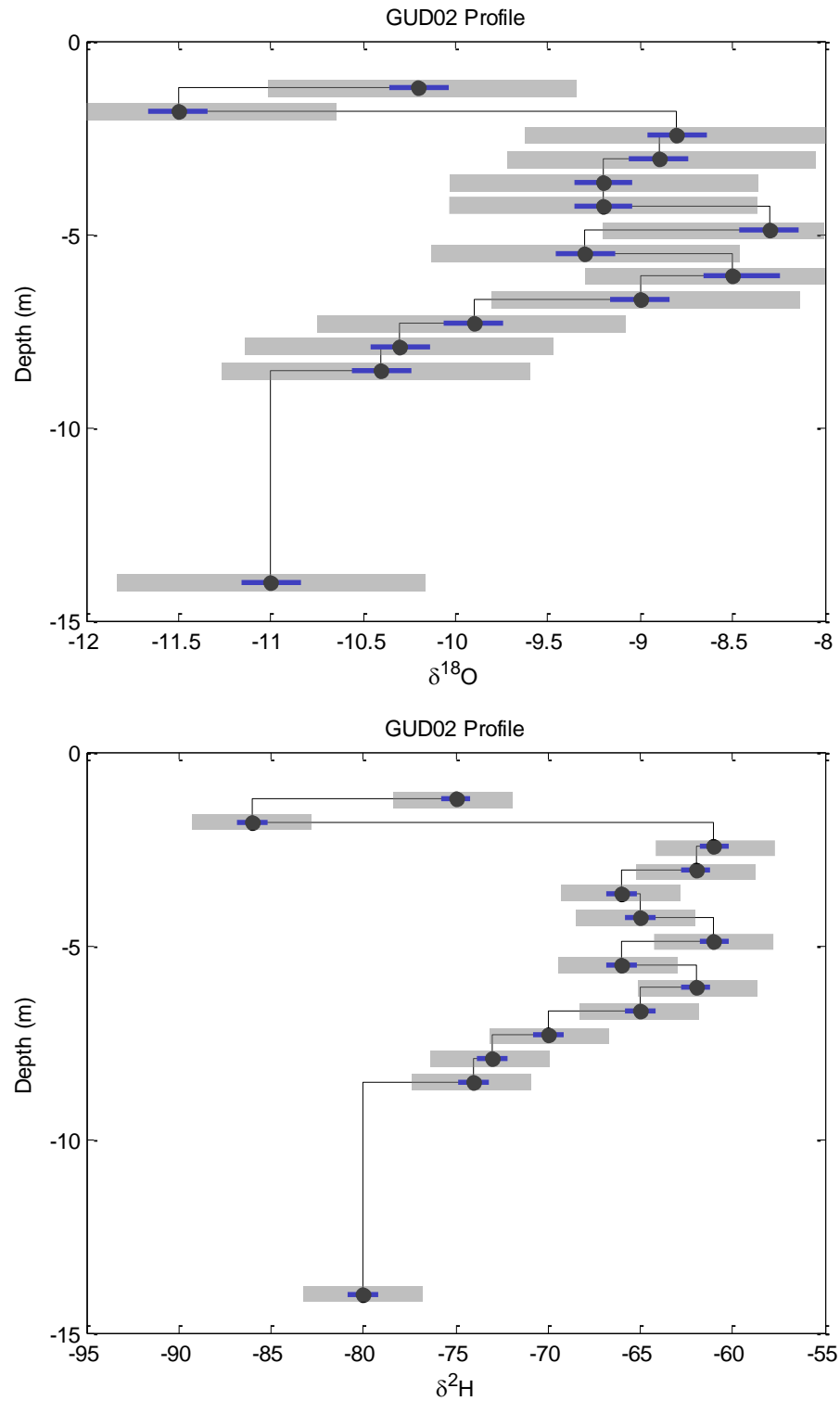


Figure 5.2a: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ versus depth for GUD02. Blue bars indicate analytical uncertainty ($\pm 0.16\text{‰}$ $\delta^{18}\text{O}$ and $\pm 0.82\text{‰}$ $\delta^2\text{H}$). Grey bars indicate adsorption based uncertainty ($\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$).

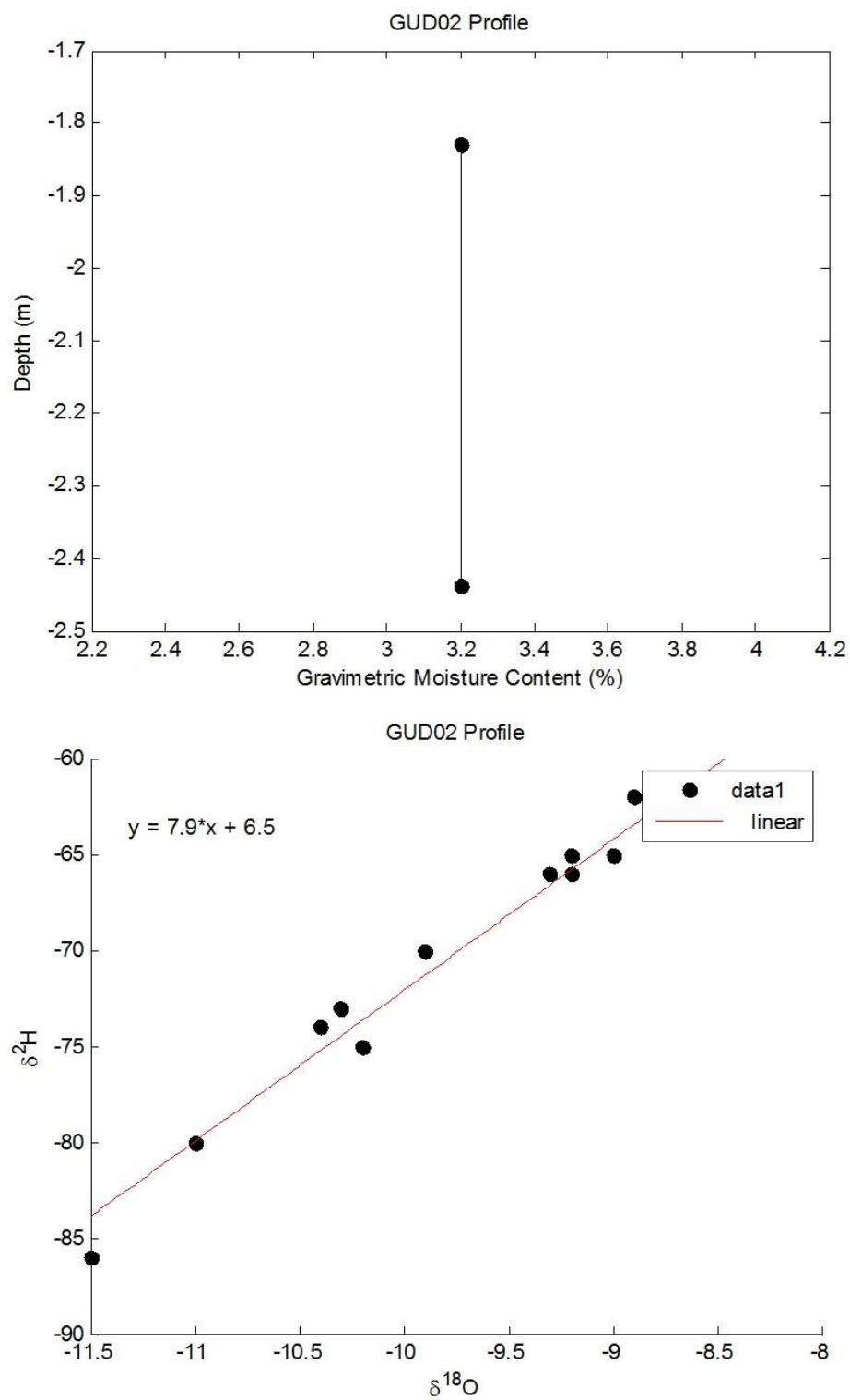


Figure 5.2b: Moisture content with depth and $\delta^{18}\text{O}/\delta^2\text{H}$ comparison for GUD02.

5.4.2 Lewis and Clark Profiles

The two Lewis and Clark profiles, LC01 (Figure 5.3a and Figure 5.3b) and LC02 (Figure 5.4a and Figure 5.4b) are similar to each other with respect to both $\delta^{18}\text{O}$ and $\delta^2\text{H}$. The $\delta^{18}\text{O}$ values for LC01 range from approximately -3‰ to -7.5‰ and from -5‰ to -8‰ for LC02. The $\delta^2\text{H}$ values range from approximately -35‰ to -63‰ for the LC01, and from -43‰ to -63‰ for LC02. The $\delta^{18}\text{O}/\delta^2\text{H}$ slopes of the LC01 profile and the LC02 profile comparison are both ~6. Although the slopes and isotopic values are similar, the moisture contents are very different. The highest moisture content for the LC01 is about 10%, whereas the highest moisture content for the LC02 is approximately 37%.

The isotopic enrichment at the surface of the LC01 profile could be due to evaporation. The depletion following the enrichment at 1-2 meters could be a result of diffusion of water vapor from the evaporation site (Barnes and Allison, 1988). The LC02 profile does not seem to reflect an evaporation signature near the surface. Both profiles have isotopic maximums around 3 to 5 meters in depth. This is most likely a result of seasonally-variable isotope signals from rainfall. Another less likely possibility could be due to fine-grained sediments. Due to the heterogeneity of the glacial tills, both profiles (LC01 and LC02) contain very fine-grained sediments with clay lenses at these layers. Based on the results in Figures 4.2-4.4, fine-grained sediments can lead to more enriched pore water because the fine-grained sediments act to adsorb the water molecules of lighter molecular weight.

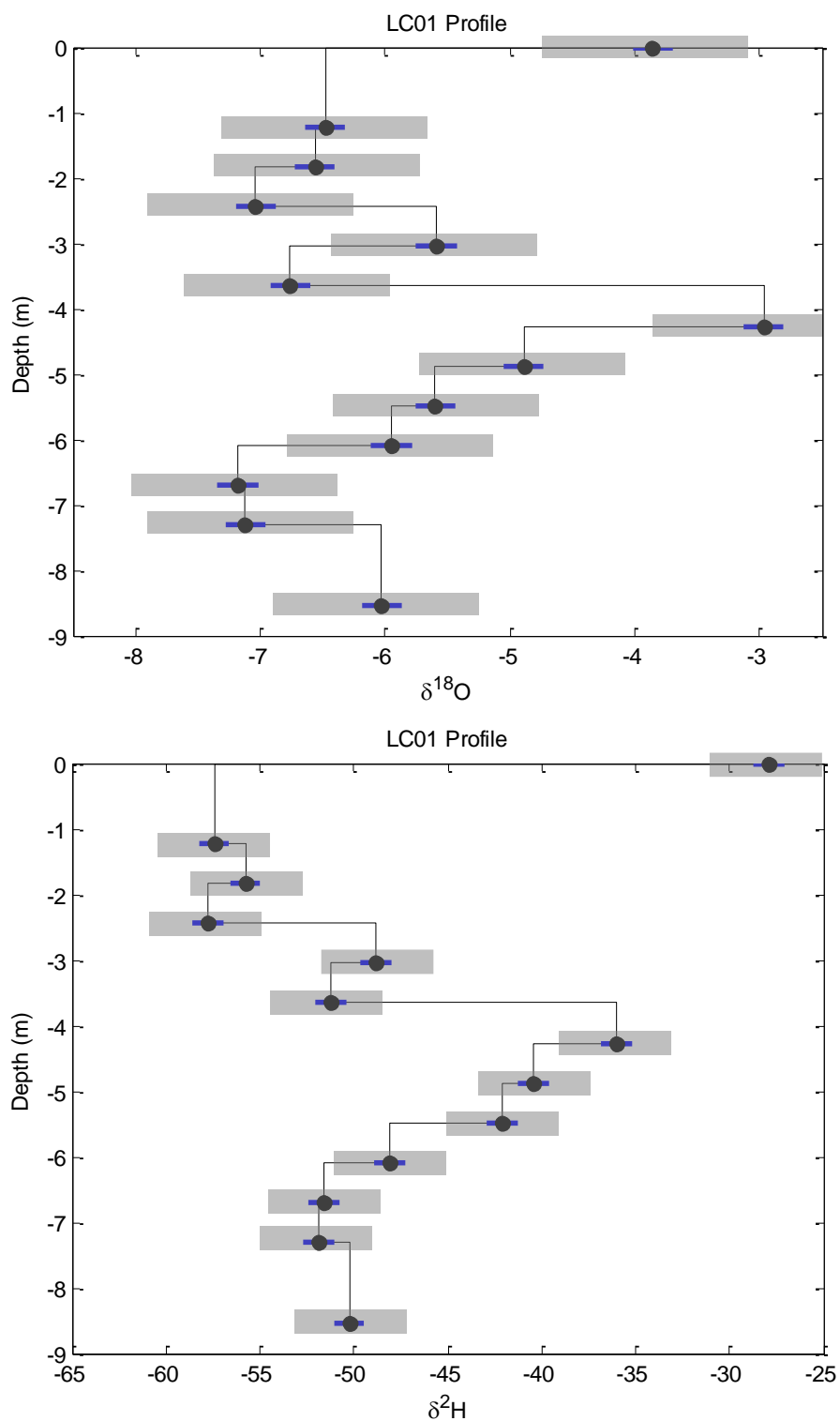


Figure 5.3a: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ versus depth for LC01. Blue bars indicate analytical uncertainty ($\pm 0.16\text{‰}$ $\delta^{18}\text{O}$ and $\pm 0.82\text{‰}$ $\delta^2\text{H}$). Grey bars indicate adsorption based uncertainty ($\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$).

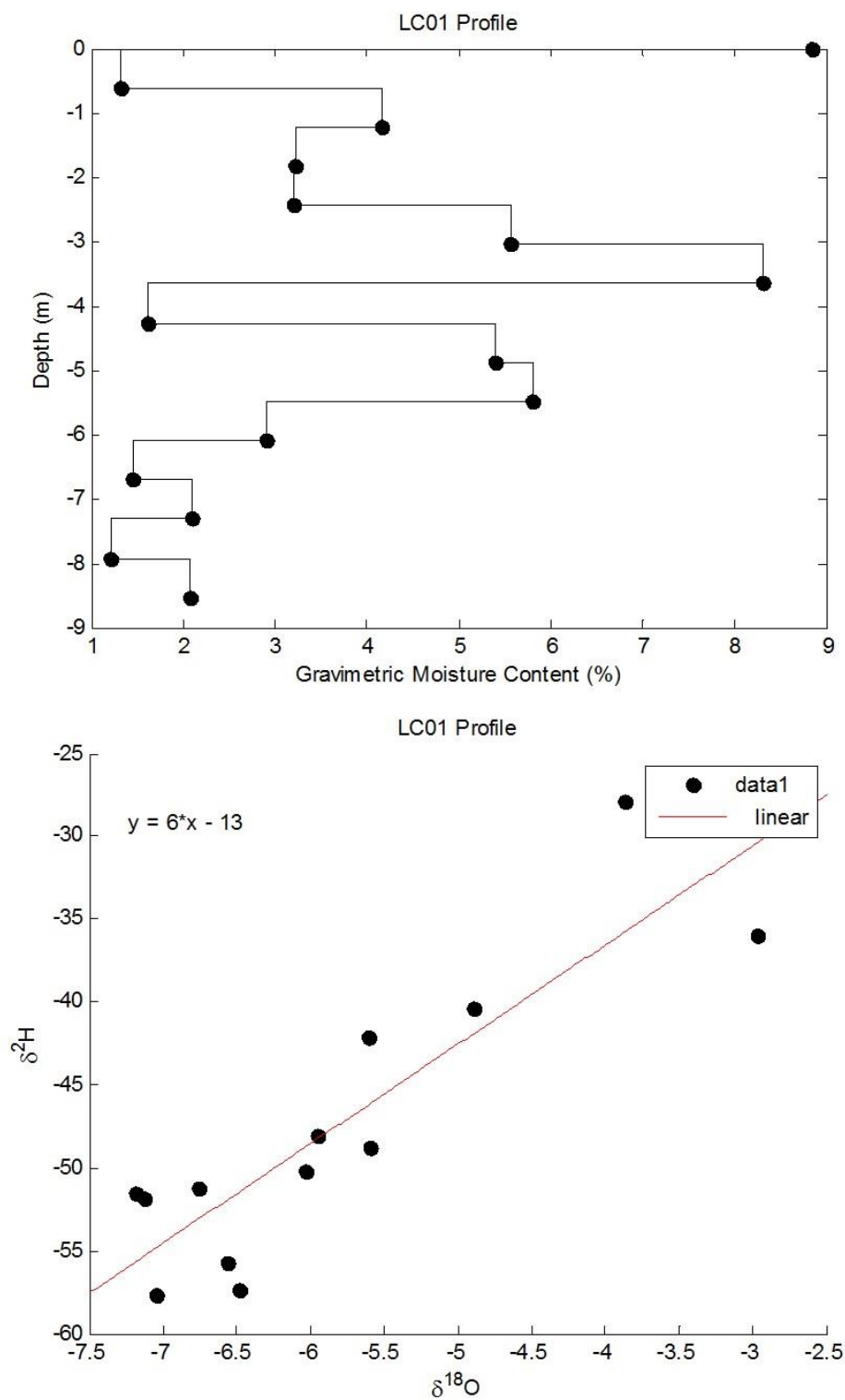


Figure 5.3b: Moisture content with depth and $\delta^{18}\text{O}/\delta^2\text{H}$ comparison for LC01.

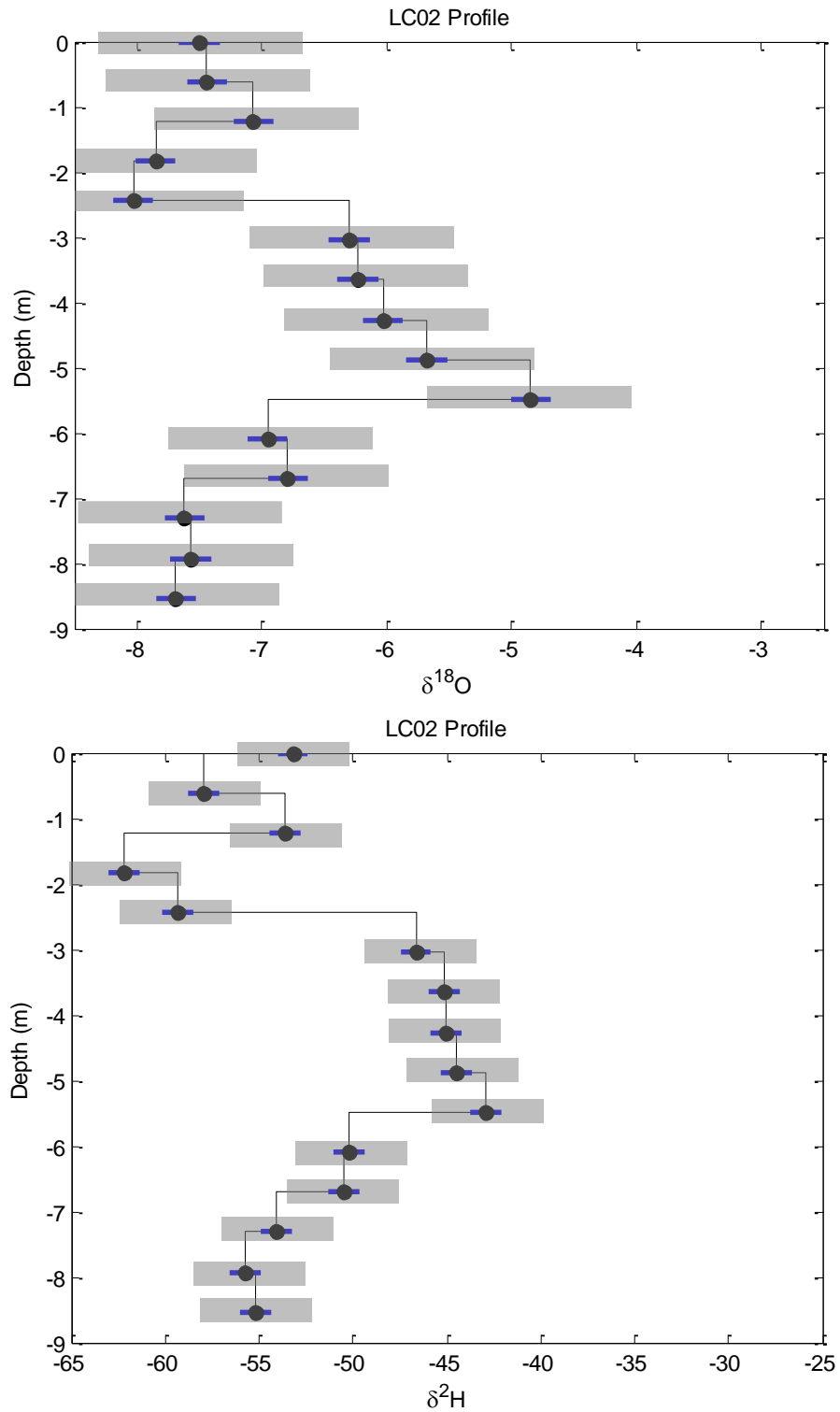


Figure 5.4a: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ versus depth for LC02. Blue bars indicate analytical uncertainty ($\pm 0.16\text{‰}$ $\delta^{18}\text{O}$ and $\pm 0.82\text{‰}$ $\delta^2\text{H}$). Grey bars indicate adsorption based uncertainty ($\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$).

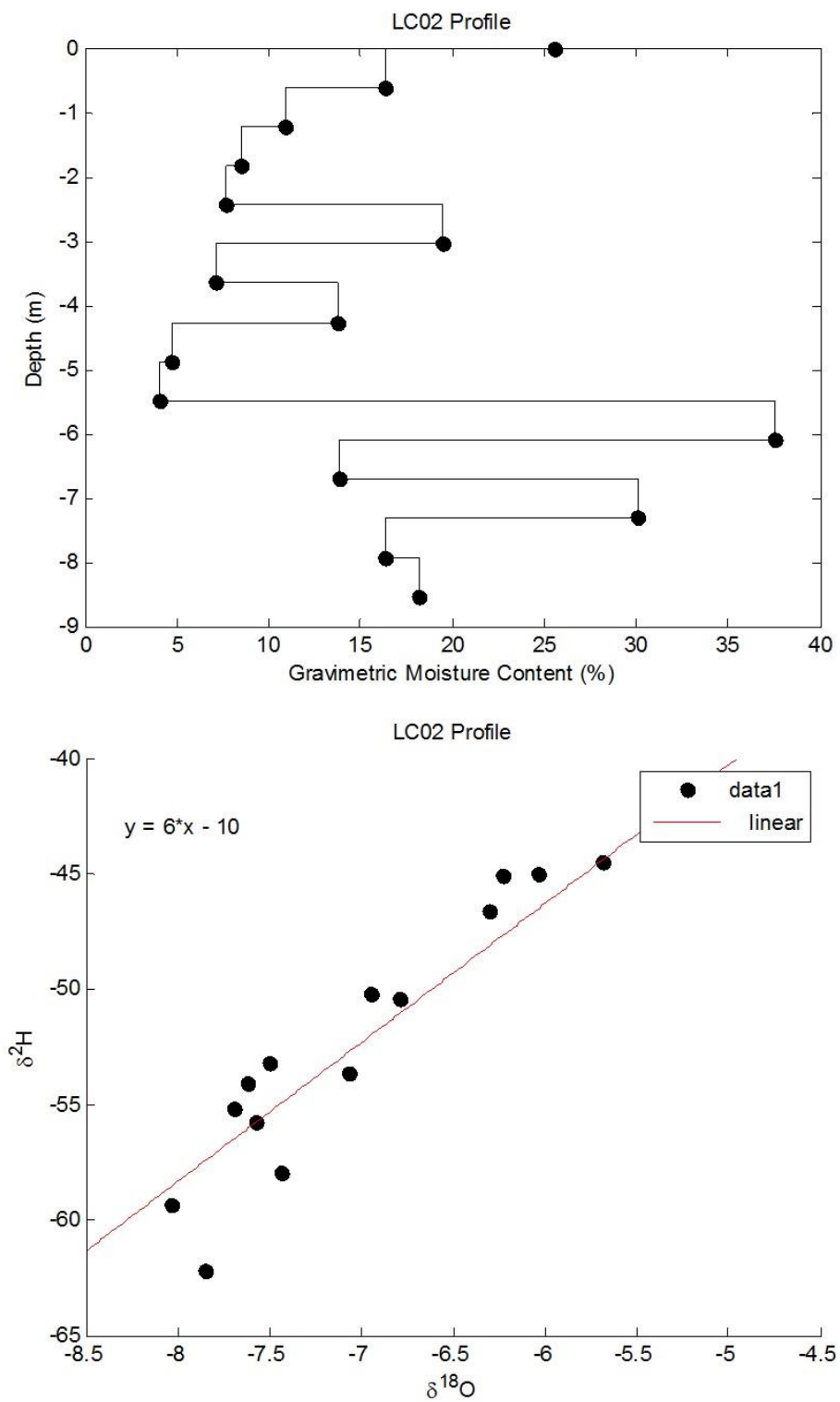


Figure 5.4b: Moisture content with depth and $\delta^{18}\text{O}/\delta^2\text{H}$ comparison for LC02.

5.4.3 Holdrege Profile

The Holdrege profile contains $\delta^{18}\text{O}$ values ranging from approximately -7.2‰ to -8.5‰, and $\delta^2\text{H}$ values ranging from -58‰ to -63‰. Vertical trends are difficult to discern given the low sampling resolution on this core. The slope of the Holdrege profile $\delta^{18}\text{O}/\delta^2\text{H}$ comparison is 3.2, although the slope is not well-defined given the small number of points. Moisture contents ranged from 14% to 24%. It is difficult to make hypotheses based on isotopic concentrations because of the low sampling resolution and lack of neighboring profile.

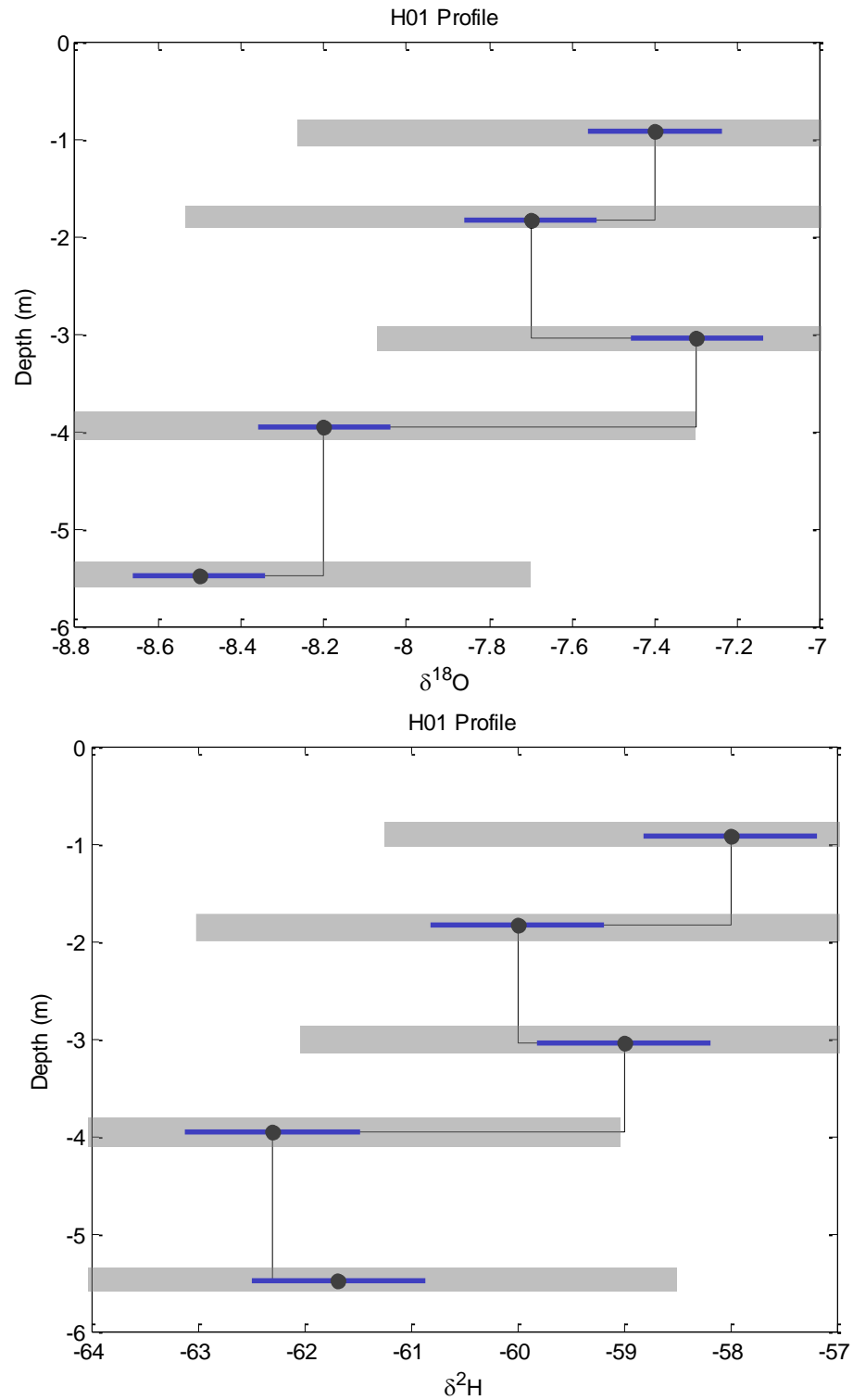


Figure 5.5a: $\delta^{18}\text{O}$ and $\delta^2\text{H}$ versus depth for H01. Blue bars indicate analytical uncertainty ($\pm 0.16\text{‰}$ $\delta^{18}\text{O}$ and $\pm 0.82\text{‰}$ $\delta^2\text{H}$). Grey bars indicate adsorption based uncertainty ($\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$).

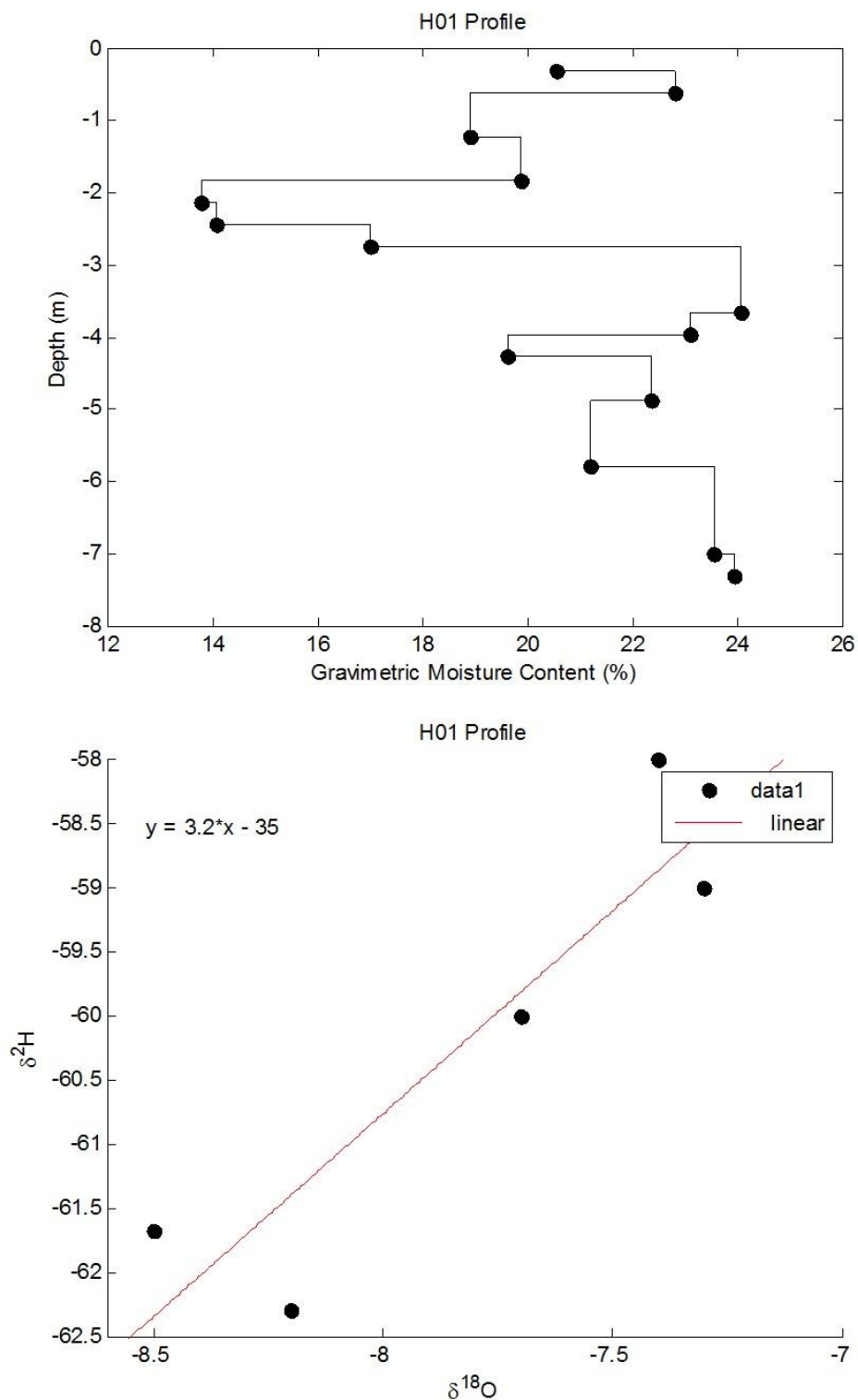


Figure 5.5b: Moisture content with depth and $\delta^{18}\text{O}/\delta^2\text{H}$ comparison for H01. Moisture content data from (Gibson, J., unpublished data).

5.4.4 Isotope Profile Comparison and Evidence for Continental Effect

The stable isotope values of the pore water from the profiles generally become more depleted from east to west (see Figure 5.6 for profile locations relative to one another). The average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the Lewis and Clark profiles are approximately -6‰ and -48‰, respectively for LC01 and -7‰ and -52‰, respectively for LC02. Further westward, the average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the H01 is approximately -8‰ and -60‰, respectively. Furthest west, the average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the Gudmundsen profiles are approximately -10‰ and -73‰, respectively for GUD01 and -10‰ and -69‰, respectively for GUD02. Figure 5.7 shows the unsaturated zone isotopic values plotted on the same graph with the GMWL and LMWL (local meteoric water line) calculated from precipitation data from Mead, Nebraska (collected from HPRCC). This pattern could be an indication of the overall continental effect influencing isotopic compositions of rainfall in the region.

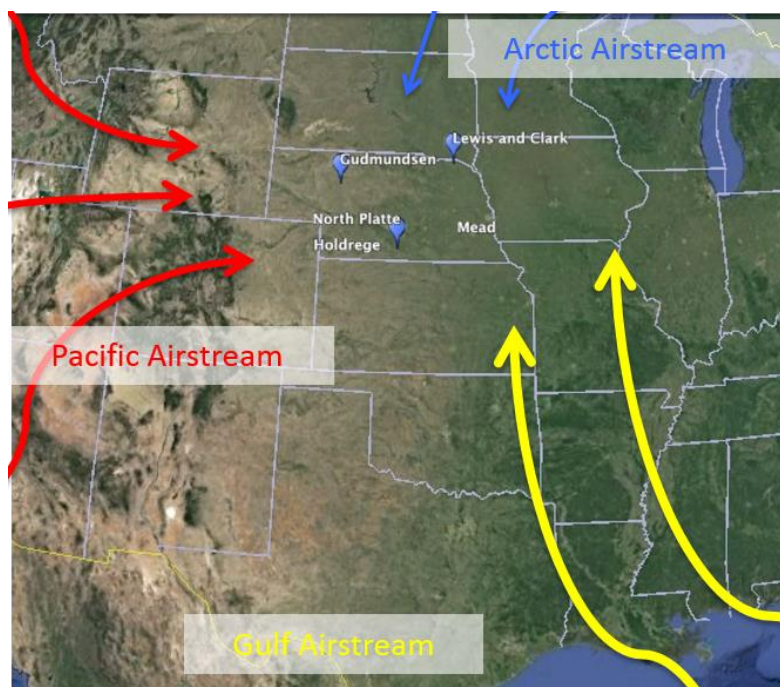


Figure 5.6: Location of profiles and competing airstreams influencing the climate and isotopic composition of precipitation in Nebraska. Adapted from Harvey and Welker (2000). From Google Earth.

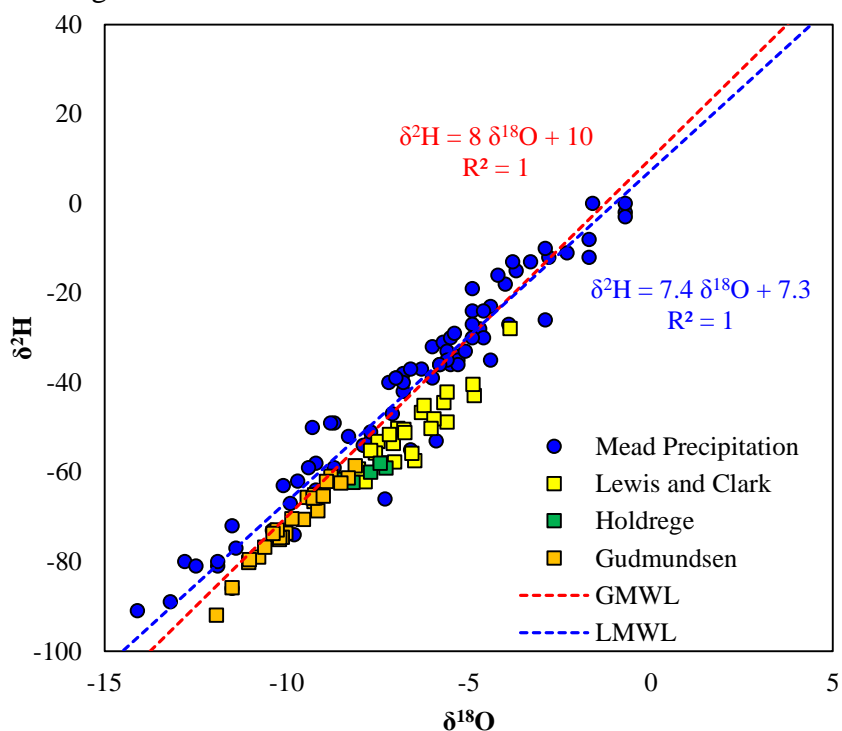


Figure 5.7: Unsaturated zone isotopic values for Gudmundsen, Lewis and Clark, and Holdrege profiles in relation to GMWL and LMWL calculated from precipitation data generated from monthly weighted averages from Mead, Nebraska.

The continental effect refers to the pattern of isotopic compositions of precipitation becoming more depleted as the air mass moves across a continent. The effect is derived from two related mechanisms: the gradual removal of moisture from the air mass during rainout, and preferential removal of heavy isotopes (Welker, 2000; Clark and Fritz, 1997; Rozanski et al., 1993). Therefore, as the Gulf airstream moves west across the state, there is preferential rain out of heavy isotopes first, resulting in a gradual isotopic depletion across the state.

Results seen in stable isotope profiles are consistent with previous isotopic precipitation studies in the area. Harvey and Welker (2000) analyzed the stable isotope compositions of precipitation from North Platte, Nebraska. These values were compared to precipitation data collected from Chicago, Illinois by the IAEA (International Atomic Energy Agency) and Mead, Nebraska, which is located in Eastern Nebraska. Harvey and Welker (2000) noted that the annual means for isotopic compositions of precipitation became more depleted further westward. For instance, the isotopic composition of precipitation in North Platte was more depleted than Mead, Nebraska; and Mead was more depleted than Chicago (Harvey and Welker, 2000). Additionally, Welker (2000) noted a coastal to continental rainout effect resulting from the Gulf of Mexico airstream moving northward. $\delta^{18}\text{O}$ values of precipitation became gradually depleted from Texas (-3‰) to Oklahoma (-5‰) and into Nebraska (-8‰; Welker, 2001).

5.4.5 Evidence of Seasonal Effects

Previous rainfall monitoring in the Great Plains region has demonstrated that strong temporal variability in rainfall isotopes occur seasonally. Seasonal variations are caused by seasonal variations in dominant moisture sources air streams (i.e. warm, moist

Gulf and Pacific streams, cold and dry Arctic winds, and warm and dry winds from the West (Harvey and Welker, 2000; Harvey, 2001). Figure 5.6 shows an illustrative interpretation of air streams affecting the state of Nebraska. This causes the climate to range from semi-arid in the western side of the state, to sub humid in the eastern side of the state (Harvey, 2001). Seasonality for mid-high latitudes is reflected through isotopically depleted precipitation in the winter months, and enriched precipitation in the summer months (Rozanski et al., 1993; Clark and Fritz, 1997; Welker, 2000 Dutton et al., 2005; Kendall and Coplen, 2001). Clark and Fritz (1997) noted the further inland, the greater the effect due to seasonality. Figure 5.8 (precipitation data from Mead, NE generated from monthly weighted averages demonstrates seasonality) further supports a seasonality effect: warmer temperatures reflect isotopically enriched precipitation, whereas cooler temperatures reflect isotopically depleted precipitation.

Harvey and Welker (2000) found that, in relation to weighted yearly averages, summer precipitation values for North Platte are much more enriched (with values of -9.8‰ $\delta^{18}\text{O}$ and -71‰ $\delta^2\text{H}$) than winter values. Harvey (2001) noted a similar pattern in Mead, Nebraska with summer values of -8.1‰ $\delta^{18}\text{O}$ and -53‰ $\delta^2\text{H}$. These values are very similar to the average values seen above. For instance, the average isotope values for all 5 profiles ranged from -6‰ to -10‰ $\delta^{18}\text{O}$ and -48‰ to -73‰ $\delta^2\text{H}$. The consistency of values suggest a seasonal effect in that temporal variations present in the unsaturated zone profiles could be due to infiltration of summer precipitation.

5.4.6 Evidence of evaporative fractionation

Calculated slopes from linear regressions are as follows: 8.2 and 7.9 for Gudmundsen profiles, 6 for Lewis and Clark profiles, and 3.2 for Holdrege. The local

meteoric water line for Mead, NE is 7.4 (values ranged from -23.6‰ to -0.7‰ $\delta^{18}\text{O}$ and -172‰ to 0‰ $\delta^2\text{H}$; n=89). The slope values for Gudmundsen and Lewis and Clark are very similar to the LMWL. Therefore, slope values for the Gudmundsen and Lewis and Clark profiles suggest that evaporation does not play a large role in evolving unsaturated zone isotopic compositions at these sites. In contrast, the slope for the Holdrege profile is much lower (3.2); and could be indicative of evaporation. However, the small number of points from the Holdrege profile is not able to constrain the slope with a high degree of confidence, and so interpretation of this slope value must remain tentative until additional analyses become available.

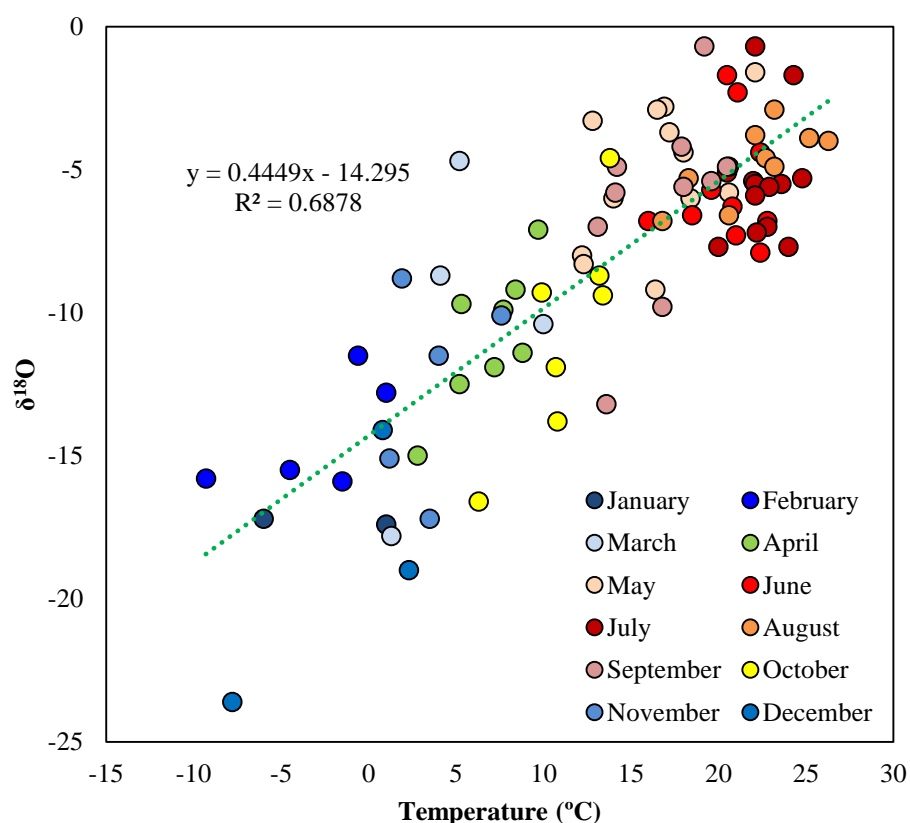


Figure 5.8: Precipitation data generated from monthly weighted averages from Mead, Nebraska. Temperature versus $\delta^{18}\text{O}$ concentrations (HPRCC).

5.4.7 Uncertainty in Profile Interpretation

Analytical errors associated with the immiscible displacement extraction method and Picarro CRDS analysis method are small relative to the apparent vertical variability found in the profiles ($\pm 0.16\text{‰}$ $\delta^{18}\text{O}$ and $\pm 0.82\text{‰}$ $\delta^2\text{H}$; indicated on figures with blue lines). However, the two standard deviations range of values from repeat spike tests is significantly larger ($\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$; indicated on figures with grey bars). This range represents the potential isotopic variability associated with adsorption-based fractionation within the profile. This error range represents a potentially confounding factor in typical stable isotope interpretation methods, which usually assume conservative tracer behavior (with the exception of evaporation). In particular, many of the apparent vertical fluctuations in isotopic values within the profiles have a magnitude less than the estimated error. For example, GUD01: depths 3-6m for $\delta^{18}\text{O}$; GUD02: depths 2-7m for $\delta^{18}\text{O}$ and $\delta^2\text{H}$; LC01: depths 1-4m for $\delta^{18}\text{O}$; LC02: depths 0-3m, 3-6m, and 6-9m for $\delta^{18}\text{O}$ and depths 3-6m and 6-9m for $\delta^2\text{H}$; and the entirety of H01. This introduces uncertainty about the robustness of many of the vertical patterns. In contrast, neighboring profiles at both the Gudmundsen site and Lewis and Clark site have very similar vertical fluctuations in isotopic values. This could be an indication that the vertical fluctuations in the profile isotopic values are primarily reflecting the temporal variability of the isotopic compositions of rainfall, rather than adsorption-based fractionation. Evaporation effects also appear to be insignificant given the similarity between unsaturated zone profile $\delta^2\text{H}/\delta^{18}\text{O}$ slope and meteoric water line $\delta^2\text{H}/\delta^{18}\text{O}$ slope.

5.5 Conclusion

Isotopic profiles across the state of Nebraska indicate the effect of two major isotopic processes, the continental effect and seasonal effect, which are superimposed to generate the overall patterns in the profiles. With the exception of the Holdrege profile, comparison to the LMWL indicates that evaporative fractionation does not significantly affect the isotopic profiles. Due to the large error associated with adsorption-based fractionation, interpreting isotopic profiles is met with some hesitation. However, some vertical fluctuations were significantly larger than the estimated error ranges. These fluctuations most likely represent a seasonality signal. In general, a possible solution to the uncertainty would be to take multiple neighboring profiles (more than two) and compare vertical fluctuations in isotopic values across an area. If vertical fluctuations are similar for all neighboring profiles, adsorption-based fractionation may not be a concern.

Chapter 6.0

Conclusion

Overall, pore water extraction from the unsaturated zone using the immiscible displacement fluid, HFE-7100, and a centrifuge has proven to be a satisfactory method for stable isotopes of water under the test conditions considered in this project. The technique is user friendly, cost-effective, and relatively quick in comparison to distillation and equilibration-based methods. Key results of the study include the following:

- HFE-7100 causes no isotopic discrimination with water exposure times up to 24 hours (maximum exposure time tested).
- Evaporation during experimentation is not a concern with the technique.
- Percent yields resulting from low moisture contents ($\leq 6\%$) indicate applicability to water-stressed regions.
- With few exceptions, the greatest percent yields resulted from high moisture contents ($> 6\%$), large grain sizes, and low clay contents.
- Pore water isotope fractionation was found in non-saline, unsaturated, highly permeable conditions, indicating a role for adsorption-related fractionation.
- Fractionation amount is not clearly associated with moisture content, clay content, or sediment chemistry, but does seem to be associated with grain size (354-710 μm grains indicate little to no fractionation).
- The standard deviation associated with fractionation due to adsorption was calculated to be $\pm 0.85\text{‰}$ $\delta^{18}\text{O}$ and $\pm 3.14\text{‰}$ $\delta^2\text{H}$ across all experiments.

- Available evidence suggests that fractionation direction is controlled by the salt effect, in which sand/clay mixtures saturated with the potassium cation become depleted relative to the spike value and mixtures saturated with sodium and magnesium cations become enriched.
- The immiscible displacement fluid technique with a centrifuge has comparable results to azeotropic distillation.
- While fractionation-related uncertainty raises concerns about the validity of unsaturated zone isotopic profile interpretations, analysis of paired field cores suggests that fractionation-related uncertainty may be smaller than the temporal variability of meteoric water in many cases.

Future research is necessary in order to refine current understanding of water isotope systematics in unsaturated zone sediments, such as mechanisms controlling fractionation amount and fractionation direction. Future work should be conducted to see if adsorption is the dominant mechanism controlling isotope fractionation, moreover, additional ions should be tested in order to determine if the salt effect is the dominant mechanism controlling fractionation direction. While fractionation-related uncertainty raises concerns about the validity of unsaturated zone isotopic profile interpretations, analysis of paired field cores suggests that fractionation-related uncertainty may be smaller than the temporal variability of meteoric water in many cases. In order to validate this, multiple neighboring profiles should be sampled, along with a greater diversity of settings.

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