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Impact of interlayer cation composition and strongly bound water on smectite δ²H, as determined by a modified TCEA method

Nadine J. Kanik, *The University of Western Ontario*

Supervisor: Longstaffe, Fred J., *The University of Western Ontario*

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Abstract

Interlayer cation composition and cation hydration enthalpy can affect the hydrogen yield and δ^{2}H of smectitic clay minerals. Condensed atmospheric water adsorbed on a clay mineral constitutes a potential additional source of hydrogen when attempting to measure the δ^{2}H of structural OH groups. To approach this problem, the δ^{2}H of different cation-saturated, dried forms of six Clay Minerals Society Source Clay smectites were measured. A modified sample drying, and on-line High-Temperature-Conversion-Elemental-Analysis (TCEA) Continuous-Flow-Isotope-Ratio-Mass-Spectrometry protocol was used to facilitate isotopic measurements. A stronger interlayer cation hydration enthalpy ($Ca^{2+}>Na^{+}>K^{+}$) caused higher residual (post-degassing) adsorbed water contents, which produced poorer smectite δ^{2}H reproducibility. Drying of K-saturated smectites for 4 hours at 220˚C produced the lowest adsorbed water contribution and the most reproducible and possibly 'accurate' δ^{2}H for smectite hydroxyl hydrogen. Notwithstanding limited rehydration potential, the TCEA method provided the lowest measurement error for hydroxyl δ^{2}H and facilitated greater sample throughput than classical methods.

Keywords

Stable isotopes, hydrogen, clay minerals, smectite, TCEA, IRMS, rehydration, dehydration, cations, adsorbed water

Summary for Lay Audience

Some clay minerals, such as smectites, are expandable and can fit positively charged ions (cations) between 2:1 layers in what is called the interlayer, similar to the filling between pieces of bread in a sandwich. Each of these cations has different abilities to hold atmospheric water vapour around itself in the interlayer. Prior to measurement of the hydrogen isotope composition (δ^2H) of hydrogen in the sheets of the clay mineral (OH hydrogen), hydrogen from adsorbed water must first be removed by heating. Accurate measurement of the δ^2H of OH hydrogen is important for understanding the history of water movement in clay-rich rocks that may be selected for underground nuclear waste storage (water that remains in the rock for millennia is best). The δ^2H of six dry smectites from the Clay Minerals Society Source Clay Project were measured to investigate how water adsorbed by cations in the interlayer, and still remaining after heating of the smectite at 220°C, can change δ^2H. A modified sample drying and on-line High-Temperature-Conversion-Elemental-Analysis (TCEA) Continuous-Flow-Isotope-Ratio-Mass-Spectrometry procedure was used for δ^2H measurements. The TCEA bakes the clay mineral at 1450°C until all hydrogen is removed, and the Mass Spectrometer measures the δ^2H of this hydrogen. The cation that held water most strongly was Ca, followed by Na, and then K. Therefore, smectites with only Ca or Na in the interlayer held onto more adsorbed water, even after being heated at 220°C for several hours, before being baked at 1450°C for δ^2H analysis. When this excess adsorbed water remained, it mixed with the OH hydrogen during baking at 1450°C and changed the measured δ^2H from what would be characteristic of OH hydrogen only. In contrast, excess adsorbed water was removed from smectites containing K in the interlayer by heating at 220°C prior to isotopic analysis. In summary, for smectites containing only interlayer K, heating for 4 hours at 220˚C prior to isotopic analysis produced the lowest adsorbed water contribution and the most reproducible and possibly 'accurate' δ^2H for smectite OH hydrogen.

Epigraph

Dedicated to my Grandmother
Dorothy Florence Kulbaba
(*August 7, 1920 - October 30, 2019*)
Your strength, humour, perseverance, and intelligence still inspire.

There once was a clay very white
Whose isotopy was not quite right
Yields were scattered
As cations mattered,
And results continue to delight.

(NJK)

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1 Introduction and Background

1.1 Project Overview

Recently, there has been increased interest in clay-rich sedimentary rock units as Deep Geologic Repositories (DGR) for the long-term storage of nuclear waste (Mazurek *et al.*, 2011; Crowe *et al.*, 2017). Clay minerals incorporate hydrogen isotopes into their structure from associated water during formation (Marumo *et al.*, 1995). The hydrogen isotope compositions obtained for a specific clay mineral can thus reflect its formation conditions (Sheppard & Glig, 1996). However, given the low permeability ($<10^{-11}$ m/s) of argillaceous sedimentary rock units (Wigger & Van Loon, 2017), long-term interaction between the clay minerals and porewater in a rock unit may modify the hydrogen isotope compositions of both (Lawrence & Taylor, 1971). If unrecognized, such isotopic exchange can lead to incorrect interpretation of the hydrogen isotope results for both clay mineral formation conditions and the origin of the porewater. An inability to identify the source of water contained in a fine-grained, low permeability sedimentary rock unit of interest for the potential location of a DGR poses safety concerns in terms of assessing its long-term hydrogeologic history (Hendry & Wasenaar, 2011). Therefore, it is imperative to understand the fundamental interactions between water and the different types of clay minerals with varying crystal chemistries, along with the associated factors and methodological considerations that can affect the hydrogen isotope compositions of clay minerals before such data can be used as a reliable proxy for porewater origin.

One such consideration concerns the methods for hydrogen isotope analysis of clay minerals. Conventional methods for analyzing the hydrogen isotope compositions of clay minerals (Godfrey, 1962; Kyser & O'Neil, 1984; Vennemann & O'Neil, 1993) are labour intensive, and largely because of sample size requirements, lack the precision and accuracy of modern instrumentation, even when conducted by the most skilled of analyst. A greatly improved method of analysis that employs High Temperature Conversion Elemental Analysis (TCEA) coupled in continuous flow mode (CF) with Isotope Ratio

Mass Spectrometry (IRMS) was introduced by Sharp *et al.* (2001) with further fundamental study undertaken by Bauer and Vennemann (2014) and VanDeVelde and Bowen (2013). A detailed, high resolution study involving a suite of specific well-characterized smectites using the TCEA-CF-IRMS method, however, is lacking in the literature. Given their expandability and high adsorptive properties, smectites can effectively adsorb water and bind water in their interlayer (Sheppard & Gilg, 1996). This makes sedimentary sites around the world that have high smectite contents of interest for the containment of nuclear waste (Keller *et al.,* 2011a&b). However, ensuring removal of this bound water for quantitative analysis is challenging as heating (degassing) at too low a temperature for a specific clay may result in incomplete removal of the bound water, whereas heating at too high a temperature may result in loss of loosely bound hydroxyl groups (Marumo *et al.*, 1995; Sheppard & Gilg, 1996).

In this study we refine and further constrain the hydrogen isotope analysis of smectite group clay minerals using the TCEA-CF-IRMS method to assess what factors contribute to the varying hydrogen isotope compositions among specific smectitic clays with different homoionic cation saturations. The investigations also suggest an approximation of what may be the 'accurate' δ^2H of the hydroxyl group hydrogen for these six standard smectites. The investigation focuses on the impacts of cation saturation and contamination by residual water contents in smectite group minerals, and how these effects are manifest in the hydrogen isotope compositions measured for such phases.

This chapter outlines the background and terminology of stable hydrogen isotope analysis, summarizes the basic principles of clay mineralogy, and explores the factors that have the potential to impact hydrogen isotope results obtained for clay minerals – smectite group minerals in particular – based on the laboratory procedures and methods used for analysis.

1.2 Stable Isotopes

Isotopes are one of two or more atoms of the same element that have the same number of protons and electrons, but which contain a different number of neutrons in their nucleus, resulting in an increase or decrease of atomic mass for a given isotope of a specific element. “Stable isotopes” refers to an isotope that has a stable nucleus, that is, it does not undergo radioactive decay, at least on timescales that can currently be measured.

The stable isotope fractionation factor (α) for a given element (E) between two phases or substances, A and B, is defined as:

$$\alpha \mathrm{E}_{\mathrm{A-B}} = \frac{\mathrm{R}_{\mathrm{A}}}{\mathrm{R}_{\mathrm{B}}} \qquad (Eq. 1.1)$$

where R_{A} is the ratio of the rare (heavy) isotope to the common (light) isotope for phase A and R_{B} is the same ratio for phase B.

For a given phase, its stable isotope results are reported in delta (δ) notation, and most commonly expressed in “per mil” (‰), which is parts per thousand. The use of the milli urey (mUr) notation has recently been suggested by Coplen (2011) and is now appearing in some papers. The ‰ designation, however, is still the most common means of reporting used by the broader isotope community and is retained here.

The δ-value is the difference between the isotope ratio of a given element in a sample (R_{A}) and a reference standard ($\mathrm{R}_{\mathrm{standard}}$) and is defined as:

$$\delta \mathrm{E}_{\mathrm{A}} = \frac{(\mathrm{R}_{\mathrm{A}} - \mathrm{R}_{\mathrm{standard}})}{\mathrm{R}_{\mathrm{standard}}} \qquad (Eq. 1.2)$$

This approach enables the differences in isotopic ratios between two substances to be measured more precisely than absolute isotope concentrations. Positive δ-values indicate the sample is enriched in the heavy isotope of a given element relative to the reference standard, whereas negative δ-values indicate that the sample is depleted of the heavy isotope relative to the reference standard. The measure of isotope fractionation between two phases is termed the α-value (*Eq*. 1.1) and is particularly important for understanding equilibrium isotope exchange between phases (Sharp, 2017).

The relationship between α and δ for phases A and B is defined as:

$$\alpha_{\text{A-B}} = \frac{1 + \delta_{\text{A}}/1000}{1 + \delta_{\text{B}}/1000} = \frac{\delta_{\text{A}} + 1000}{\delta_{\text{B}} + 1000} \qquad (Eq. 1.3)$$

The isotopic fractionation factor (α) is temperature-dependent provided equilibrium is established between the two phases being described. For an ideal gas, lnα varies as a continuum of $1/T^2$ (K) at high temperatures and 1/T (K) at low temperatures. This behaviour is commonly expressed as “per mil” fractionation, which is defined as 1000lnα. As expected, “per mil (‰)” fractionation decreases with increasing temperature in an equilibrium system.

1.2.1 Hydrogen

Hydrogen was initially produced during the ‘Big Bang’ and is the most abundant element in our solar system. It is also abundant and important on Earth as water (H_2O) and in combination with other elements (Faure & Mensing, 2005; Sharp, 2017). Hydrogen has two stable isotopes ^{1}H (protium) and ^{2}H (deuterium). On Earth, the mean natural abundance of ^{1}H is 99.985 %, with ^{2}H accounting for only 0.015 % (Faure & Mensing, 2005). The masses of the two isotopes differ, with ^{2}H being 99.8 % (2.0140amu) heavier than ^{1}H (1.007825 amu). This mass difference subsequently affects the strength of covalent bonds formed between the isotopes of hydrogen and atoms of other elements (Faure & Mensing, 2005). The δ^2H of ocean water is ~0 ‰ by nature of how the international standard in the δ-definition is defined (see below). Most other natural materials on Earth have negative δ^2H (Sharp, 2017).

Stable hydrogen isotope compositions reported in this study are expressed using δ-notation, with VSMOW (Vienna Standard Mean Ocean Water) as the standard (Coplen, 2011):

$$\delta^2\text{H} = \frac{(^2\text{H}/^1\text{H})_{\text{sample}} - (^2\text{H}/^1\text{H})_{\text{standard}}}{(^2\text{H}/^1\text{H})_{\text{standard}}} \qquad (Eq. 1.4)$$

where $(^{2}H/^{1}H)_{sample}$ is the ratio of the ^{2}H and ^{1}H molar concentrations in the measured sample and $(^{2}H/^{1}H)_{standard}$ is the isotope ratio of the reference standard. While $\delta^{2}H$ is reported relative to VSMOW, the measured values are pinned to a two-point calibration defined by accepted values for VSMOW (0 ‰) at one end and Standard Light Antarctic Precipitation 2 (SLAP2) (–427.5 ‰) at the other end (Sharp, 2017; International Atomic Energy Agency, 2017).

1.2.2 Hydrogen Isotopes in the Environment

An example of hydrogen isotope fractionation in nature arises from the effects of latitude during a process termed Rayleigh distillation, whereby water vapour and precipitation from an airmass undergo fractionation of hydrogen isotopes as the air mass migrates from low to high latitudes (Clark & Fritz, 1997). As an airmass moves to higher latitudes it cools and increasingly loses its ability to carry moisture (Clark & Fritz, 1997). This results in a preference for the heavy isotope (^{2}H) of hydrogen to enter rainout as precipitation, causing the water vapour remaining in the airmass, and any subsequent precipitation, to have increasingly negative $\delta^{2}H$ with increasing latitude. Therefore, the value of precipitation from an airmass at low latitudes initially having $\delta^{2}H$ of ~ –6 ‰ would subsequently decrease to ~ –30 ‰ by mid-latitudes and ~ –110 ‰ upon reaching high latitudes (Attendorn & Bowen, 2012).

These differences in the $\delta^{2}H$ of precipitation subsequently impact the $\delta^{2}H$ of water in the local environment, resulting in differences in $\delta^{2}H$ of minerals formed in different geographical locations during weathering or other processes involving meteoric water (Lawrence & Taylor, 1971; Sharp, 2017; Faure & Mensing, 2005).

This behaviour is illustrated in diagrams by Lawrence and Taylor (1971) and Sharp (2017) in which hydrogen and oxygen isotope data for soil kaolinite demonstrate that its $\delta^{2}H$ at different latitudes is reflective of the average meteoric $\delta^{2}H$ at the sampling location.

1.3 Clay Minerals

Clay minerals are phyllosilicates that are characterized by a large surface area associated with a very small grain size, typically $<2\mu m$ (Grim, 1968; Brindley & Brown, 1980; Moore & Reynolds, 1989). The large surface to volume ratio of clay minerals contributes to their unique properties, which include highly reactive surfaces, plasticity, expandability, water retention properties when wet, high cation exchange capacities, and catalytic activity (Brindley & Brown, 1980; Moore & Reynolds, 1989).

In clay mineralogy nomenclature a *plane* refers to a flat surface connecting points on a straight line, a *sheet* refers to a homogenous linkage of tetrahedra or octahedra, a *layer* consists of joined tetrahedral and octahedral sheets. A *structure unit* indicates a complete layer and interlayer assemblage containing one or more chemical formula units, as described by Brindley and Brown (1980).

Clay minerals contain both tetrahedral and octahedral sheets. The tetrahedral sheets are composed of SiO_4 tetrahedra, where the silicon atom is situated between one unshared apical oxygen and three basal oxygens, which link the tetrahedra together to form a sheet. The edge-linked octahedra, which make up octahedral sheets, are composed of six hydroxyl groups surrounding a central cation, most commonly Al^{3+}, Mg^{2+}, Fe^{2+} or Fe^{3+}. Whether a clay mineral is dioctahedral or trioctahedral is defined by the cation or cations within the octahedral sheet, with cation substitution occurring most commonly in the octahedral sheet. To meet the 6-charge unit structure requirement, dioctahedral minerals have one vacant site and two octahedral sites filled with 3+ cations, and trioctahedral minerals have all three octahedral sites filled with 2+ cations, per $O_{10}(OH)_2$ unit formula.

There are major groups of layer silicate minerals, based on a 1:1 or 2:1 layer type, layer charge, and type of interlayer. Further classification of species and sub-groups is based on chemical composition, octahedral sheet type, and the layer and interlayer geometry of superposition (Brindley & Brown, 1980; Moore & Reynolds, 1989). The 1:1 layer is formed when a single tetrahedral and octahedral sheet are bonded, where hydroxyl (OH) groups comprise the uppermost unshared plane of anions in the octahedral sheet. A common example of a 1:1 structured clay is kaolinite. A 2:1 layer, which is characteristic of smectite, is formed by bonding an octahedral sheet between two tetrahedral sheets; this is facilitated by an inversion of the upper tetrahedral sheet, which enables bonding of the apical oxygens with the octahedral sheet (Brindley & Brown, 1980) (Fig. 1.1).

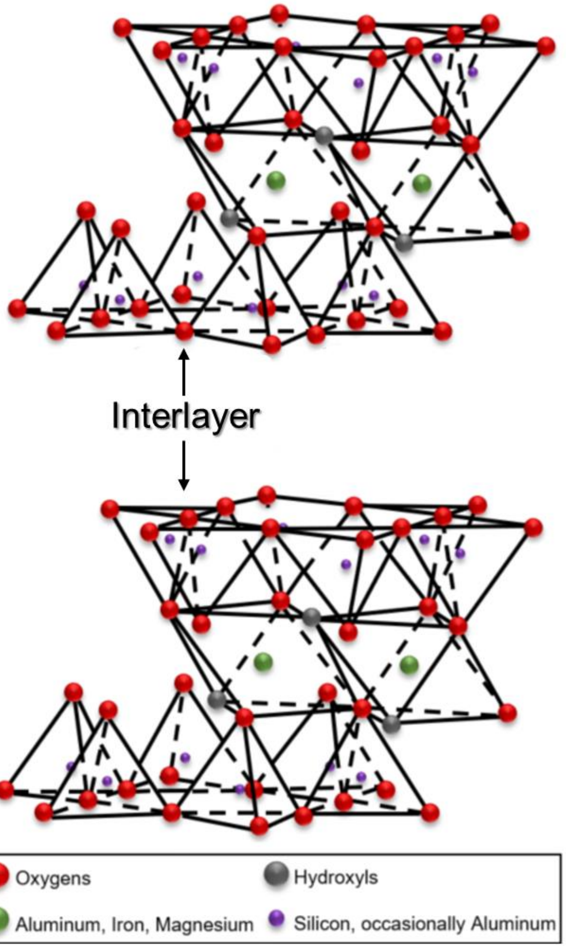

Figure 1.1. Structure of a 2:1 clay mineral, depicting two tetrahedral-octahedral-tetrahedral three-sheet layers with the interlayer space between the two layers (after Longstaffe, 2000).

Therefore, the shared apical oxygens and unshared OH groups in the middle of each six-fold tetrahedral ring form a common plane of junction between the tetrahedral and octahedral sheets (Brindley & Brown, 1980).

The surface and interlayer spaces of a clay mineral are typically negatively charged, which then attracts cations. The negative charge results when ions, possessing a lesser charge, substitute into the sheets. Common possibilities include Al^{3+} replacing Si^{4+} in the tetrahedral sheet, and Mg^{2+} or Fe^{2+} replacing Al^{3+} or Fe^{3+} in the octahedral sheet (Brindley & Brown, 1980). This produces a layer with a negative charge of 0 to 1 per formula unit, where the composition of the formula unit, to be balanced by cations, is $[O_{10}(OH)_2]$ (Bailey, 1980). The layer charge provides a means of further classifying 2:1 clay minerals, with that of smectite, being negative and ranging between 0.2 to 0.6 (e^-) per formula unit, compared to that of vermiculite and mica, with negative layer charges of 0.6 to 0.9 and 1, respectively (Bailey, 1980). The presence of a layer charge indicates an electrical imbalance between the tetrahedral and octahedral sheets. This charge can be balanced by adsorbing ions to the surface or incorporating them within the interlayer spaces (Grim, 1968). The adsorbed/incorporated ions are typically Na^+, Ca^{2+}, and Mg^{2+}, but exchange reactions may also introduce other cations or organic ions (Brindley & Brown, 1980). These cations are then hydrated in the presence of H_2O and effectively bind H_2O to the surface and interlayer spaces of the clay mineral. The effects of the layer charge and incorporation of cations and further hydration enables the expansion of the interlayer in some 2:1 clay minerals. The 2:1 clay minerals may be either expandable or non-expandable upon hydration. A typical example of a non-expandable 2:1 clay mineral is illite, while expandable types include smectite and vermiculite.

Clay minerals are the primary products of the rock weathering process and are formed at the surface of the Earth by chemical reactions between mineral materials and water. Clay minerals may be neoformed, transformed or detrital, depending on the geotectonic setting and thermal history of the formation environment (Merriman, 2005). Detrital clay minerals are those physically transported into new locations, (*e.g.*, sedimentary basins, continental shelves) from weathering of outcrops. During direct transport, modification of the clay mineral is minimal; detrital clay minerals deposited into sedimentary basins may be thought of as having inherited characteristics from their source, at least prior to having undergone any diagenetic or metamorphic changes at their new location. An example is provided by the inherited clay minerals that occur within foreland basins near eroded mountain belts (Merriman, 2002). Neoformed, meaning newly formed, clay minerals are formed by *in situ* precipitation from solutions, such as ferromagnesium-rich clay minerals formed around submarine hydrothermal vents where hot, Mg-rich seawater and basaltic crust react (Merriman, 2002, 2005). Neoformed clay minerals may also form in many other settings, such as hypersaline, sedimentary basin environments, where volcanic glass or ash may be deposited and altered to smectite by the high alkalinity (Hillier, 1993). Transformation refers to clay minerals that have been modified from one variety to another during largely solid-state reactions, which are posited to occur during burial diagenesis by some researchers (*e.g.*, Eberl, 1984). In other words, a clay mineral may be partially modified by a chemical reaction, while still keeping some of its original or 'inherited' structure intact. A couple of chemical reactions, as stated by Eberl (1984), that result in transformation of clay minerals are ion exchange and layer transformation. For ion exchange, ions that are loosely bound to the clay are exchanged with ions from the surrounding environment. During layer transformation, modifications occur in the arrangement of cations fixed in the interlayer or in the tetrahedral and octahedral sheets. Natural examples of these reactions include acid leaching of potassium ions (K^+) from illite to form smectite and the conversion of randomly ordered illite-smectite, to ordered illite-smectite, and finally illite, with increasing depth and temperature, and addition of the necessary components (*e.g.*, K^+).

Clay minerals contain both hydrogen and oxygen. This feature provides a valuable dual system for assessing the paleoclimate of a location by using the hydrogen and oxygen isotope signatures captured by a clay mineral during weathering (Lawrence & Taylor, 1971) or water-rock interaction during diagenesis and hydrothermal alteration (Bechtel & Hoernes, 1993; Marumo *et al.*, 1995). The transition from smectite to illite, for example, has been used to provide information on past thermal regimes within sedimentary basins dominated by fine-grained mudstones and shales (Altaner *et al.*, 1984; Altaner *et al.*, 1989).

Clay minerals are also valuable in multiple industrial applications. A few examples include their use as effective binders for pharmaceutical drugs to slow the rate that medications are released in the body (Djebbi *et al.*, 2018) and to identify complications that can be associated with extraction of oil from oil-sands using hot water and steam (McKay & Longstaffe, 2013).

An extremely important use of clay minerals concerns the storage of nuclear waste. A full understanding of clay mineral crystal-chemistry in this application is relevant both for the host rock selected for a potential Deep Geologic Repository (DGR) (Mazurek *et al.*, 2011) and for the choice of the major material to be used in the barrier system to envelop used nuclear fuel cell during placement and storage in a DGR (Crowe *et al.*, 2017). The advantage of using clay-rich rocks and barrier materials for nuclear waste storage is related to the properties of clay-rich rocks. These properties include extremely low hydraulic conductivities ($<10^{-11}$ m/s) and a strong adsorption of radionuclides, which slows migration of radionuclides through molecular diffusion and reduces the possibility of fast radionuclide transport via advective water movement (Wigger & Van Loon, 2017). Argillaceous (clay-rich) rock formations are considered as host lithologies for DGRs, as a result of their small pore sizes (1 to 100 nm), which create a high sealing capacity (Keller *et al.*, 2011b). In addition to clay minerals in the host rock, bentonites, which are primarily composed of smectite, are of interest as a barrier material around the metal canisters holding the used nuclear fuel cells, creating a dual barrier system (Keller *et al.*, 2011a; Kaufhold *et al.*, 2017).

1.3.1 Smectites

This study focuses on smectites, which are a group of clay minerals that may be dioctahedral or trioctahedral and possess the ability to maintain their two-dimensional crystallographic integrity while undergoing expansion or contraction of their interlayer space (Moore & Reynolds, 1989). In general, the variations of aluminum (Al^{3+}), magnesium (Mg^{2+}), and iron (Fe^{3+}, Fe^{2+}) concentrations in the octahedral sheet enable differentiation among smectites, whereas the tetrahedral sheet is primarily composed of silicon (Si^{4+}) and oxygen (O^{2-}). A smectite is considered dioctahedral if it is Al-rich, as it takes two Al^{3+} to neutralize the layer charge, and trioctahedral if it is Mg-rich, as it requires three Mg^{2+} to neutralize the layer charge.

The ideal structural formulae for dioctahedral and trioctahedral clay minerals are:

$$M^{+}_{A+B}(Al_{2-A}Mg_{A})(Si_{4-B}Al_{B})O_{10}(OH)_{2}\text{, and}$$
$$M^{+}_{B-A}(Mg_{3-A}Al_{A})(Si_{4-B}Al_{B})O_{10}(OH)_{2}\text{,}$$

respectively, where M^+ is an exchangeable cation (usually Ca^{2+}, Na^+, Mg^{2+}, K^+). The expandability of smectites enables the interlayer cation to be readily exchanged with another cation, which facilitates an increased cation exchange capacity compared with that of other clay minerals (Moore & Reynolds, 1989). Smectites expand variably depending on relative humidity and cation saturation (Cases *et al.*, 1997). The types of water associated with smectitic clay minerals include: (i) adsorbed water, on the surface of the clay mineral, and (ii) interlayer water, which forms hydration spheres around the cations within the expandable interlayers of smectites, and can collectively be called bound water (BW) (Brindley & Brown, 1980; Cases *et al.*, 1997; Longstaffe, 2000; Kuligiewicz & Derkowski, 2017). A third source of hydrogen occurs in the form of hydroxyl groups (OH), which is tightly bound within the structure of the clay mineral (Brindley & Brown, 1980; Sheppard & Gilg, 1996).

The size, valency, and hydration enthalpy of a cation determines how tightly it will bond with the structural oxygen and hydroxyl groups in a smectite and affects how many equivalent layers of water can exist within the interlayer space at a specific relative humidity (Berend *et al*., 1995; Cases *et al.*, 1997). A monovalent or large cation (*e.g.*, Cs^{+1}, K^{+1}) can sustain one stable water layer in the smectite interlayer, over a large range of relative humidity (RH); in the same domain, smaller, divalent cations (*e.g.*, Ca^{2+}, Mg^{2+}) can support two stable water layers (Berend *et al.*, 1995). This means that at a given RH below 100˚C, the quantity of adsorbed water in a smectite is primarily controlled by the hydration enthalpy of the interlayer cation (Berend *et al.*, 1995; Cases *et al.*, 1997).

Different amounts of interlayer water are associated with each cation, and thus have the potential to produce different hydrogen isotope compositions for the types of water associated with smectites of varying cation saturations (Marumo *et al.*, 1995).
As such, it is necessary to remove – commonly by thermal methods – the adsorbed, bound water (BW) from the surface and interlayer of a clay mineral prior to isotopic analysis of its structural hydroxyl hydrogen. If both the BW and structural hydroxyl are removed together, the resulting contamination from BW leads to inaccurate measurement of hydroxyl δ^2H (Marumo *et al.*, 1995). Determining the temperature at which BW can be removed completely without also removing more loosely bound hydroxyl groups from the smectite is difficult (Marumo *et al.*, 1995). In one study, all smectites observed still contained up to 3 water molecules for each interlayer cation after being dried at 110°C, with amounts of BW decreasing in relation to the type of interlayer cation as follows, Mg>Ca>Na>Cs (Kuligiewicz & Derkowski, 2017).

The temperature required for complete BW removal has previously been suggested to range from 150 to 250°C (Wolters & Emmerich, 2007; Bauer & Vennemann, 2014; VanDeVelde & Bowen, 2013). The exact temperatures of heating at which BW is completely removed, and loss of structural hydroxyl begins, however, is variable among smectites (Longstaffe, 2000; Kuligiewicz & Derkowski, 2017). For complete dehydroxylation, very high temperatures are required, typically >1000°C for full decomposition of the clay structure (Marumo *et al.*, 1995; Bauer & Vennemann, 2014; Qi *et al.*, 2017). The general range at which 2:1 clay minerals dehydroxylate typically lies between 300 and 800°C for dioctahedral varieties and 700 to 1000°C for trioctahedral varieties (Vedder & Wilkins, 1969; Kawano & Tomita, 1991a). These temperatures are only a guide, however; Fe-rich nontronite, for example, can dehydroxylate at < 300˚C, compared to Fe-poor smectites, which dehydroxylate at >300˚C (Kuligiewicz & Derkowski, 2017).

1.4 Stable Isotopes in Clay Minerals

The isotope compositions of structural oxygen and hydrogen in clay minerals have been widely used to facilitate paleoclimate reconstruction and obtain geologic information, such as: the origin or formation conditions of a mineral (Mizota & Longstaffe, 1996); temperature of crystallization (Hornibrook & Longstaffe, 1996); water origin (*e.g.*, fresh water, sea water, brine) associated with clay formation, particularly during diagenesis (Longstaffe, 1983, 1984; Gilg *et al.*, 2013; Savin & Lee, 1988); and extent of isotopic equilibrium among the clay minerals, fluids, and other minerals (Lawrence & Taylor, 1971). Interpretation of the isotopic data, however, is dependent on the clay mineral having retained its original isotopic composition and not having undergone change during post-formation processes such as dissolution, isotopic exchange, or inheritance from previous/other minerals (Longstaffe & Ayalon, 1990; Mizota & Longstaffe, 1996; Longstaffe, 2000; He *et al.*, 2019). To improve the interpretive power of such investigations, better knowledge of the isotopic discrimination/exchange among water in contact with clay minerals, clay mineral BW and structural hydroxyl groups is required (Marumo *et al.*, 1995).

The primary factors controlling the hydrogen isotope composition of a clay mineral have previously been identified to be the crystal chemistry, crystallite size, temperature, and surface area (Savin & Epstein, 1970; Longstaffe, 1987, 2000). While there are a number of studies that address the general dehydration of smectite (Marumo *et al.*, 1995; Wolters & Emmerich, 2007; Derkowski *et al.*, 2012a,b; Kuligiewicz & Derkowski, 2017; Derkowski & Kuligiewicz, 2017), very few comprehensively address the hydrogen isotope discrimination/exchange among mobile water, bound water, and hydroxyl groups in clay-rich rocks (Savin & Lee, 1988; Longstaffe, 2000). The idea that the hydrogen isotope composition of a clay mineral might be modified by post-formation isotopic exchange with its environment was considered but rejected in several foundational studies (Sheppard *et al.*, 1969; Savin & Epstein, 1970; Yeh & Savin, 1976; Lawrence & Taylor, 1971; Yeh & Epstein, 1978; Yeh & Eslinger, 1986). Those works generally concluded that hydrogen isotope exchange between clay minerals and water was insignificant at surface and near-surface temperatures. More recently, other researchers have argued that such exchange can and does occur at temperatures as low as 30°C, depending on water/rock ratio and duration of post-formation contact with water (Bird & Chivas, 1988; Longstaffe & Ayalon, 1990; Mizota & Longstaffe, 1996; see below).

A few early studies attempted to quantify the hydrogen isotope fractionation factor (α) for smectite-water, but the results have remained variable. The hydrogen isotope fractionation factor of 0.94 reported by Savin and Epstein (1970) for smectite-water at deep sea temperatures was later determined to be unreliable (Savin & Lee, 1988), as those authigenic smectite samples from deep sea sediments did not undergo removal of potentially contaminating hydroxide minerals before isotope analysis was done.

Lawrence and Taylor (1971) also noted that during the dehydration procedures intended to remove BW from smectite, there was partial exchange between the hydroxyl hydrogen and interlayer water, thus allowing only an approximate measurement of the smectite-water hydrogen isotope fractionation. However, this issue for smectite was not reported by other workers (Savin & Lee, 1988). Lawrence and Taylor (1971) also estimated the smectite-water hydrogen isotope fractionation to be ~0.97 for all smectites at weathering temperatures. They further observed that iron-poor smectite contains more ^{2}H than iron-rich smectite from the same profile.

Based on the hydrogen isotope compositions of illite-smectite from thick shale sequences of the U.S. Gulf Coast over 29 to 120°C, Yeh (1980) proposed an illite/smectite-water hydrogen isotope geothermometer of:

$$1000 \ln \alpha_{\text{(clay-water)}} = -19.6 \times 10^{3} T^{-1} + 25,$$

where T is in kelvin.

Capuano (1992) proposed an illite/smectite-water hydrogen isotope geothermometer of:

$$1000 \ln \alpha_{\text{(clay-water)}} = -45.3 \times 10^{3} T^{-1} + 94.7,$$

where T is in kelvin.

The assumptions associated with such geothermometers are that 1000 ln$\alpha_{\text{illite/smectite-water}}$ change linearly with 1/T over the measured temperature range. In the case of the Yeh (1980) geothermometer, $\alpha_{\text{illite/smectite-water}}$ at 25°C is ~ 0.96.

As mentioned above, more recent research has indicated that post-formational exchange of hydrogen isotopes between clay minerals and water can occur independently of oxygen isotope exchange (Bird & Chivas, 1988; Longstaffe & Ayalon, 1990; Sheppard & Gilg, 1996). Experiments conducted by O'Neil & Kharaka (1976) demonstrated that hydrogen exchange was very slow at low temperatures but nonetheless was notably faster than for oxygen. Below 100°C a significant amount of hydrogen isotope exchange can occur; by 200°C hydrogen isotope exchange is extensive and can still occur exclusive of exchange of oxygen isotopes in clay minerals (Longstaffe, 2000). A possible cause of this behavior is that hydrogen isotope exchange between clay minerals and water may be controlled by replacement of H^+ as opposed to OH at lower temperatures (O'Neil & Kharaka, 1976; Kharaka *et al.*, 1986). In contrast, OH replacement becomes more important for controlling clay-hydrogen isotope exchange with water at higher temperatures (Longstaffe, 2000).

1.5 Rehydration Effects

Beyond the uncertainty surrounding hydrogen isotope fractionation factors and exchange temperatures between clay minerals and water, atmospheric rehydration causes a further methodological complication when attempting to determine the hydrogen isotope composition of smectitic clay minerals. As mentioned above, clay minerals, particularly expandable 2:1 varieties such as smectite, are extremely hydrophilic. Therefore, rehydration from laboratory atmospheric water vapour has the potential to modify the hydrogen isotope compositions obtained for clay mineral samples (Bauer & Vennemann, 2014). As such, it is imperative to limit any potential for rehydration of a clay mineral sample after the drying process used to prepare the sample for hydrogen isotope analysis (Longstaffe, 2000). There is high potential for partial rehydration, for example, during the transfer of the sample from a drying chamber into the device being used to make the isotopic measurements.

The potential for rehydration is particularly important for expandable clay minerals such as smectite. For example, a Clay Minerals Society (CMS) smectite standard (SWy-1) analyzed by Bauer and Vennemann (2014) had a reported δ^2H of ~ –130 ‰. According to the structural formula of SWy-1:

$(Ca_{0.18}Na_{0.01}K_{0.01})(Al_{1.54}Mg_{0.25}Fe^{3+}_{0.21})(Si_{3.88}Al_{0.12})O_{10}(OH)_2$ (Srodon & McCarty, 2008),

SWy-1 has a corresponding structural water yield of 4.74 wt. %. Addition of adsorbed water with a δ^2H of ~ –60.9 ‰, condensed onto the smectite from laboratory atmospheric water vapour with a δ^2H of ~ –133 ‰ (a not uncommon value in lower latitude laboratories), has significant potential to modify the isotopic composition presumed to be obtained for the structural hydroxyl hydrogen isotope composition of SWy-1. As modeled in Figure 1.2, the δ^2H of SWy-1 is highly susceptible to change over a range of adsorbed water contents.

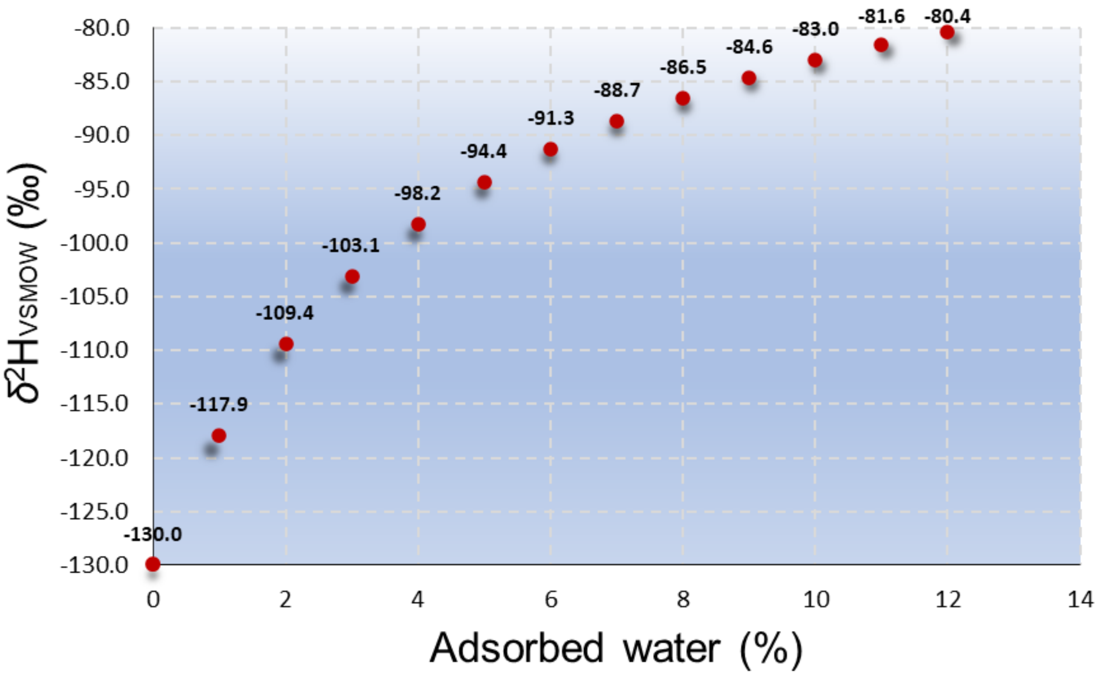

Figure 1.2. Plot of δ^2H for the SWy-1 smectite for a modeled range of adsorbed water contents from 0 to 14 %, assuming an average δ^2H of –60.9 ‰ for water condensed and adsorbed onto the clay at 21°C from laboratory atmospheric water vapour with an δ^2H of –133 ‰.

For example, starting from a smectite δ^2H of –130 ‰ for hydroxyl hydrogen in a completely dehydrated state, the measured δ^2H increases by ~ 50 ‰ for an adsorbed water content of 10 %. An adsorbed water content of 10 % is common for swelling clay minerals at a relative humidity of only ~ 20 %, with the potential for the smectite to hold > 30% of its weight in adsorbed water at a relative humidity of ~ 90 % (Michot & Villieras, 2006). For the same parameters, Figure 1.3 provides a higher resolution of the model of how smectite δ^2H can vary in the range of 0 to 2 % adsorbed water contents, which is the range that typically has the most impact on the apparent δ^2H of a dried smectite during analytical procedures (Kuligiewicz & Derkowski, 2017).

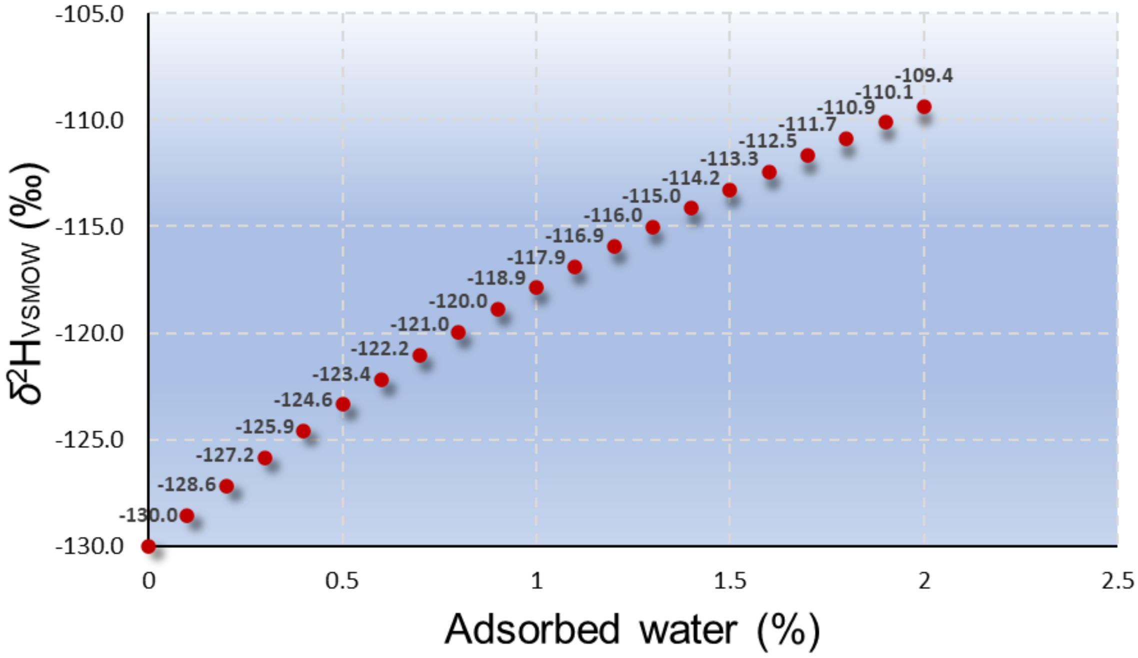

Figure 1.3. Plot of δ^2H for SWy-1 containing up to 2 % adsorbed water and assuming an average δ^2H of –60.9 ‰ for water condensed and adsorbed onto the clay at 21°C from laboratory atmospheric water vapour with an δ^2H of –133 ‰.

1.6 Hydrogen Isotope Measurement Methodology

The conventional method of water extraction from hydrous minerals for hydrogen isotope analysis is based on the approaches of Godfrey (1962), Kyser and O'Neil (1984), and Vennemann and O'Neil (1993). The principle of the method is based on prior complete removal of bound water at a given temperature (see previous discussion) from the clay mineral and subsequent dehydroxylation and/or dehydrogenation of the hydroxyl groups in the structure of the clay mineral by thermal decomposition at ~ 1000°C.

Two models have been proposed for dehydroxylation. The first, which is common in dioctahedral 2:1 clay minerals, proceeds via the formation of water (H_2O) by neighboring hydroxyl groups (OH). The newly formed water molecules diffuse out of the clay structure through the interlayer, leaving behind residual oxygen (O_r) according to the following equation (Vedder & Wilkins, 1969; Guggenheim *et al.*, 1987; Drits *et al.*, 1995):

$$(OH)_{2n} \rightarrow nH_2O + nO_r \qquad (Eq. 1.5)$$

The second model, which applies to trioctahedral 2:1 clay minerals, proceeds through migration of an H^+ proton to a OH group, thereby forming and releasing an H_2O molecule as follows (Wang *et al.*, 2015):

$$H^+ + (OH)^- \rightarrow H_2O \qquad (Eq. 1.6)$$

Dehydrogenation takes place where iron is associated with the clay mineral, and reduces the quantity of OH groups available for dehydroxylation by the release of hydrogen from oxidation of Fe^{2+}, thus forming hydrogen gas ($H_{2(gas)}$) from hydrogen radicals ($2H\bullet\uparrow$) as follows (Rouxh *et al.*, 1972; Rancourt *et al.*, 2001; Steudel *et al.*, 2016):

$$Fe^{2+} + OH^- \rightarrow Fe^{3+} + O_r^{2-} + H\bullet\uparrow \qquad (Eq. 1.7)$$

The conventional analytical method typically involves heating several tens of mg of clay mineral sample in a quartz glass tube, within a tube furnace, under vacuum, for a desired time, at a specific temperature, to remove adsorbed water. If desired, a step-wise heating pretreatment procedure may be employed, whereby adsorbed water evolved over successive temperature ranges (*e.g.*, 25-100°C, 100-200°C, 200-300°C, 300-400°C) for a given period of time can be collected and its δ^2H analyzed (Marumo *et al.*, 1995). The furnace temperature is then increased to ~1000°C to fully decompose and dehydroxylate the clay mineral structure to ensure the complete release of H_2O – presumed to contain only hydroxyl group hydrogen – which is then trapped at −196°C. Alternatively, a fuel gas-oxygen torch may be used to heat the sample for ~10 minutes, instead of heating in a tube furnace, to decompose the sample; this latter method relies heavily on the skill and consistency of the operator. Copper oxide, at ~550°C, is then used to oxidize any molecular hydrogen produced at this time to water. Hydrogen gas ($H_{2(g)}$) is then produced from the total water collected, by reacting the collected water over powdered chromium (or depleted uranium, if available) at ~900°C. The $H_{2(g)}$ is then transferred quantitatively to a glass tube filled with activated charcoal held at −196°C. Once all $H_{2(g)}$ has been collected, the glass tube is sealed and transferred to an inlet port on an IRMS, where the $H_{2(g)}$ is released and its δ^2H measured.

The conventional method is still used for measurement of clay mineral δ^2H, particularly as a baseline / gold standard during development of new analytical methods. A major advantage of this approach is that samples are never exposed to atmospheric contamination following dehydration but prior to isotopic analysis. The method, however, has several disadvantages. These include: (i) the need for a large amount of sample (typically ~30-100 mg, depending on the clay mineral); (ii) operator inconsistency during torch-induced dehydroxylation; (iii) each analysis may take 45-60 minutes; (iv) sample preparation and quality control measures are lengthy for this method, which allows analysis of only 3-4 samples per day, and (v) very little of the analysis can be automated, which makes it very labour-intensive. These factors prompted the need for development of new methods that are faster, require smaller samples and achieve equivalent or better accuracy and precision.

1.7 Previous Work

The development of continuous-flow isotope ratio mass spectrometry (CF-IRMS) coupled to a high temperature conversion elemental analyzer (TCEA) in the late 1990s enabled the δ^2H analysis of hydrogen-bearing solids, water samples, and gases to be faster, more economical, and sometimes more precise (Qi *et al.*, 2017; Begley & Scrimgeour, 1996; Burgoyne & Hayes, 1998; Hilkert *et al.*, 1999). Sharp *et al.* (2001) first applied the on-line TCEA coupled with CF-IRMS method to non-expanding hydrous minerals, including amphibole, biotite, and muscovite. This method has the advantage of being rapid, at ~4 minutes per sample and requires a very small amount, 1-20 mg, of sample material depending on its hydrogen content (Qi *et al.*, 2017). This advance has resulted in a change in project analytical designs from those investigating only a few samples to studies involving the much larger numbers of samples and sample replicates needed to facilitate meaningful statistical analysis.

Bauer and Vennemann (2014) built on the TCEA CF-IRMS method of Sharp *et al.* (2001) by analyzing the δ^2H of expandable hydrous minerals, which included smectitic clay minerals, mainly montmorillonite from the Molasse sediments from the Northern Foreland Basin of the European Alps. The study comprehensively explored variables that may impact the δ^2H of the hydrous minerals and notably identified the potential for atmospheric contamination of samples, between heating/degassing under active vacuum to remove bound water and the transfer to the autosampler of the TCEA CF-IRMS.

The standards analyzed by Bauer and Vennemann (2014) were an in-house biotite and kaolinite, along with the SWy-1 montmorillonite from the CMS Source Clay Repository. Samples were degassed under active vacuum from 150 to 250°C for 3 to 9 hours to remove adsorbed water, then torch-sealed in a glass vial for storage, which was opened only immediately prior to loading in the TCEA autosampler to minimize rehydration of the samples. They compared the δ^2H obtained for the clay minerals from the TCEA-CF-IRMS method to the conventional method and concluded that a degassing temperature of 250°C for three hours effectively removed adsorbed water and did not cause differences in δ^2H for smaller crystallite sizes contrary to what was noted for degassing at 150°C. Simply put, when samples, having a specific crystallite size range were degassed at 150°C, the samples with a relatively smaller grain size (<0.1 μm compared with <2 μm) returned variable δ^2H. Bauer and Vennemann (2014) also noted that when dehydrated samples were stored under vacuum and quickly transferred to the TCEA autosampler, contamination by atmospheric water vapour was greatly reduced.

A subsequent study by VanDeVelde and Bowen (2013) used the TCEA-CF-IRMS method to evaluate how several common chemical pretreatments used for the removal of organic matter and carbonate minerals during the analysis of 2:1 clay minerals impacted the δ^2H of hydroxyl hydrogen. This study also offers some insights into the temperature and time needed to remove BW and minimize readsorption of atmospheric water during transfer to the TCEA-CF-IRMS system. The methods of Van DeVelde and Bowen (2013) followed Sharp *et al.* (2001), but used a purpose-built vacuum glass line and muffle furnace for degassing and heating prior to TCEA-CF-IRMS analysis. Among the smectites analyzed, the crystal-chemistry of one in particular, SCa-3 (montmorillonite), was well-constrained, as it is another of the CMS Source Clay Repository materials. The sample transfer time, and hence exposure to laboratory atmosphere, between their drying and the TCEA was stated to be <5 minutes. Multiple degassing temperatures were used in order to find the temperature that produced minimum $H_{2(g)}$ yields, thus indicating that adsorbed water had been removed. To determine if a minimum hydrogen yield had been achieved, was calculated from the difference between the theoretical hydrogen yield of the hydroxyl groups- based on the structural formula of the clay- and the actual hydrogen yield, obtained during analysis. The difference between these yield values indicates the excess hydrogen remaining in the form of adsorbed water (or other H-bearing contaminants) from that theoretically derived from the hydroxyl hydrogen present in an ideally ‘dry’ clay mineral. Therefore, the minimum hydrogen yield represents the lowest amount of excess hydrogen derived from adsorbed water after degassing at a given temperature, compared to the hydroxyl hydrogen yield expected from a dry clay mineral. Importantly, the temperature must be high enough to effectively remove adsorbed water, but still low enough so as not to remove loosely bound hydroxyl group hydrogen.

For montmorillonite, minimum $H_{2(g)}$ yields were obtained after 4 hours of degassing at 200°C, with no changes noted for samples heated for a longer time. When the same montmorillonite was degassed at 350°C, it reached the same minimum yields in only 2 hours; however, the measured δ^2H were ~6 % higher than samples degassed at 200°C, likely resulting from dehydroxylation of structural OH groups (Van DeVelde & Bowen, 2013). Samples degassed at 100°C produced $H_{2(g)}$ yields well above the minimum attained at the higher temperatures, indicating that this temperature was not high enough to remove all adsorbed water, despite a longer heating time of 8 hours being used.

Therefore, Van DeVelde and Bowen (2013) recommended that the drying (degassing) temperature not exceed 200°C, in contrast to the 250°C recommenced by Bauer and Vennemann (2014), and that 4 hours at 200°C was required to remove all adsorbed water. The longer heating time of 4 hours, compared with shorter periods suggested in other studies, was attributed to the tightly folded metal capsules in which the samples were contained for degassing and subsequent isotopic analysis using the TCEA-CF-IRMS method. Bauer and Vennemann (2014) also cautioned more generally that care should be employed to quantify any procedures related to TCEA-CF-IRMS analysis that have the potential to alter the hydrogen isotope compositions of the samples.

The studies of Sharp *et al*. (2001), Bauer and Vennemann (2014) and VanDeVelde and Bowen (2013) provide a fundamental starting point for accurate analysis of the hydroxyl hydrogen isotope composition of smectites, and indeed the method has been employed in several studies of the δ^2H of the hydroxyl hydrogen in hydrous phyllosilicates (Bojar *et al.*, 2009; Dekoninck *et al.*, 2015; Buatier *et al.*, 2016; Compendex & Elsevier, 2016; Grujic *et al.*, 2018). That said, there is still uncertainty regarding the degassing time and temperature that should be used. In general, the chemical composition of smectite group minerals, and its possible impact on δ^2H measurements has not been quantified in detail. In particular, the effects of differing cation-saturations on the degassing and rehydration properties of various types of smectites, and the attendant consequences for δ^2H, have not been fully considered.

There is one additional complication associated with the previous foundational studies (*e.g.*, Sharp *et al*., 2001; Bauer & Vennemann, 2014; VanDeVelde & Bowen, 2013) that used the TCEA-CF-IRMS method to determine the hydrogen isotope compositions of hydrous minerals. In these studies, the international biotite reference standard NBS 30 was used for calibration of phyllosilicate δ^2H. Recent work, however, showed that δ^2H obtained for this standard using the TCEA-CF-IRMS method are unreliable (Qi *et al*., 2014). Another problem is that the NBS 30 biotite supply is now exhausted and no longer available. This prompted the development of two new standards for the hydrogen isotope analysis of hydrous minerals using the TCEA-CF-IRMS method (Qi *et al*., 2017). These new standards are USGS-57 (biotite) and USGS-58 (muscovite), and were shown to avoid the problems that arose with NBS 30. Therefore, USGS-57 and USGS-58 were used in this study to provide a robust two-point calibration for the hydrogen isotope results obtained for all phyllosilicate minerals.

1.8 Thesis Structure

The current study investigates whether the δ^2H of smectite hydroxyl hydrogen can be precisely and “accurately” determined using the efficient and cost-effective TCEA-CF-IRMS method. The focus here is on smectites for which the interlayer cation has been controlled, and the consequences of that approach for accurate and precise measurement of hydroxyl hydrogen δ^2H. Chapter 2 describes the mineralogical characterization of the materials used in this study, Chapter 3 describes the methods for isotopic and thermogravimetric data collection, Chapter 4 presents the results, which are then discussed in Chapter 5. The main conclusions are summarized in Chapter 6.

Chapter 2

2 Geological, Mineralogical, and Particle-Size Characterization of Samples

2.1 Clay Samples

Sample materials for this study were selected from the Clay Minerals Society (CMS) Source Clay Repository, currently housed at Purdue University. These are natural, homogenous mega-samples of individual clay minerals, which contain minimal impurities and have well-studied physical and chemical properties. The current study focuses on smectites from the CMS collection, and includes three montmorillonites, one saponite, one hectorite, and one nontronite (also considered a Fe-rich montmorillonite). The selection of the six smectites was based on the differing chemical and physical properties of each, where smectites STx-1, SAz-1, SWy-1, and SWa-1 are dioctahedral and SapCa-1 and SHCa-1 are trioctahedral (Table 2.1).

Table 2.1. Characteristics of smectite samples used in this study (Moll, 2001; Baker & Strawn, 2014) with δ^2H (Fagan, 2001) and structural formulae (Srodon & McCarty, 2008).

Sample	Species	Octahedral Structure	Origin (U.S.A.)	Age	Formation Conditions	Structural Formula	$\delta^2H_{\mathrm{VSMOW}}$ (‰)
STx-1	Montmorillonite	dioctahedral	Gonzales, Texas	Eocene	marine, sedimentary	$(Ca_{0.21}Na_{0.01}K_{0.00})(Al_{1.54}Mg_{0.39}Fe^{3+}_{0.07})(Si_{3.96}Al_{0.04})O_{10}(OH)_2$	–118±2 (n=9)
SAz-1	Montmorillonite	dioctahedral	Apache County, Arizona	Pliocene	marine, sedimentary	$(Ca_{0.23}Na_{0.02}K_{0.01})(Al_{1.39}Mg_{0.54}Fe^{3+}_{0.09})Si_4O_{10}(OH)_2$	–122±11 (n=7)
SWy-1	Montmorillonite	dioctahedral	Crook County, Wyoming	Cretaceous	non-marine, sedimentary	$(Ca_{0.18}Na_{0.01}K_{0.01})(Al_{1.54}Mg_{0.25}Fe^{3+}_{0.21})(Si_{3.88}Al_{0.12})O_{10}(OH)_2$	–135±6 (n=8)
SapCa-1	saponite	trioctahedral	near Ballart, California	Pliocene	hydrothermal	$(Ca_{0.20}Na_{0.00}K_{0.00})(Mg_{2.91}Fe^{3+}_{0.06}Al_{0.01})(Si_{3.58}Al_{0.42})O_{10}(OH)_2$	–133±7 (n=6)
SHCa-1	hectorite	trioctahedral	Hector, California	Pliocene	hydrothermal	$(Ca_{0.16}Na_{0.01}K_{0.01})(Mg_{2.57}Li_{0.32}Al_{0.04})(Si_{3.96}Al_{0.04})O10(OH_{1.35}F_{0.65})$	–130±15 (n=3)
SWa-1	nontronite	dioctahedral	Grant County, Washington	Mid-Miocene	hydrothermal	$(Ca_{0.22}Na_{0.00}K_{0.01})(Fe_{1.20}Al_{0.65}Mg_{0.13})(Si_{3.74}Al_{0.26})O_{10}(OH)_2$	–156±7 (n=6)

The following information regarding the origin and possible formation mechanisms of these smectites has been described by Moll (2001) and references therein. The STx-1 montmorillonite occurs at the base of the Manning Formation in eastern Gonzales County, Texas, U.S.A. It was formed by alteration of volcanic ash of rhyolitic composition. A couple of mechanisms have been proposed for its formation, in order to account for its Mg content. One mechanism suggests that ash fell into a lagoon or coastal water body and the Mg was acquired from seawater. The other suggests that alteration of the ash was caused by ascension of subterranean brines along fault planes. The SAz-1 montmorillonite has its origin in the Biadhochi Formation near Defiance Plateau in Apache County, Arizona. U.S.A. It was formed by ashfall into lakes and streams, wherein occurred the conversion of vitric tuff to smectite. Magnesium for formation was supplied by the surrounding rocks or lake and stream waters. The SWy-1 montmorillonite was collected from the Newcastle Formation in Crook County Wyoming, U.S.A. It was formed by deposition of volcanic rhyolitic ash into a sea or lake. This smectite is naturally rich in Na, suggesting that a Na-rich solution moved through the deposit, perhaps after the main period of alteration.

According to the descriptions of Post (1984), the SapCa-1 saponite was found at an elevation of ~ 488 m, on a steep hillside, near Ballarat, California, U.S.A. It occurs within open fracture zones and joints in metamorphosed dolomitic limestone that are part of the Late Cambrian Noonday Dolomite Formation, located near the base of the Panamint Range. In the last 100,000 years, it is stated that Lake Panamint submerged the limestone structure containing the saponite, at least five times. However, during recent episodes of flexing and faulting in the area, hydrothermal replacement of the dolomitic limestone may have occurred at a depth below the weathering profile. As the saponite is confined to the fracture zones and not found nearby in the playa, is has been surmised that the source of Mg for the saponite was from phreatic ground water, as opposed to being supplied by the dolomite, leading to the conclusion that the saponite likely formed via hydrothermal alteration.

Volcanic rocks in the Mohave Desert near Hector, California, U.S.A. are associated with the formation of the SHCa-1 hectorite. It originates from a complex igneous terrain in southeastern California. The SHCa-1 hectorite is Li-bearing. One scenario for its formation is alteration of dacitic volcanic ash, with recrystallization of the overlying limestone adding calcite to the deposit. Another possible scenario for formation of SHCa-1 has been suggested to be the combination of volcanic ash deposition into an ancient lake overlying a fault and the flow of hotsprings from the fault, with addition of Mg from the lake water.

The location and formation conditions of SWa-1 have been investigated in detail by Baker, 2017 and are as follows. The SWa-1 nontronite / iron-rich montmorillonite originates from near Trinidad, Washington, U.S.A, and was collected from directly below a basalt-paleosol contact, where the basalt flowed over the paleosol. The overlying basalt flow is part of the Frenchman Springs Member of the Wanapum Basalt of the Columbia River Basalt Group. The paleosol was stated to have developed on top of the underlying Grand Ronde Basalt. Features at the contact are suggested to indicate that the paleosol was wet at the time it was covered by the basalt flow. The mixing of the hot lava and wet soil likely resulted in hydrothermal alteration of both the lava and the soil. This suggests formation of this smectite by alteration of the aluminous paleosol by hot hydrothermal fluids containing dissolved Si, Mg, and Fe (Baker and Strawn, 2014) (Baker, 2017).

The sampling location, geologic age, formation conditions and structural formulae of these samples are summarized in Table 2.1. The montmorillonites (STx-1, Saz-1, SWy-1) used in this study are all Al-rich, with much smaller amounts of Mg and Fe. In contrast, the saponite (SapCa-1) and hectorite (SHCa-1) are Mg-rich. The nontronite (SWa-1) is Fe-rich and is dioctahedral. The hectorite (SHCa-1) contains extensive Li^+ substituted for Mg^{2+}, and F^- substituted for OH^-, in its octahedral sheet.

Kaolinite (KGa-1) and illite (IMt-1), also from the CMS Source Clay Repository, were chosen as respective 1:1 and 2:1, non-expandable reference materials for comparison with the results obtained for the expandable smectitic clay minerals. The KGa-1 aliquot used in this study is referred to as KGa-1 RT, where RT refers to maintenance of the standard at room temperature when not in use.

2.2 Sample Preparation

Size fractionation was performed at *The* University *of* Western Ontario's Laboratory for Stable Isotope Science (LSIS). The <2 μm size fraction was obtained via dispersion of ~10 g of each of the six smectites in 1000 mL of distilled water, followed by gravity settling in a 30-cm column, according to Stoke's law (Jackson, 1968). This step was repeated several times until the water in the upper portion of the settling column was clear, to ensure capture of all the <2 μm clay size fraction. The same approach was used for the first batch (#1) of illite (IMt-1). A second batch (#2) of the <2 μm size fraction of IMt-1 was prepared by centrifugation (Jackson, 1968). The KGa-1 kaolinite was analyzed directly as shipped and not processed in anyway. This unprocessed KGa-1 has well-understood characteristics as it has been used in the LSIS as both an oxygen and hydrogen isotope standard for the conventional analysis of hydrous minerals for more than 30 years.

The six smectites were treated to remove hydrogen-bearing organic matter by addition of ~200-400 ml (depending on clay flocculation) of 6 % sodium hypochlorite to the ~1000 ml beaker containing the clay solution and placed in a 65 °C water bath overnight (Jackson, 1968; Ignasiak *et al.*, 1983; Sheppard & Gilg, 1996). The samples were then stirred and transferred to several 15 mL centrifuge tubes. The samples were then washed with DI water using ultrasonication at 700 watts for one minute and centrifuged for ~12 minutes at ~ 17,000 rpms in a refrigerated centrifuge held at 18°C. These latter steps were repeated several times to ensure complete removal of bleach and other reaction byproducts. Following Ignasiak *et al.* (1983), the washed samples were then each split into three portions. Two portions were saturated with ~15 mL 2M KCl and ~15 mL 2M $CaCl_2$, respectively, to produce K-saturated and Ca-saturated samples. The KCl and $CaCl_2$ treated samples were again washed several times and the supernatant tested with 1 % silver nitrate solution to ensure the complete remove of KCl or $CaCl_2$. The third aliquot of each washed sample was deemed to have become Na-saturated during the bleaching process. The illite and kaolinite samples were not bleached or treated to produce a specific exchangeable cation saturation.

The samples did not undergo any further chemical purification; for example, there was no use of hydrogen peroxide, sodium/acetic acetate buffers, toluene-soxhlet extractions or buffered sodium dithionite to remove trace carbonates, organics, or Fe-(oxy) hydroxides as the possibility of altering the original hydrogen and oxygen isotope compositions of the clay minerals outweighed the benefits of removing very small trace impurities (Fagan, 2001; VanDeVelde & Bowen, 2013).

The cation-saturated and washed samples were then covered with a KimWipe, frozen, and then cryophilized using a LabConco Triad freeze-dryer (collector temperature -85˚C, shelf temperature -5˚C) in the plastic centrifuge tubes. Following drying, the samples were lightly ground by hand with a glass stir rod and transferred to sealed glass scintillation vials for storage until needed.

2.3 XRD Analysis

The character and purity of the <2 μm size fractions of the smectite samples were determined using a Rigaku rotating anode X-ray diffractometer (XRD) (Co Kα radiation = 1.790210 Å, 45 kV potential, 160 mA current). Briefly, a basal plane preferred orientation of ~20 mg of each sample was obtained by its suspension in water, pipetting the suspension onto a glass slide, and allowing the wet suspension to air-dry on the glass slides (Moore & Reynolds, 1989). Broadly following Ignasiak *et al*. (1983), XRD patterns for each of the K-saturated samples was then obtained after: (i) heating at 107˚C for 12 hours (0 % relative humidity (RH)) and analyzed while still hot, then (ii) following overnight equilibration over saturated $MgNO_3$ (54 % RH), then (iii) heating at 300˚C for 3 hours, and finally (iv) heating at 550˚C for 2 hours. Separate analyses were performed for the Ca-saturated sample, first (i) after overnight equilibration over saturated $MgNO_3$ (54 % RH) and then (ii) following overnight ethylene glycol vapour saturation under static vacuum at 65°C and further equilibration at room temperature for at least 24 hours. The XRD patterns were obtained over the range 2-42 ˚2Θ Co Kα at 10°/minute at a 0.02

2Θ interval, for all sample preparations, except for those saturated with ethylene glycol, which were analyzed from 2-82 °2Θ Co Kα.

2.3.1 XRD Interpretation

The XRD diffraction results confirmed that the clay mineral samples are smectites with only minimal traces of impurities. Sharp 001 peaks with a *d*-spacing of ~15 Å, which is indicative of Ca-saturated smectite at 54 % relative humidity (RH), were observed for all samples (Moore & Reynolds, 1989; Brindley & Brown, 1980) (Figs. 2.1-2.6).

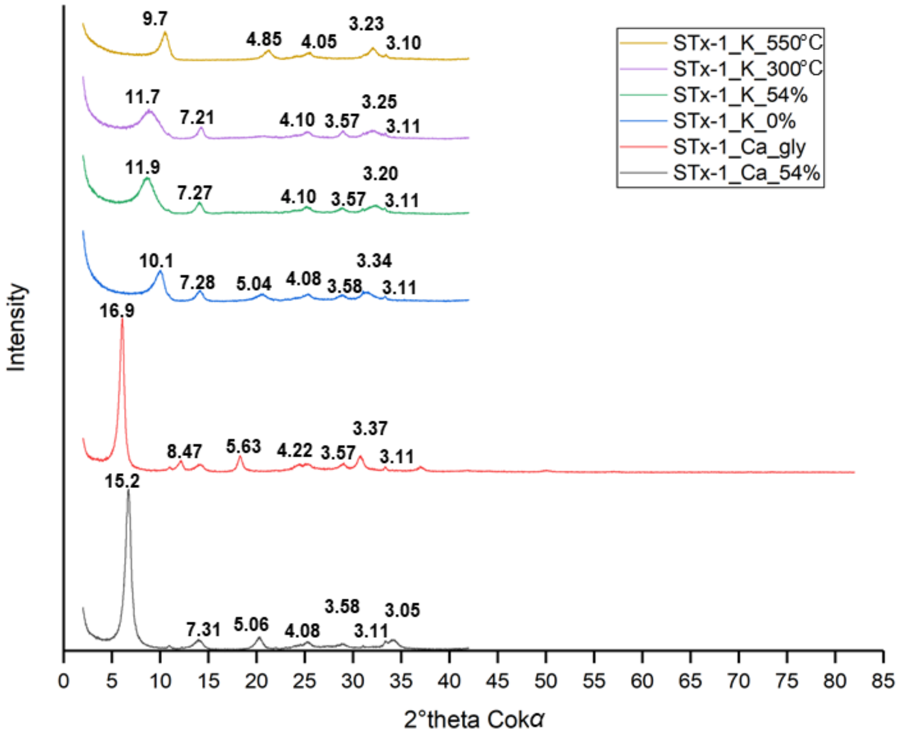

Figure 2.1. XRD patterns of each of the six different treatments for preferred-orientations of the Ca- and K-saturated forms of STx-1 (montmorillonite). The letters K and Ca in the legend refer to the exchangeable cation-saturation. Temperatures of heating are denoted by 300°C and 550°C, and 'gyl' = glycolated sample.

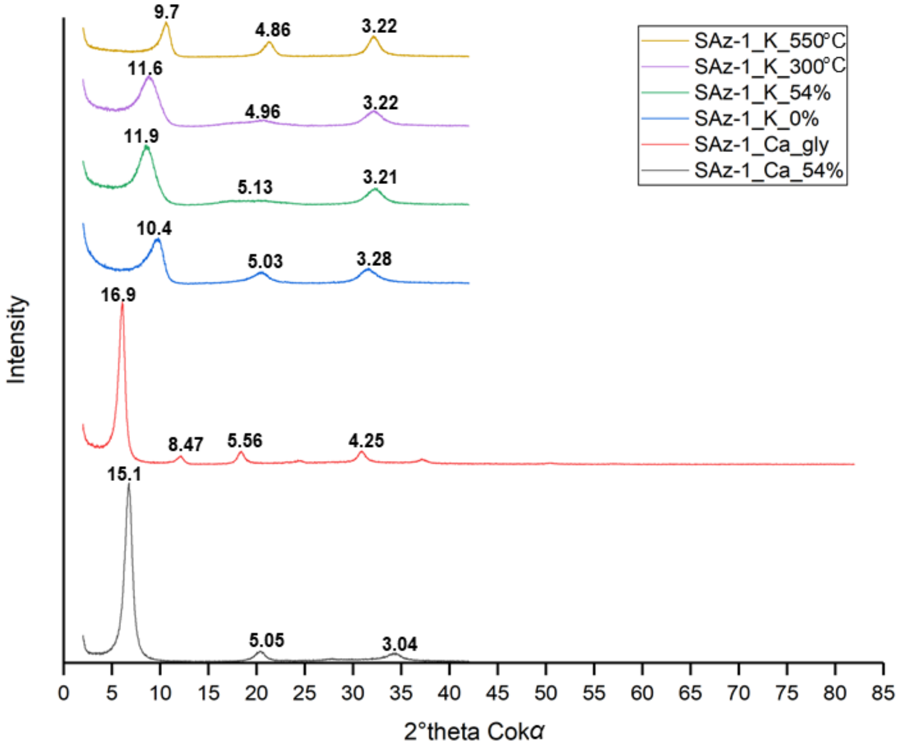

Figure 2.2. XRD patterns of each of the six different treatments for preferred-orientations of the Ca- and K-saturated forms of SAz-1 (montmorillonite). The letters K and Ca in the legend refer to the exchangeable cation-saturation. Temperatures of heating are denoted by 300°C and 550°C, and 'gyl' = glycolated sample.

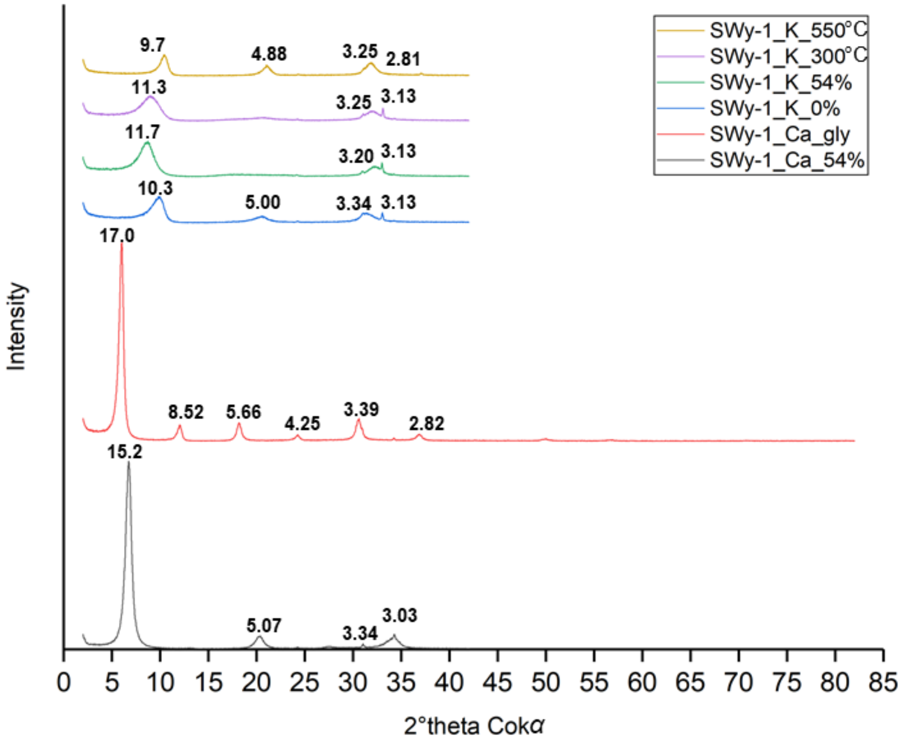

Figure 2.3. XRD patterns of each of the six different treatments for preferred-orientations of the Ca- and K-saturated forms of SWy-1 (montmorillonite). The letters K and Ca in the legend refer to the exchangeable cation-saturation. Temperatures of heating are denoted by 300°C and 550°C, and 'gyl' = glycolated sample.

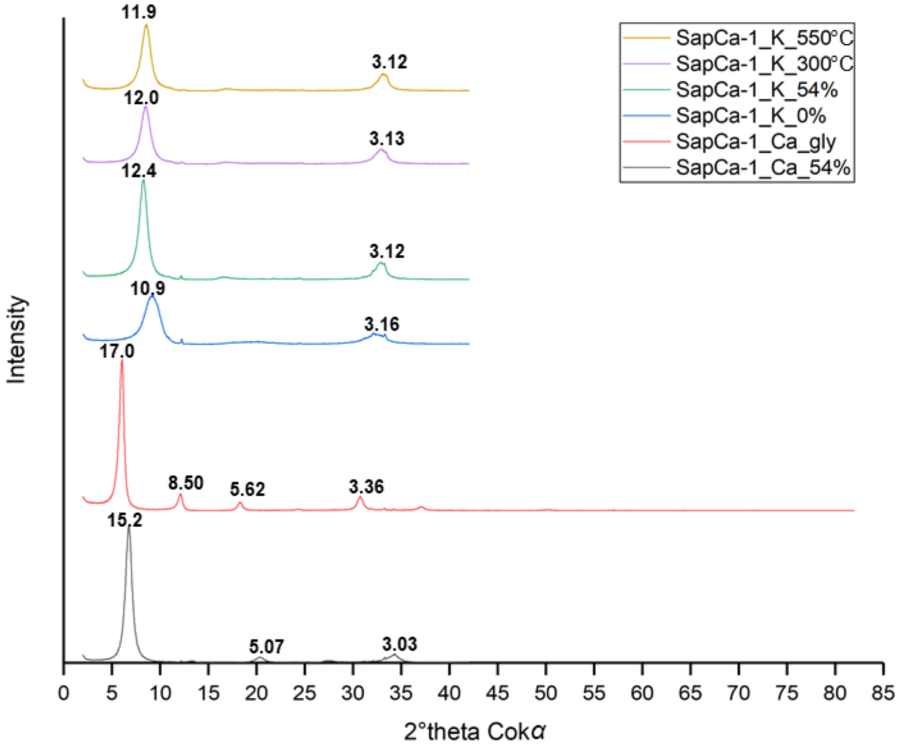

Figure 2.4. XRD patterns of each of the six different treatments for preferred-orientations of the Ca- and K-saturated forms of SapCa-1 (saponite). The letters K and Ca in the legend refer to the exchangeable cation-saturation. Temperatures of heating are denoted by 300°C and 550°C, and 'gyl' = glycolated sample.

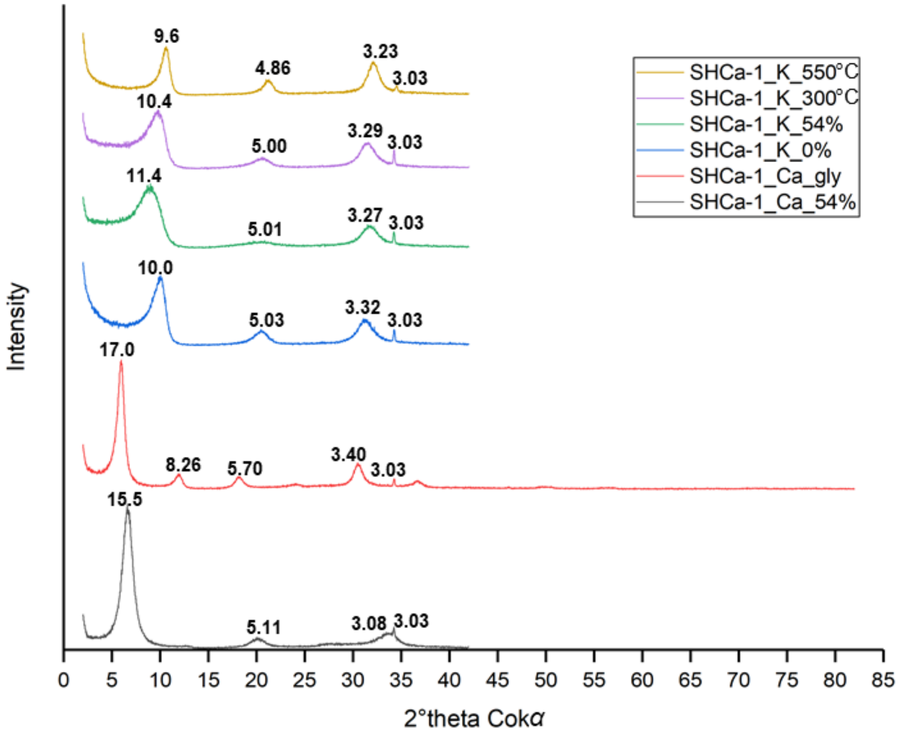

Figure 2.5. XRD patterns of each of the six different treatments for preferred-orientations of the Ca- and K-saturated forms of SHCa-1 (hectorite). The letters K and Ca in the legend refer to the exchangeable cation-saturation. Temperatures of heating are denoted by 300°C and 550°C, and 'gyl' = glycolated sample.

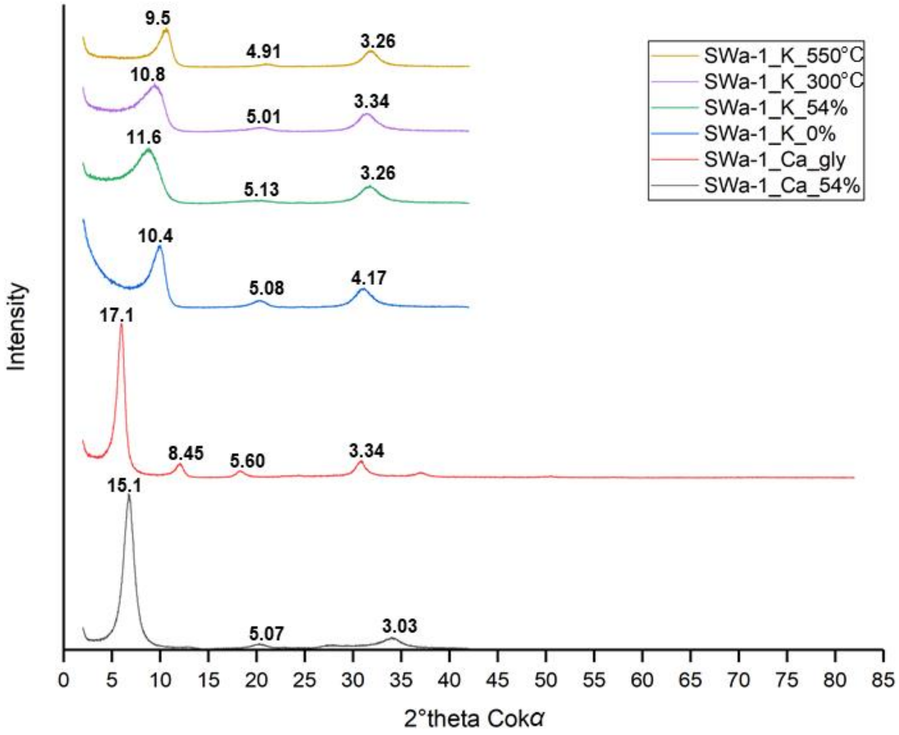

Figure 2.6. XRD patterns of each of the six different treatments for preferred-orientations of the Ca- and K-saturated forms of SWa-1 (nontronite). The letters K and Ca in the legend refer to the exchangeable cation-saturation. Temperatures of heating are denoted by 300°C and 550°C, and 'gly' = glycolated sample.

The <2 μm size fraction has previously been shown to be purer than the bulk sample, of the same material, for these CMS Source Clay Repository smectites (Chipera & Bish, 2001). For most of the smectite samples selected, the common trace impurity detected was quartz at ~3.343 Å and for STx-1 and SWy-1, quartz was also detected at ~4.26 Å. Other trace impurities included: (i) a calcite peak at ~3.03 Å for SHCa-1, (ii) an opal-CT peak between ~4.08 and 4.10 Å, and a kaolinite peak at ~7.2 Å that disappeared after heating to 550°C (Brindley & Brown, 1980) for STx-1, and (iii) a trace peak at ~3.13 Å (pyrolusite or hornblende?) in SWy-1, which was not previously noted in the analysis of Chipera and Bish (2001).

Further tests confirmed the identification of the clay mineral samples as smectite. Upon exposure to ethylene glycol vapour, the d(001) of all Ca-saturated samples expanded to

~17 Å (Figs. 2.1-2.6). K-saturated forms of all tested at 0 % and 54 % RH, respectively, displayed the characteristic collapse of the interlayer toward a d(001) of ~10 Å and its subsequent expansion to ~12 Å at 54 % RH (Moore & Reynolds, 1989; Brindley & Brown, 1980) (Figs. 2.1-2.6). After heating to 300°C, all K-saturated samples displayed a partial collapse of the d(001) to between ~10 and 12 Å; the absence of a full collapse to ~10 Å likely arose from rehydration in the laboratory atmospheric humidity during handling for XRD analysis, as the samples had to be allowed to cool before being placed in the X-ray diffractometer. A final heating to 550°C produced a complete collapse of the d(001) to ~9.5 to 9.7 Å for all samples, except SapCa-1, for which a d(001) of ~11.9 Å was recorded but is not yet fully explained (Figs. 2.1-2.6).

2.4 Grain Size Analysis

Grain size analysis of the Ca, K, and Na cation-saturated forms of the <2 μm size-fractions of smectites SWy-1, SWa-1, and SapCa-1 was conducted at the Control and Crystallization of Pharmaceuticals Laboratory (CCPL) at *The* University *of* Western Ontario. A Malvern Mastersizer 2000 capable of grain-size measurement between 0.02 to 2000 μm in diameter was used for the measurements. While it is termed "grain size analysis" and is typically used for grain size measurements, in this case it was used to obtain a measure of particle size distribution in the <2 μm separate. The analyzer uses the volume of a grain to calculate the size and diameter equivalent to the measured volume using an equivalent spheres technique (Xiao *et al*., 2009). This approach assumes that each grain is a perfect sphere. About 80 mg of freeze-dried smectite was determined to be the minimum amount of material required for analysis. This limitation restricted grain size analysis to SWy-1, SWa-1, and SapCa-1; insufficient <2 μm material remained for the other samples. The main purpose of these measurements was to test the effectiveness of the settling column method in isolating the <2 μm size fraction from these smectites.

About 80 mg of each cation-form of these smectites was placed in separate 15 mL plastic centrifuge tubes, deflocculated in 10 mL of 0.1 % sodium hexametaphosphate solution ($Na(PO_3)_6$) (Chipera & Bish, 2001), hand stirred, and then dispersed using an ultrasonic probe for ~30 seconds at 700 watts. The mixture was then capped and transported to the

CCPL for particle-size analysis. Each mixture was added to 500 mL of DI water, which is pumped into the Mastersizer 2000 laser diffractometer using the control settings for average China clay. The analyzer produced three separate particle-size analyses, with 20 seconds between each analysis and one weighted average particle-size analysis per sample.

2.4.1 Grain Size Distribution Interpretation

Large peaks in the 1000 μm particle range were observed for either one or all of the cation-saturated forms for each of the SWy-1, SapCa-1, and SWa-1 smectite samples (Figs. 2.7-2.9). These peaks were determined to be artefacts, arising from interference generated from the glass beaker in which the samples were dispersed during particle-size analysis.

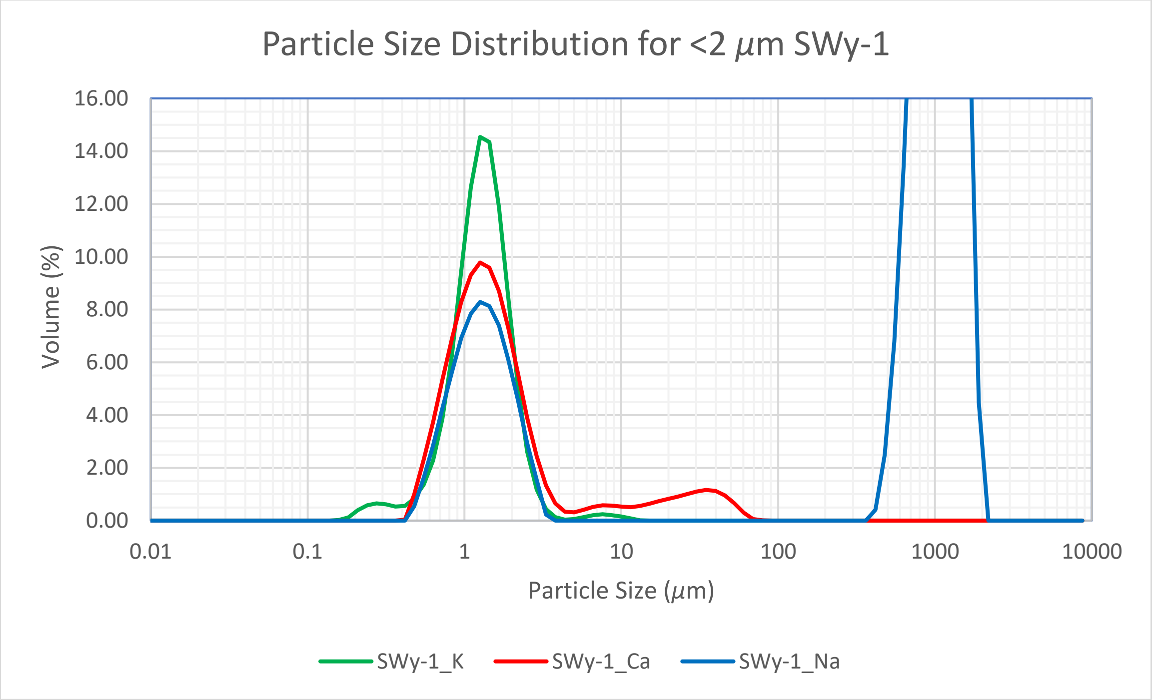

Figure 2.7. Particle-size distribution of the K-, Ca-, and Na-saturated forms of SWy-1, initially size separated to < 2 μm using the settling column method.

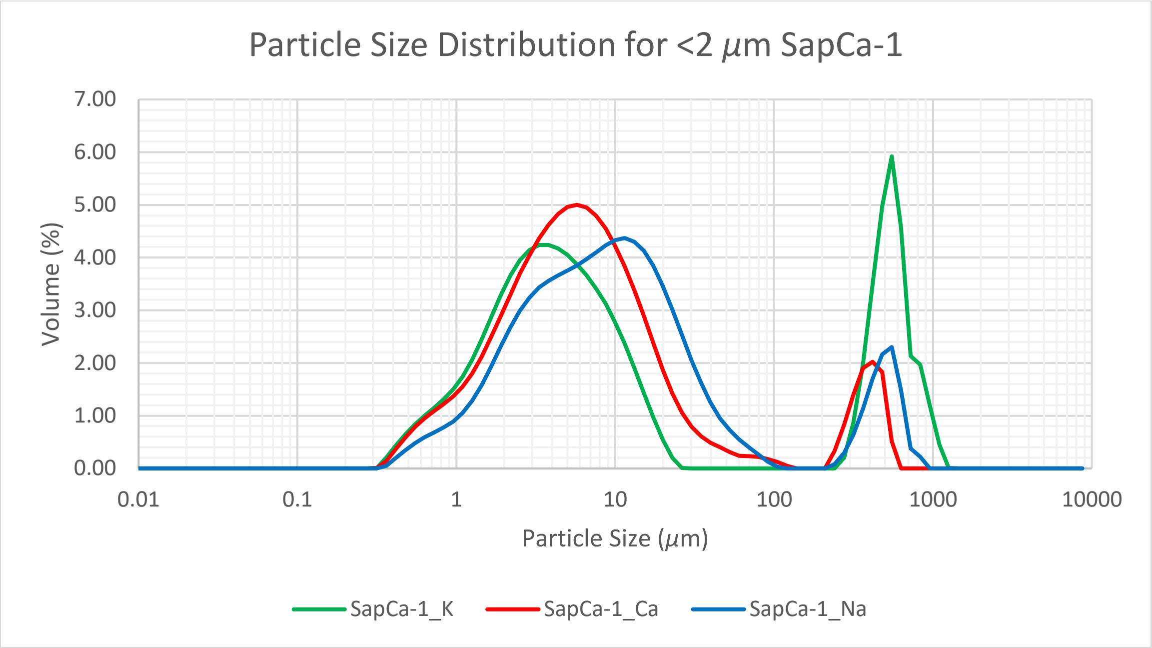

Figure 2.8. Particle-size distribution of the K-, Ca-, and Na-saturated forms of SapCa-1, initially size separated to < 2 μm using the settling column method.

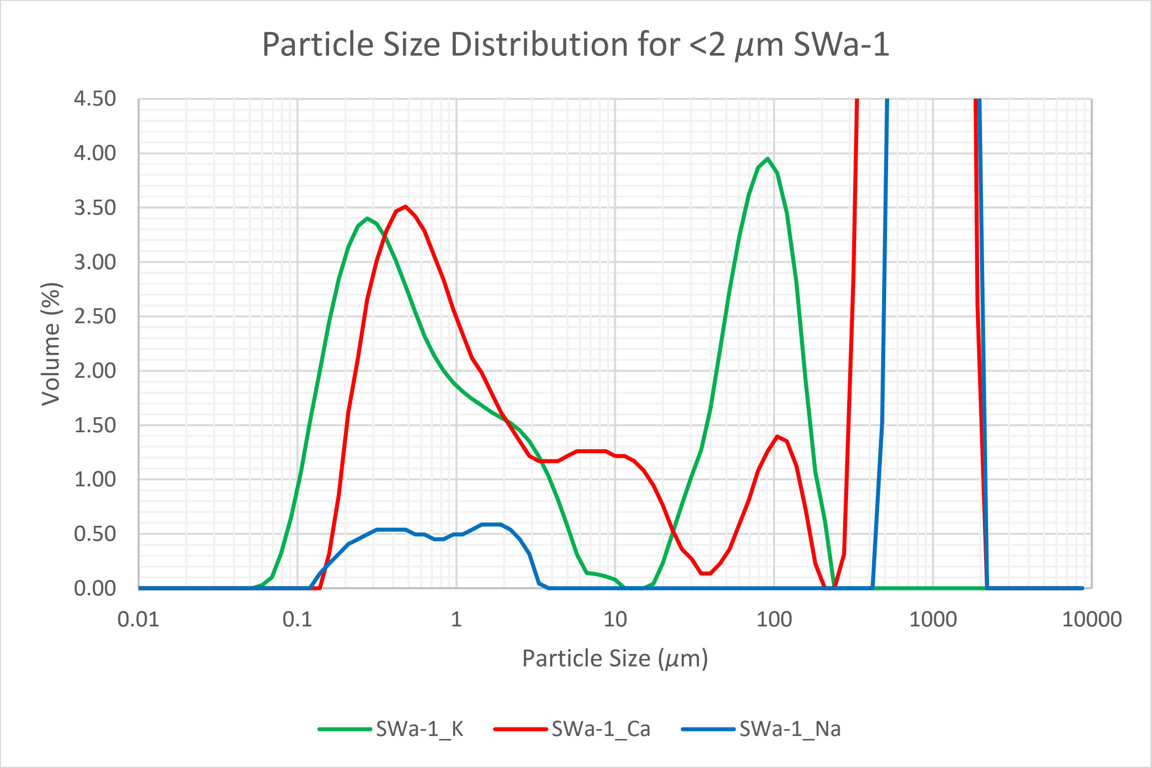

Figure 2.9. Particle-size distribution of the K-, Ca-, and Na-saturated forms of SWa-1, initially size separated to < 2 μm using the settling column method.

The particle-size distribution for the <2 μm size fraction of SWy-1 shows that most of the particles are 1 μm in size, with the Ca-saturated sample displaying a minor peak of particles also in the 50 μm size range (Fig. 2.7). This result is consistent with the fact that the SWy-1 sample, in all cation forms, was the easiest to deflocculate – as observed visually – of the three smectites considered here.

The particle-size distribution for the <2 μm SapCa-1 extended into the <2 μm range in the Mastersizer analysis, but particle-size peaks occurred at 3 μm, 6 μm, and 10 μm for the K, Ca, and Na exchangeable cation-saturated forms, respectively (Fig. 2.8). This sample was moderately difficult to disperse for all cation saturations, which is reflected in larger apparent size fractions (> 2 μm) that almost certainly arise from particle agglomeration.

The Mastersizer particle-size distribution for the SWa-1 <2 μm size fraction varied greatly among cation-saturations (Fig. 2.9). The Ca-saturated sample showed three primary particle-size peaks in the <2 μm, 10 μm, and 100 μm ranges, whereas there were two particle-size peaks in the <2 μm and 100 μm ranges for the K-saturated sample, and one peak in the <2 μm range for the Na-saturated form. These observations are consistent with the ease of dispersal for each exchangeable cation form. The Na-saturated form dispersed readily in the sodium hexametaphosphate solution during stirring and ultrasonication. The peaks at higher average particle sizes for the Ca- and K-saturated forms reflect greater difficulty in dispersion, and almost certainly particle agglomeration.

In short, despite the use of sodium hexametaphosphate for deflocculation of the samples (Chipera & Bish, 2001) and sonication prior and during the Mastersizer particle-size analysis, many samples exhibited particle agglomeration. Use of the settling column method according to Stoke’s Law for initial size separation of the samples, and the care taken while employing this method, make it unlikely that the larger size particles (> 2 μm) arose from incomplete initial <2 μm size fractionation. While the Mastersizer method has been applied previously to determine grain size distributions for lake sediments and soils (Callesen *et al*., 2018; Xiao *et al.*, 2013; Xiao *et al.*, 2009; Peng *et* *al.*, 2005), it is likely that the high purity (nearly pure smectite) of the samples examined in the present study resulted in incomplete dispersal and agglomeration in most cases. The viscous nature of the smectites and their saturation in particular with K^+ and $Ca^{2+,}$ which are of high ionic strength, made their particles difficult to disperse using a solution that minimizes the potential for cation exchange with the dispersal solution. Additional uncertainties arise from: (i) the assumption of particles as perfect spheres, whereas clay mineral particles have a platy shape (Callesen *et al*., 2018), and (ii) use of an 80 mg sample rather than the standard 1 g for which this method is intended.

Ultimately, this method of grain size analysis was not optimal for the present study. However, as all the clay mineral size fractions were prepared using the same settling column method at the same time under the same conditions, the results for the SWy-1 sample that was easily dispersed provide some general confirmation that the <2 μm size fraction was indeed isolated from the initial samples.

Chapter 3

3 Analytical Methods – Hydrogen Isotope and Thermogravimetric Analysis

3.1 TCEA Hydrogen Isotope Standards for Hydrous Minerals

Non-expandable 2:1 phyllosilicates, such as biotite and muscovite, contain hydrogen only in structural hydroxyls and are minimally affected by the extent of rehydration that affects swelling clay minerals such as smectite. As such, they are ideal as hydrogen isotope standards during the analysis of phyllosilicate samples (Brindley & Brown, 1980; Qi *et al.*, 2017).

New standards, USGS-57 (biotite) and USGS-58 (muscovite), have been specifically developed to provide a robust two-point calibration for the δ^2H of hydrous minerals analyzed by the TCEA-CF-IRMS method (Qi *et al.*, 2017):

USGS-57 (biotite)
$\delta^2H_{VSMOW-SLAP} = -91.5 \pm 2.4$ ‰ (n= 24)
Mass fraction hydrogen = 0.416 ± 0.002 % (n= 4)
Mass fraction water = 3.74 ± 0.02 % (n= 4)

USGS-58 (muscovite)
$\delta^2H_{VSMOW-SLAP} = -28.4 \pm 1.6$ ‰ (n= 24)
Mass fraction hydrogen = 0.448 ± 0.002 % (n= 4)
Mass fraction water = 4.03 ± 0.02 % (n= 4).

Qi *et al.* (2017) note that both standards were also analyzed using conventional off-line methods (at LSIS) and produced values of $\delta^2H = -92.9 \pm 2.8$ ‰ for USGS-57 and −28.1 ± 0.8 ‰ for USGS-58. These results are identical within error to those obtained by TCEA-CF-IRMS methods.

3.2 Degassing Pretreatment Procedure

All samples and standards in each analytical session were treated identically, including during procedures to remove bound water (BW) from external mineral surfaces and the interlayer of smectites. Approximately 2 mg of the smectite samples, < 1 mg of KGa-1 RT (kaolinite), ~2.5 mg of IMt-1 (illite), and between 2 to ~3.5 mg of the USGS standards and GBS biotite were weighed into 3.5 x 5 mm silver capsules. The amounts weighed were scaled to the presumed hydroxyl hydrogen content of each phyllosilicate.

For most experiments, the silver capsules containing the samples and standards were then completely folded closed with tweezers and placed in individual, numbered wells that had been bored into an aluminum tray (Al-tray). Prior to implementation (analytical sessions [analyses] 1-9 and 11) (see Appendix 1 for complete data files) of the Al-tray, each folded silver capsule was placed in an individual, open glass vial; the vials were then placed in a wire rack loosely covered by Al-foil. The Al-tray / wire rack with vials were then placed in an oven and heated at a specific temperature under active vacuum. Heating duration and temperature were varied from experiment to experiment as part of the development of the degassing protocol.

3.3 TCEA-CF-IRMS

The δ^2H of the samples and standards was analyzed following Sharp *et al.* (2001), Bauer and Vennemann (2014), VanDeVelde and Bowen (2013), and Qi *et al.* (2017). Following a prescribed time and temperature pretreatment, discussed below, the seal on the vacuum oven was released and the Al-tray / wire rack and glass vials containing the samples and standards was immediately removed and taken to the He-flushed Costech Zero-Blank autosampler attached to the furnace port of the TCEA. The capsules bearing the standards and samples were then quickly transferred from the still hot, Al-tray / wire rack into the He-flushed autosampler in < 2.5 minutes. The autosampler was immediately closed, leak checked, and purged under He flow to ensure that any contact or rehydration of the samples with the laboratory atmosphere was limited. The samples were maintained under He-flush in the autosampler for at least 4 hours prior to analysis by TCEA-CF-IRMS.

The samples were combusted in the LSIS Thermo Scientific^{TM} High Temperature Conversion Elemental Analyzer (TCEA) connected to a Thermo Scientific^{TM} Delta^{TM} XL Plus isotope ratio mass spectrometer (IRMS), run in continuous flow (CF), via a Conflo^{TM} III open-split interface, with an automated sequence time of ~4 minutes per sample or standard. For this study, the TCEA reactor was composed of a glassy carbon tube inserted inside a ceramic sleeve and filled with glassy carbon chips, with quartz and silver wool at the bottom. A graphite crucible is situated on top of the chips in the glassy carbon tube for collection of silver and ash residue from sample/standard combustion. The thermal decomposition of the phyllosilicates produces water, which then reacts with the glassy carbon tube to produce H_2 and CO gas. The He carrier gas then transfers these gases through the gas chromatographic (GC) column to the IRMS for measurement of hydrogen gas ($H_{2(g)}$) content and isotopic composition. During analysis, the TCEA reactor temperature was set at 1450°C and the GC column at 120°C. with a He flow of 90 ml/minute.

Another option for the TCEA furnace, not employed here, is a chromium (Cr) packed reactor. Chromium-packed reactors are generally better for samples that may contain substances of halogens and sulfur, which was not a major concern for the samples and standards used in this study. According to Qi *et al.* (2017), there is no appreciable difference between the values of δ^2H obtained for typical hydrous minerals analyzed using Cr or glassy carbon reactors.

Following Sharp *et al.* (2001), the IRMS hydrogen reference gas (δ^2H = –124.69 ‰, VSMOW) was introduced through the dual inlet system of the IRMS. This enabled the use of minimal reference gas while still maintaining the quality of the isotopic analysis. The USGS-57 and USGS-58 were included, at minimum in duplicate, in each analytical session to ensure accurate calibration to the VSMOW-SLAP scale.

An in-house biotite (GBS) standard with an expected δ^2H of −64±2 ‰ was also included in each analytical session in this study to monitor the accuracy of the USGS-57 / USGS-58 two-point VSMOW-SLAP calibration curve. In addition to GBS, KGa-1 RT (kaolinite), and IMt-1 (1) and (2) (illite) were included as an extra control on accuracy in some analysis during early method testing, but were not used in later analyses as the positions in the autosampler were limited to 48 samples.

Sample and standard weights and the surface area under the hydrogen gas $3H_2/2H_2$ signal peak ($^2H+^1H=3H_{2(g)}$ and $^1H+^1H=2H_{2(g)}$), produced by evolved hydrogen gas from the sample material, were combined to determine the hydrogen content of each sample and standard. Hydrogen yields (H_2) are reported in μmol H_2/mg of clay minerals, as calibrated using the known hydroxyl hydrogen contents of USGS-57 (biotite). Virtually identical results were obtained if the known hydroxyl hydrogen contents of USGS-58 (muscovite) was employed. That said, further testing and precise quantification of the exact structural formulas and thermo behavior for both standards would be of interest in this regard.

3.4 Thermogravimetric (TG) Analysis

Thermal mass loss profiles for the smectite samples were obtained at the Institute of Geological Sciences of the Polish Academy of Sciences, using a TA Discovery thermal analyzer from TA Instruments. This instrument has an absolute weighing error of < 1 μg, weight measurement resolution of <0.1 μg, and a thermal drift between 200 and 1000°C of <4 μg. For each sample, 15 mg was weighed onto individual platinum pans and placed in the TG autosampler. The TG measurements were performed in a dry nitrogen (purity >99.999 %; supplied by Air Products) flow at a rate of 50 mL/min. All samples except SapCa-1 in Ca-saturated form and all cation forms of SWy-1, underwent a preliminary isothermal drying at 40°C for 15 minutes. This was followed by isothermal drying for 4 hours at 220°C for all the samples, which were then ramp-heated (dynamically) to 1000°C at a rate of 10°C/minute.

Chapter 4

4 Results

4.1 Method Development

4.1.1 Terminology and Exclusion of Outliers

In this study a sample refers to one type of material of a specific amount. A batch is composed of multiple individual samples that have been loaded into the TCEA autosampler at the same time and analyzed together in sequence. The data produced from a batch of samples is termed an ‘Analysis’ with a corresponding number (i.e., Analysis 20).

The USGS-57 (biotite) and USGS-58 (muscovite) standards were determined to have respective 1-sigma standard deviations (SD) for δ^2H of 2.4 ‰ and 1.6 ‰ (n= 24) during testing and development across six different laboratories (Qi *et al.*, 2017). For the present study, USGS-57 and USGS-58 standards returned respective SDs of 1.42 ‰ (n= 29, 14 batches) and 0.80 ‰ (n= 29, 14 batches) for analysis 18 to 31. That the SDs were lower than those reported by Qi *et al.* (2017) was expected, as this variability resulted from use of only one analytical set of instrumentation.

Outliers of δ^2H for samples from each batch that were more than 2.8 ‰, 2-sigma SD were excluded from further consideration, based on a doubling of the precision obtained for USGS-57. Smectite δ^2H was expected to be less reproducible than possible for the well-crystallized and non-expandable USGS phyllosilicate standards. The reproducibility of the laboratory GBS biotite standard was 1.97 ‰ (n= 44, 14 batches), which is also higher than for the better-constrained USGS-57 biotite standard. Any samples that were impacted by equipment malfunctions or unstable analytical conditions during operation and method development were also excluded from further consideration.

Values of δ^2H obtained for USGS-57, USGS-58, and GBS standards during Analyses 1 to 17 were not included in the calculations described above, as those analyses comprised the method development. When referring to Analyses 1 to 17, only the initial δ^2H and averages are considered.

4.1.2 Material Amounts

During Analysis 1, hydrogen oversaturation of the IRMS peak resulting from evolved gas from the sample material was observed for the KGa-1 RT samples, due to the use of too much sample. The amount of KGa-1 RT sample material was then reduced to < 1 mg from ~ 1.9 mg, which resolved the problem of IRMS peak oversaturation. Oversaturation was not encountered for the smectite samples or the biotite and muscovite standards when using material amounts in the range of ~ 2 to ~ 3.6 mg.

4.1.3 TCEA Maintenance

According to the maintenance and care manual, best practices for TCEA maintenance involving organic samples generally state that the ash/waste crucible be changed after every 150 samples to avoid overflow of waste into the glassy carbon reactor packing, thus hindering gas flow from the sample to the MS. For phyllosilicates, much more waste builds up in the graphite crucible. Therefore, the recommended standard TCEA maintenance for clay minerals, as observed in this study, includes changing the crucible after analysis of every 70 to 90 samples.

4.1.4 He-flush Time Test

Initially during method development (Analyses 1 to 13, Appendix 1), samples were loaded into the Costech Zero blank autosampler, sealed, and equilibrated under He-flush overnight (12-18 hours). The same samples, with the same pretreatment, however, produced comparable average δ^2H for both overnight and 4-hour He-flushed samples (Table 4.1: Analysis 13 versus Analysis 14). This observation has the benefit of saving both time and the cost of consumable He. A He-flush time shorter than 4 hours was not tested but may still be possible, provided the TCEA CF-IRMS system has sufficient time to reach a stable CO background after loading the samples into the autosampler but prior to analysis.

Table 4.1. The δ^2H and hydrogen (H_2) yields for K-saturated smectite, illite, and kaolinite for comparison of He-flush times in the TCEA autosampler.

Sample	δ^2H_{VSMOW} (‰)	δ^2H_{VSMOW} (‰) Average	δ^2H_{VSMOW} (‰) SD	H-yield (H_2) (μmol H_2/mg)	H-yield (H_2) Average (μmol H_2/mg)	H-yield (H_2) SD (μmol H_2/mg)
4 hour He-flush time (Analysis 14)						
SWy-1_K	–140.9	–140.4	0.64	3.11	3.10	0.03
SWy-1_K	–140.0			3.08		
SapCa-1_K	–130.7	–128.95	2.45	2.55	2.48	0.11
SapCa-1_K	–127.2			2.40		
SWa-1_K	–158.2	–159.23	1.52	3.35	3.38	0.05
SWa-1_K	–160.3			3.42		
SAz-1_K	–122.0	–121.19	1.19	3.36	3.39	0.03
SAz-1_K	–120.4			3.41		
IMt-1_K (2)	–103.1	–102.41	0.94	3.23	3.22	0.01
IMt-1_K (2)	–101.7			3.21		
KGa-1 RT	–55.9	–56.9	0.93	8.42	8.40	0.06
KGa-1 RT	–57.7			8.44		
KGa-1 RT	–57.1			8.33		
Overnight He-flush time (Analysis 13)						
SWy-1_K	–143.0	–143.4	0.51	3.06	3.07	0.01
SWy-1_K	–143.7			3.08		
SapCa-1_K	–132.2	–131.2	1.42	2.36	2.43	0.10
SapCa-1_K	–130.2			2.50		
SWa-1_K	–163.0	–162.8	0.31	3.40	3.41	0.02
SWa-1_K	–162.5			3.42		
SAz-1_K	–121.4	–122.2	1.22	2.96	3.44	0.69
SAz-1_K	–123.1			3.93		
IMt-1_K (2)	–104.5	–104.7	0.38	3.19	3.21	0.02
IMt-1_K (2)	–105.0			3.22		
KGa-1	–55.4	–55.4	0.39	8.44	8.40	0.11
KGa-1	–56.0			8.53		
KGa-1	–55.2			8.26		
KGa-1	–55.1			8.36		

SD = 2-sigma standard deviation

4.1.5 Glass Vials versus Al-Tray

For some of the initial method development batches, Analyses 1 to 9 and 11, the samples were heated in a vacuum oven in individual glass test tube vials, following Bauer and Vennemann (2014). After removal from the vacuum oven, however, the vials were not sealed, as the samples they contained were loaded immediately into the TCEA autosampler. As the glass vials were difficult to handle when hot, two people were needed to safely transfer the samples to each slot in the autosampler. This issue was resolved with the use of the Al-tray fabricated by the University of Western Ontario, Earth Science Machine Shop, based on a similar design developed by Justin Drummond at Queen’s University, Kingston, Ontario, Canada. The wells in the Al-tray that hold individual samples were drilled ~ 1 cm deep, in order to keep the samples hot during the transfer from the vacuum oven to the He-flushed autosampler and thus limit sample rehydration from atmospheric water vapour during the transfer. The use of the Al-tray enabled one operator to quickly move the tray containing the samples from the vacuum oven to the autosampler, and load the samples from the Al-tray to the autosampler with precision tweezers.

Samples heated in glass vials (Analysis 8) and heated in the Al-tray (Analysis 13) returned comparable average isotopic results when all other variables were kept constant, such as heating time and temperature under active vacuum (Table 4.2). Therefore, all subsequent analyses were performed using the Al-tray. A temperature of 200°C was used in these early analyses, as the maximum temperature that would not cause the rubber seal on the vacuum oven to begin melting was 220°C. In later analyses, the temperature was raised to the 220°C, after establishing the integrity of the rubber seal at the maximum temperature.

Table 4.2. Comparison of δ^2H for smectite degassed in glass vials versus Al-tray.

Sample	δ^2H_{VSMOW} (‰)	Average (‰)	SD (‰)
Degassed at 200°C for 24 hours in glass vials (Analysis 8)			
SWy-1_K	–139.6	–141.6	1.73
SWy-1_K	–142.8		
SWy-1_K	–142.5		
SapCa-1_K	–131.6	–130.5	1.36
SapCa-1_K	–130.8		
SapCa-1_K	–129.0		
SWa-1_K	–167.5	–166.6	1.28
SWa-1_K	–165.2		
SWa-1_K	–167.3		
Degassed at 200°C for 24 hours in Al-tray (Analysis 13)			
SWy-1_K	–143.0	–143.4	0.51
SWy-1_K	–143.7		
SapCa-1_K	–132.2	–131.2	1.42
SapCa-1_K	–130.2		
SWa-1_K	–163.0	–162.8	0.31
SWa-1_K	–162.5		

SD = 2-sigma standard deviation

4.2 Hydrogen Isotope Results

4.2.1 All Smectites Test

Analyses 23, 24, 28, and 31 (Appendix 1) established baseline values of δ^2H and hydrogen yields (H_2) for the six smectites. Analyses 23, 24, and 28 examined the δ^2H and H_2 yields for Ca-, K-, and Na-saturated forms of the six smectites that were degassed at 220°C for 4 hours under active vacuum prior to TCEA-CF-IRMS analysis. Analysis 31 consisted of the K-saturated form of each of the six smectites, as in analysis 24, but was degassed at 220°C for 24 hours under active vacuum before TCEA-CF-IRMS analysis (Table 4.3 and Appendix 1). All samples in these four batches underwent a He-flush for 4 hours in the autosampler after degassing but before TCEA-CF-IRMS analysis.

Table 4.3. Average δ^2H and hydrogen yield for each smectite, by cation saturation.

Sample	*n*	Average $\delta^2\mathrm{H}_{\mathrm{VSMOW}}$ (‰)	$\delta^2\mathrm{H}_{\mathrm{VSMOW}}$ (‰) SD	Average H_2 yield (μmol/mg)	SD H_2 yield (μmol/mg)
Degassed at 220°C for 4 hours					
SAz-1_K	4	–114.0	0.76	3.00	0.01
SAz-1_Ca	5	–118.7	1.57	3.79	0.09
SAz-1_Na	4	–121.0	0.61	3.44	0.03
SWy-1_K	4	–134.6	0.94	2.84	0.03
SWy-1_Ca	5	–129.2	0.84	3.45	0.07
SWy-1_Na	4	–129.5	1.17	3.20	0.02
SapCa-1_K	4	–125.5	0.79	2.34	0.02
SapCa-1_Ca	5	–128.5	0.74	3.61	0.10
SapCa-1_Na	4	–126.4	1.66	2.54	0.08
STx-1_K	4	–74.5	0.84	3.00	0.03
STx-1_Ca	5	–88.8	1.22	3.42	0.06
STx-1_Na	3	–87.5	0.57	3.38	0.03
SHCa-1_K	4	–110.5	0.89	1.61	0.03
SHCa-1_Ca	5	–119.0	1.47	2.65	0.03
SHCa-1_Na	3	–111.2	0.80	2.01	0.02
SWa-1_K	4	–156.6	1.53	2.94	0.03
SWa-1_Ca	5	–149.0	2.54	3.57	0.04
SWa-1_Na	4	–152.3	1.17	3.30	0.05
Degassed at 220°C for 24 hours					
SAz-1_K	4	–118.5	0.38	3.18	0.03
SWy-1_K	4	–136.7	1.14	2.75	0.25
SapCa-1_K	4	–125.8	0.19	2.32	0.03
STx-1_K	4	–79.0	0.75	3.12	0.07
SHCa-1_K	4	–113.6	1.09	1.73	0.01
SWa-1_K	4	–154.3	0.76	3.11	0.02

n = number of samples; SD = 2-sigma standard deviation

The various cation-saturated forms of each smectite have δ^2H that cluster together within ~5 to 13 ‰ (Fig. 4.1). However, the δ^2H of replicate samples of each cation-saturated form generally show a significantly smaller range of variation (<5 ‰). The δ^2H of the Ca- and Na-saturated forms plotted variably in relation to the K-saturated samples for each smectite (Fig. 4.1). Four of the K-saturated smectites degassed at 4 versus 24 hours have similar δ^2H (Fig. 4.1). SAz-1 and STx-1 K-saturated smectites, however have slightly lower δ^2H after degassing for 24 hours versus 4 hours.

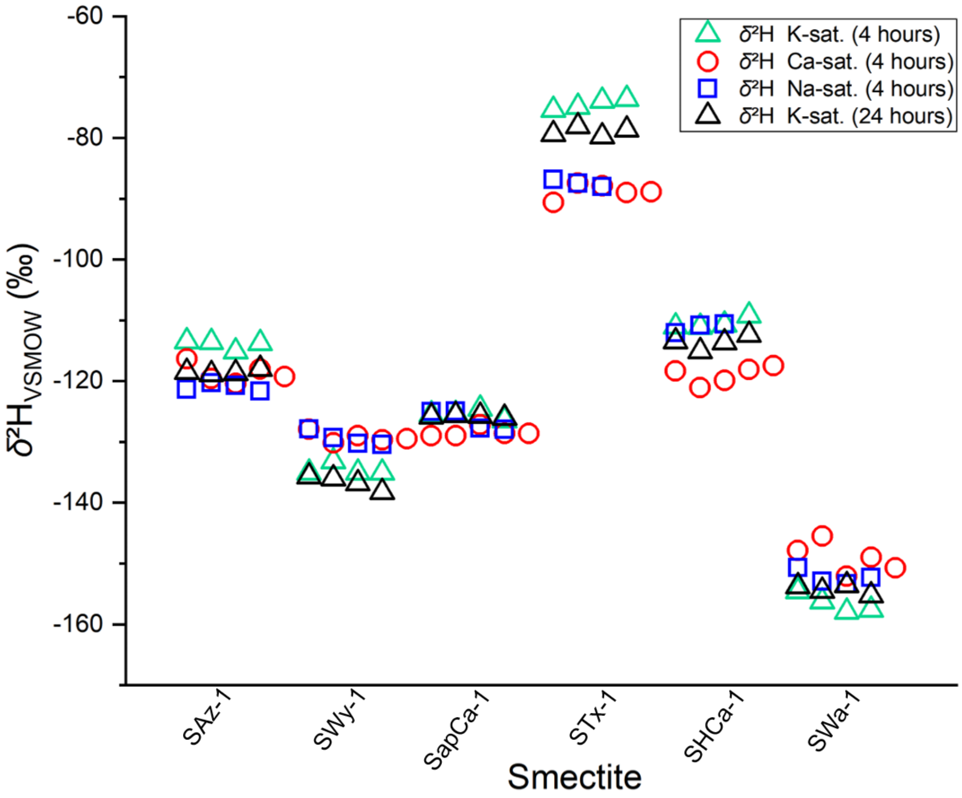

Figure 4.1. **δ^2H for three exchangeable cation-saturations of each smectite, degassed under active vacuum at 220°C for 4 or 24 hours.**

In general, the hydrogen yield data for each of the smectites follow a similar trend, with the highest yields recorded for Ca-saturated aliquots of a given smectite and the lowest yields recorded for K-saturated aliquots of the same smectite (Fig. 4.2). However, there was a greater difference between hydrogen yields obtained for the trioctahedral Ca-saturated SapCa-1 and SHCa-1 samples and their Na- and K-saturated forms, than was observed for the other smectites. Heating time duration (24 versus 4 hours) appeared to have little effect on the hydrogen yields obtained for the K-saturated forms of the smectites.

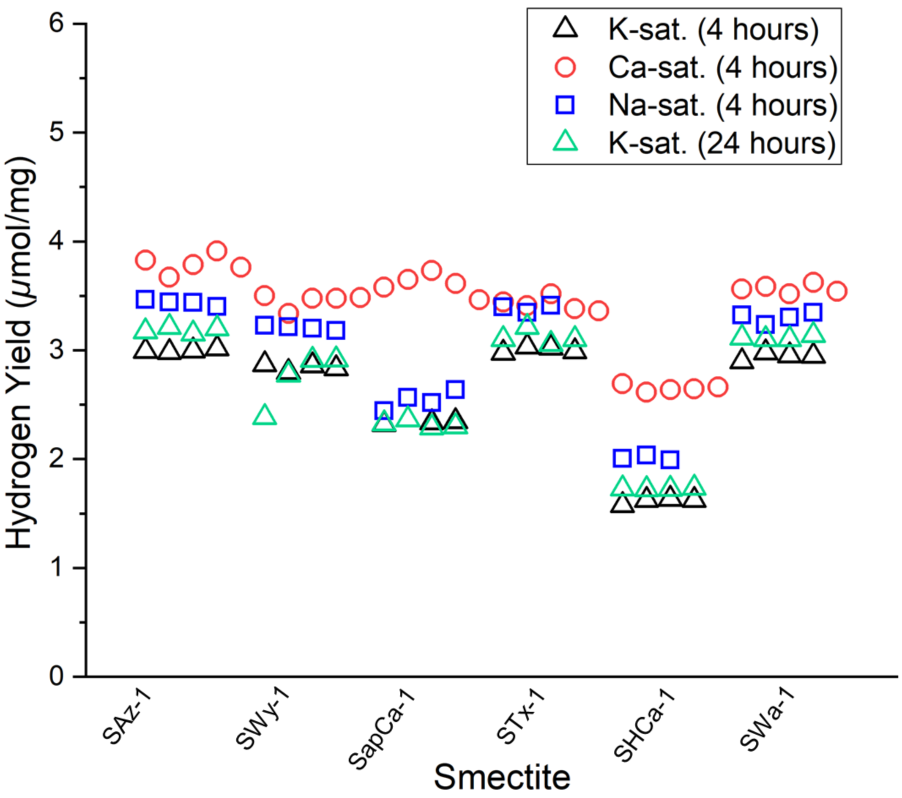

Figure 4.2. Hydrogen yields associated with δ^2H illustrated in Figure 13, for three exchangeable cation saturations of each smectite, degassed under active vacuum at 220°C for 4 or 24 hours.

4.2.2 Loading Time Test

The effects of autosampler loading time on smectite δ^2H and hydrogen yield was tested using SAz-1 during Analysis 19, 20, and 21 (Appendix 1) for all three cation-saturated forms. Loading time was defined as the time elapsed between breaking the seal on the vacuum oven, completely loading all samples into the autosampler under helium flush, and sealing the autosampler. Times tested were 2, 4, and 10 minutes after degassing at 200°C for four hours. Samples were held under helium flush in the autosampler for four hours prior to TCEA analysis.

The 2 and 4 minute loadings produced very comparable δ^2H, particularly for the Na-saturated form. The Ca- and K-saturated samples also had overlapping δ^2H; however, a few of the 4-minute samples had δ^2H ~1 to 3 ‰ higher than the 2 minute samples (Fig. 4.3).

In contrast to the 2- and 4-minute results, the 10-minute loading test displayed higher δ^2H for all of the cation-saturated forms of the SAz-1 sample (Fig. 4.3).

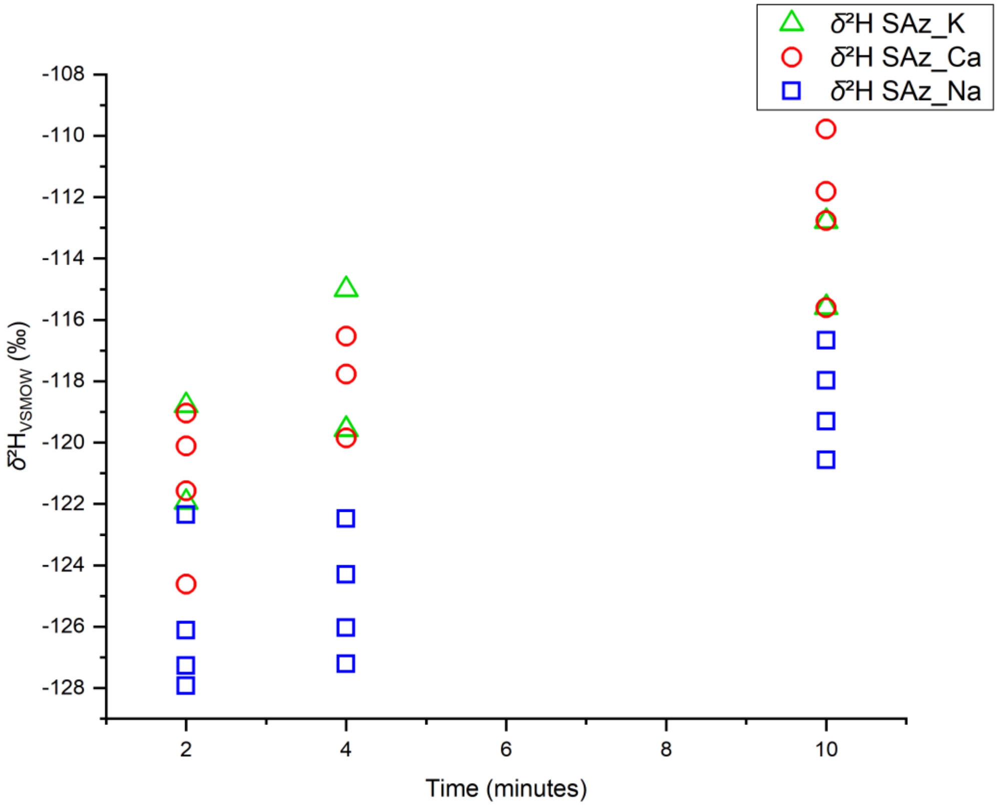

Figure 4.3. **δ^2H for each of the three cation-saturated forms of the SAz-1 smectite, for 2, 4, and 10 minute autosampler loading times. Loading time is calculated from the moment that the seal on the vacuum oven is broken until the samples are sealed under He-flush in the TCEA autosampler.**

In terms of hydrogen yield, K-saturated SAz-1 did not change appreciably among the three loading times (Fig. 4.4). Hydrogen yields for Ca- and Na-saturated aliquots overlap, but are higher than those of the K-saturated aliquot at 2 and 4 minutes. At 10 minutes, the hydrogen yields show the widest separation among the cation saturations, with the Ca-saturated aliquot having the highest values.

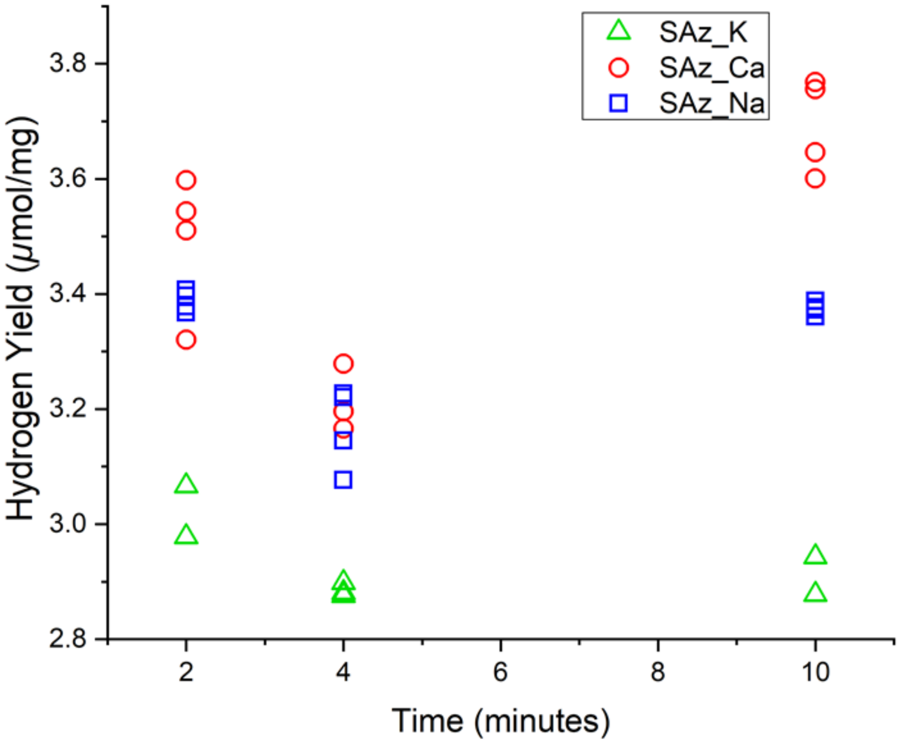

Figure 4.4. Hydrogen yields associated with δ^2H illustrated in Figure 15 for three exchangeable cation saturations of SAz-1, for autosampler loading time of 2, 4, and 10 minutes.

4.2.3 Triple Temperature Test

Aliquots of the K-, Na-, and Ca-saturated smectites were pretreated at 21°C, 100°C and 220°C, prior to TCEA-CF-IRMS measurement, to track the progressive removal of adsorbed water from the samples, and the subsequent response of the different cation forms through this degassing sequence, in relation to smectite δ^2H and hydrogen yields. The 21°C pretreatment consisted simply of loading the material into the silver capsules, folding them closed, and leaving them exposed to laboratory atmosphere and temperature prior to loading in the autosampler. The 220°C pretreatment involved degassing under active vacuum, at 220°C, in the Al-tray for 20 hours. The temperature was then decreased to 100°C, the vacuum oven opened, and the 100°C samples were added to the Al-tray. The vacuum oven was returned to active vacuum pumping and both sets of samples were heated at 100°C for four hours. The 21°C samples were then loaded to the autosampler, after which the vacuum oven was opened, and the heated samples were then quickly added to the autosampler as well. The autosampler was then sealed under He-flush.

The smectite δ^2H and hydrogen yields are illustrated in Figures 4.5-4.16. The K-saturated samples generally returned very similar δ^2H for the 100°C and 220°C treatments, while there was a noticeable, though slight, shift to higher δ^2H for K-saturated samples left exposed to the atmosphere at room temperature.

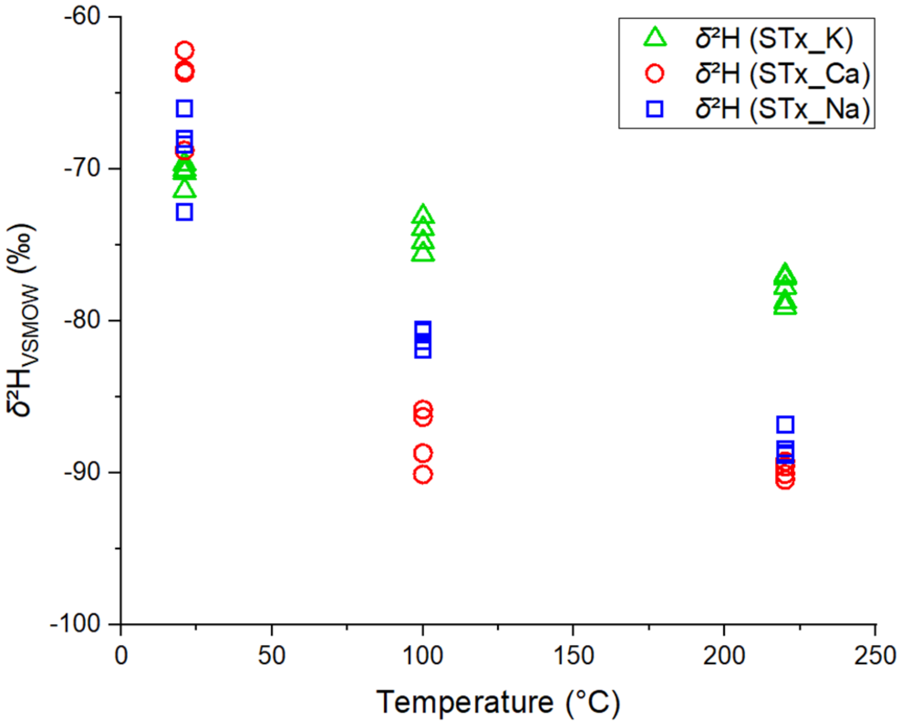

Figure 4.5. **δ^2H for the three cation-saturated forms of STx-1 at the three pretreatment conditions.**

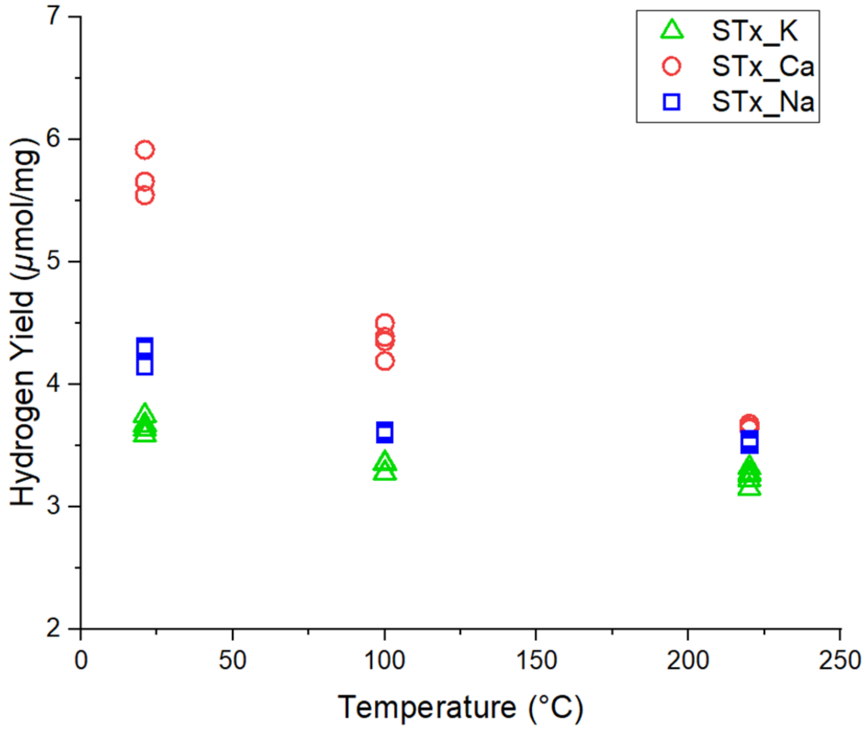

Figure 4.6. Hydrogen yields for STx-1 for the same samples illustrated in Figure 4.5.

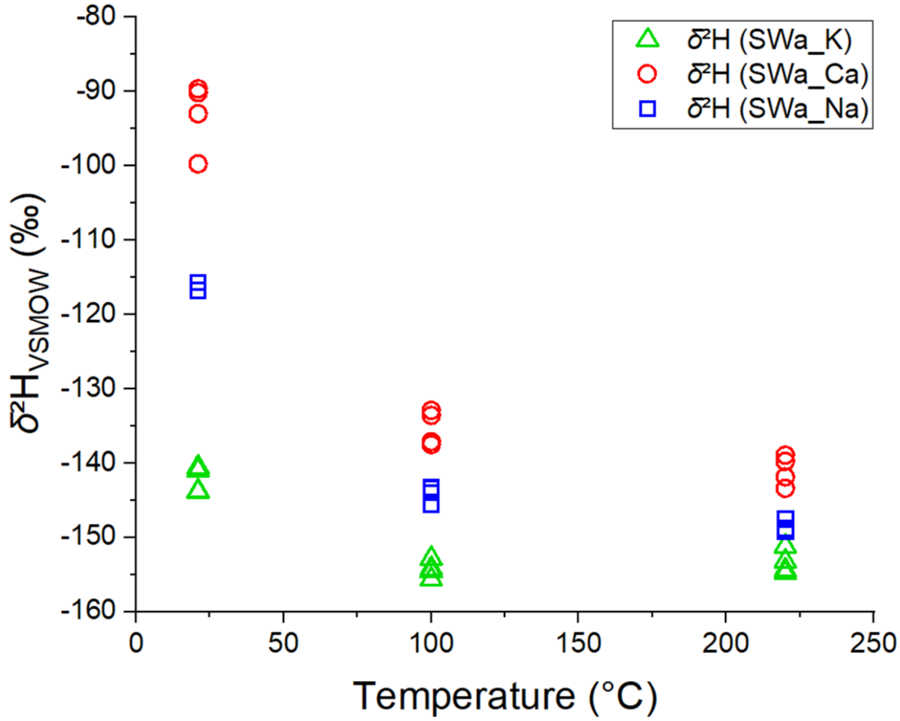

Figure 4.7. δ^2H for the three cation-saturated forms of SWa-1 at the three pretreatment conditions.

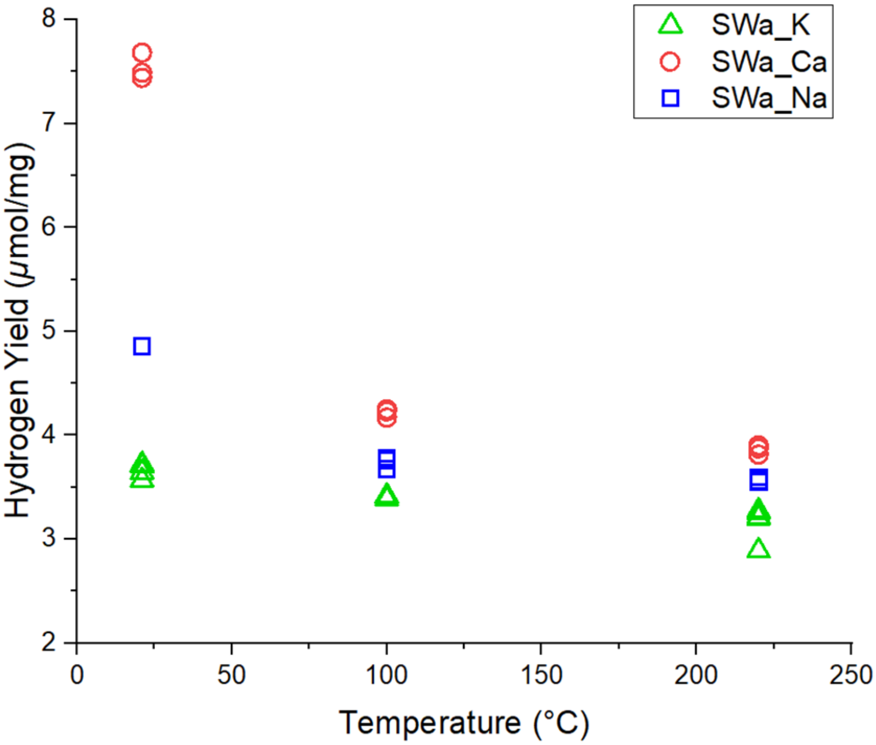

Figure 4.8. Hydrogen yields for SWa-1 for the same samples illustrated in Figure 4.7.

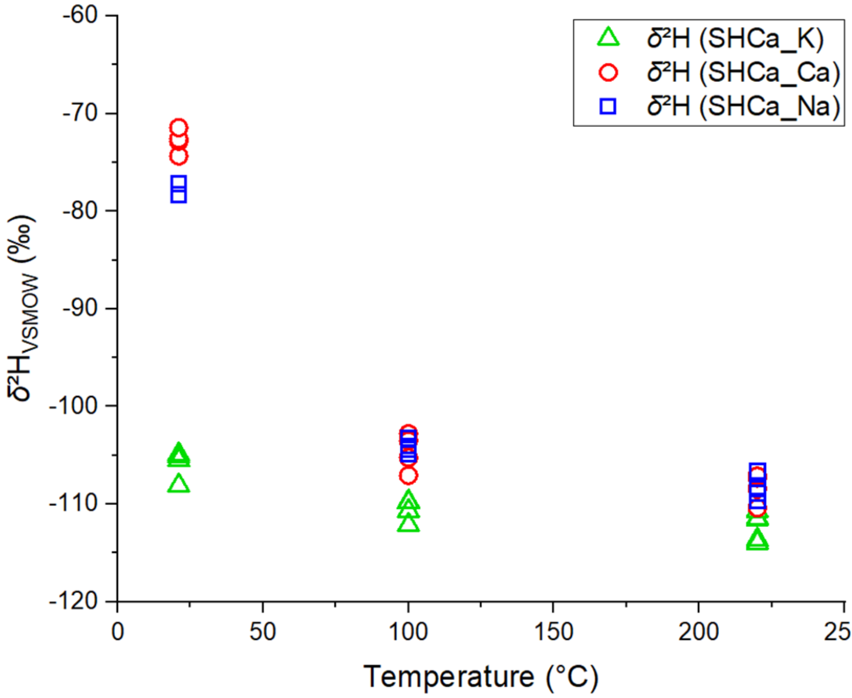

Figure 4.9. δ^2H for the three cation-saturated forms of SHCa-1 at the three pretreatment conditions.

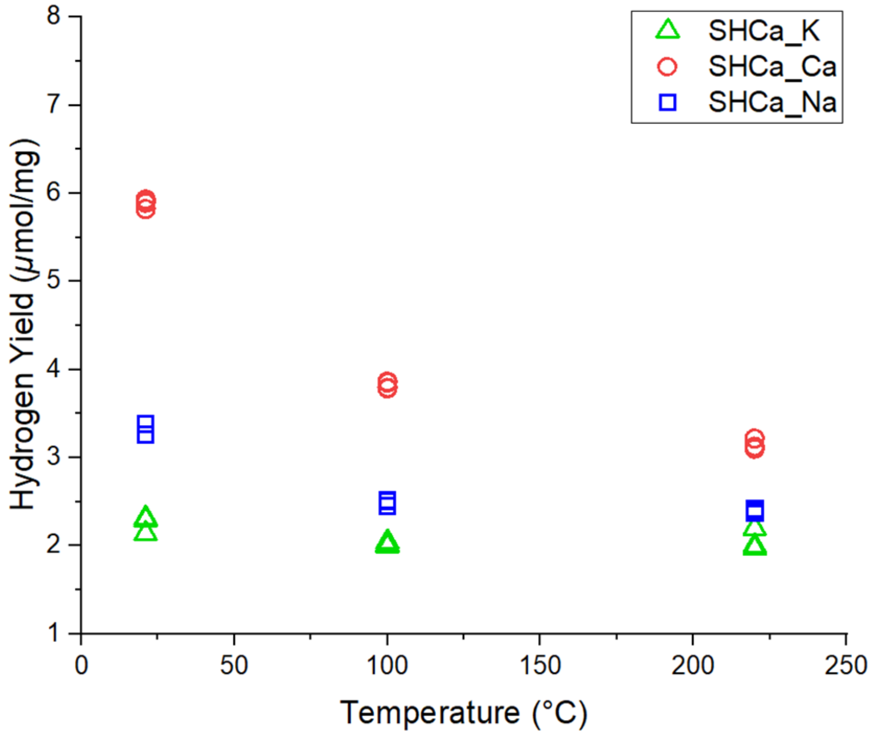

Figure 4.10. Hydrogen yields for SHCa-1 for the same samples illustrated in Figure 4.9.

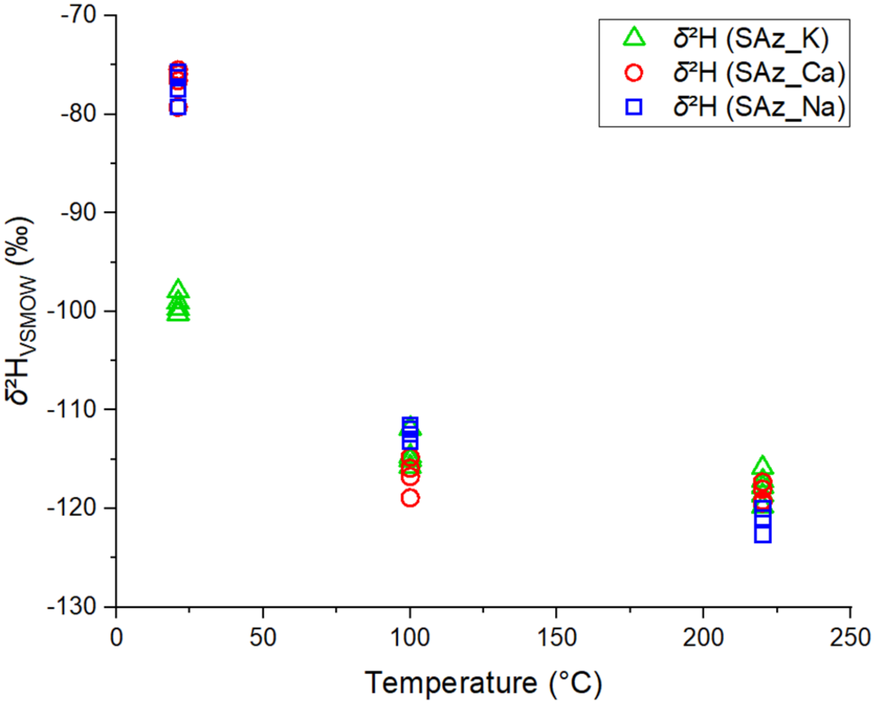

Figure 4.11. δ^2H for the three cation-saturated forms of the SAz-1 at the three pretreatment conditions.

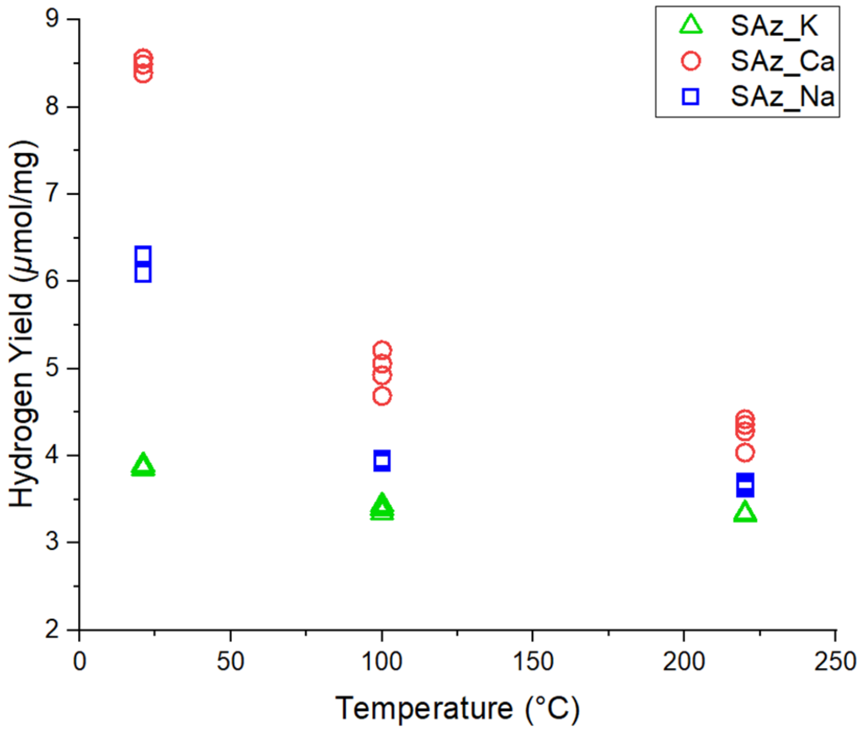

Figure 4.12. Hydrogen yields for SAz-1 for the same samples as illustrated in Figure 4.11.

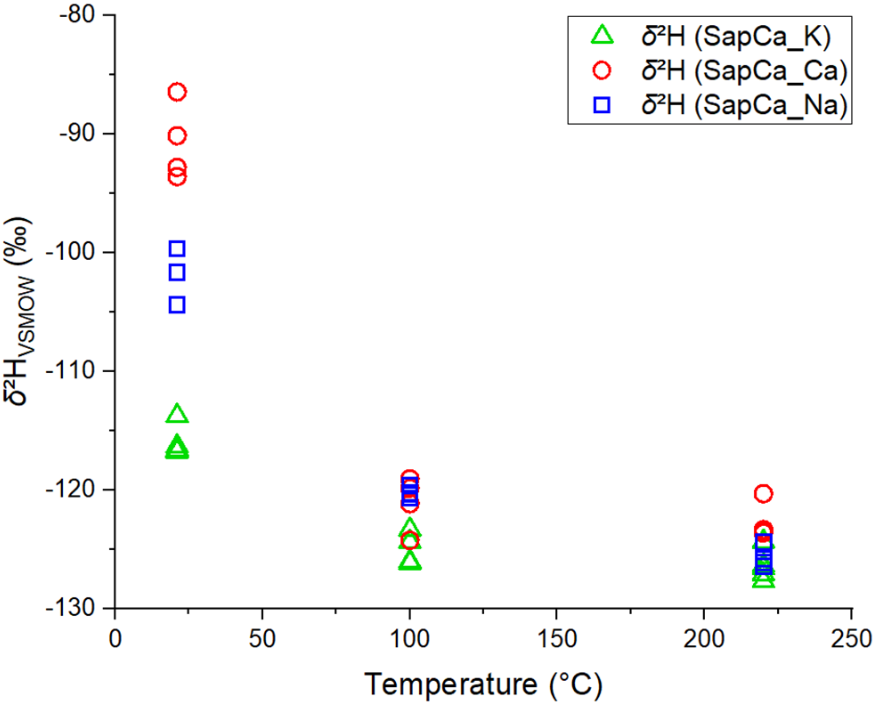

Figure 4.13. δ^2H for the three cation-saturated forms of SapCa-1 at the three pretreatment conditions.

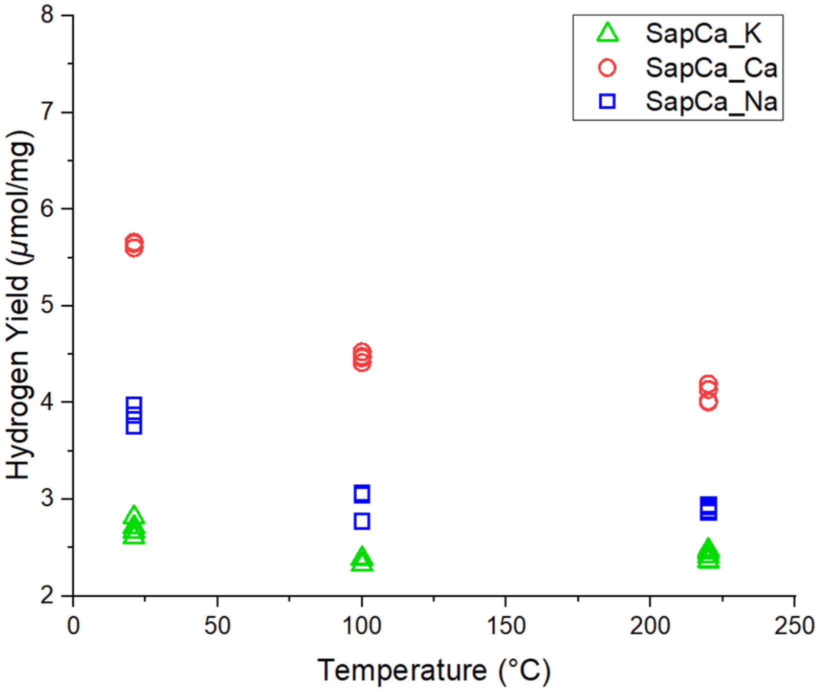

Figure 4.14. Hydrogen yields for SapCa-1 for the same samples illustrated in Figure 4.13.

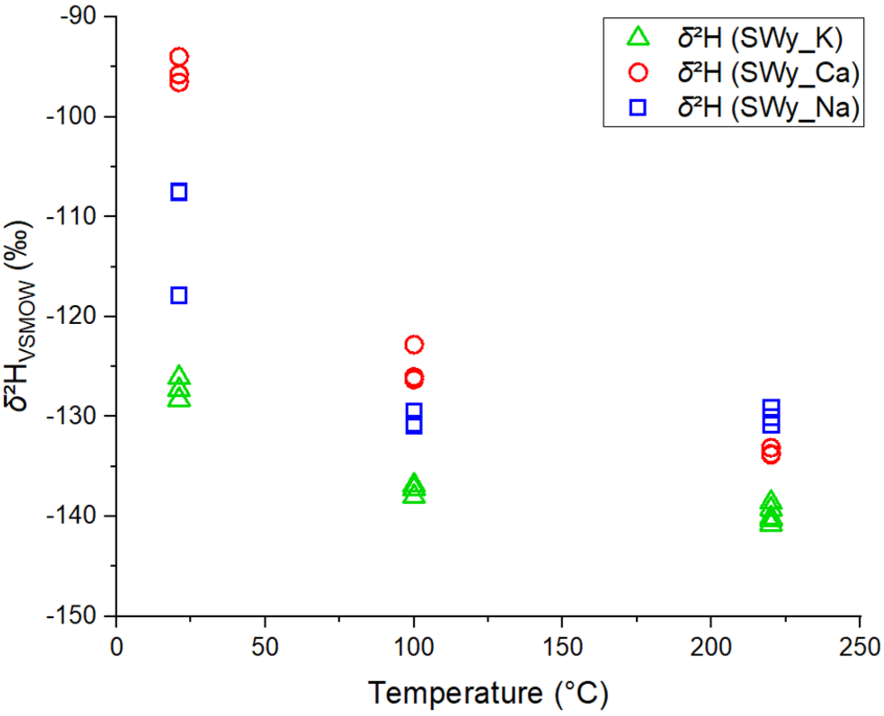

Figure 4.15. δ^2H for the three cation-saturated forms of SWy-1 at the three pretreatment conditions.

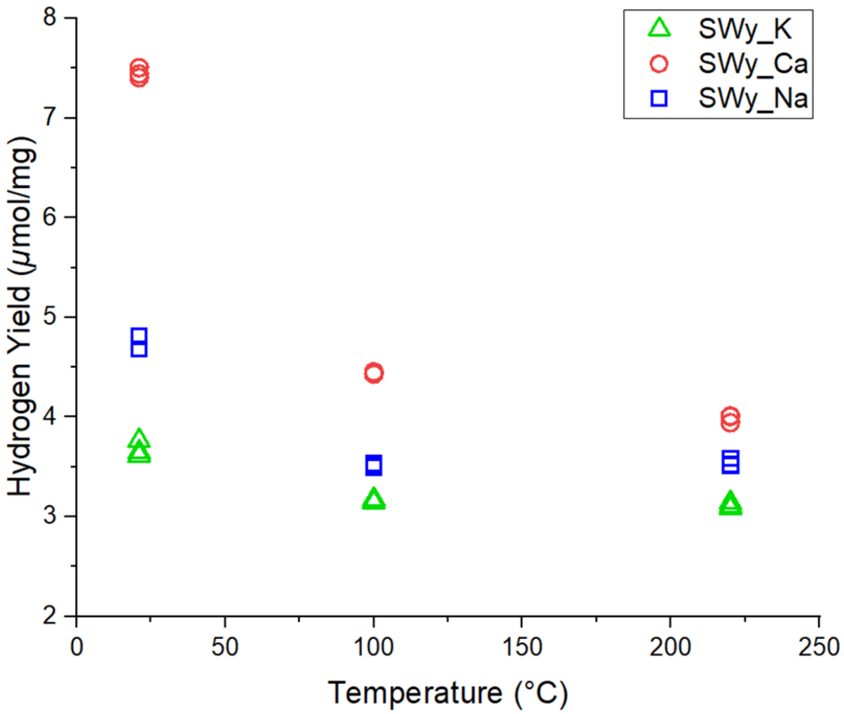

Figure 4.16. Hydrogen yields for SWy-1 for the same samples illustrated in Figure 4.15.

In contrast to the K-saturated samples, the Ca- and Na-saturated forms displayed large shifts to more negative δ^2H between the 21°C samples and samples degassed at 100°C. For samples degassed at 100°C versus those degassed at 220°C + 100°C, δ^2H either remained similar or shifted to somewhat more negative values for the latter treatment.

Except for STx-1 (Fig. 4.5), there was also a distinct difference among the δ^2H obtained for a given sample pretreated at 21°C, depending on cation saturation. For SWy-1, SWa-1, SHCa-1, and SapCa-1, Ca-saturated samples had the highest δ^2H, which subsequently decreased in order for Na- and K-saturated samples (Figs. 4.7, 4.9, 4.13, 4.15). The δ^2H of the SAz-1 21°C sample were similar for the Ca and Na forms, but decreased by nearly 20 ‰ for the K-saturated sample (Fig. 4.11). The SAz-1, SapCa-1, and SHCa-1 samples degassed at 100°C and 220°C had closely overlapping δ^2H for all cation saturations (Figs. 4.9, 4.11, 4.13). For STx-1, SWy-1, and SWa-1 there was still a difference in δ^2H for the different cation saturations up to 220° + 100°C treatment (Figs. 4.5, 4.7, 4.15).

The hydrogen yields followed a similar pattern for all smectites; Ca-saturated forms had the highest yields followed by the Na- and K-saturated forms (Figs. 4.7, 4.8, 4.10, 4.12, 4.14, 4.16). The 21°C samples displayed distinct differences in yield among the cation forms. This separation narrowed progressively between samples degassed at 100°C and 220° + 100°C. The decrease in hydrogen yield from the 21°C treatment to degassing at 220° + 100°C was largest for Ca-saturated forms, much smaller for Na-saturated forms, and smallest for K-saturated forms. After degassing at 220°+100°C, all cation forms of SAz-1, SWa-1, STx-1, and SWy-1 returned the narrowest spread in hydrogen yields (Figs. 4.6, 4.8, 4.12, 4.16), while SapCa-1 and SHCa-1 continued to have significantly higher yields for the Ca-saturated aliquot compared to the other cation forms (Figs. 4.10 and 4.14).

4.3 Thermogravimetric (TG) Analysis Results

At the beginning of the TG analysis, an isothermal heating segment of 4 hours at 220°C was added to simulate the vacuum oven conditions of four-hour heating at 220°C prior to TCEA-CF-IRMS isotopic measurements. As with the vacuum oven preheating, this step is intended to remove adsorbed water from the clay mineral, so that the mass loss of the evolved water from the structural hydroxyl groups can be measured accurately, and thus correspond to what should be a “dry sample”. Mass loss for each cation form of each of the six smectite samples was calculated beginning at, and normalized to the apparent “dry mass” at the end of the isothermal heating segment to the end of the ramp heating at ~1000°C (Table 4.4).

Table 4.4. Temperature of the major mass loss event for the different cation-saturated forms of each smectite.

Sample	Major mass loss temperature (°C)	Mass loss (%)
SapCa-1_K	820	4.69
SapCa-1_Ca	825	5.44
SapCa-1_Na	810	4.68
SAz-1_K	595	5.16
SAz-1_Ca	615	5.77
SAz-1_Na	610	5.52

SHCa-1_K	625	6.64
SHCa-1_Ca	620	6.60
SHCa-1_Na	625	6.13
STx-1_K	475	4.77
STx-1_Ca	480	5.34
STx-1_Na	480	4.93
SWa-1_K	440	5.16
SWa-1_Ca	450	5.57
SWa-1_Na	445	5.36
SWy-1_K	605	6.28
SWy-1_Ca	650	6.62
SWy-1_Na	630	6.82

The TG patterns for all samples and their various exchangeable cation saturations are illustrated in Figures 4.17-4.22 below.

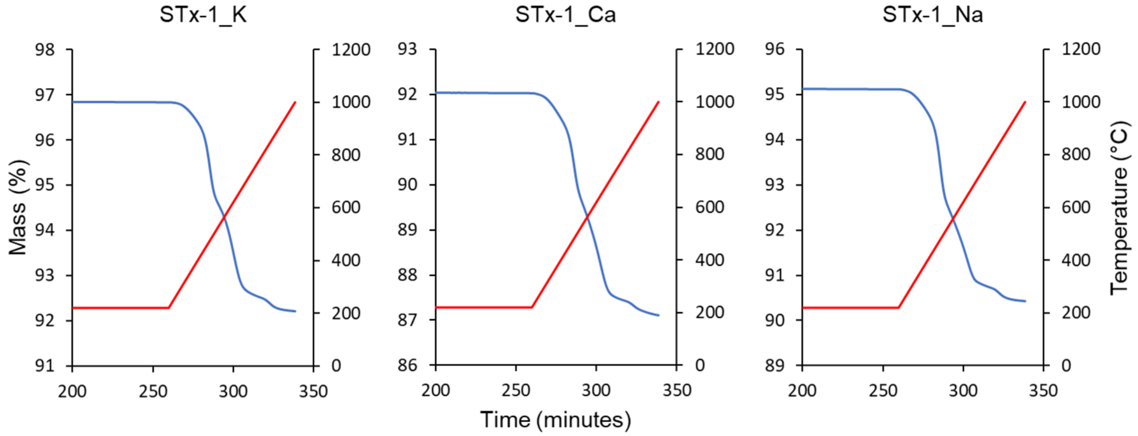

Figure 4.17. TG analysis of the <2 *μ*m STx-1, K-, Ca-, and Na-saturated smectite. The blue line represents the mass loss curve and the red line the isothermal heating segments.

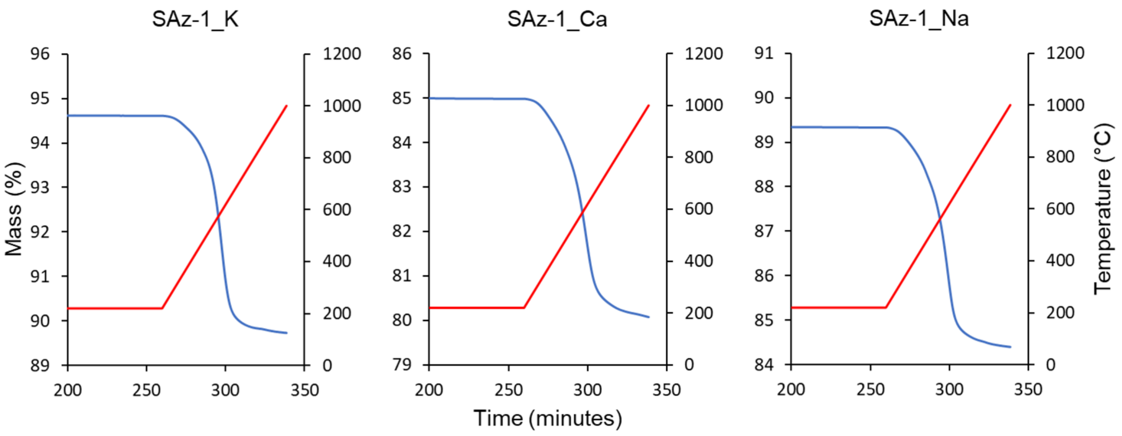

Figure 4.18. TG analysis of the <2 μm SAz-1, K-, Ca-, and Na-saturated smectite. The blue line represents the mass loss curve and the red line the isothermal heating segments.

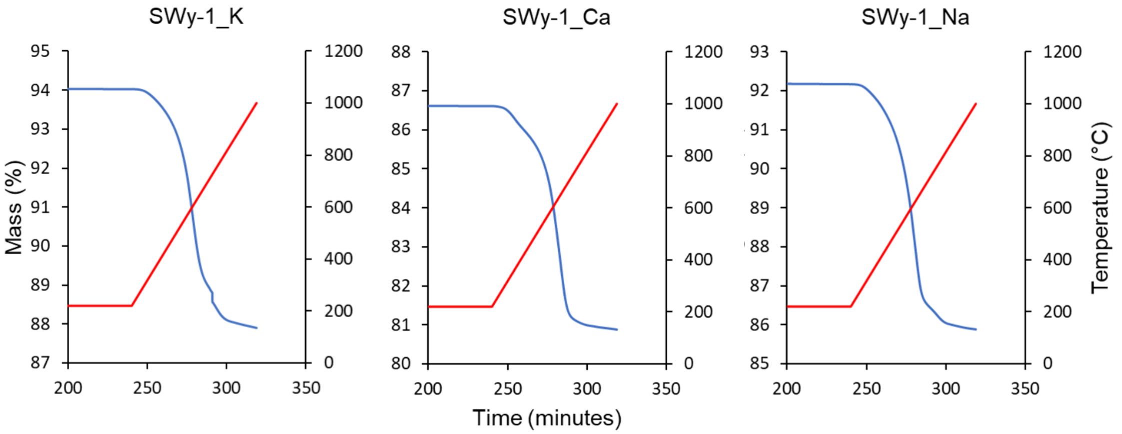

Figure 4.19. TG analysis of the <2 μm SWy-1, K-, Ca-, and Na-saturated smectite. The blue line represents the mass loss curve and the red line the isothermal heating segments.

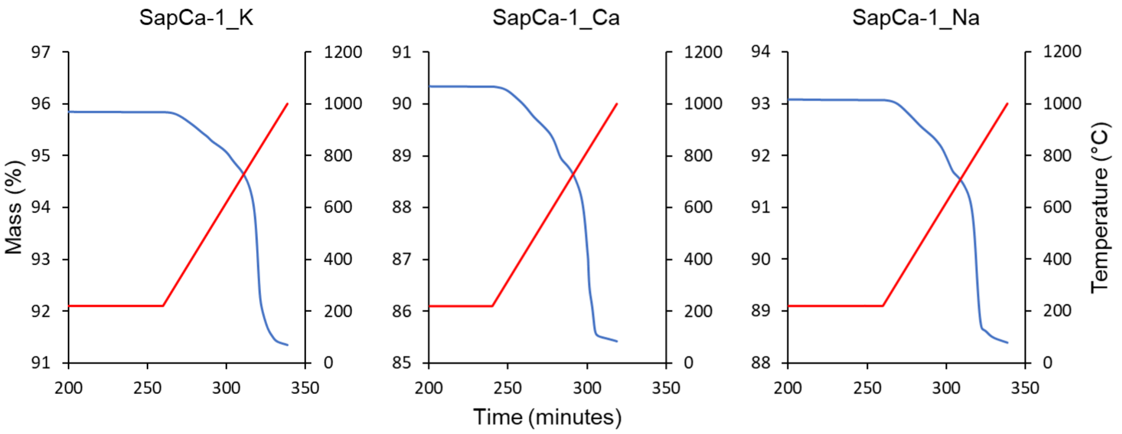

Figure 4.20. TG analysis of the <2 μm SapCa-1, K-, Ca-, and Na-saturated smectite. The blue line represents the mass loss curve and the red line the isothermal heating segments.

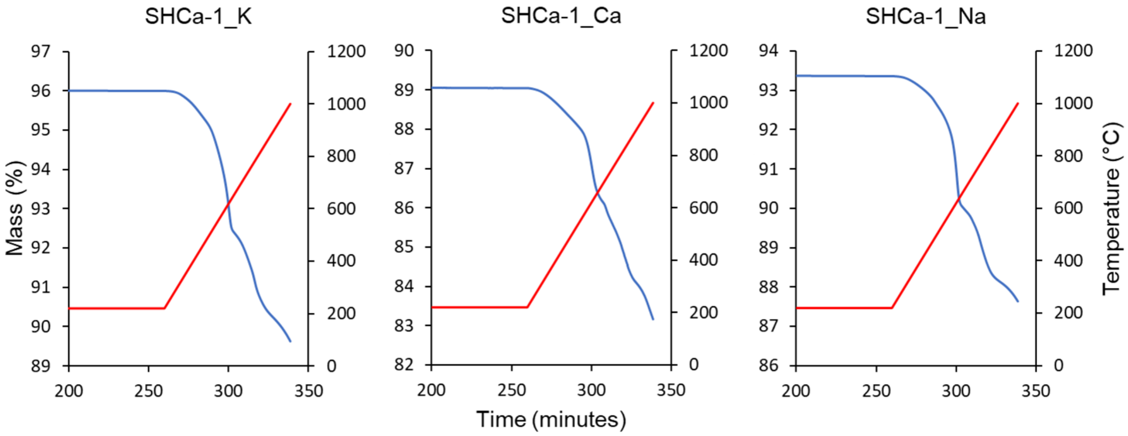

Figure 4.21. TG analysis of the <2 *μ*m SHCa-1, K-, Ca-, and Na-saturated smectite. The blue line represents the mass loss curve and the red line the isothermal heating segments.

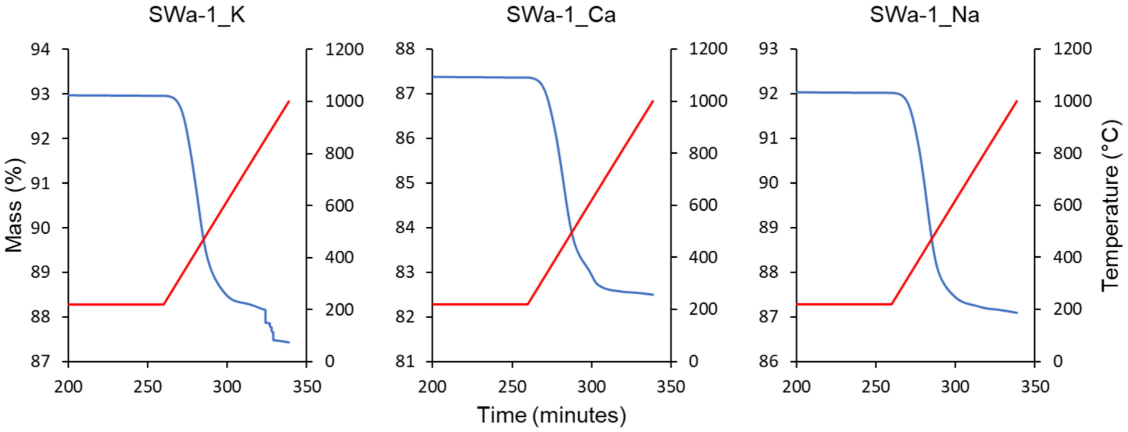

Figure 4.22. TG analysis of the <2 *μ*m SWa-1, K-, Ca-, and Na-saturated smectite. The blue line represents the mass loss curve and the red line the isothermal heating segments.

Relatively high temperature mass loss was observed for all cation forms of SapCa-1, which showed primary mass loss event peaks in the 800°C range (Figs. 4.20). The lowest temperature mass loss event occurred at slightly above 400°C for all cation-saturations of SWa-1 (Figs. 4.22). The other four smectites displayed primary mass loss events in the 600°C range for all cation forms (Figs. 4.17-4.19 and 4.21). Dehydroxylation was the primary mass loss event for all samples.

A slight difference in the temperature of the primary mass loss events was noticed among the different cation-saturations of all smectites (Table 4.4). The general trends were for the Ca-saturated forms of the smectites to have the highest temperatures for their primary mass loss events. The K- and Na-saturated forms typically displayed similar or the same temperatures for primary mass loss, with the K-saturated form trending to lower temperatures than the Na-saturated form for four of the six smectites (Table 4.4).

A few steps of mass loss also occurred at the end of the ramp heating segment for the SWa-1 K-saturated form. These are experimental artefacts, however, resulting from sample material movement on the analysis pan during heating (Fig. 4.22), and were excluded from the mass loss calculations. This technical problem also affected the SWy-1 K-saturated sample, but as the movement occurred during a mass loss event, the mass loss at the point of the drop was calculated and added to the main mass.

With the exception of SHCa-1, the highest mass loss was observed for Ca-saturated forms of the smectites, followed by Na-saturated forms (Table 4.4). The lowest mass loss was measured for K-saturated forms of each smectite sample (Table 4.4).

Chapter 5

5 Discussion

5.1 Dehydration

The complete removal of adsorbed water from a clay mineral is imperative in order to accurately measure the δ^2H of its structural hydroxyl hydrogen. Previous studies, however, do not agree on an ideal heating/degassing temperature or length of time for complete removal of adsorbed water from clay mineral surfaces (Berend *et al.*, 1995;VanDeVelde & Bowen, 2013; Bauer & Vennemann, 2014; Kuligiewicz & Derkowski, 2017). Complexity arises when attempting to find the temperature and time at which adsorbed water is completely removed without initiating removal of loosely bound hydroxyl groups (Marumo *et al.*, 1995; Sheppard & Gilg, 1996; Emmerich *et al.*, 1999; Kuligiewicz & Derkowski, 2017).

The TG curves obtained in this study provided information on the temperature of the start of dehydroxylation and major mass loss temperature for each of the smectites (Figs. 4.17-4.22). For example, the SWa-1 nontronite reached the start of its major mass loss event at ~300°C, which was previously reported to be the onset of dehydroxylation for nontronite (Kuligiewicz & Derkowski, 2017). Saturation with a particular cation has also been previously reported to change the temperature of dehydroxylation by up to 60°C (Wolters & Emmerich, 2007). This effect was also observed in the present study; the temperatures of the major mass loss events typically increased from K- to Na- to Ca-saturation (Table 4.4).

Mass loss from the TG, as evolved water, can also be compared with the water-equivalent mass loss, calculated from the TCEA-CF-IRMS hydrogen yield for each sample. The assumptions in this comparison are that water evolution is the same for both the TG and TCEA high temperature conversion and that all mass loss or H_2-yield arises from dehydroxylation and formation of water only.

The theoretical mass loss for hydroxyl groups evolved as water can be calculated as follows:

$$[18.0/SW] \times 100 = EW\ \% , \qquad (Eq. 5.1)$$

based on a smectite structural formula with two hydroxyl groups per formula unit, where 18.0 (g/mol) is the molecular weight of one H_2O molecule formed from dehydroxylation of the two hydroxyl groups, SW is the molecular weight of the smectite based on its structural formula, and EW is the theoretical weight loss, in percent, of evolved water from the smectite.

The calculation for the mass loss of actual evolved water from an individual smectite sample determined by TCEA-CF-IRMS can be determined by:

$$[USGS57_{H\text{-}yield} / USGS57_{avg.amp}] \times [S_{amp} / S_{wt}] = S_{H\text{-}yield} , \qquad (Eq. 5.2)$$

where the hydrogen content an individual sample (S_{amp}) is measured from the mass spectrometer peak height for m/z = 2 for hydrogen, and sample weight in mg is denoted as S_{wt}. The amplitude (m/z =2 for hydrogen, as above) ($USGS57_{avg.amp}$) and weight ($USGS_{avg.wt}$) in mg used in the equation are the averages of the individual amplitude and weights of two or more USGS 57 standards included in TCEA-CF-IRMS batch. The H_2-yield for USGS 57 ($USGS57_{H\text{-}yield}$) in μmol/mg was calculated from the $USGS_{avg.wt}$ in mg x 2.135, which is derived from the expected H_2-yield (μmol) for an ideal structural formula of biotite. This equals the H_2-yield of the individual sample ($S_{H\text{-}yield}$) calculated from USGS 57 standard in μmol/mg.

Therefore, for a given sample:

$$[S_{avg.H\text{-}yield} \times 18.0 / 1000] \times 100 = S_{TCEA\text{-}H2Oequiv.} \qquad (Eq. 5.3)$$

where $S_{avg.H\text{-}yield}$ is the average of the $S_{H\text{-}yield}$ for several aliquots of the same sample in a TCEA-CF-IRMS batch, division by 1000 is required for unit conversion, equaling the mass loss in percentage water equivalent from the sample H_2-yield ($S_{TCEA\text{-}H2Oequiv.}$).

The TCEA-CF-IRMS hydrogen yields obtained after degassing at 220°C (Table 4.3) for each sample were converted to an equivalent mass loss for water and are plotted against the actual TG mass loss data in Figure 5.1. Two distinct groups emerged. In the first group, SapCa-1, STx-1, SAz-1, and SWa-1 of all cation-saturations displayed linearity and a near 1:1 ratio in mass loss between the two methods, and showed the same trend in hydrogen yield by cation saturation (hydrogen yield for K-saturation < Na-saturation < Ca-saturation).

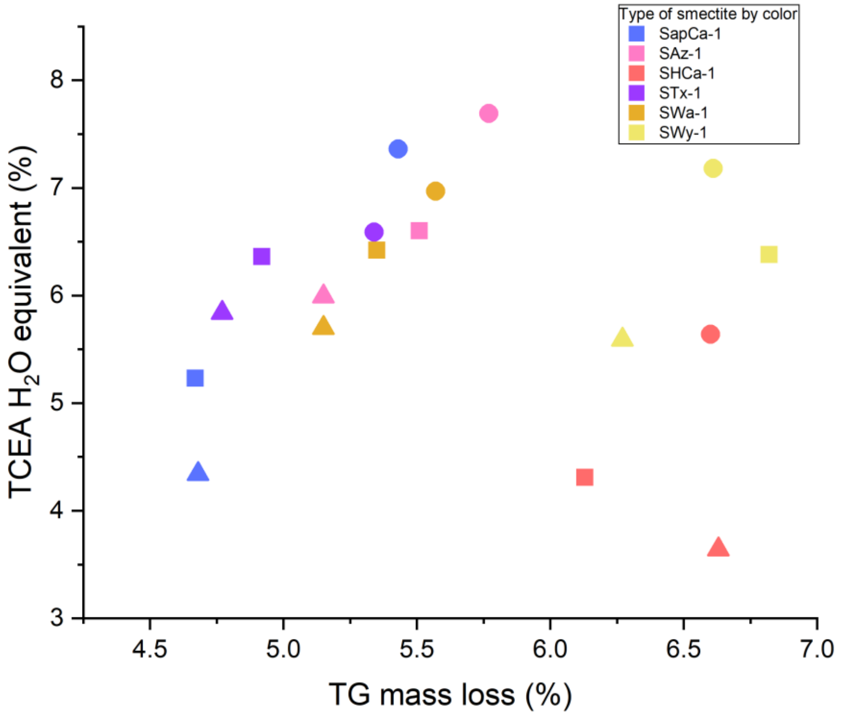

Figure 5.1. The water equivalent evolved from the six smectites by thermal conversion in the TCEA-CF-IRMS plotted against the TG mass loss from each sample in percentage. Shapes indicate cation-saturated forms: Ca= circle, K= triangle, and Na= square. All TCEA-CF-IRMS data are averaged from the triple temperature test where samples were degassed at 220°C.

The second group, consisting of SHCa-1 and SWy-1, followed the cation-saturation trend in yields as above, but did not show linearity between the TG and TCEA-CF-IRMS methods. This offset from linearity arises from the TG data, suggesting that impurities were released during heating in the TG. This is probable for SHCa-1, which contained calcite, as noted during the XRD analysis. Release of carbon dioxide during TG heating of the calcite would have caused additional mass loss. No major impurities, however, were noticed in the XRD pattern of SWy-1, although their putative presence may be undetectable (*e.g.*, amounts below XRD detection limit and/or amorphous material).

In Figures 5.2 to 5.7, the δ^2H for the different cation-saturated forms of each smectite are plotted versus hydrogen yield. As heating time and temperature increase, the difference between the cation-saturated forms of the smectites, in terms of δ^2H and hydrogen yields, decreases. Conversely, for shorter degassing times and lower temperatures, smectite δ^2H and hydrogen yields increase according to cation-saturation in the order K < Na < Ca.

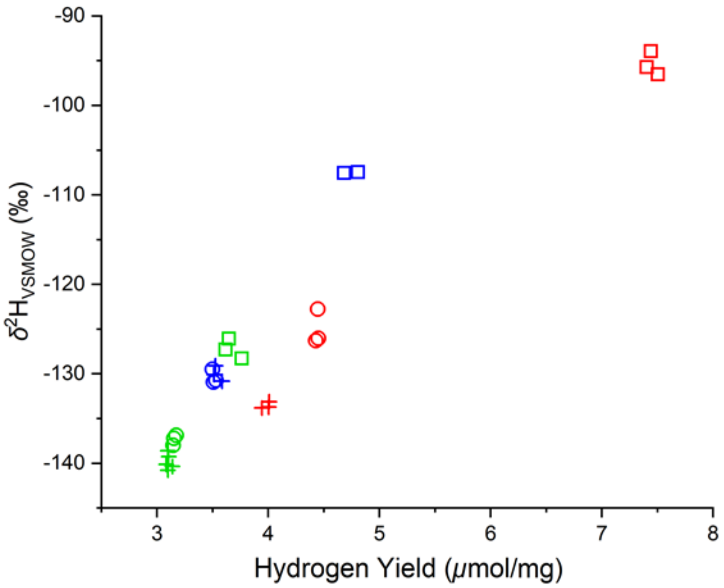

Figure 5.2. Plot of δ^2H versus hydrogen yield for SWy-1. Colors indicate cation-saturated forms: Ca (red), K (green), and Na (blue). Shapes represent pretreatment temperatures of 21°C (squares), 100°C (circles), and 220°C (crosses).

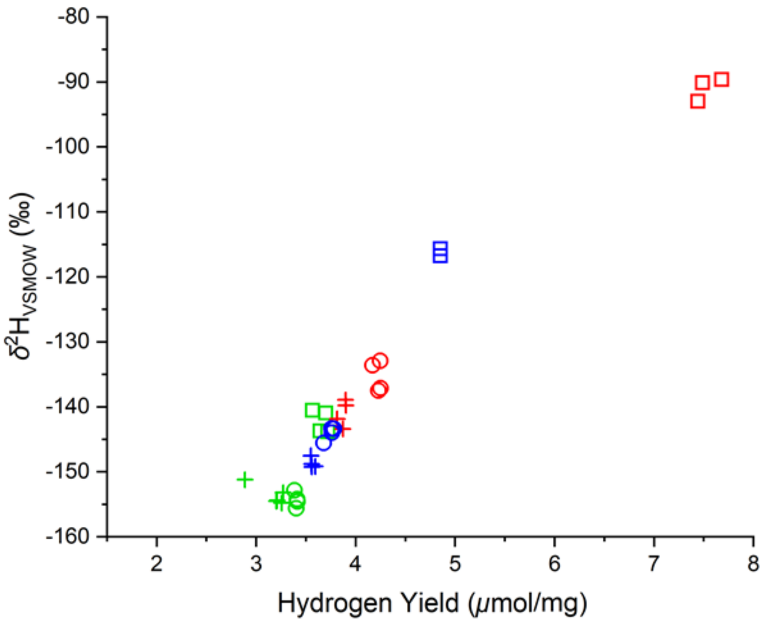

Figure 5.3. Plot of *δ*²H versus hydrogen yield for the SWa-1. Colors indicate cation-saturated forms: Ca (red), K (green), and Na (blue). Shapes represent pretreatment temperatures of 21°C (squares), 100°C (circles), and 220°C (crosses).

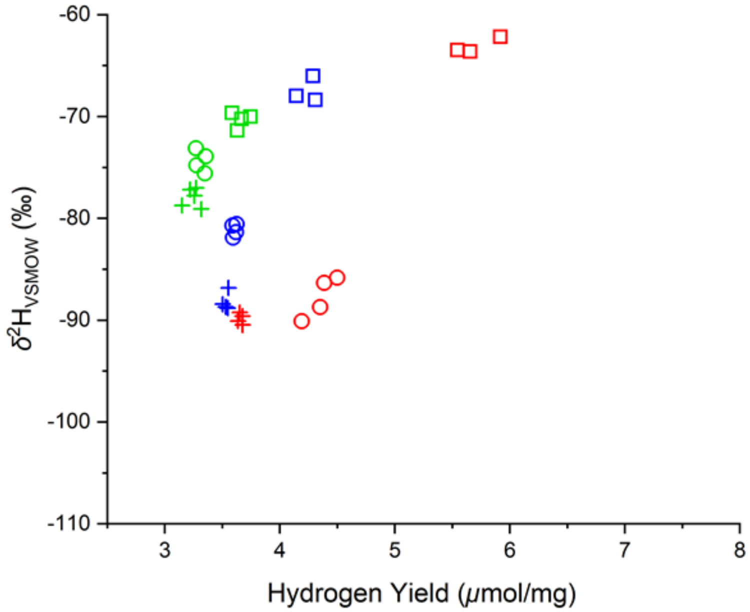

Figure 5.4. Plot of *δ*²H versus hydrogen yield for STx-1. Colors indicate cation-saturated forms: Ca (red), K (green), and Na (blue). Shapes represent pretreatment temperatures of 21°C (squares), 100°C (circles), and 220°C (crosses).

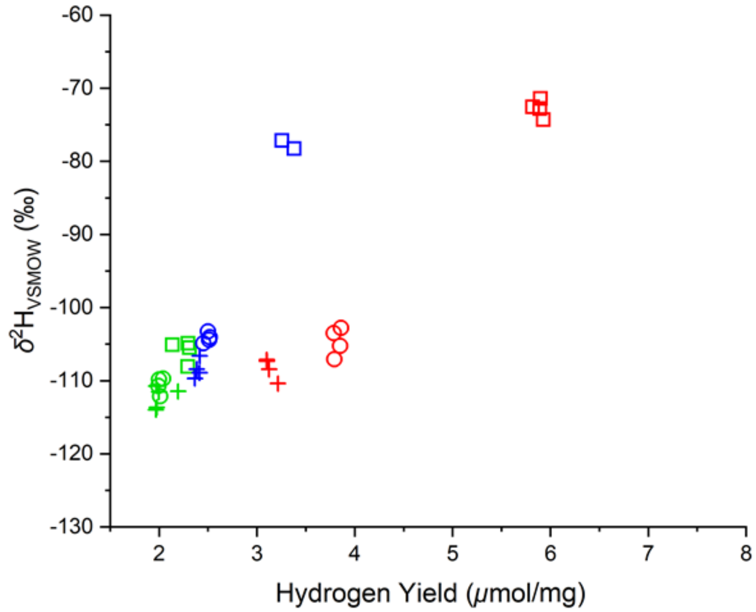

Figure 5.5. Plot of δ^2H versus hydrogen yield for SHCa-1. Colors indicate cation-saturated forms: Ca (red), K (green), and Na (blue). Shapes represent pretreatment temperatures of 21°C (squares), 100°C (circles), and 220°C (crosses).

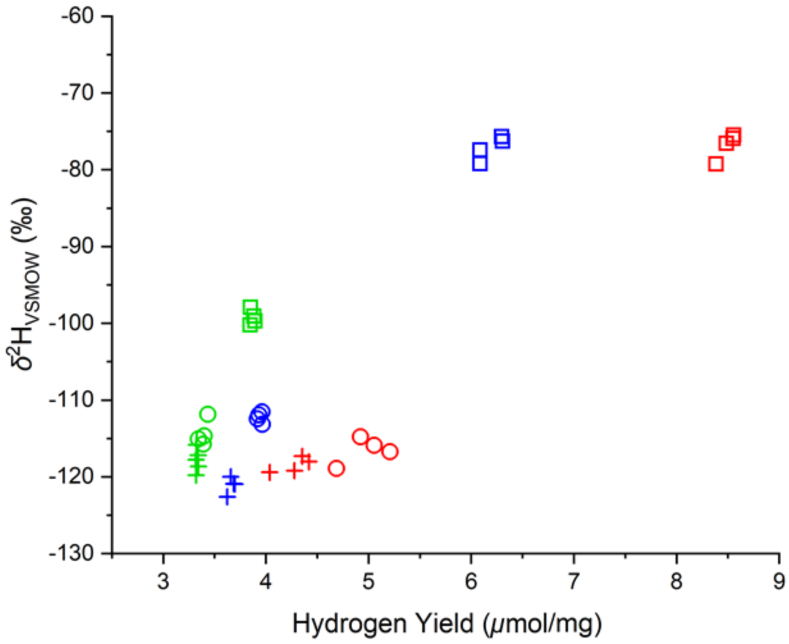

Figure 5.6. Plot of δ^2H versus hydrogen yield for SAz-1. Colors indicate cation-saturated forms: Ca (red), K (green), and Na (blue). Shapes represent pretreatment temperatures of 21°C (squares), 100°C (circles), and 220°C (crosses).

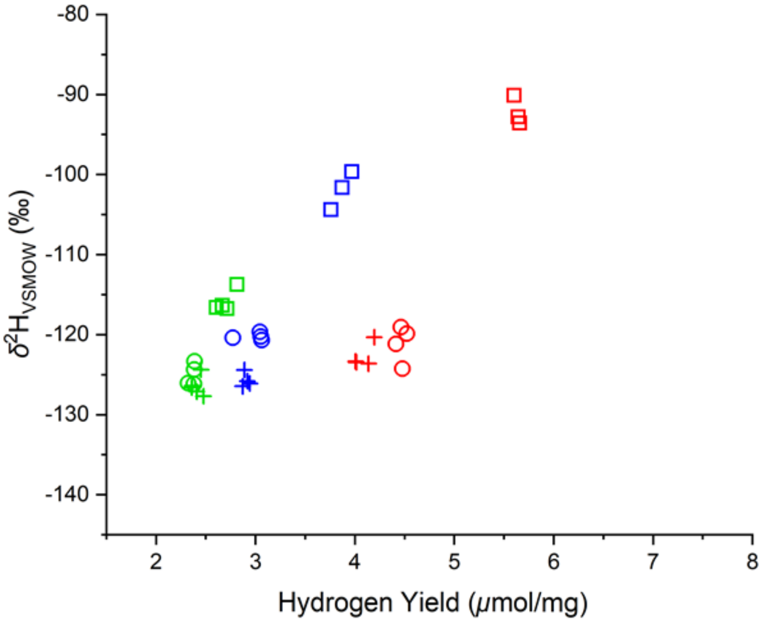

Figure 5.7. Plot of δ^2H versus hydrogen yield for SapCa-1. Colors indicate cation-saturated forms: Ca (red), K (green), and Na (blue). Shapes represent pretreatment temperatures of 21°C (squares), 100°C (circles), and 220°C (crosses).

The change in δ^2H and hydrogen yields for room temperature samples and those degassed at 100°C, 200°C, and 350°C for 0, 2, 4, and 6 hours was previously studied by VanDeVelde and Bowen (2013) for a montmorillonite of unknown cation-saturation. They observed that δ^2H and hydrogen yields showed comparable values for degassing times of 4 and 6 hours. The δ^2H for the K-saturated smectites in this study are also similar for 4 and 24 hour degassing times at 220°C (Table 4.3). The hydrogen yields and subsequent excess water, calculated from the difference between theoretical and actual yields, for the K-saturated forms degassed at 220°C for 4 and 24 hours were also comparable within analytical error (Table 5.1). Thus, extending the degassing time past 4 hours at this temperature does not appear to remove any additional adsorbed water. For comparison, hydrogen yield data is also shown for the 100°C degassing temperature and shows a much higher excess water content (~ 2x for most samples) than the 220°C degassing time, with amounts of adsorbed water following the same cation-saturation order (K < Na < Ca) (Table 5.1).

When assessing excess water retained by each of the smectites (Table 5.1), SapCa-1_K, SapCa-1_Na, and SHCa-1_K returned negative values. As the theoretical hydrogen yield is calculated from an ideal formula that assumes a homoionic cation saturation (*e.g.*, all original cations in the interlayer are replaced by K^+, Ca^{2+}, or Na^+ and no mix of cations remains), the actual occurrence of other cations in the interlayer could result in the observed yield calculation discrepancy. The negative values may also be related to early dehydroxylation; however, this is unlikely considering the dehydroxylation temperatures provided by the TG analyses for these particular clay minerals.

Table 5.1. Comparison of theoretical and actual H_2 yields with excess water obtained from each cation form. The theoretical yields calculated from smectite formulas are after Srodon and McCarty (2008) and assume complete homoionic cation saturation and the absence of impurities. Actual yields for the 220°C degassing temperature are as reported in Table 4.3 and those degassed at 100°C are averaged from the Triple Temperature Tests in Section 4.2.3.

Sample	Theoretical H_2 yield (μmol/mg) per formula unit	Actual H_2 yield (μmol/mg)	Difference	Weight % of excess water per unit of clay dry mass
		Degassed at 220°C for 4 hours		
STx-1_K	2.65	3.00	0.36	0.63
STx-1_Ca	2.70	3.42	0.72	1.29
STx-1_Na	2.70	3.38	0.69	1.23
SAz-1_K	2.62	3.00	0.38	0.67
SAz-1_Ca	2.69	3.79	1.10	1.98
SAz-1_Na	2.68	3.44	0.76	1.36
SWy-1_K	2.62	2.84	0.23	0.40
SWy-1_Ca	2.67	3.45	0.78	1.40
SWy-1_Na	2.66	3.20	0.54	0.96
SapCa-1_K	2.53	2.34	-0.19	-0.33
SapCa-1_Ca	2.58	3.61	1.03	1.86
SapCa-1_Na	2.57	2.54	-0.03	-0.05
SHCa-1_K	1.75	1.61	-0.14	-0.36
SHCa-1_Ca	1.78	2.65	0.87	2.35
SHCa-1_Na	1.77	2.01	0.24	0.64
SWa-1_K	2.43	2.94	0.51	0.91
SWa-1_Ca	2.48	3.57	1.09	1.96
SWa-1_Na	2.48	3.30	0.83	1.48
		Degassed at 220°C for 24 hours		
STx-1_K	2.65	3.12	0.47	0.85

SAz-1_K	2.62	3.18	0.56	1.01
SWy-1_K	2.62	2.75	0.13	0.23
SapCa-1_K	2.53	2.32	-0.21	-0.38
SHCa-1_K	1.75	1.73	0.02	0.04
SWa-1_K	2.43	3.11	0.68	1.22
Degassed at 100°C for 4 hours				
STx-1_K	2.65	3.31	0.66	1.19
STx-1_Ca	2.70	4.36	1.66	2.99
STx-1_Na	2.70	3.61	0.91	1.64
SAz-1_K	2.62	3.39	0.77	1.39
SAz-1_Ca	2.69	4.97	2.28	4.10
SAz-1_Na	2.68	3.94	1.26	2.27
SWy-1_K	2.62	3.16	0.54	0.97
SWy-1_Ca	2.67	4.44	1.77	3.19
SWy-1_Na	2.66	3.51	0.85	1.53
SapCa-1_K	2.53	2.37	-0.16	-0.29
SapCa-1_Ca	2.58	4.47	1.89	3.40
SapCa-1_Na	2.57	2.98	0.41	0.74
SHCa-1_K	1.75	2.01	0.26	0.47
SHCa-1_Ca	1.78	3.82	2.04	3.67
SHCa-1_Na	1.77	2.50	0.73	1.31
SWa-1_K	2.43	3.40	0.97	1.75
SWa-1_Ca	2.48	4.22	1.74	3.13
SWa-1_Na	2.48	3.75	1.27	2.29

While VanDeVelde and Bowen (2013) also did not notice an appreciable difference between the δ^2H and hydrogen yields for their montmorillonite degassed at 200 and 350°C for the 4-hour time period, these tests were not applied to any specific cation-saturated form. In the present study, there is convergence towards similar δ^2H and hydrogen yields for the Ca, Na and K cation-saturated forms of the smectites when degassed at 220°C (Figs. 5.2-5.7). Despite this convergence at 220°C, however, a clear separation still exists for most smectites between the different cation-saturations for both δ^2H and hydrogen yield. The K-saturated forms of all smectites have the lowest hydrogen yields, with similar results obtained for any given smectite whether degassed at 100°C or 220°C. In contrast, higher and more variable hydrogen yields are associated with the Na-saturated forms, with the highest and most variable yields being obtained for the Ca-saturated forms. This behaviour can be attributed to the size, hydration enthalpy, and number of water molecules that each cation can bind (Cases *et al.*, 1997). As the K-saturated forms are the least affected by rehydration, given the low hydration enthalpy of the K^+ ion, the δ^2H obtained for the K-saturated forms of each smectite are likely closest to the “accurate” results for the δ^2H of hydroxyl hydrogen in each smectite.

For smectites heated at the same temperature, the hydration enthalpy of the interlayer cation was determined to be the primary factor controlling differences in residual water content (Kuligiewicz & Derkowski, 2017). After drying at 110°C, interlayer cations in smectites may still facilitate retention of up to three water molecules each (Kuligiewicz & Derkowski, 2017). This behaviour was also observed for the hydrogen yields at different degassing temperatures in this study. The potassium ion (K^+) has a very low hydration enthalpy and is large in size, which reduces the expansion ability of a K-saturated smectite and limits the amount of residual water this cation can bind in the interlayer (Kawano & Tomita, 1989). Therefore, for smectites saturated with a monovalent cation, dehydration may be complete between 200 and 300°C (Kuligiewicz & Derkowski, 2017). The opposite is true for Ca^{2+}, which has a high hydration enthalpy that effectively binds residual water in the interlayer of a Ca-saturated smectite, even after drying at >300°C (Kawano & Tomita, 1989; Kuligiewicz & Derkowski, 2017; Cases *et al.*, 1992). While Na^+ and K^+ both have low hydration enthalpies relative to Ca^{2+}, Na^+ is much smaller in diameter than K^+ (Cases *et al.*, 1992). This enables Na^+ to more readily adsorb or desorb residual interlayer water than K^+ (Kawano & Tomita, 1989). Given that Ca- and Na-saturated forms can still contain adsorbed water above 220°C, dehydroxylation may commence before complete removal of adsorbed water is achieved (Kuligiewicz & Derkowski, 2017). This was noted by Sheppard and Gilg (1996) who speculated that complete removal of adsorbed water, without some degree of structural hydrogen loss, may not be possible for some smectites, thus causing permanent bias in clay hydroxyl hydrogen isotope results.

5.1.1 External Controls on Dehydration

These samples were analyzed during the month of September, in London, Ontario, Canada. Accordingly, the average δ^2H (–133 ± 27 ‰, SD, n= 49; Longstaffe, unpublished data) was calculated for laboratory atmospheric water vapour from a thirteen-year record of atmospheric water vapor, collected at weekly intervals for the month of September in London, Ontario, Canada at a location situated 100 m from the LSIS laboratory. As previously shown on Figures 1.2 and 1.3 and discussed by Bauer and Vennemann (2014), the δ^2H of the surrounding atmospheric water vapour can significantly modify the δ^2H obtained for a clay mineral, even if only a small percentage is adsorbed and then not completely removed prior to analysis of the hydroxyl hydrogen.

The δ^2H of water that would condense from laboratory atmospheric water vapour (–133 ‰) was calculated for a temperature range of 0 to 220°C using the equation of Horita and Wesolowski (1994):

$$10^3 \ln\alpha_{(l\text{-}v)} = 1158.8(T^3/10^9) - 1620.1(T^2/10^6) + 794.84(T/10^3) - 161.04 + 2.9992(10^9/T^3) \qquad (Eq. 5.4)$$

The condensed-water δ^2H was selected with consideration of general atmospheric condensation systematics following Rayleigh distillation, whereby water condensed from the vapour to liquid state, at a given temperature, is enriched in ^{2}H relative to the vapour (Clark & Fritz, 1997). This approach assumes that: (i) the supply of atmospheric water vapour was infinite relative to the amount of water condensed onto the clay minerals, and (ii) condensation occurred at equilibrium.

Figure 5.8 illustrates the δ^2H of water condensed onto the clay mineral from atmospheric water vapour (δ^2H = –133 ‰) at 21, 100 and 220°C. Average values of δ^2H and hydrogen yield for the SWy-1 smectite (Analysis 22) in all cation forms are also shown. Consistent with the values in Table 5.1, the hydrogen yield varies predictably for each cation form depending on the amount of adsorbed water remaining after degassing, following the order Ca > Na > K. The adsorbed water remaining after degassing also appears to impact the δ^2H of the different cation forms. The Ca- and Na-saturated forms shift toward the δ^2H of the condensed water, indicating incomplete removal of adsorbed water – a feature also indicated by hydrogen yields in excess of theoretical values. In contrast, the δ^2H of K-saturated form remains relatively unchanged between 100 and 220°C, and does not exhibit a high excess hydrogen yield, both of which indicate that retention of residual adsorbed water was limited. To test this observation further, the δ^2H of the STx-1 smectite (Analysis 30) was plotted in Figure 5.9 on the same curve for the condensed water δ^2H. The δ^2H of the STx-1 Ca- and Na-saturated forms again move towards the δ^2H of the condensed water, while the δ^2H of the K-saturated form remains relatively unchanged, with the size of excess hydrogen yields also following the pattern observed for SWy-1. In short, the higher hydration enthalpy of Ca^{2+}, and to a lesser degree Na^+, and hence their greater ability to bind residual water in the smectite interlayer relative to K^+, causes the effects of residual adsorbed water on hydroxyl δ^2H (and hydrogen yield) to be highest for Ca-saturated smectites and lowest for K-saturated smectites (Figs. 5.2-5.7).

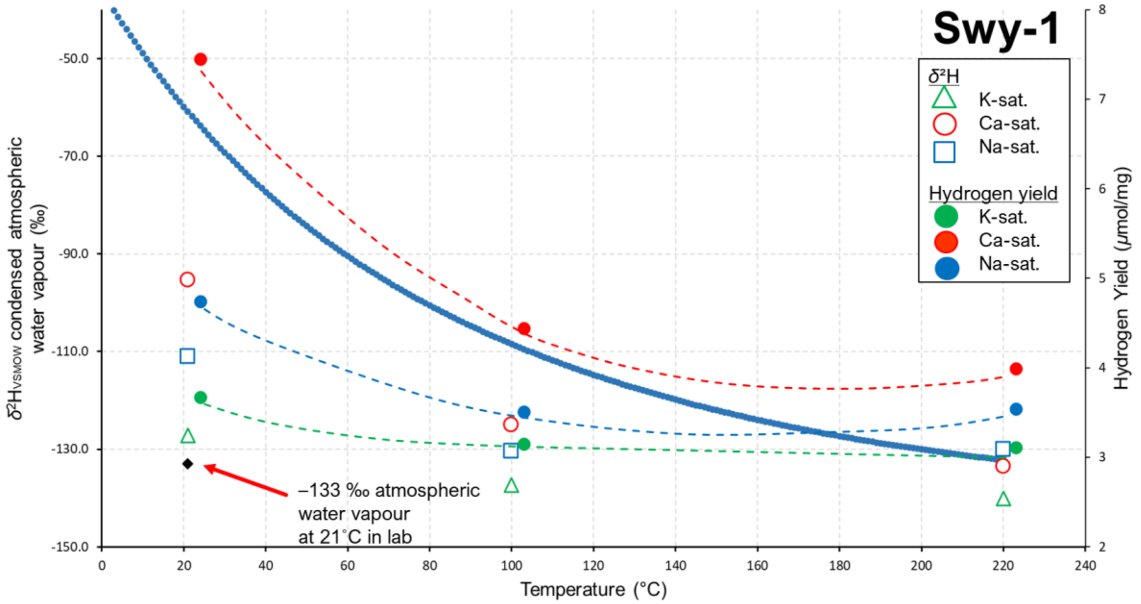

Figure 5.8. Average δ^2H and average hydrogen yields for the three cation-saturated (K-, Na-, or Ca-sat.) forms of the SWy-1 smectite for three different temperatures (hydrogen yields displayed with 3°C offset). The δ^2H (–133 ‰; black diamond) of local atmospheric water vapour at 21°C is also shown. The blue curve represents the calculated δ^2H of water condensed onto the smectite from the atmosphere from 0 to 220°C. Dashed curves highlight smectite hydrogen yield changes relative to the degassing temperature used to remove adsorbed water.

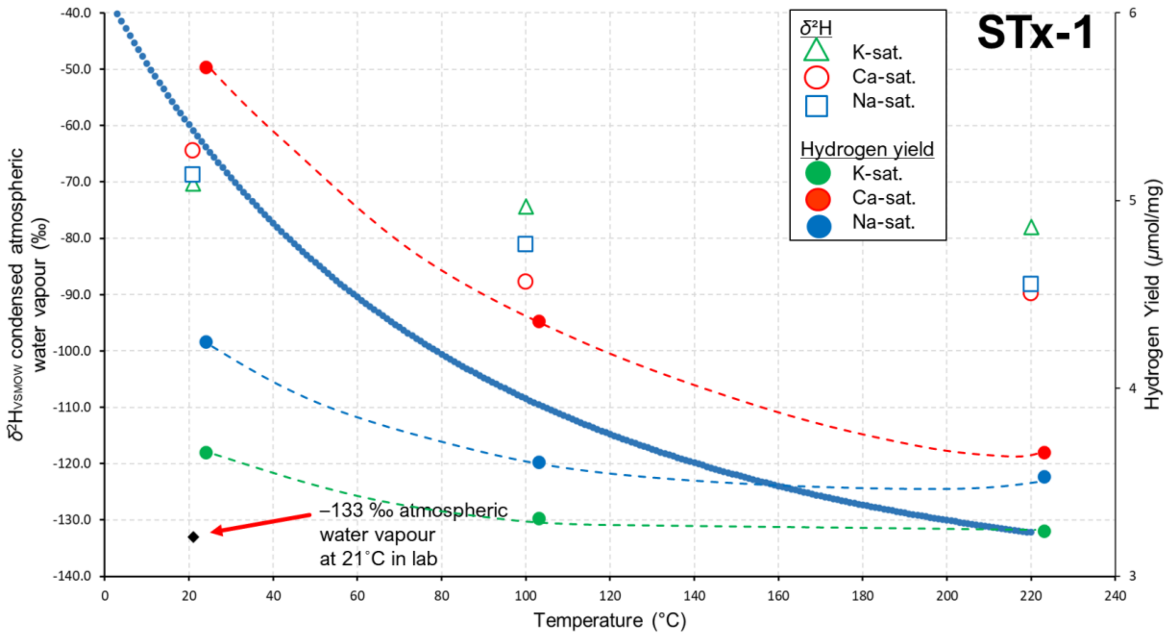

Figure 5.9. Average δ^2H and average hydrogen yields for the three cation-saturated (K-, Na-, or Ca-sat.) forms of the STx-1 smectite for three different temperatures (hydrogen yields displayed with 3°C offset). The δ^2H (–133 ‰; black diamond) of local atmospheric water vapour at 21°C is also shown. The blue curve represents the calculated δ^2H of water condensed onto the smectite from the atmosphere from 0 to 220°C. Dashed curves highlight smectite hydrogen yield changes relative to the degassing temperature used to remove adsorbed water.

5.2 Rehydration

The SAz-1 loading time experiment tested, for each cation saturation, whether, and for how long, heat retained by the Al-tray would inhibit rehydration of smectite, and hence attenuate modification its δ^2H resulting from atmospheric water vapour contamination. For a given cation saturation, the smectite δ^2H obtained for the 2- and 4-minute tests displayed similar compositions and hydrogen yields. The 4-minute samples show some slight movement toward higher δ^2H, but this may be related to inter-batch variability, as the corresponding hydrogen yields do not increase. Overall, the minimal impact on δ^2H indicates that use of the Al-tray, along with the samples being wrapped in silver foil, effectively limited rehydration for the 1 to 2.5 minute loading times achieved in this study, at least for our laboratory where the average RH is ~41-45 %, but maybe vary at a higher or lower relative humidity.

The shift to higher δ^2H and higher hydrogen yields at 10 minutes is almost certainly driven by the hydrogen isotope composition of local atmospheric water vapour. As noted by Bauer & Vennemann (2014), the δ^2H of atmospheric water vapour in a laboratory can vary by ± 10s of ‰ in relation to dominant airmasses and heating/cooling systems. Relative humidity could also be expected to have an impact on rehydration, whereby clay minerals may adsorb more water and at a quicker rate at higher relative humidity (Michot & Villieras, 2006). Fortunately, the relative humidity in the LSIS laboratory was relatively low during the month of September compared with other months, ranging between 41-45 %.

The δ^2H of atmospheric water vapour and water condensed from that vapour at 21°C provide information on whether such contamination should increase or decrease the δ^2H of a particular smectite. Figure 5.10 illustrates hydrogen isotope results for the SAz-1 smectite along with the calculated δ^2H (−60.9 ‰) of condensed local atmospheric water vapour. Adsorbed water with a higher δ^2H than the hydroxyl group hydrogen should cause an increase in the δ^2H measured for a partially rehydrated smectite.

As expected, rehydration proceeded differently for each of the three cation-saturated forms of the SAz-1 smectite. Between 4 and 10 minutes, the hydrogen yields for the K-saturated form did not indicate any appreciable rehydration from adsorption of atmospheric moisture, an observation supported by the very limited change in δ^2H over this time (Fig. 5.10). As discussed earlier, the minimal rehydration for the K-saturated sample can be attributed to the large size of K^+ and its low hydration enthalpy, thus limiting water adsorption in the interlayer (Kawano & Tomita, 1989; Kawano & Tomita, 1991b; Cases *et al.*, 1997). In contrast, the δ^2H of the Ca-and Na-saturated forms increased by ~5 ‰ over this time period (Fig. 5.10). Compared to K^+, the smaller size of Na^+ enables water to be adsorbed more efficiently, and for the Ca-saturated form, increased rehydration reflects its higher hydration enthalpy and ability to more strongly bind water in the smectite interlayer (Cases *et al.*, 1997).

Figures 5.8 and 5.9 can also be informative in the context of rehydration. The curve of δ^2H for condensed atmospheric moisture can be used to approximate the δ^2H of water adsorbed by the smectite as the Al-tray cools from 220°C.

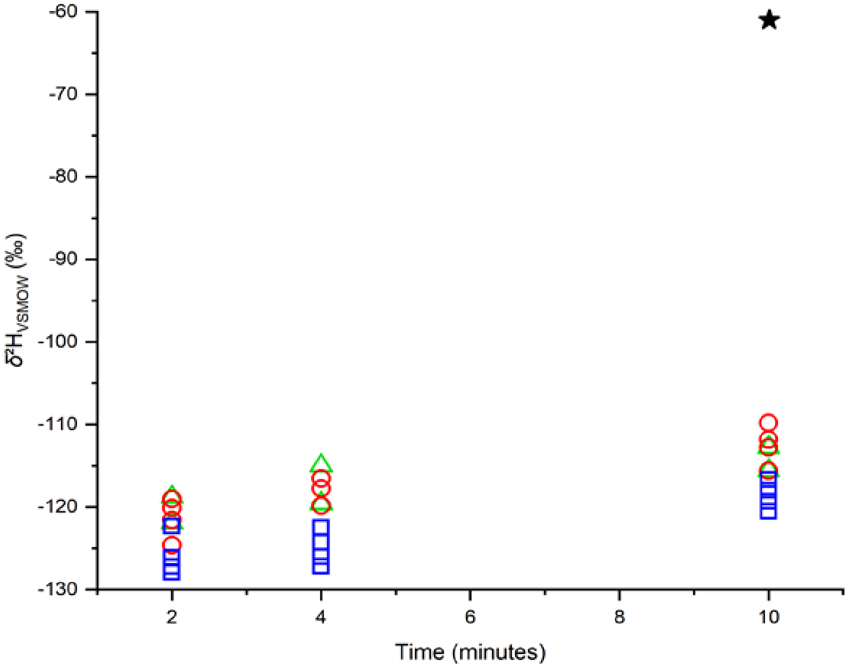

Figure 5.10. δ^2H of SAz-1 K- (green triangle), Ca- (red circle), and Na-saturated (blue square) smectite for autosampler loading times of 2, 4, and 10 minutes. The calculated δ^2H of water (−60.9 ‰, black star) condensed from local atmospheric water vapour is also shown.

5.3 Comparison of TCEA and Conventional Method Smectite δ^2H

Fagan (2001) used conventional methods that followed Godfrey (1962), as modified by Kyser and O'Neil (1984) to obtain δ^2H for the same CMS Source Clay smectites as analyzed in the present study. These analyses were also completed at Western's Laboratory for Stable Isotope Science.

The measurements were performed on untreated, <2 μm size fractions of these smectites. The analyses involved on-line degassing of ~70 mg of each smectite in a quartz tube at 150°C under active vacuum for 2-3 hours to remove adsorbed and interlayer water. The samples were then heated under static vacuum to 1000°C to release hydroxyl groups from the smectite, mostly as water vapour. Any $H_{2(g)}$ also released at this step was converted to H_2O by reaction with copper oxide at 550°C, and then combined cryogenically with the water already released. The water was then reacted with depleted uranium heated to ~800°C to quantitatively form $H_{2(g)}$. The $H_{2(g)}$ was cryogenically condensed on activated charcoal and submerged in liquid nitrogen, and then released into a VG Prism II dual-inlet, triple collecting IRMS for measurement of δ^2H.

Figures 5.11 to 5.16 illustrate the δ^2H obtained by Fagan (2001) using the conventional method for untreated <2 μm smectite samples of unknown interlayer cation saturation (most likely Ca- and/or Na-dominated). These results are compared the δ^2H obtained in the present study by TCEA-CF-IRMS for the three cation-saturated forms of the same smectite samples.

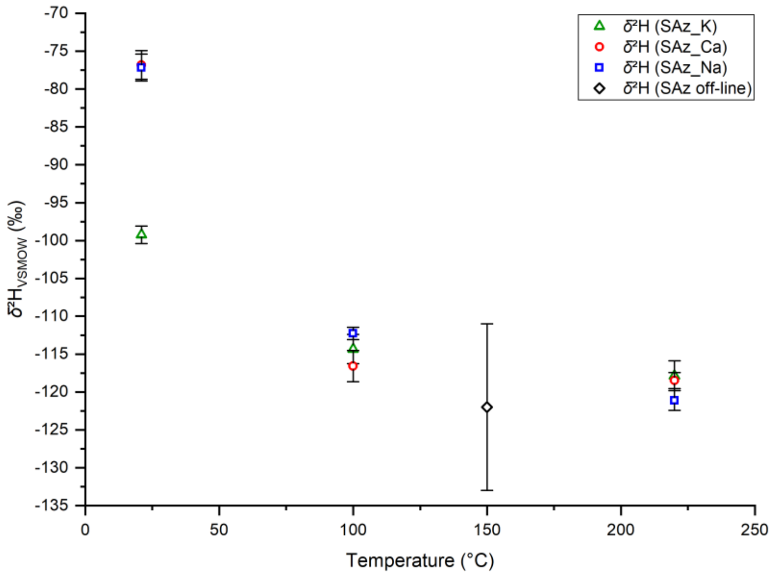

Figure 5.11. Average δ^2H of SAz-1 for the TCEA-CF-IRMS method (error bars from the triple temperature test for each cation form) compared with a range of −135 to −108 ‰ (average = –122 ‰, n=7; open diamond) obtained using the conventional method by Fagan (2001).

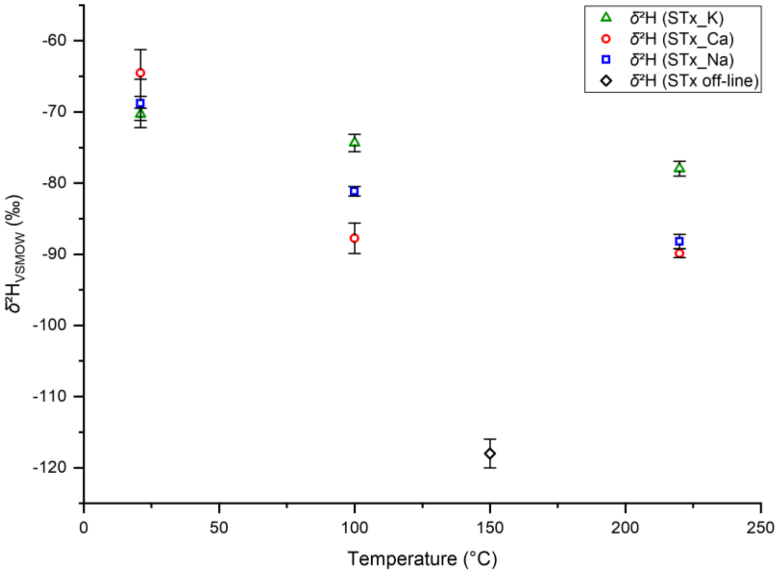

Figure 5.12. Average δ^2H of STx-1 for the TCEA-CF-IRMS method (error bars from the triple temperature test for each cation form) compared with a range of −122 to −115 ‰ (average = –118 ‰; n=9; open diamond) obtained using the conventional method by Fagan (2001).

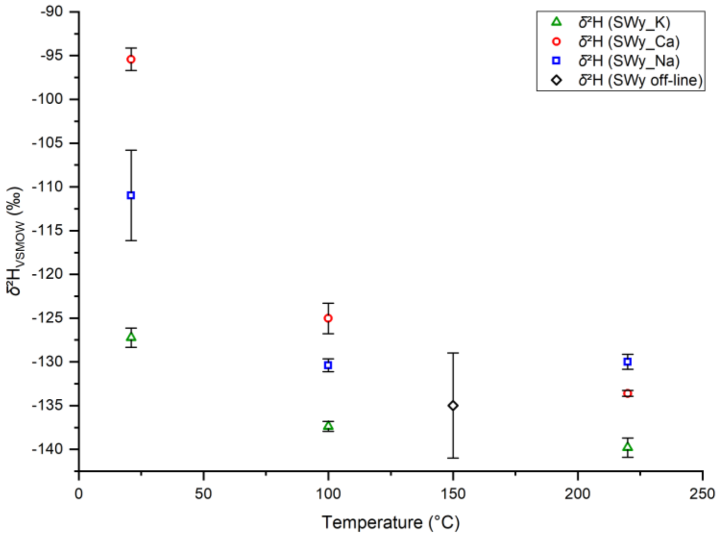

Figure 5.13. Average δ^2H of SWy-1 for the TCEA-CF-IRMS method (error bars from the triple temperature test for each cation form) compared with a range of −145 to −127 ‰ (average = –135 ‰; n=8; open diamond) obtained using the conventional method by Fagan (2001).

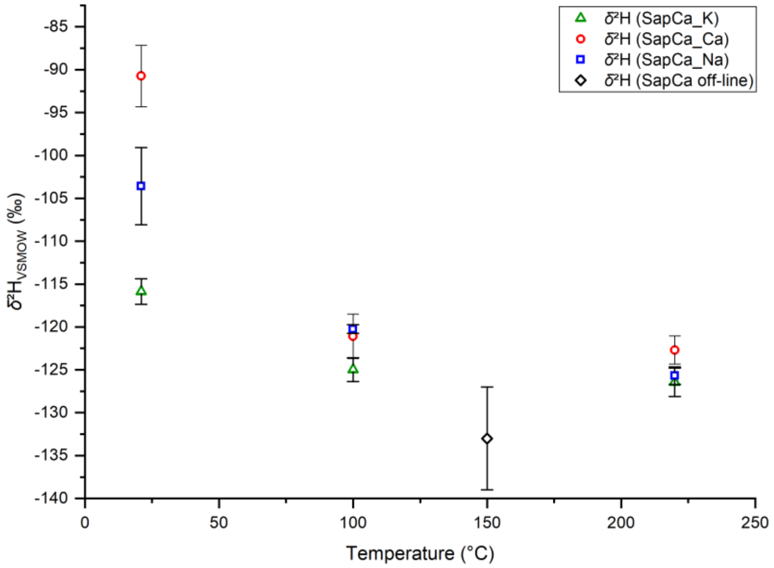

Figure 5.14. Average δ^2H of SapCa-1 for the TCEA-CF-IRMS method (error bars from the triple temperature test for each cation form) compared with a range of −141 to −132 ‰ (average = –133 ‰; an n=6; open diamond) obtained using the conventional method by Fagan (2001).

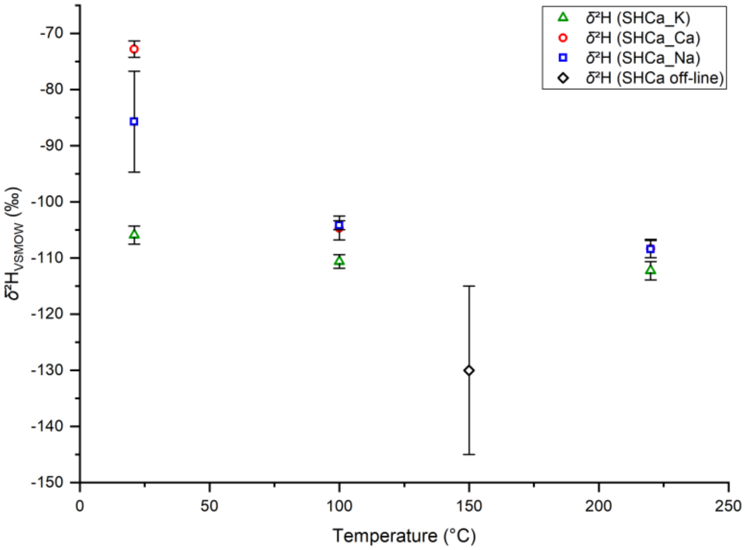

Figure 5.15. Average δ^2H of SHCa-1 for the TCEA-CF-IRMS method (error bars from the triple temperature test for each cation form) compared with a range of −144 to −114 ‰ (average = –130 ‰; n=3; open diamond) obtained using the conventional method by Fagan (2001).

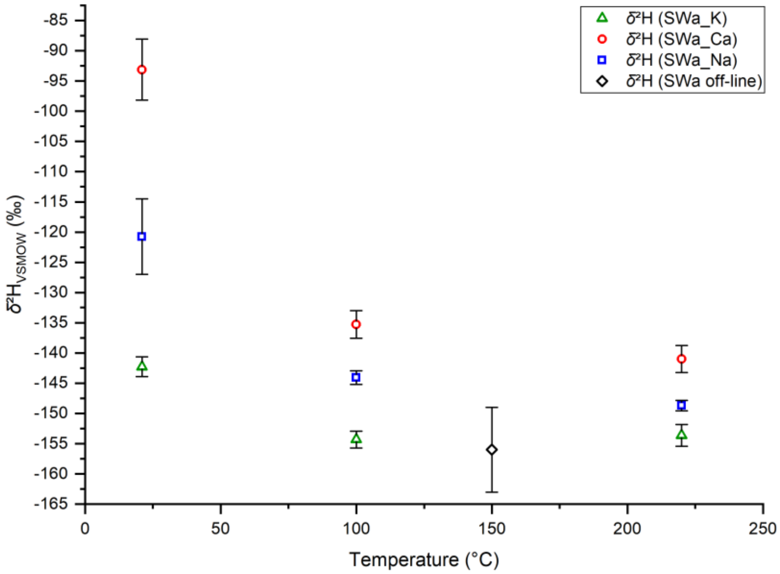

Figure 5.16. Average δ^2H of SWa-1 for the TCEA-CF-IRMS method (error bars from the triple temperature test for each cation form) compared with a range of −167 to −148 ‰ (average = –156 ‰: n=6; open diamond) obtained using the conventional method by Fagan (2001).

In this comparison, outliers in the TCEA-CF-IRMS data were not removed in order to provide as realistic a comparison as possible with results from the conventional method. The comparison shows that the conventional method has much poorer reproducibility and may be less accurate than the TCEA-CF-IRMS method. This is illustrated by the error bars shown in Figures 5.11 to 5.16, where variances for δ^2H from the conventional method range from 7 to 30 ‰, compared to typical variances of <1 to <5 ‰ for the TCEA-CF-IRMS method. Despite the improved precision of the TCEA-CF-IRMS method, accuracy is still a question for both methods. The conventional method, in theory, should provide the most accurate results as the smectites are not exposed to rehydration during degassing or dehydroxylation. However, given the large degree of variation in δ^2H obtained using the conventional method, other factors may limit the accuracy of this method. These might include incomplete removal of bound water during degassing, sample inhomogeneity, and skill of the analyst. Currently, the best estimation of accurate δ^2H for each smectite is provided by the K-saturated forms, degassed at 220°C; these aliquots are least affected by rehydration and have returned the most consistent δ^2H throughout this study.

With the exception of STx-1 (Fig. 5.12), the average δ^2H obtained using the conventional method for smectite aliquots of unknown cation saturation degassed at 150°C are broadly similar to those obtained using the TCEA-CF-IRMS method for K-, Na- and Ca-saturated aliquots degassed at 100°C or 220°C (Figs. 5.11, 5.13-5.16). This provides some general verification that the TCEA-CF-IRMS method employed here is suitable for determining the δ^2H of smectite group minerals. The cause of the large discrepancy between methods in the average δ^2H obtained for STx-1 remains unclear.

These results also show that the TCEA-CF-IRMS method, inclusive of outliers, produces less variability in δ^2H than the conventional method, even though the latter approach virtually eliminates the possibility of sample rehydration.

The poorer reproducibility of the conventional analytical method may be a result of sample inhomogeneity. No treatments were applied to these samples other than physical isolation of a <2 μm size fraction; procedures to remove potential organic matter or to control exchangeable cation-saturation were not performed (Fagan, 2001). By comparison, analysis of USGS-57 (biotite) and USGS-58 (muscovite) by the conventional method at LSIS produced much better reproducibility with mean δ^2H (±SD) of −92.9 ± 2.8 ‰ and −28.1 ± 0.8 ‰, respectively (Qi *et al*., 2017). However, these phyllosilicates have a larger grain size and are non-expandable, which limits the potential impacts of rehydration on δ^2H.

5.4 Proposed Hydroxyl Hydrogen Isotope Compositions for the CMS Smectites

Table 5.2 summarizes the δ^2H of the K-saturated forms of the six CMS smectites with the mineralogical and geological information for these samples. The K-saturated form outgassed for 4 hours achieved the most complete dehydration and therefore appears to provide the most accurate δ^2H for the hydroxyl hydrogen of each smectite. It is recommended that these values for these smectites be adopted for wider use by the scientific community.

Table 5.2. Characteristics of smectite samples used in this study (Moll, 2001; Baker and Strawn, 2014; Srodon & McCarty, 2008) with the δ^2H of the K-saturated forms degassed at 220°C for 4 hours.

Sample	Species	Octahedral Structure	Origin (U.S.A.)	Age	Formation Conditions	Structural Formula	TCEA method δ^2H_{VSMOW} (‰)
STx-1	Montmorillonite	dioctahedral	Gonzales, Texas	Eocene	marine, sedimentary	$(M^{+}_{0.43})(Al_{1.54}Mg_{0.39}Fe^{3+}_{0.07})(Si_{3.96}Al_{0.04})O_{10}(OH)_2$	–74.5 ±0.75 (n=4)
SAz-1	Montmorillonite	dioctahedral	Apache County, Arizona	Pliocene	marine, sedimentary	$(M^{+}_{0.49})(Al_{1.39}Mg_{0.54}Fe^{3+}_{0.09})Si_4O_{10}(OH)_2$	–114.0 ±0.38 (n=4)
SWy-1	Montmorillonite	dioctahedral	Crook County, Wyoming	Cretaceous	non-marine, sedimentary	$(M^{+}_{0.38})(Al_{1.54}Mg_{0.25}Fe^{3+}_{0.21})(Si_{3.88}Al_{0.12})O_{10}(OH)_2$	–134.6 ±1.14 (n=4)
SapCa-1	saponite	trioctahedral	near Ballart, California	Pliocene	hydrothermal	$(M^{+}_{0.40})(Mg_{2.91}Fe^{3+}_{0.06}Al_{0.01})(Si_{3.58}Al_{0.42})O_{10}(OH)_2$	–125.5 ±0.19 (n=4)
SHCa-1	hectorite	trioctahedral	Hector, California	Pliocene	hydrothermal	$(M^{+}_{0.34})(Mg_{2.57}Li_{0.32}Al_{0.04})(Si_{3.96}Al_{0.04})O10(OH_{1.35}F_{0.65})$	–110.5 ±1.09 (n=4)
SWa-1	nontronite	dioctahedral	Grant County, Washington	Mid-Miocene	hydrothermal	$(M^{+}_{0.45})(Fe_{1.20}Al_{0.65}Mg_{0.13})(Si_{3.74}Al_{0.26})O_{10}(OH)_2$	–156.6 ±0.76 (n=4)

Chapter 6

6 Conclusions

6.1 Major Conclusions

Here we considered the effects of cation-saturation, degassing temperature under active vacuum, and laboratory procedures on the δ^2H of six, well-characterized CMS Source Clay Repository smectites. The goals were to gain an enhanced understanding of how these factors impact the 'hydroxyl hydrogen' δ^2H measured for 2:1 expandable hydrous phyllosilicates using the TCEA-CF-IRMS method, and establish the true δ^2H of hydroxyl group hydrogen in these six standard smectites.

The exchangeable cation type in the smectite interlayer emerged as a primary factor controlling the measured hydrogen isotope compositions for the hydroxyl hydrogen. The calculated difference between the theoretical hydrogen yields for each smectite based on its structural formula and the actual hydrogen yields obtained during analysis was instrumental in determining how much adsorbed water was retained by the smectites for each of the cation saturations.

The effectiveness of a specific temperature selected for removal of adsorbed / interlayer water (degassing) pretreatments prior to isotopic analysis was variable for the different cation saturations of the same smectite. For effective removal of bound water from a given smectite, different degassing temperatures were required depending on cation saturation, with progressively higher temperatures required from K^+ to Na^+ to Ca^{2+}.

In this study, degassing at 100°C was insufficient to completely remove bound water from any of the cation-saturated forms of the smectites. By 220°C, the hydrogen yields for the K-saturated forms of the smectites heated under vacuum for four hours indicated that nearly all bound water had been degassed. After degassing at 220°C, however, the hydrogen yields for the Ca- and Na-saturated smectite forms were still significantly in excess of theoretical values, indicating that contamination of the δ^2H by condensed atmospheric moisture was likely. For the K-saturated forms, increasing the degassing time beyond 4 hours at 220°C showed no further improvement, within analytical error, for removal of excess bound water from the smectites. However, hydrogen yields and resulting δ^2H suggested that temperatures greater than the maximum of 220°C tested in this study would be needed for complete removal of bound water from the Ca- and Na-saturated forms. This aspect should be investigated further.

This study also showed that use of a custom-milled Al-tray prevented significant rehydration of the smectite samples during transfer from the degassing oven to the TCEA autosampler, provided that the entire transfer was completed in < 4 minutes at a laboratory relative humidity of between 41-45 % at 21°C. As the smectites began to rehydrate, their hydrogen isotope compositions shifted toward the hydrogen isotope composition of the condensed atmospheric moisture. These effects were most pronounced for Ca-saturated samples, with the effects diminishing from Na-saturated to K-saturated forms.

While the TCEA-CF-IRMS method employed here does not eliminate all potential for rehydration of samples during preparation for isotopic analysis, the error measured for replicate analyses of δ^2H was much lower (<1 to <5 ‰) than the 7 to 30 ‰ range previously achieved for these samples using conventional methods.

The protocol recommended by this study for obtaining the most ‘accurate’ δ^2H for hydroxyl hydrogen in smectites is to use homoionic K-saturated forms. The low hydration enthalpy of the potassium cation limits the amount of contaminating adsorbed water. As the amount of bound water adsorbed by the K-saturated forms is limited, a degassing time of 4 hours at 220°C appears effective for bound water removal prior to hydrogen isotope analysis. Quick transfer (<4 minutes) of samples contained in a hot Al-tray between the vacuum oven and the TCEA autosampler is also required to reduce the potential for rehydration of the samples.

The results of this study provide the best estimates for the hydroxyl hydrogen δ^2H of these six smectites. In a comparison of the SWy-1 and STx-1 samples, the δ^2H of the K-saturated sample remained at a ‘fixed’ δ^2H after heating at 220°C, in contrast to the δ^2H of the Ca- and Na-saturated forms. This behaviour was related to the higher amount of adsorbed water retained after heating at 220°C by the Ca- and Na-saturated forms. As the Ca- and Na-saturated forms retained more residual adsorbed water, their δ^2H was shifted towards the δ^2H of the condensed local atmospheric moisture. This shift was not observed for the K-saturated forms of the smectites, leading to the conclusion that the K-saturated forms are most closely indicative of the ‘accurate’ δ^2H of hydroxyl hydrogen for each of the smectites.

The recommended δ^2H for the hydroxyl hydrogen of each of the smectites examined in this study are as follows:

STx-1= –74.5 ±0.75 ‰,
SAz-1= –114.0 ±0.38 ‰,
SWy-1= –134.6 ±1.14 ‰,
SapCa-1= –125.5 ±0.19 ‰,
SHCa-1= –110.5 ±1.09 ‰, and
SWa-1= –156.6 ±0.76 ‰.

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Appendices

Appendix 1 – Summary of Analytical Data for each Analysis

This appendix contains the raw data files for every analysis discussed in this study. Its inclusion is meant to be an accessible record of all the raw data and parameters employed during method development and sample analysis to supplement the data summaries presented in this study and to assist with future work. Text references in the body of this study refer to Analysis #s, which are labelled below as [Analysis-1 through -supplemental] for easy location of each file.

Information contained in the files include: Date of analysis, operator and laboratory director information, equipment identification and operating parameters, file approval by director date, method and procedural information, pre-treatment conditions of samples, equipment and error notes, number of samples and standards, information on standards, sample weights, hydrogen isotope and hydrogen yield data results, mass spectrometer reference number, and in some cases sample loading time and notes on laboratory environmental condition

[Analysis-01]

Project: Kanik NWMO_TCEA-HM-H19-01 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik & Li Huang
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: May 4, 2019 (May 16, 2019; revised by FJL)

Date Analyzed: Apr 17, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 23 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	44.73	-91.5
USGS 58	115.65	-28.4

Ampl 2	weight (mg)	umole	reference	
8248.50	0.150	8.33	USGS 47	water
8017.25	3.247	7.97	USGS 58	muscovite
6223.00	2.976	6.35	USGS 57	biotite

slope: 0.88973
Intercept: -131.30
r squared 0.999
Calculated equation: d2H = 0.890 *raw -131.3

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	Yield water umole/mg	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
1	GBS biotite	3.259	5340	76.27	-62.5	-63.4	1.65	1.67	1.63	1.940	-64.4	0.7	28511	NWMO TCEA book 1	
2	GBS biotite	2.965	4923	75.206	-62.5	-64.4	1.68	1.70	1.65	1.940			28512	NWMO TCEA book 1	
3	USGS 47	0.15	8384	-15.754	-150.2	-145.3	56.42	57.07	55.55	55.508	-146.0	1.0	28513	NWMO TCEA book 1	
4	USGS 47	0.15	8113	-17.318	-150.2	-146.7	54.60	55.23	53.75	55.508			28514	NWMO TCEA book 1	
5	NBS 22	0.15	7869	16.595	-120.0	-116.5	52.95	53.57	52.13	72.5?	-115.2	1.9	28515	NWMO TCEA book 1	
6	NBS 22	0.15	7999	19.669	-120.0	-113.8	63.33	54.45	53.00	72.5?			28516	NWMO TCEA book 1	
7	VSMOW	0.15	8163	146.951	0.0	-0.6	64.63	55.57	54.08	72.5?	0.1	0.9	28517	NWMO TCEA book 1	
8	VSMOW	0.15	7904	148.351	0.0	0.7	53.19	53.81	52.37	72.5?			28518	NWMO TCEA book 1	
9	USGS 57	2.912	6179	45.517	-91.5	-90.8	2.14	2.17	2.11	2.135	-91.0	0.8	28519	NWMO TCEA book 1	
10	USGS 57	2.956	6254	45.551	-91.5	-90.8	2.14	2.16	2.10	2.135			28520	NWMO TCEA book 1	
11	USGS 57	2.836	5694	46.078	-91.5	-90.3	2.03	2.05	2.00	2.135			28521	NWMO TCEA book 1	
12	USGS 57	3.201	6765	43.949	-91.5	-92.2	2.13	2.16	2.10	2.135			28522	NWMO TCEA book 1	
13	GBS biotite	3.001	5287	73.239	-62.5	-66.1	1.78	1.80	1.75	1.940			28523	NWMO TCEA book 1	
14	USGS 58	3.229	8063	115.128	-28.4	-28.9	2.52	2.55	2.48	2.454	-28.4	1.0	28524	NWMO TCEA book 1	
15	USGS 58	3.28	8104	114.798	-28.4	-29.2	2.49	2.52	2.46	2.454			28525	NWMO TCEA book 1	
16	USGS 58	3.376	8422	115.31	-28.4	-28.7	2.52	2.55	2.48	2.454			28526	NWMO TCEA book 1	
17	USGS 58	3.102	7480	117.377	-28.4	-26.9	2.43	2.46	2.40	2.454			28527	NWMO TCEA book 1	
18	GBS biotite	3.054	5487	77.926	-62.5	-62.0	1.81	1.83	1.79	1.940			28528	NWMO TCEA book 1	
19	KGa-1 RT	2.001	13787	208.549	-57.0	54.3	6.95	7.04	6.85	7.750	-27.0	54.2	28529	NWMO TCEA book 1	oversaturated
20	KGa-1 RT	1.97	1861	87.177	-57.0	-53.7	0.95	0.96	0.94	7.750			28531	NWMO TCEA book 1	oversturated, gas split dilution method used, yield inaccurate
21	KGa-1 RT	1.813	1848	87.642	-57.0	-53.3	1.03	1.04	1.01	7.750			28532	NWMO TCEA book 1	oversturated, gas split dilution method used, yield inaccurate
22	KGa-1 RT	1.976	2009	85.527	-57.0	-55.2	1.03	1.04	1.01	7.750			28533	NWMO TCEA book 1	oversturated, gas split dilution method used, yield inaccurate
23	GBS biotite	2.922	5166	73.341	-62.5	-66.0	1.78	1.81	1.76	1.940			28534	NWMO TCEA book 1	
	The following samples were loaded and analized immediately following the analysis of the previous samples														
24	USGS 47	0.15	4791	-6.576	-150.2	-137.2	32.24	32.61	31.74	55.508	-140.9	3.8	28535	NWMO TCEA book 1	used single and double weights to check linearity
25	USGS 47	0.15	8632	-16.643	-150.2	-146.1	58.09	58.76	57.19	55.508			28536	NWMO TCEA book 1	used single and double weights to check linearity
26	USGS 47	0.3	1642	-9.044	-150.2	-139.3	5.52	5.59	5.44	55.508			28537	NWMO TCEA book 1	used single and double weights to check linearity
27	USGS 47	0.3	1880	-11.113	-150.2	-141.2	6.33	6.40	6.23	55.508			28538	NWMO TCEA book 1	used single and double weights to check linearity
28	NBS22	0.15	8008	15.401	-120.0	-117.6	53.89	54.51	53.06	72.5?	-112.4	5.5	28539	NWMO TCEA book 1	used single and double weights to check linearity
29	NBS22	0.15	7944	17.217	-120.0	-116.0	53.46	54.08	52.63	72.5?			28540	NWMO TCEA book 1	used single and double weights to check linearity
30	NBS22	0.3	1876	23.256	-120.0	-110.6	6.31	6.39	6.21	72.5?			28541	NWMO TCEA book 1	used single and double weights to check linearity
31	NBS22	0.3	1889	28.937	-120.0	-105.6	6.36	6.43	6.26	72.5?			28542	NWMO TCEA book 1	used single and double weights to check linearity
32	VSMOW	0.15	7853	141.579	0.0	-5.3	52.85	53.46	52.03	?	2.6	6.8	28543	NWMO TCEA book 1	used single and double weights to check linearity
33	VSMOW	0.15	8147	146.861	0.0	-0.6	54.82	55.46	53.98	?			28544	NWMO TCEA book 1	used single and double weights to check linearity
34	VSMOW	0.3	1937	156.117	0.0	7.6	6.52	6.59	6.42	?			28545	NWMO TCEA book 1	used single and double weights to check linearity
35	VSMOW	0.3	1954	157.502	0.0	8.8	6.57	6.65	6.47	?			28546	NWMO TCEA book 1	used single and double weights to check linearity

# of samples: 0 (development project)
# of standards, duplicates, failed: 34,0,1

[Analysis-02]

Project: Kanik NWMO_TCEA-HM-H19-02 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik & Li Huang
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: April 25, 2019 (revised May 16, 2019)

Date Analyzed: Apr 23, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 19 hours followed by loading into He purged autosamper, equillibrated in autosampler He atmosphere overnight.

Reference gas: -124.69

	Raw	Accepted Value
USGS 57	41.50	-91.5
USGS 58	110.83	-28.4

Ampl 2	weight (mg)	umole	reference	
6782.5	3.259	**6.96**	USGS 57	biotite
7828.0	3.235	7.94	USGS 58	muscovite

slope: 0.91013
Intercept: -129.27
r squared 0.999
Calculated equation: d2H = 0.910 *raw -129.3

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite based umole/mg	yield muscovite based umole/mg	yield expected umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
													#	
1	GBS	3.491	6180	70.197	**-62.5**	**-65.4**	**1.82**	**1.80**	**1.940**	**-64.3**	**2.0**	28554	NWMO TCEA book 1	
2	USGS 57	3.317	6932	42.249	**-91.5**	**-90.8**	**2.14**	**2.12**	**2.135**	**-91.5**	**1.0**	28555	NWMO TCEA book 1	
3	USGS 58	3.198	7807	110.758	**-28.4**	**-28.5**	**2.50**	**2.48**	**2.454**	**-28.4**	**0.1**	28556	NWMO TCEA book 1	
4	GBS	3.582	6400	73.887	**-62.5**	**-62.0**	**1.83**	**1.81**	**1.940**			28557	NWMO TCEA book 1	
5	KGa-1	0.999	8288	78.054	**-57.0**	**-58.2**	**8.51**	**8.41**	**7.750**	**-59.14**	**0.6**	28558	NWMO TCEA book 1	
6	KGa-1	1.07	8881	76.98	**-57.0**	**-59.2**	**8.51**	**8.42**	**7.750**			28559	NWMO TCEA book 1	
7	KGa-1	0.885	7279	76.443	**-57.0**	**-59.7**	**8.44**	**8.34**	**7.750**			28560	NWMO TCEA book 1	
8	KGa-1	1.035	8670	76.745	**-57.0**	**-59.4**	**8.59**	**8.49**	**7.750**			28561	NWMO TCEA book 1	
9	USGS 57	3.201	6633	40.746	**-91.5**	**-92.2**	**2.13**	**2.10**	**2.135**			28562	NWMO TCEA book 1	
10	USGS 58	3.271	7849	110.899	**-28.4**	**-28.3**	**2.46**	**2.43**	**2.454**			28563	NWMO TCEA book 1	
11	GBS	3.77	6344	70.097	**-62.5**	**-65.5**	**1.73**	**1.71**	**1.940**			28564	NWMO TCEA book 1	

# of samples: 0 (development project)
# of standards, duplicates, failed: 11,0,0

[Analysis-03]

Project: Kanik NWMO_TCEA-HM-H19-03 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik & Li Huang
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: May 2, 2019 (revised May 16, 2019)

Date Analyzed: Apr 30, 2019

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 4 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	42.16	-91.5
USGS 58	112.49	-28.4

Ampl 2	weight (mg)	umole	reference	
6706.5	3.178	**6.79**	USGS 57	biotite
8256.0	3.294	8.08	USGS 58	muscovite

slope:		0.89726		
Intercept:		-129.33		
r squared		0.999		
Calculated equation:	d2H =	0.897	*raw	-129.3

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite based umole/mg	yield muscovite based umole/mg	yield expected umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
													#	
50	USGS 57	3.210	6721	42.771	**-91.5**	**-91.0**	**2.12**	**2.05**	**2.135**	**-91.5**	**0.8**	28568	NWMO TCEA book 1	
51	USGS 58	3.258	8163	114.349	**-28.4**	**-26.7**	**2.53**	**2.45**	**2.454**	**-28.4**	**2.4**	28569	NWMO TCEA book 1	
52	GBS biotite	3.525	6335	74.298	**-62.5**	**-62.7**	**1.82**	**1.76**	**1.940**	**-64.9**	**3.2**	28570	NWMO TCEA book 1	
53	KGa-1 RT	1.029	8711	85.162	**-57.0**	**-52.9**	**8.56**	**8.29**	**7.750**	**-53.7**	**0.8**	28571	NWMO TCEA book 1	
54	KGa-1 RT	0.947	7975	83.11	**-57.0**	**-54.8**	**8.52**	**8.25**	**7.750**			28572	NWMO TCEA book 1	
55	KGa-1 RT	0.873	7285	84.873	**-57.0**	**-53.2**	**8.44**	**8.17**	**7.750**			28573	NWMO TCEA book 1	
56	KGa-1 RT	0.862	7192	83.971	**-57.0**	**-54.0**	**8.44**	**8.17**	**7.750**			28574	NWMO TCEA book 1	
57	USGS 57	3.146	6692	41.551	**-91.5**	**-92.0**	**2.15**	**2.08**	**2.135**			28575	NWMO TCEA book 1	
58	USGS 58	3.330	8349	110.623	**-28.4**	**-30.1**	**2.54**	**2.45**	**2.454**			28576	NWMO TCEA book 1	
59	IMt-1_K <2 µm	2.667	8740	28.47	**?**	**-103.8**	**3.32**	**3.21**	**?**	**-105.78**	**1.5**	28577	NWMO TCEA book 1	
60	IMt-1_K <2 µm	2.461	8026	26.418	**?**	**-105.6**	**3.30**	**3.19**	**?**			28578	NWMO TCEA book 1	
61	IMt-1_K <2 µm	2.599	8510	25.66	**?**	**-106.3**	**3.31**	**3.21**	**?**			28579	NWMO TCEA book 1	
62	IMt-1_K <2 µm	2.545	8253	24.43	**?**	**-107.4**	**3.28**	**3.18**	**?**			28580	NWMO TCEA book 1	
63	GBS biotite	**3.652**	6618	69.223	**-62.49**	**-67.2**	**1.83**	**1.77**	**1.940**			28581	NWMO TCEA book 1	

# of samples: 0 (development project)
# of standards, duplicates, failed: 11,0,0

[Analysis-04]

Project: Kanik NWMO_TCEA-HM-H19-04 (hydrous minerals)

Isotope(s): Hydrogen

Preparation: Nadine Kanik

Analyst: Nadine Kanik & Li Huang

Data Treatment and QA/QC: F. Longstaffe

Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS

Date Approved by Director: May 2, 2019 (revised May 16, 2019)

Date Analyzed: May 2, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C (±9C, door opening to load diff.) active vacuum oven for 8 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight (16:00 to 9:00)

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	45.04	-91.5
USGS 58	114.41	-28.4

Ampl 2	weight (mg)	umole	reference	
7403.0	3.367	7.19	USGS 57	biotite
8410.0	3.557	8.73	USGS 58	muscovite

slope:		0.90959		
Intercept:		-132.47		
r squared		0.999		
Calculated equation:	d2H =	0.910	*raw	-132.5

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite based umole/mg	yield muscovite based umole/mg	yield expected umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
													#	
1	GBS biotite	3.5230	6069	76.549	**-62.5**	**-62.8**	**1.67**	**1.79**	**1.940**	**-64.0**	**1.9**	28586	NWMO TCEA book 3	
2	USGS 57	3.1900	7267	46.647	**-91.5**	**-90.0**	**2.21**	**2.36**	**2.135**	**-91.5**	**2.1**	28587	NWMO TCEA book 3	
3	USGS 58	3.8800	8828	114.882	**-28.4**	**-28.0**	**2.21**	**2.36**	**2.454**	**-28.4**	**0.6**	28588	NWMO TCEA book 3	
4	GBS biotite	3.7050	6869	76.371	**-62.5**	**-63.0**	**1.80**	**1.92**	**1.940**			28589	NWMO TCEA book 3	
5	KGa-1 RT	0.9300	7730	84.17	**-57.0**	**-55.9**	**8.07**	**8.63**	**7.750**	**-55.51**	**0.7**	28590	NWMO TCEA book 3	
6	KGa-1 RT	0.7730	6339	84.308	**-57.0**	**-55.8**	**7.96**	**8.51**	**7.750**			28591	NWMO TCEA book 3	
7	KGa-1 RT	0.9200	7680	84.227	**-57.0**	**-55.9**	**8.11**	**8.66**	**7.750**			28592	NWMO TCEA book 3	
8	KGa-1 RT	0.7770	6422	85.699	**-57.0**	**-54.5**	**8.03**	**8.58**	**7.750**			28593	NWMO TCEA book 3	
9	USGS 57	3.5440	7539	43.428	**-91.5**	**-93.0**	**2.07**	**2.21**	**2.135**			28594	NWMO TCEA book 3	
10	USGS 58	3.2340	7992	113.937	**-28.4**	**-28.8**	**2.40**	**2.56**	**2.454**			28595	NWMO TCEA book 3	
11	IMt-1_K<2 µm	2.9220	9570	33.337	**?**	**-102.1**	**3.18**	**3.40**	**?**	**-103.76**	**1.1**	28596	NWMO TCEA book 3	
12	IMt-1_K<2 µm	2.8630	9334	30.545	**?**	**-104.7**	**3.17**	**3.38**	**?**			28597	NWMO TCEA book 3	
13	IMt-1_K<2 µm	2.7380	8793	31.455	**?**	**-103.9**	**3.12**	**3.33**	**?**			28598	NWMO TCEA book 3	
14	IMt-1_K<2 µm	2.6760	8686	30.896	**?**	**-104.4**	**3.15**	**3.37**	**?**			28599	NWMO TCEA book 3	
15	GBS biotite	3.4810	6339	72.761	**-62.49**	**-66.3**	**1.77**	**1.89**	**1.940**			28600	NWMO TCEA book 3	

# of samples: 0 (development project)

# of standards, duplicates, failed: 11,0,0

[Analysis-05]

Project: Kanik NWMO_TCEA-HM-H19-05 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik & Li Huang
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: May 10, 2019 (revised by FJL)

Date Analyzed: May 8, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 12 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	44.88	-91.5
USGS 58	115.46	-28.4

				Ampl 2	weight (mg)	umole	reference	
						0.00	USGS 47	water
slope:		0.89413		7810.50	3.101	7.61	USGS 58	muscovite
Intercept:		-131.63		6896.00	3.219	6.87	USGS 57	biotite
r squared		0.999						
Calculated equation:	d2H =	0.894	*raw	-131.6				

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
82	GBS biotite	3.8170	6721	74.412	**-62.5**	**-65.1**	**1.75**	**1.72**	**1.940**	**-65.6**	**1.0**	28604	NWMO TCEA book 3	
83	USGS 57	3.2260	6994	44.545	**-91.5**	**-91.8**	**2.16**	**2.11**	**1.940**	**-91.5**	**0.4**	28605	NWMO TCEA book 3	
84	USGS 58	3.2000	8151	116.037	**-28.4**	**-27.9**	**2.54**	**2.48**	**55.508**	**-28.4**	**0.7**	28606	NWMO TCEA book 3	
85	GBS biotite	3.4190	6118	74.585	**-62.5**	**-64.9**	**1.78**	**1.74**	**55.508**			28607	NWMO TCEA book 3	
86	KGa-1	1.0200	8634	85.067	**-57.0**	**-55.6**	**8.43**	**8.25**	**7.750**	**-54.9**	**0.6**	28608	NWMO TCEA book 3	***Weight entries were reversed between this sample***
87	KGa-1	0.8040	6672	85.713	**-57.0**	**-55.0**	**8.27**	**8.09**	**7.750**			28609	NWMO TCEA book 3	***and the one that follows; fixed***
88	KGa-1	0.9550	8004	85.865	**-57.0**	**-54.9**	**8.35**	**8.17**	**7.750**			28610	NWMO TCEA book 3	
89	KGa-1	0.7830	6486	86.602	**-57.0**	**-54.2**	**8.25**	**8.07**	**7.750**			28611	NWMO TCEA book 3	
90	USGS 57	3.2110	6798	45.224	**-91.5**	**-91.2**	**2.11**	**2.06**	**2.135**			28612	NWMO TCEA book 3	
91	USGS 58	3.0020	7470	114.875	**-28.4**	**-28.9**	**2.48**	**2.42**	**2.135**			28613	NWMO TCEA book 3	
92	IMt-1_K	2.3130	7477	37.682	**?**	**-97.9**	**3.22**	**3.15**	**2.135**	**-99.8**	**1.6**	28614	NWMO TCEA book 3	
93	IMt-1_K	2.5360	8240	34.562	**?**	**-100.7**	**3.24**	**3.17**	**2.135**			28615	NWMO TCEA book 3	
94	IMt-1_K	2.1740	6992	34.427	**?**	**-100.9**	**3.20**	**3.13**	**1.940**			28616	NWMO TCEA book 3	
95	GBS biotite	3.7700	7028	72.503	**-62.5**	**-66.8**	**1.86**	**1.82**	**2.454**			28617	NWMO TCEA book 3	

# of samples: 0 (development project)
# of standards, duplicates, failed: 14,0,0

[Analysis-06]

Project: Kanik NWMO_TCEA-HM-H19-06 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik & Li Huang
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: May 10, 2019 (May 16, revised by FJL)

Date Analyzed: May 9, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 16 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	45.97	-91.5
USGS 58	115.35	-28.4

slope:	0.90947			
Intercept:	-133.31			
r squared	0.999			
Calculated equation: d2H =	0.909	*raw	-133.3	

Ampl 2	weight (mg)	umole	reference	
		0.00	USGS 47	water
7386.00	3.076	7.55	USGS 58	muscovite
6387.00	3.137	6.70	USGS 57	biotite

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
97	GBS biotite	3.420	6048	78.997	**-62.5**	**-61.5**	**1.85**	**1.81**	**1.940**	**-64.0**	**2.7**	28625	NWMO TCEA book 3	
98	USGS 57	3.132	6333	47.356	**-91.5**	**-90.2**	**2.12**	**2.07**	**2.135**	**-91.5**	**1.8**	28626	NWMO TCEA book 3	
99	USGS 58	3.020	7241	116.209	**-28.4**	**-27.6**	**2.51**	**2.45**	**2.454**	**-28.4**	**1.1**	28627	NWMO TCEA book 3	
100	GBS biotite	3.824	6527	76.516	**-62.5**	**-63.7**	**1.79**	**1.74**	**1.940**			28628	NWMO TCEA book 3	
101	KGa-1	1.016	8286	81.569	**-57.0**	**-59.1**	**8.55**	**8.33**	**7.750**	**-58.9**	**1.4**	28629	NWMO TCEA book 3	
102	KGa-1	1.127	9281	79.842	**-57.0**	**-60.7**	**8.64**	**8.42**	**7.750**			28630	NWMO TCEA book 3	
103	KGa-1	0.731	5793	82.853	**-57.0**	**-58.0**	**8.31**	**8.10**	**7.750**			28631	NWMO TCEA book 3	
104	KGa-1	0.827	6605	83.209	**-57.0**	**-57.6**	**8.37**	**8.16**	**7.750**			28632	NWMO TCEA book 3	
105	USGS 57	3.142	6441	44.582	**-91.5**	**-92.8**	**2.15**	**2.10**	**2.135**			28633	NWMO TCEA book 3	
106	USGS 58	3.132	7531	114.491	**-28.4**	**-29.2**	**2.52**	**2.46**	**2.454**			28634	NWMO TCEA book 3	
107	IMt-1_K	2.317	7077	34.318	**?**	**-102.1**	**3.20**	**3.12**	**?**	**-102.7**	**0.5**	28635	NWMO TCEA book 3	
108	IMt-1_K	2.346	7174	33.303	**?**	**-103.0**	**3.21**	**3.13**	**?**			28636	NWMO TCEA book 3	
109	IMt-1_K	2.260	6471	33.485	**?**	**-102.9**	**3.00**	**2.93**	**?**			28637	NWMO TCEA book 3	
110	GBS biotite	3.843	6543	73.119	**-62.5**	**-66.8**	**1.79**	**1.74**	**1.940**			28638	NWMO TCEA book 3	

# of samples: 0 (development project)
# of standards, duplicates, failed: 14,0,0

[Analysis-07]

Project: Kanik NWMO_TCEA-HM-H19-07 (hydrous minerals)

Isotope(s): Hydrogen

Fred's note: see changes in red; make sure these are carried through in subsequent files.

Preparation: Nadine Kanik

Analyst: Nadine Kanik & Li Huang

Data Treatment and QA/QC: F. Longstaffe

Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS

Date Approved by Director: May 16, 2019 (revised by FJL)

Date Analyzed: May 10, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 28 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	49.14	-91.5
USGS 58	119.91	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
7381.50	3.057	7.50	USGS 58	muscovite
6495.50	3.121	6.66	USGS 57	biotite

slope: 0.89164

Intercept: -135.31

r squared 0.999

Calculated equation: d2H = 0.892 *raw -135.3

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes	
112	GBS biotite	3.615	6346	81.664	**-62.5**	**-62.5**	**1.80**	**1.78**	**1.940**	**-64.7**	**2.5**	28643	NWMO TCEA book 3		
113	USGS 57	3.044	6350	51.202	**-91.5**	**-89.7**	**2.14**	**2.12**	**2.135**	**-91.5**	**2.6**	28644	NWMO TCEA book 3		
114	USGS 58	3.078	7414	121.051	**-28.4**	**-27.4**	**2.47**	**2.45**	**2.454**	**-28.4**	**1.4**	28645	NWMO TCEA book 3		**CHECK WEIGHT; IT APPEARS A ZERO WAS DROPPED; I CHANGED IT.**
115	GBS biotite	3.665	6765	79.76	**-62.5**	**-64.2**	**1.89**	**1.88**	**1.940**			28646	NWMO TCEA book 3		
116	KGa-1 RT	0.724	5855	89.213	**-57.0**	**-55.8**	**8.29**	**8.22**	**7.750**	**-57.2**	**1.0**	28647	NWMO TCEA book 3		
117	KGa-1 RT	0.753	6098	86.957	**-57.0**	**-57.8**	**8.31**	**8.23**	**7.750**			28648	NWMO TCEA book 3		
118	KGa-1 RT	0.8	6557	86.843	**-57.0**	**-57.9**	**8.41**	**8.33**	**7.750**			28649	NWMO TCEA book 3		
119	KGa-1 RT	0.797	6484	87.202	**-57.0**	**-57.6**	**8.34**	**8.27**	**7.750**			28650	NWMO TCEA book 3		
120	USGS 57	3.197	6641	47.071	**-91.5**	**-93.3**	**2.13**	**2.11**	**2.135**			28651	NWMO TCEA book 3		
121	USGS 58	3.036	7349	118.759	**-28.4**	**-29.4**	**2.48**	**2.46**	**2.454**			28652	NWMO TCEA book 3		
122	IMt-1_K	2.102	6551	39.728	**?**	**-99.9**	**3.20**	**3.17**	**?**	**-102.6**	**2.6**	28653	NWMO TCEA book 3		
123	IMt-1_K	2.258	7050	36.444	**?**	**-102.8**	**3.20**	**3.17**	**?**			28654	NWMO TCEA book 3		
124	IMt-1_K	2.609	8232	34	**?**	**-105.0**	**3.24**	**3.21**	**?**			28655	NWMO TCEA book 3		
125	GBS biotite	3.687	6707	76.066	**-62.5**	**-67.5**	**1.87**	**1.85**	**1.940**			28656	NWMO TCEA book 3		

# of samples: 0 (development project)

# of standards, duplicates, failed: 14

[Analysis-08]

Project: Kanik NWMO_TCEA-HM-H19-08 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik & Li Huang
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: May 16, 2019 (FJL)

Date Analyzed: May 15, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, 1350C, **Pre-treatment=** heated in 200C active vacuum oven for 24 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	39.62	-91.5
USGS 58	112.11	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
7734.50	3.310	8.12	USGS 58	muscovite
6223.00	3.138	6.70	USGS 57	biotite

slope:		0.87042		
Intercept:		-125.99		
r squared		0.999		
Calculated equation:	d2H =	0.870	*raw	-126.0

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
127	GBS biotite	3.499	5978	75.249	**-62.5**	**-60.5**	**1.84**	**1.79**	**1.940**			28660	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
128	USGS 57	3.699	7458	41.142	**-91.5**	**-90.2**	**2.17**	**2.12**	**2.135**			28661	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
129	USGS 58	3.1	7414	113.969	**-28.4**	**-26.8**	**2.57**	**2.51**	**2.454**			28662	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
130	GBS biotite	3.902	6825	71.543	**-62.5**	**-63.7**	**1.88**	**1.84**	**1.940**			28663	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
131	KGa-1 RT	0.839	6753	79.226	**-57.0**	**-57.0**	**8.66**	**8.45**	**7.750**			28664	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
132	KGa-1 RT	0.989	8104	76.023	**-57.0**	**-59.8**	**8.82**	**8.60**	**7.750**			28665	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
133	KGa-1 RT	0.938	7630	76.005	**-57.0**	**-59.8**	**8.76**	**8.54**	**7.750**			28666	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
134	KGa-1 RT	0.858	6940	76.458	**-57.0**	**-59.4**	**8.71**	**8.49**	**7.750**			28667	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
135	GBS biotite	3.992	6748	70.371	**-62.5**	**-64.7**	**1.82**	**1.77**	**1.940**			28668	NWMO TCEA book 3	Reactor only at 1350C, so these samples not included in calculations
136	IMt-1_K	2.604	7600	28.01	**?**	**-101.6**	**3.14**	**3.06**	**?**	**-100.5**	**1.4**	28670	NWMO TCEA book 3	
137	IMt-1_K	2.411	7048	31.179	**?**	**-98.8**	**3.15**	**3.07**	**?**			28671	NWMO TCEA book 3	
138	IMt-1_K	2.924	8653	28.801	**?**	**-100.9**	**3.19**	**3.11**	**?**			28672	NWMO TCEA book 3	
139	IMt-1 (2)	2.589	7700	29.302	**?**	**-100.5**	**3.20**	**3.12**	**?**	**-99.9**	**0.6**	28673	NWMO TCEA book 3	
140	IMt-1 (2)	2.417	7262	30.647	**?**	**-99.3**	**3.23**	**3.15**	**?**			28674	NWMO TCEA book 3	
141	IMt-1 (2)	2.178	6493	29.82	**?**	**-100.0**	**3.21**	**3.13**	**?**			28675	NWMO TCEA book 3	
142	IMt-1_K (2)	2.375	6731	32.183	**?**	**-98.0**	**3.05**	**2.98**	**?**	**-99.06**	**0.96**	28676	NWMO TCEA book 3	
143	IMt-1_K (2)	2.704	7718	30.114	**?**	**-99.8**	**3.07**	**3.00**	**?**			28677	NWMO TCEA book 3	
144	IMt-1_K (2)	2.56	7054	30.511	**?**	**-99.4**	**2.97**	**2.89**	**?**			28678	NWMO TCEA book 3	
145	USGS 57	3.171	6362	40.767	**-91.5**	**-90.5**	**2.16**	**2.11**	**2.135**	**-91.50**	**1.41**	28679	NWMO TCEA book 3	
146	USGS 58	3.116	7246	113.949	**-28.4**	**-26.8**	**2.50**	**2.44**	**2.454**	**-28.40**	**2.26**	28680	NWMO TCEA book 3	
147	GBS biotite	3.447	6184	75.076	**-62.5**	**-60.6**	**1.93**	**1.88**	**1.940**	**-61.04**	**0.57**	28681	NWMO TCEA book 3	
148	SCa-3	2.916	10107	0.067	**?**	**-125.9**	**3.73**	**3.64**	**?**	**-126.39**	**0.58**	28682	NWMO TCEA book 3	
149	SCa-3	2.704	9859	-1.207	**?**	**-127.0**	**3.92**	**3.83**	**?**			28683	NWMO TCEA book 3	
150	SCa-3	2.157	7722	-0.249	**?**	**-126.2**	**3.85**	**3.76**	**?**			28684	NWMO TCEA book 3	
151	SWy-1_K	2.212	6041	-15.698	**?**	**-139.6**	**2.94**	**2.87**	**?**	**-141.64**	**1.73**	28685	NWMO TCEA book 3	
152	SWy-1_K	2.519	6875	-19.328	**?**	**-142.8**	**2.94**	**2.87**	**?**			28686	NWMO TCEA book 3	
153	SWy-1_K	2.425	6691	-18.917	**?**	**-142.5**	**2.97**	**2.90**	**?**			28687	NWMO TCEA book 3	
154	SapCa-1_K	2.363	5396	-6.439	**?**	**-131.6**	**2.46**	**2.40**	**?**	**-130.46**	**1.36**	28688	NWMO TCEA book 3	
155	SapCa-1_K	2.36	5411	-5.574	**?**	**-130.8**	**2.47**	**2.41**	**?**			28689	NWMO TCEA book 3	
156	SapCa-1_K	2.218	4992	-3.406	**?**	**-129.0**	**2.42**	**2.36**	**?**			28690	NWMO TCEA book 3	
157	SWa-1_K	2.631	7492	-47.683	**?**	**-167.5**	**3.07**	**2.99**	**?**	**-166.64**	**1.28**	28691	NWMO TCEA book 3	
158	SWa-1_K	2.151	5890	-45.008	**?**	**-165.2**	**2.95**	**2.88**	**?**			28692	NWMO TCEA book 3	
159	SWa-1_K	2.268	6391	-47.414	**?**	**-167.3**	**3.03**	**2.96**	**?**			28693	NWMO TCEA book 3	
160	USGS 57	3.104	6084	38.472	**-91.5**	**-92.5**	**2.11**	**2.06**	**2.135**			28694	NWMO TCEA book 3	
161	USGS 58	3.503	8223	110.277	**-28.4**	**-30.0**	**2.53**	**2.46**	**2.454**			28695	NWMO TCEA book 3	
162	GBS biotite	3.913	6548	74.153	**-62.5**	**-61.4**	**1.80**	**1.76**	**1.940**			28696	NWMO TCEA book 3	

# of samples: 0 (development project)
# of standards, duplicates, failed:27,0,9

[Analysis-09]

Project: Kanik NWMO_TCEA-HM-H19-09 (hydrous minerals)

Isotope(s): Hydrogen

Preparation: Nadine Kanik

Analyst: Nadine Kanik & Li Huang

Data Treatment and QA/QC: F. Longstaffe

Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS

Date Approved by Director: May 17 , 2019 (revised by FJL)

Date Analyzed: May 16, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 4 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight, samples heated in glass vials with silver capsules closed.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	47.46	-91.5
USGS 58	117.15	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
7463.00	3.206	7.87	USGS 58	muscovite
6112.50	3.012	6.43	USGS 57	biotite

slope:		0.90544		
Intercept:		-134.47		
r squared		0.999		
Calculated equation:	d2H =	0.905	*raw	-134.5

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
164	GBS biotite	3.618	6298	83.509	-62.5	-58.9	1.83	1.84	1.940	-63.6	5.1	28701	NWMO TCEA book 3	
165	USGS 57	3.012	6139	50.409	-91.5	-88.8	2.14	2.15	2.135	-91.5	3.8	28702	NWMO TCEA book 3	
166	USGS 58	3.117	7277	120.668	-28.4	-25.2	2.46	2.46	2.454	-28.4	4.5	28703	NWMO TCEA book 3	
167	KGa-1 RT	1.098	8937	85.156	-57.0	-57.4	8.56	8.58	7.750	-56.0	2.0	28704	NWMO TCEA book 3	
168	KGa-1 RT	0.745	6001	89.141	-57.0	-53.8	8.47	8.49	7.750			28705	NWMO TCEA book 3	
169	KGa-1 RT	0.824	6655	85.663	-57.0	-56.9	8.50	8.51	7.750			28706	NWMO TCEA book 3	
170	IMt-1_K (2)	2.124	5993	38.019	?	-100.0	2.97	2.97	?	-101.1	1.4	28707	NWMO TCEA book 3	
171	IMt-1_K (2)	2.215	6338	35.758	?	-102.1	3.01	3.02	?			28708	NWMO TCEA book 3	
172	GBS biotite	3.331	5664	78.917	-62.5	-63.0	1.79	1.79	1.940			28709	NWMO TCEA book 3	
173	SCa-3	2.293	8564	16.222	?	-119.8	3.93	3.94	?	-123.2	3.0	28710	NWMO TCEA book 3	
174	SCa-3	2.859	10860	11.153	?	-124.4	4.00	4.00	?			28711	NWMO TCEA book 3	
175	SCa-3	3.167	11489	10.074	?	-125.3	3.82	3.82	?	-149.0	2.2	28712	NWMO TCEA book 3	
176	SWy-1_K	3.022	9194	-18.276	?	-151.0	3.20	3.21	?			28713	NWMO TCEA book 3	
177	SWy-1_K	2.301	6404	-13.401	?	-146.6	2.93	2.93	?			28714	NWMO TCEA book 3	
178	SWy-1_K	2.54	7107	-16.492	?	-149.4	2.94	2.95	?			28715	NWMO TCEA book 3	
179	USGS 57	3.011	6086	44.501	-91.50	-94.2	2.13	2.13	2.135			28716	NWMO TCEA book 3	
180	SapCa-1_K	2.925	6738	-2.608	?	-136.8	2.42	2.43	?	-139.03	1.92	28717	NWMO TCEA book 3	
181	SapCa-1_K	2.928	7112	-6.437	?	-140.3	2.55	2.56	?			28718	NWMO TCEA book 3	
182	SapCa-1_K	2.748	6562	-6.088	?	-140.0	2.51	2.52	?			28719	NWMO TCEA book 3	
183	SWa-1_K	3.061	8594	-47.526	?	-177.5	2.95	2.96	?	-178.49	1.47	28720	NWMO TCEA book 3	
184	SWa-1_K	3.199	8636	-50.485	?	-180.2	2.84	2.85	?			28721	NWMO TCEA book 3	
185	SWa-1_K	2.77	7984	-47.837	?	-177.8	3.03	3.04	?			28722	NWMO TCEA book 3	
186	GBS biotite	3.464	6115	72.293	-62.5	-69.0	1.86	1.86	1.940			28723	NWMO TCEA book 3	
187	USGS 58	3.295	7649	113.622	-28.4	-31.6	2.44	2.45	2.454			28724	NWMO TCEA book 3	

# of samples: 0

# of standards, duplicates, failed: 24

[Analysis-10]

Project: Kanik NWMO_TCEA-HM-H19-10 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik & Li Huang
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: May 17, 2019 (revised by FJL)

Date Analyzed: May 16, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 4 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight, samples heated in Al-tray with open capsules.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	43.73	-91.5
USGS 58	114.99	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
7134.00	3.038	7.45	USGS 58	muscovite
6120.00	3.033	6.47	USGS 57	biotite

slope: 0.88554
Intercept: -130.22
r squared 0.999
Calculated equation: d2H = 0.886 *raw -130.2

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
188	GBS biotite	3.935	6600	74.412	**-62.5**	**-64.3**	**1.77**	**1.75**	**1.940**	**-64.99**	**4.4**	28725		
189	USGS 57	2.979	5881	46.815	**-91.5**	**-88.8**	**2.09**	**2.06**	**2.135**	**-91.5**	**3.9**	28726	NWMO TCEA book 3	
190	USGS 58	2.927	6918	115.886	**-28.4**	**-27.6**	**2.50**	**2.47**	**2.454**	**-28.4**	**1.1**	28727	NWMO TCEA book 3	
191	KGa-1 RT	0.738	5851	90.105	**-57.0**	**-50.4**	**8.39**	**8.28**	**7.750**	**-50.9**	**1.0**	28728	NWMO TCEA book 3	
192	KGa-1 RT	0.826	6330	90.279	**-57.0**	**-50.3**	**8.11**	**8.01**	**7.750**			28729	NWMO TCEA book 3	
193	KGa-1 RT	0.823	6285	88.191	**-57.0**	**-52.1**	**8.08**	**7.98**	**7.750**			28730	NWMO TCEA book 3	
194	IMt-1_K (2)	2.637	7096	34.01	**?**	**-100.1**	**2.85**	**2.81**	**?**	**-97.1**	**4.2**	28731	NWMO TCEA book 3	
195	IMt-1_K (2)	2.187	4252	40.752	**?**	**-94.1**	**2.06**	**2.03**	**?**			28732	NWMO TCEA book 3	
196	GBS biotite	3.758	3105	78.202	**-62.5**	**-61.0**	**0.87**	**0.86**	**1.940**			28733	NWMO TCEA book 3	
197	SCa-3	2.421	2618	1.825	**?**	**-128.6**	**1.14**	**1.13**	**?**	**-131.9**	**3.7**	28734	NWMO TCEA book 3	Did not drop into reactor properly, delta values s from manual peak estimate
198	SCa-3	2.714	2334	-6.372	**?**	**-135.9**	**0.91**	**0.90**	**?**			28735	NWMO TCEA book 3	Did not drop into reactor properly, delta values s from manual peak estimate
199	SCa-3	2.506	2111	-1.004	**?**	**-131.1**	**0.89**	**0.88**	**?**			28736	NWMO TCEA book 3	Did not drop into reactor properly, delta values s from manual peak estimate
200	SWy-1_K	2.832	1739	-17.754	**?**	**-145.9**	**0.65**	**0.64**	**?**	**-138.1**	**8.5**	28737	NWMO TCEA book 3	Did not drop into reactor properly, delta values s from manual peak estimate
201	SWy-1_K	2.533	6547	1.349	**?**	**-129.0**	**2.73**	**2.70**	**?**			28738	NWMO TCEA book 3	Delta values for this sample still a bit off, likely as a result of previous
202	SWy-1_K	2.404	6520	-10.225	**?**	**-139.3**	**2.87**	**2.83**	**?**			28739	NWMO TCEA book 3	
203	USGS 57	3.086	6359	40.644	**-91.5**	**-94.2**	**2.18**	**2.15**	**2.135**			28740	NWMO TCEA book 3	
204	USGS 58	3.148	7350	114.085	**-28.4**	**-29.2**	**2.47**	**2.44**	**2.454**			28741	NWMO TCEA book 3	
205	SapCa-1_K	3.193	7625	-4.306	**?**	**-134.0**	**2.53**	**2.50**	**?**	**-136.30**	**2.42**	28742	NWMO TCEA book 3	
206	SapCa-1_K	3.074	7608	-6.519	**?**	**-136.0**	**2.62**	**2.59**	**?**			28743	NWMO TCEA book 3	
207	SapCa-1_K	3.263	8591	-9.75	**?**	**-138.9**	**2.79**	**2.75**	**?**			28744	NWMO TCEA book 3	
208	SWa-1_K	2.504	7397	-45.224	**?**	**-170.3**	**3.13**	**3.09**	**?**	**-172.41**	**1.97**	28745	NWMO TCEA book 3	
209	SWa-1_K	2.939	8679	-48.076	**?**	**-172.8**	**3.12**	**3.09**	**?**			28746	NWMO TCEA book 3	
210	SWa-1_K	3.041	9024	-49.613	**?**	**-174.2**	**3.14**	**3.10**	**?**			28747	NWMO TCEA book 3	
211	GBS biotite	3.38	5586	68.388	**-62.5**	**-69.7**	**1.75**	**1.73**	**1.940**			28748	NWMO TCEA book 3	

# of samples: 0
# of standards, duplicates, failed: 19,0,5

[Analysis-11]

Project: Kanik NWMO_TCEA-HM-H19-11 (hydrous minerals)

Isotope(s): Hydrogen

Preparation: Nadine Kanik

Analyst: Nadine Kanik & Li Huang

Data Treatment and QA/QC: F. Longstaff

Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS

Date Approved by Director: May 17 , 2019 (FJL)

Date Analyzed: May 17, 2019

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 24 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight, samples heated in glass vials with silver capsules closed.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	46.56	-91.5
USGS 58	118.74	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
6925.00	3.046	7.47	USGS 58	muscovite
6575.00	3.348	7.15	USGS 57	biotite

slope: 0.87412

Intercept: -132.19

r squared 0.999

Calculated equation: d2H = 0.874 *raw -132.2

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
	GBS biotite													lost while leak checking autosampler
	USGS 57													lost while leak checking autosampler
213	USGS 58	3.048	6912	120.189	**-28.4**	**-27.1**	**2.47**	**2.45**	**2.454**	**-28.4**	**1.8**	28751	NWMO TCEA book 3	
214	GBS biotite	3.563	6521	79.156	**-62.5**	**-63.0**	**1.99**	**1.98**	**1.940**	**-64.2**	**1.7**	28752	NWMO TCEA book 3	
215	KGa-1 RT	0.919	7195	80.943	**-57.0**	**-61.4**	**8.51**	**8.45**	**7.750**	**-62.8**	**1.8**	28753	NWMO TCEA book 3	
216	KGa-1 RT	1.045	6708	80.009	**-57.0**	**-62.3**	**6.98**	**6.93**	**7.750**			28754	NWMO TCEA book 3	
217	KGa-1 RT	1.032	8192	76.313	**-57.0**	**-65.5**	**8.63**	**8.57**	**7.750**			28755	NWMO TCEA book 3	
218	KGa-1 RT	0.906	7106	80.247	**-57.0**	**-62.0**	**8.53**	**8.47**	**7.750**			28756	NWMO TCEA book 3	
219	GBS biotite	3.903	6656	76.44	**-62.5**	**-65.4**	**1.85**	**1.84**	**1.940**			28757	NWMO TCEA book 3	
220	USGS 57	3.348	6575	46.555	**-91.5**	**-91.5**	**2.14**	**2.12**	**2.135**			28758	NWMO TCEA book 3	
221	USGS 58	3.044	6938	117.294	**-28.5**	**-29.7**	**2.48**	**2.46**	**2.454**			28759	NWMO TCEA book 3	

# of samples: 0 (development project)

# of standards, duplicates, failed: 9,0,2

[Analysis-12]

Project: Kanik NWMO_TCEA-HM-H19-12 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik & Li Huang
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: May 17, 2019 (FJL)

Date Analyzed: May 17, 2019,

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 24 hours followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere overnight, samples heated in Al-tray with capsules open.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	44.64	-91.5
USGS 58	116.67	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
6492.50	2.868	7.04	USGS 58	muscovite
6084.00	3.156	6.74	USGS 57	biotite

slope: 0.87598
Intercept: -130.60
r squared 0.999
Calculated equation: d2H = 0.876 *raw -130.6

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
	GBS biotite													GBS analysis manually stopped
225	USGS 57	2.923	5807	46.872	**-91.5**	**-89.5**	**2.20**	**2.15**	**2.135**	**-91.5**	**2.8**	28761	NWMO TCEA book 3	
226	USGS 58	2.838	6507	117.758	**-28.4**	**-27.5**	**2.54**	**2.49**	**2.454**	**-28.4**	**1.3**	28762	NWMO TCEA book 3	
227	KGa-1 RT	0.826	6524	87.543	**-57.0**	**-53.9**	**8.75**	**8.56**	**7.750**	**-57.5**	**3.3**	28763	NWMO TCEA book 3	
228	KGa-1 RT	1.03	8205	82.548	**-57.0**	**-58.3**	**8.82**	**8.64**	**7.750**			28764	NWMO TCEA book 3	
229	KGa-1 RT	1.23	10043	80.107	**-57.0**	**-60.4**	**9.04**	**8.85**	**7.750**			28765	NWMO TCEA book 3	
230	IMt-1_K (2)	2.374	6931	35.571	**?**	**-99.4**	**3.23**	**3.16**	**?**	**-100.1**	**0.9**	28766	NWMO TCEA book 3	
231	IMt-1_K (2)	2.616	7637	34.06	**?**	**-100.8**	**3.23**	**3.16**	**?**			28767	NWMO TCEA book 3	
232	GBS biotite	3.523	5849	76.314	**-62.5**	**-63.8**	**1.84**	**1.80**	**1.940**	**-63.8**	**#DIV/0!**	28768	NWMO TCEA book 3	
233	SCa-3	2.394	9328	1.832	**?**	**-129.0**	**4.32**	**4.22**	**?**	**-128.7**	**1.4**	28769	NWMO TCEA book 3	
234	SCa-3	2.485	9383	3.907	**?**	**-127.2**	**4.18**	**4.09**	**?**			28770	NWMO TCEA book 3	
235	SCa-3	2.47	9725	0.813	**?**	**-129.9**	**4.36**	**4.27**	**?**			28771	NWMO TCEA book 3	
236	SWy-1_K	2.38	6028	-10.368	**?**	**-139.7**	**2.81**	**2.75**	**?**	**-140.7**	**1.4**	28772	NWMO TCEA book 3	
237	SWy-1_K	2.312	6382	-13.462	**?**	**-142.4**	**3.06**	**2.99**	**?**			28773	NWMO TCEA book 3	
238	SWy-1_K	2.19	5680	-10.909	**?**	**-140.2**	**2.87**	**2.81**	**?**			28774	NWMO TCEA book 3	
239	USGS 57	3.389	6361	42.407	**-91.5**	**-93.5**	**2.08**	**2.03**	**2.135**			28775	NWMO TCEA book 3	
240	USGS 58	2.898	6478	115.589	**-28.4**	**-29.3**	**2.48**	**2.42**	**2.454**			28776	NWMO TCEA book 3	
241	SapCa-1_K	2.721	5492	3.272	**?**	**-127.7**	**2.24**	**2.19**	**?**	**-128.94**	**1.30**	28777	NWMO TCEA book 3	
242	SapCa-1_K	2.821	5080	0.33	**?**	**-130.3**	**1.99**	**1.95**	**?**			28778	NWMO TCEA book 3	
243	SapCa-1_K	2.955	4289	2.089	**?**	**-128.8**	**1.61**	**1.57**	**?**			28779	NWMO TCEA book 3	
244	SWa-1_K	2.954	3551	-34.548	**?**	**-160.9**	**1.33**	**1.30**	**?**	**-160.87**	**#DIV/0!**	28780	NWMO TCEA book	took MS longer to register peak ampl2&raw d2H values, d2H looks ok
245	SWa-1_K	2.777	2246	-42.778	**?**	**-168.1**	**0.90**	**0.88**	**?**			28781	NWMO TCEA book	TCEA GC needs maintenance, poor peak shape
246	SWa-1_K	2.216	1432	-54.197	**?**	**-178.1**	**0.72**	**0.70**	**?**			28783	NWMO TCEA book	TCEA GC needs maintenance, poor peak shape
	GBS biotite													GBS analysis manually stopped, TCEA GC needs maintenance
	# of samples: 0 (development project)													
	# of standards, duplicates, failed:19,0,5													

[Analysis-13]

Project: Kanik NWMO_TCEA-HM-H19-13 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: June 24, 2019 (FJL)

Nadine's Notes: for degassing, Al-tray gave comparable d2H values to previous (and end of current) analysis for 1:1, 2:1 swelling & non-swelling HM. Reactor maintenance caused higher d2H in first several samples (see notes below)
For future reference: monitor number of samples needed to stabilize d2H values for new vs re-packed reactors, monitor drift.

Date Analyzed: June 12, 2019,
Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 24 hours followed by loading into He purged autosamper (glass vials and Al-tray), equilibrated in autosampler He atmosphere overnight.
Capsules closed, maintenance done on reactor, reactor re-packed, and new crucible.
Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	45.02	-91.5
USGS 58	115.39	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
7263.00	3.175	7.79	USGS 58	muscovite
6923.67	3.528	7.53	USGS 57	biotite

slope: 0.89666
Intercept: -131.86
r squared 0.999
Calculated equation: d2H = 0.897 *raw -131.9

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes	
														2 blanks done before first GBS, to help condition reactor	
251	GBS biotite	3.858	6675	92.89	-62.5	-48.6	1.88	1.86	1.940			28793	NWMO TCEA book 3	expected and actual d2H values differ, likely resulting from changes to reactor	degassed in glass vials
252	USGS 57	3.672	7300	60.206	-91.5	-77.9	2.16	2.13	2.135			28794	NWMO TCEA book 3	expected and actual d2H values differ, likely resulting from changes to reactor	degassed in glass vials
253	USGS 58	3.19	7404	128.788	-28.4	-16.4	2.53	2.49	2.454			28795	NWMO TCEA book 3	expected and actual d2H values differ, likely resulting from changes to reactor	degassed in glass vials
254	KGa-1	0.941	7358	90.946	-57.0	-50.3	8.51	8.39	7.750			28796	NWMO TCEA book 3	expected and actual d2H values differ, likely resulting from changes to reactor	degassed in glass vials
255	KGa-1	0.988	7696	89.586	-57.0	-51.5	8.47	8.36	7.750			28797	NWMO TCEA book 3	d2H values improve starting here, but still trend high, excluded from avg & stdev calcs	degassed in glass vials
256	KGa-1	0.836	6469	88.665	-57.0	-52.4	8.42	8.30	7.750			28798	NWMO TCEA book 3		degassed in glass vials
257	KGa-1	0.91	7086	87.935	-57.0	-53.0	8.47	8.35	7.750			28799	NWMO TCEA book 3		degassed in glass vials
258	GBS biotite	3.823	6666	81.978	-62.5	-58.4	1.90	1.87	1.940			28800	NWMO TCEA book 3		degassed in glass vials
259	SCa-3	2.663	10586	12.105	?	-121.0	4.32	4.26	?			28801	NWMO TCEA book 3		degassed in glass vials
260	SCa-3	2.52	9972	9.235	?	-123.6	4.30	4.24	?			28802	NWMO TCEA book 3		degassed in glass vials
261	SWy-1_K	2.653	7099	-6.52	?	-137.7	2.91	2.87	?			28803	NWMO TCEA book 3		degassed in glass vials
262	SWy-1_K	2.691	7145	-6.592	?	-137.8	2.89	2.85	?			28804	NWMO TCEA book 3		degassed in glass vials
263	SapCa-1_K	2.509	5505	9.818	?	-123.1	2.39	2.35	?			28805	NWMO TCEA book 3		degassed in glass vials
264	SapCa-1_K	3.065	7103	3.963	?	-128.3	2.52	2.49	?			28806	NWMO TCEA book 3		degassed in glass vials
265	SWa-1_K	2.488	7487	-26.372	?	-155.5	3.27	3.23	?			28807	NWMO TCEA book 3		degassed in glass vials
266	SWa-1_K	2.895	9041	-29.984	?	-158.7	3.40	3.35	?			28808	NWMO TCEA book 3		degassed in glass vials
267	IMt-1_K (2)	2.395	6935	37.591	?	-98.2	3.15	3.11	?	-100.91	4.52	28809	NWMO TCEA book 3	d2H values become very close to previous analysis starting here	degassed in glass vials
268	IMt-1_K (2)	2.359	6739	40.007	?	-96.0	3.11	3.06	?			28810	NWMO TCEA book 3		degassed in glass vials
269	SAz-1_K	2.606	8115	11.631	?	-121.4	3.39	3.34	?	-122.22	0.94	28811	NWMO TCEA book 3		degassed in glass vials
270	SAz-1_K	3.018	9453	9.927	?	-123.0	3.41	3.36	?			28812	NWMO TCEA book 3		degassed in glass vials
271	USGS 57	3.535	6963	46.301	-91.5	-90.3	2.14	2.11	2.135	-91.50	3.14	28813	NWMO TCEA book 3		degassed in glass vials
272	USGS 58	3.149	7230	117.404	-28.4	-26.6	2.50	2.46	2.454	-28.40	2.19	28814	NWMO TCEA book 3		degassed in glass vials
273	GBS biotite	3.807	6441	78.48	-62.5	-61.5	1.84	1.81	1.940	-62.55	1.85	28815	NWMO TCEA book 3	this GBS in glass vial	degassed in glass vials
274	GBS biotite	3.943	6767	78.663	-62.5	-61.3	1.87	1.84	1.940			28816	NWMO TCEA book 3	this GBS in Al-tray, use of tray does not seem to cause d2H difference	degassed in Al-tray
275	USGS 57	3.306	6474	47.699	-91.5	-89.1	2.13	2.10	2.135			28817	NWMO TCEA book 3		degassed in Al-tray
276	USGS 58	3.146	7221	116.091	-28.4	-27.8	2.50	2.46	2.454			28818	NWMO TCEA book 3		degassed in Al-tray
277	KGa-1	0.892	6920	85.33	-57.0	-55.4	8.44	8.32	7.750	-55.44	0.39	28819	NWMO TCEA book 3		degassed in Al-tray
278	KGa-1	0.999	7831	84.602	-57.0	-56.0	8.53	8.41	7.750			28820	NWMO TCEA book 3		degassed in Al-tray
279	KGa-1	0.814	6182	85.446	-57.0	-55.2	8.26	8.15	7.750			28821	NWMO TCEA book 3		degassed in Al-tray
280	KGa-1	0.834	6409	85.566	-57.0	-55.1	8.36	8.24	7.750			28822	NWMO TCEA book 3		degassed in Al-tray
281	GBS biotite	3.653	5906	77.822	-62.5	-62.1	1.76	1.73	1.940			28823	NWMO TCEA book 3		degassed in Al-tray
282	SCa-3	2.695	11474	6.678	?	-125.9	4.63	4.57	?	-125.54	0.47	28824	NWMO TCEA book 3		degassed in Al-tray
283	SCa-3	2.427	9691	7.427	?	-125.2	4.34	4.28	?			28825	NWMO TCEA book 3		degassed in Al-tray
284	SWy-1_K	2.835	7978	-12.423	?	-143.0	3.06	3.02	?	-143.36	0.51	28826	NWMO TCEA book 3		degassed in Al-tray
285	SWy-1_K	2.805	7931	-13.229	?	-143.7	3.08	3.03	?			28827	NWMO TCEA book 3		degassed in Al-tray
286	SapCa-1_K	3.043	6609	-0.346	?	-132.2	2.36	2.33	?	-131.17	1.42	28828	NWMO TCEA book 3		degassed in Al-tray
287	SapCa-1_K	2.563	5899	1.899	?	-130.2	2.50	2.47	?			28829	NWMO TCEA book 3		degassed in Al-tray
288	SWa-1_K	2.664	8321	-34.69	?	-163.0	3.40	3.35	?	-162.75	0.31	28830	NWMO TCEA book 3		degassed in Al-tray
289	SWa-1_K	2.405	7562	-34.208	?	-162.5	3.42	3.37	?			28831	NWMO TCEA book 3		degassed in Al-tray
290	IMt-1_K (2)	2.499	7338	30.551	?	-104.5	3.19	3.15	?			28832	NWMO TCEA book 3		degassed in Al-tray
291	IMt-1_K (2)	2.854	8451	29.938	?	-105.0	3.22	3.18	?			28833	NWMO TCEA book 3		degassed in Al-tray
292	SAz-1_K	2.572	6996	11.688	?	-121.4	2.96	2.92	?			28834	NWMO TCEA book 3		degassed in Al-tray
293	SAz-1_K	2.246	8110	9.771	?	-123.1	3.93	3.87	?			28835	NWMO TCEA book 3		degassed in Al-tray
294	USGS 57	3.743	7334	41.048	-91.5	-95.1	2.13	2.10	2.135			28836	NWMO TCEA book 3		degassed in Al-tray
295	USGS 58	3.229	7338	112.67	-28.4	-30.8	2.47	2.44	2.454			28837	NWMO TCEA book 3		degassed in Al-tray
296	GBS biotite	3.952	6627	74.248	-62.5	-65.3	1.82	1.80	1.940			28838	NWMO TCEA book 3		degassed in Al-tray

# of samples: 24
# of standards, duplicates, failed: 6,0,16

[Analysis-14]

Project: Kanik NWMO_TCEA-HM-H19-14 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: June 24, 2019 (FJL)

Date Analyzed: June 14, 2019
Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 24 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = 1min: 46sec
Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	42.38	-91.5
USGS 58	113.88	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
6604.50	2.961	7.27	USGS 58	muscovite
5947.50	3.108	6.63	USGS 57	biotite

slope: 0.88247
Intercept: -128.90
r squared 0.999
Calculated equation: d2H = 0.882 *raw -128.9

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
301	GBS biotite	3.009	5237	76.258	**-62.5**	**-61.6**	**1.94**	**1.91**	**1.940**	**-63.0**	**1.2**	28846	NWMO TCEA book 3	
302	GBS biotite	3.155	5131	75.286	**-62.5**	**-62.5**	**1.81**	**1.79**	**1.940**			28847	NWMO TCEA book 3	
303	USGS 57	3.059	5828	43.89	**-91.5**	**-90.2**	**2.13**	**2.10**	**2.135**	**-91.5**	**1.9**	28848	NWMO TCEA book 3	
304	USGS 58	2.911	6489	114.646	**-28.4**	**-27.7**	**2.49**	**2.45**	**2.454**	**-28.4**	**1.0**	28849	NWMO TCEA book 3	
305	KGa-1 RT	0.826	6236	82.729	**-57.0**	**-55.9**	**8.42**	**8.30**	**7.750**	**-56.9**	**0.9**	28850	NWMO TCEA book 3	
306	KGa-1 RT	0.879	6651	80.645	**-57.0**	**-57.7**	**8.44**	**8.32**	**7.750**			28851	NWMO TCEA book 3	
307	KGa-1 RT	0.743	5550	81.39	**-57.0**	**-57.1**	**8.33**	**8.22**	**7.750**			28852	NWMO TCEA book 3	
308	GBS biotite	3.165	4754	72.936	**-62.5**	**-64.5**	**1.68**	**1.65**	**1.940**			28853	NWMO TCEA book 3	
309	SCa-3	2.174	8582	8.013	**?**	**-121.8**	**4.40**	**4.34**	**?**	**-122.9**	**1.5**	28854	NWMO TCEA book 3	
310	SCa-3	2.377	9396	5.649	**?**	**-123.9**	**4.41**	**4.35**	**?**			28855	NWMO TCEA book 3	
311	SWy-1_K	2.493	6958	-13.594	**?**	**-140.9**	**3.11**	**3.07**	**?**	**-140.4**	**0.6**	28856	NWMO TCEA book 3	
312	SWy-1_K	1.989	5487	-12.566	**?**	**-140.0**	**3.08**	**3.03**	**?**			28857	NWMO TCEA book 3	
313	SapCa-1_K	2.484	5688	-2.028	**?**	**-130.7**	**2.55**	**2.52**	**?**	**-129.0**	**2.4**	28858	NWMO TCEA book 3	
314	SapCa-1_K	2.138	4601	1.897	**?**	**-127.2**	**2.40**	**2.37**	**?**			28859	NWMO TCEA book 3	
315	SWa-1_K	2.398	7193	-33.16	**?**	**-158.2**	**3.35**	**3.30**	**?**	**-159.23**	**1.52**	28860	NWMO TCEA book 3	
316	SWa-1_K	2.179	6683	-35.596	**?**	**-160.3**	**3.42**	**3.37**	**?**			28861	NWMO TCEA book 3	
317	IMt-1_K (2)	2.548	7370	29.262	**?**	**-103.1**	**3.23**	**3.18**	**?**	**-102.41**	**0.94**	28862	NWMO TCEA book 3	
318	IMt-1_K (2)	2.292	6603	30.765	**?**	**-101.7**	**3.21**	**3.17**	**?**			28863	NWMO TCEA book 3	
319	SAz-1_K	2.405	7254	7.773	**?**	**-122.0**	**3.36**	**3.32**	**?**	**-121.19**	**1.19**	28864	NWMO TCEA book 3	
320	SAz-1_K	2.181	6661	9.685	**?**	**-120.4**	**3.41**	**3.36**	**?**			28865	NWMO TCEA book 3	
321	USGS 57	3.156	6067	40.865	**-91.5**	**-92.8**	**2.14**	**2.11**	**2.135**			28866	NWMO TCEA book 3	
322	USGS 58	3.01	6720	113.117	**-28.4**	**-29.1**	**2.49**	**2.46**	**2.454**			28867	NWMO TCEA book 3	
323	GBS biotite	2.928	4773	74.342	**-62.5**	**-63.3**	**1.82**	**1.79**	**1.940**			28868	NWMO TCEA book 3	

# of samples: 19
# of standards, duplicates, failed: 4,0,0

[Analysis-15]

Project: Kanik NWMO_TCEA-HM-H19-15 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: June 28, 2019 (FJL)

Date Analyzed: June 18, 2019
Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 24 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = 2min: 30sec
Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	46.03	-91.5
USGS 58	116.79	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
5817.00	2.721	6.68	USGS 58	muscovite
5354.00	2.885	6.16	USGS 57	biotite

slope:		0.89178		
Intercept:		-132.55		
r squared		0.999		
Calculated equation:	d2H =	0.892	*raw	-132.5

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
327	GBS biotite	3.294	5077	81.8	-62.5	-59.6	1.77	1.77	1.940	-62.8	3.1	28873	NWMO TCEA book 3	
328	USGS 57	2.846	5361	48.945	-91.5	-88.9	2.17	2.16	2.135	-91.5	3.7	28874	NWMO TCEA book 3	
329	USGS 58	2.883	6171	118.903	-28.4	-26.5	2.46	2.46	2.454	-28.4	2.7	28875	NWMO TCEA book 3	
330	KGa-1 RT	0.625	4509	89.262	-57.0	-52.9	8.30	8.28	7.750	-54.2	1.7	28876	NWMO TCEA book 3	
331	KGa-1 RT	0.762	5592	86.532	-57.0	-55.4	8.44	8.42	7.750			28877	NWMO TCEA book 3	
332	GBS biotite	3.403	5034	79.161	-62.5	-62.0	1.70	1.70	1.940			28878	NWMO TCEA book 3	
333	SAz-1_K	1.762	4868	13.656	?	-120.4	3.18	3.17	?	-121.9	1.5	28879	NWMO TCEA book 3	
334	SAz-1_K	1.68	4571	11.721	?	-122.1	3.13	3.12	?			28880	NWMO TCEA book 3	
335	SAz-1_K	2.29	6473	10.303	?	-123.4	3.25	3.24	?			28881	NWMO TCEA book 3	
336	SAz-1_Ca	1.58	5179	12.318	?	-121.6	3.77	3.76	?	-124.3	2.4	28882	NWMO TCEA book 3	
337	SAz-1_Ca	2.04	7217	8.027	?	-125.4	4.07	4.06	?			28883	NWMO TCEA book 3	
338	SAz-1_Ca	2.106	7448	7.372	?	-126.0	4.07	4.06	?			28884	NWMO TCEA book 3	
339	SAz-1_Na	1.95	6218	2.877	?	-130.0	3.67	3.66	?	-130.4	1.5	28885	NWMO TCEA book 3	
340	SAz-1_Na	1.771	5622	3.806	?	-129.2	3.65	3.64	?			28886	NWMO TCEA book 3	
341	SAz-1_Na	2.165	6846	0.468	?	-132.1	3.64	3.63	?			28887	NWMO TCEA book 3	
342	IMt-1_K (2)	1.973	5323	33.995	?	-102.2	3.10	3.10	?	-102.02	0.30	28888	NWMO TCEA book 3	
343	IMt-1_K (2)	1.955	5332	34.472	?	-101.8	3.14	3.13	?			28889	NWMO TCEA book 3	
344	SWa-1_K	2.228	6211	-37.557	?	-166.0	3.21	3.20	?	-165.17	2.93	28890	NWMO TCEA book 3	
345	SWa-1_K	1.74	4814	-32.919	?	-161.9	3.18	3.18	?			28891	NWMO TCEA book 3	
346	SWa-1_K	2.115	5940	-39.27	?	-167.6	3.23	3.22	?			28892	NWMO TCEA book 3	
347	SWa-1_Ca	1.769	5842	-26.89	?	-156.5	3.80	3.79	?	-157.48	1.19	28893	NWMO TCEA book 3	
348	SWa-1_Ca	1.958	6527	-27.521	?	-157.1	3.84	3.83	?			28894	NWMO TCEA book 3	
349	SWa-1_Ca	2.038	6712	-29.461	?	-158.8	3.79	3.78	?			28895	NWMO TCEA book 3	
350	SWa-1_Na	2.22	6690	-35.348	?	-164.1	3.47	3.46	?	-162.81	1.30	28896	NWMO TCEA book 3	
351	SWa-1_Na	2.127	6529	-32.428	?	-161.5	3.53	3.52	?			28897	NWMO TCEA book 3	
352	SWa-1_Na	1.93	5913	-34.023	?	-162.9	3.52	3.52	?			28898	NWMO TCEA book 3	
353	GBS biotite	3.302	4594	73.502	-62.5	-67.0	1.60	1.60	1.940			28899	NWMO TCEA book 3	
354	SWy-1_K	2.073	5289	-11.483	?	-142.8	2.94	2.93	?	-143.36	0.67	28900	NWMO TCEA book 3	
355	SWy-1_K	2.029	5231	-11.948	?	-143.2	2.97	2.96	?			28901	NWMO TCEA book 3	
356	SWy-1_K	2.229	5789	-12.944	?	-144.1	2.99	2.98	?			28902	NWMO TCEA book 3	
357	SWy-1_Ca	2.525	8117	-8.787	?	-140.4	3.70	3.69	?	-138.88	1.75	28903	NWMO TCEA book 3	
358	SWy-1_Ca	2.291	7195	-7.579	?	-139.3	3.61	3.61	?			28904	NWMO TCEA book 3	
359	SWy-1_Ca	1.908	6031	-4.953	?	-137.0	3.64	3.63	?			28905	NWMO TCEA book 3	
360	SWy-1_Na	1.924	5392	-4.197	?	-136.3	3.22	3.22	?	-136.51	0.35	28906	NWMO TCEA book 3	
361	SWy-1_Na	1.894	5310	-4.237	?	-136.3	3.23	3.22	?			28907	NWMO TCEA book 3	
362	SWy-1_Na	1.88	5273	-4.898	?	-136.9	3.23	3.22	?			28908	NWMO TCEA book 3	
363	USGS 57	2.924	5347	43.111	-91.5	-94.1	2.10	2.10	2.135			28909	NWMO TCEA book 3	
364	USGS 58	2.559	5463	114.668	-28.4	-30.3	2.46	2.45	2.454			28910	NWMO TCEA book 3	
365	GBS biotite	2.799	4342	78.412	-62.5	-62.6	1.78	1.78	1.940			28911	NWMO TCEA book 3	

# of samples: 29
# of standards, duplicates, failed:10,0,0

[Analysis-16]

Project: Kanik NWMO_TCEA-HM-H19-16 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: June 28, 2019 (FJL)

Date Analyzed: June 20, 2019
Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 4 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for ~4 hours then analyzed.

Loading time with Al-tray and operator = 2min: 46sec. New reactor and packing, reactor baked out at 1450C for ~9 hours prior to analysis

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	37.26	-91.5
USGS 58	108.57	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
5373.50	2.784	6.83	USGS 58	muscovite
4824.00	2.897	6.18	USGS 57	biotite

slope: 0.88483
Intercept: -124.46
r squared 0.999
Calculated equation: d2H = 0.885 *raw -124.5

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
369	GBS biotite	3.321	4626	67.9	-62.5	-64.4	1.79	1.77	1.940	-64.8	0.9	28917	NWMO TCEA book 3	d2H values may be altered resulting from new reactor
370	GBS biotite	2.755	3774	66.473	-62.5	-65.6	1.76	1.74	1.940			28918	NWMO TCEA book 3	d2H values may be altered resulting from new reactor
371	GBS biotite	3.212	4712	66.237	-62.5	-65.9	1.88	1.86	1.940			28919	NWMO TCEA book 3	d2H values may be altered resulting from new reactor
372	GBS biotite	3.335	4793	66.624	-62.5	-65.5	1.84	1.83	1.940			28920	NWMO TCEA book 3	d2H values may be altered resulting from new reactor
373	USGS 57	2.595	4379	38.013	-91.5	-90.8	2.16	2.15	2.135	-91.5	0.9	28921	NWMO TCEA book 3	
374	USGS 58	2.984	5837	108.236	-28.4	-28.7	2.51	2.49	2.454	-28.4	0.4	28922	NWMO TCEA book 3	
375	KGa-1 RT	0.756	5039	80.788	-57.0	-53.0	8.54	8.47	7.750	-52.6	0.5	28923	NWMO TCEA book 3	
376	KGa-1 RT	0.703	4648	81.613	-57.0	-52.3	8.48	8.40	7.750			28924	NWMO TCEA book 3	
377	GBS biotite	2.615	3732	68.234	-62.5	-64.1	1.83	1.81	1.940			28925	NWMO TCEA book 3	
378	SAz-1_K	1.694	4308	4.707	?	-120.3	3.26	3.23	?	-120.1	1.3	28926	NWMO TCEA book 3	
379	SAz-1_K	1.636	4148	6.512	?	-118.7	3.25	3.22	?			28927	NWMO TCEA book 3	
380	SAz-1_K	1.927	4972	3.534	?	-121.3	3.31	3.28	?			28928	NWMO TCEA book 3	
381	SAz-1_Ca	1.904	5953	-1.27	?	-125.6	4.01	3.97	?	-123.6	1.8	28929	NWMO TCEA book 3	
382	SAz-1_Ca	1.917	7085	2.415	?	-122.3	4.74	4.70	?			28930	NWMO TCEA book 3	
383	SAz-1_Ca	1.675	5972	1.944	?	-122.7	4.57	4.53	?			28931	NWMO TCEA book 3	
384	SAz-1_Na	1.869	5523	0.604	?	-123.9	3.79	3.76	?	-122.96	0.85	28932	NWMO TCEA book 3	
385	SAz-1_Na	1.6	4688	2.364	?	-122.4	3.76	3.72	?			28933	NWMO TCEA book 3	
386	SAz-1_Na	1.518	4460	2.131	?	-122.6	3.77	3.73	?			28934	NWMO TCEA book 3	
387	IMt-1_K (2)	1.674	4101	26.251	?	-101.2	3.14	3.11	?	-100.70	0.77	28935	NWMO TCEA book 3	
388	IMt-1_K (2)	1.82	4479	27.475	?	-100.2	3.15	3.13	?			28936	NWMO TCEA book 3	
389	SWa-1_K	1.61	3958	-41.596	?	-161.3	3.15	3.13	?	-162.82	1.76	28937	NWMO TCEA book 3	
390	SWa-1_K	1.785	4498	-45.505	?	-164.7	3.23	3.20	?			28938	NWMO TCEA book 3	
391	SWa-1_K	1.582	3919	-42.942	?	-162.5	3.18	3.15	?			28939	NWMO TCEA book 3	
392	SWa-1_Ca	1.829	5699	-29.469	?	-150.5	3.99	3.96	?	-152.44	1.96	28940	NWMO TCEA book 3	
393	SWa-1_Ca	2.107	6405	-33.889	?	-154.5	3.90	3.86	?			28941	NWMO TCEA book 3	
394	SWa-1_Ca	1.855	5714	-31.505	?	-152.3	3.95	3.92	?			28942	NWMO TCEA book 3	
395	SWa-1_Na	1.797	4907	-37.347	?	-157.5	3.50	3.47	?	-157.64	1.80	28943	NWMO TCEA book 3	
396	SWa-1_Na	1.548	4278	-35.547	?	-155.9	3.54	3.51	?			28944	NWMO TCEA book 3	
397	SWa-1_Na	1.518	4137	-39.596	?	-159.5	3.49	3.46	?			28945	NWMO TCEA book 3	
398	GBS biotite	2.584	3490	67.86	-62.5	-64.4	1.73	1.72	1.940			28946	NWMO TCEA book 3	
399	SWy-1_K	1.881	4244	-18.558	?	-140.9	2.89	2.87	?	-141.70	0.71	28947	NWMO TCEA book 3	
400	SWy-1_K	2.05	4584	-19.882	?	-142.1	2.87	2.84	?			28948	NWMO TCEA book 3	
401	SWy-1_K	2.078	4630	-20.004	?	-142.2	2.86	2.83	?			28949	NWMO TCEA book 3	
402	SWy-1_Ca	1.809	5210	-8.866	?	-132.3	3.69	3.66	?	-132.07	0.22	28950	NWMO TCEA book 3	
403	SWy-1_Ca	2.148	5959	-8.542	?	-132.0	3.56	3.53	?			28951	NWMO TCEA book 3	
404	SWy-1_Ca	1.809	5115	-8.382	?	-131.9	3.62	3.59	?			28952	NWMO TCEA book 3	
405	SWy-1_Na	1.877	4644	-10.819	?	-134.0	3.17	3.15	?	-133.08	1.54	28953	NWMO TCEA book 3	
406	SWy-1_Na	1.752	4334	-10.661	?	-133.9	3.17	3.14	?			28954	NWMO TCEA book 3	
407	SWy-1_Na	1.755	4357	-7.731	?	-131.3	3.18	3.16	?			28955	NWMO TCEA book 3	
408	USGS 57	3.198	5269	36.497	-91.5	-92.2	2.11	2.09	2.135			28956	NWMO TCEA book 3	
409	USGS 58	2.583	4910	108.9	-28.4	-28.1	2.44	2.42	2.454			28957	NWMO TCEA book 3	
410	GBS biotite	2.823	3947	68.861	-62.5	-63.5	1.79	1.78	1.940			28958	NWMO TCEA book 3	

# of samples: 29 (development project)
# of standards, duplicates, failed, blanks: 13,0,0,2

[Analysis-17]

Project: Kanik NWMO_TCEA-HM-H19-17 (hydrous minerals)A1:O59/
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: , 2019 (FJL)

Date Analyzed: June 23, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 200C active vacuum oven for 24 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = 3min: 03sec. Varification analysis with previous reactor data with new reactor data

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	36.76	-91.5
USGS 58	109.61	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4945.50	2.536	6.22	USGS 58	muscovite
5586.50	3.255	6.95	USGS 57	biotite

slope: 0.86617
Intercept: -123.34
r squared 0.999
Calculated equation: d2H = 0.866 *raw -123.3

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														1 conditioning blanks at start
413	GBS biotite	3.681	5591	67.456	**-62.5**	**-64.9**	**1.89**	**1.91**	**1.940**	**-64.8**	**1.8**	28961	NWMO TCEA book 3	
414	USGS 57	3.207	5516	36.655	**-91.5**	**-91.6**	**2.14**	**2.16**	**2.135**	**-91.5**	**0.1**	28962	NWMO TCEA book 3	
415	USGS 58	2.539	4989	109.326	**-28.4**	**-28.6**	**2.44**	**2.47**	**2.454**	**-28.4**	**0.4**	28963	NWMO TCEA book 3	
416	KGa-1 RT	0.707	4748	75.3	**-57.0**	**-58.1**	**8.35**	**8.45**	**7.750**	**-57.8**	**0.4**	28964	NWMO TCEA book 3	
417	KGa-1 RT	0.749	4037	75.945	**-57.0**	**-57.6**	**6.70**	**6.78**	**7.750**			28965	NWMO TCEA book 3	
418	GBS biotite	3.647	5598	68.178	**-62.5**	**-64.3**	**1.91**	**1.93**	**1.940**			28966	NWMO TCEA book 3	
419	SAz-1_K	1.841	5054	7.823	**?**	**-116.6**	**3.41**	**3.45**	**?**	**-115.4**	**1.2**	28967	NWMO TCEA book 3	
420	SAz-1_K	1.584	4310	10.59	**?**	**-114.2**	**3.38**	**3.42**	**?**			28968	NWMO TCEA book 3	
421	SAz-1_K	1.883	5201	9.008	**?**	**-115.5**	**3.44**	**3.48**	**?**			28969	NWMO TCEA book 3	
422	SAz-1_Ca	2.012	8104	-0.577	**?**	**-123.8**	**5.01**	**5.07**	**?**	**-122.9**	**0.8**	28970	NWMO TCEA book 3	
423	SAz-1_Ca	1.86	7258	0.784	**?**	**-122.7**	**4.85**	**4.91**	**?**			28971	NWMO TCEA book 3	
424	SAz-1_Ca	1.582	6181	1.281	**?**	**-122.2**	**4.86**	**4.92**	**?**			28972	NWMO TCEA book 3	
425	SAz-1_Na	1.867	5817	0.734	**?**	**-122.7**	**3.88**	**3.92**	**?**	**-121.9**	**0.7**	28973	NWMO TCEA book 3	
426	SAz-1_Na	1.84	5689	1.812	**?**	**-121.8**	**3.85**	**3.89**	**?**			28974	NWMO TCEA book 3	
427	SAz-1_Na	1.594	4878	2.304	**?**	**-121.3**	**3.81**	**3.85**	**?**			28975	NWMO TCEA book 3	
428	IMt-1_K (2)	1.828	4620	28.923	**?**	**-98.3**	**3.14**	**3.18**	**?**			28976	NWMO TCEA book 3	
429	SWa-1_K	1.808	4883	-39.274	**?**	**-157.4**	**3.36**	**3.40**	**?**	**-157.78**	**0.77**	28977	NWMO TCEA book 3	
430	SWa-1_K	1.828	4921	-40.789	**?**	**-158.7**	**3.35**	**3.39**	**?**			28978	NWMO TCEA book 3	
431	SWa-1_K	1.715	4587	-39.211	**?**	**-157.3**	**3.33**	**3.37**	**?**			28979	NWMO TCEA book 3	
432	SWa-1_Ca	2.048	6864	-28.281	**?**	**-147.8**	**4.17**	**4.22**	**?**	**-145.91**	**2.18**	28980	NWMO TCEA book 3	
433	SWa-1_Ca	2.08	7086	-26.554	**?**	**-146.3**	**4.24**	**4.29**	**?**			28981	NWMO TCEA book 3	
434	SWa-1_Ca	1.835	6237	-23.325	**?**	**-143.5**	**4.23**	**4.28**	**?**			28982	NWMO TCEA book 3	
435	SWa-1_Na	1.866	5671	-31.644	**?**	**-150.8**	**3.78**	**3.82**	**?**	**-149.77**	**0.88**	28983	NWMO TCEA book 3	
436	SWa-1_Na	1.733	5153	-29.686	**?**	**-149.1**	**3.70**	**3.74**	**?**			28984	NWMO TCEA book 3	
437	SWa-1_Na	1.956	5805	-30.184	**?**	**-149.5**	**3.69**	**3.73**	**?**			28985	NWMO TCEA book 3	
438	GBS biotite	3.798	5397	64.892	**-62.5**	**-67.1**	**1.77**	**1.79**	**1.940**			28986	NWMO TCEA book 3	
439	SWy-1_K	1.673	3929	-15.983	**?**	**-137.2**	**2.92**	**2.96**	**?**	**-137.90**	**0.67**	28987	NWMO TCEA book 3	
440	SWy-1_K	1.962	4720	-16.941	**?**	**-138.0**	**2.99**	**3.03**	**?**			28988	NWMO TCEA book 3	
441	SWy-1_K	1.636	3758	-17.507	**?**	**-138.5**	**2.86**	**2.89**	**?**			28989	NWMO TCEA book 3	
442	SWy-1_Ca	1.676	5176	-6.999	**?**	**-129.4**	**3.84**	**3.89**	**?**	**-130.58**	**1.02**	28990	NWMO TCEA book 3	
443	SWy-1_Ca	2.036	6162	-8.929	**?**	**-131.1**	**3.76**	**3.81**	**?**			28991	NWMO TCEA book 3	
444	SWy-1_Ca	1.907	5901	-9.15	**?**	**-131.3**	**3.85**	**3.89**	**?**			28992	NWMO TCEA book 3	
445	SWy-1_Na	1.727	4470	-6.169	**?**	**-128.7**	**3.22**	**3.26**	**?**	**3.19**	**0.02**	28993	NWMO TCEA book 3	
446	SWy-1_Na	2.026	5171	-7.902	**?**	**-130.2**	**3.18**	**3.21**	**?**			28994	NWMO TCEA book 3	
447	SWy-1_Na	1.722	4402	-7.113	**?**	**-129.5**	**3.18**	**3.22**	**?**			28995	NWMO TCEA book 3	
448	USGS 57	3.303	5657	36.873	**-91.5**	**-91.4**	**2.13**	**2.16**	**2.135**			28996	NWMO TCEA book 3	
449	USGS 58	2.533	4902	109.901	**-28.4**	**-28.2**	**2.41**	**2.44**	**2.454**			28997	NWMO TCEA book 3	
450	GBS biotite	3.29	4713	69.79	**-62.5**	**-62.9**	**1.78**	**1.80**	**1.940**			28998	NWMO TCEA book 3	

# of samples: 27 (development project)
# of standards, duplicates, failed, blanks: 11,0,0,1

[Analysis-18]

Project: Kanik NWMO_TCEA-HM-H19-18 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: September 30, 2019 (FJL)

Date Analyzed: Sept 5, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 25 hours, and vac opened samples added to Al-tray and heated for 5 hours at 100C, and non-heated samples added in the analysis with both sets of heated samples, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 3 hours then analyzed. Loading time with Al-tray and operator = breaking vac seal to AS= 41sec. and loading AS to closing AS= 50sec., total time = 2min. 31 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	43.70	-91.5
USGS 58	110.95	-28.4

slope: 0.93823
Intercept: -132.50
r squared 0.999
Calculated equation: d2H = 0.938 *raw -132.5

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4459.00	2.345	5.75	USGS 58	muscovite
5554.00	3.327	7.10	USGS 57	biotite

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
455	GBS biotite	3.668	5054	74.000	**-62.5**	**-63.1**	**1.76**	**1.78**	**1.940**	**-64.9**	**1.4**	29497	NWMO TCEA book 3	
456	GBS biotite	3.161	4486	70.492	**-62.5**	**-66.4**	**1.81**	**1.83**	**1.940**			29498	NWMO TCEA book 3	
457	GBS biotite	3.288	4446	73.387	**-62.5**	**-63.6**	**1.73**	**1.75**	**1.940**			29499	NWMO TCEA book 3	
458	USGS 57	3.387	5719	44.372	**-91.5**	**-90.9**	**2.16**	**2.18**	**2.135**	**-91.5**	**0.6**	29500	NWMO TCEA book 3	
459	USGS 58	2.381	4521	111.655	**-28.4**	**-27.7**	**2.43**	**2.45**	**2.454**	**-28.4**	**0.8**	29501	NWMO TCEA book 3	
460	KGa-1 RT (220C-25h)	0.93	6207	76.131	**-57.0**	**-61.1**	**8.53**	**8.61**	**7.750**	**-62.5**	**0.9**	29502	NWMO TCEA book 3	
461	KGa-1 RT (220C-25h)	1.019	6679	75.311	**-57.0**	**-61.8**	**8.38**	**8.46**	**7.750**			29503	NWMO TCEA book 3	
462	KGa-1 RT (220C-25h)	0.865	5597	75.146	**-57.0**	**-62.0**	**8.27**	**8.35**	**7.750**			29504	NWMO TCEA book 3	
463	KGa-1 RT (220C-25h)	0.878	5792	73.853	**-57.0**	**-63.2**	**8.44**	**8.51**	**7.750**			29505	NWMO TCEA book 3	
464	KGa-1 RT (220C-25h)	0.896	5932	74.039	**-57.0**	**-63.0**	**8.47**	**8.54**	**7.750**			29506	NWMO TCEA book 3	
465	KGa-1 RT (220C-25h)	0.86	5647	73.361	**-57.0**	**-63.7**	**8.40**	**8.47**	**7.750**			29507	NWMO TCEA book 3	
466	KGa-1 RT (220C-25h)	0.839	5469	74.207	**-57.0**	**-62.9**	**8.34**	**8.41**	**7.750**			29508	NWMO TCEA book 3	
467	GBS biotite	3.559	5087	72.577	**-62.5**	**-64.4**	**1.83**	**1.84**	**1.940**			29509	NWMO TCEA book 3	
468	USGS 57	3.254	5400	43.096	**-91.5**	**-92.1**	**2.12**	**2.14**	**2.135**			29510	NWMO TCEA book 3	
469	USGS 58	2.383	4569	111.209	**-28.4**	**-28.2**	**2.45**	**2.47**	**2.454**			29511	NWMO TCEA book 3	
470	KGa-1 RT (100C-5h)	0.844	5559	87.855	**-57.0**	**-50.1**	**8.42**	**8.50**	**7.750**	**-51.98**	**0.98**	29512	NWMO TCEA book 3	
471	KGa-1 RT (100C-5h)	0.855	5542	86.575	**-57.0**	**-51.3**	**8.29**	**8.37**	**7.750**			29513	NWMO TCEA book 3	
472	KGa-1 RT (100C-5h)	0.846	5455	85.541	**-57.0**	**-52.2**	**8.25**	**8.32**	**7.750**			29514	NWMO TCEA book 3	
473	KGa-1 RT (100C-5h)	0.903	5858	85.361	**-57.0**	**-52.4**	**8.30**	**8.37**	**7.750**			29515	NWMO TCEA book 3	
474	KGa-1 RT (100C-5h)	0.869	5703	85.393	**-57.0**	**-52.4**	**8.39**	**8.47**	**7.750**			29516	NWMO TCEA book 3	
475	KGa-1 RT (100C-5h)	0.832	5456	85.043	**-57.0**	**-52.7**	**8.39**	**8.46**	**7.750**			29517	NWMO TCEA book 3	
476	KGa-1 RT (100C-5h)	0.855	5591	84.938	**-57.0**	**-52.8**	**8.36**	**8.44**	**7.750**			29518	NWMO TCEA book 3	
477	GBS biotite	3.446	4466	70.959	**-62.5**	**-65.9**	**1.66**	**1.67**	**1.940**			29519	NWMO TCEA book 3	
478	USGS 57	3.339	5543	43.624	**-91.5**	**-91.6**	**2.12**	**2.14**	**2.135**			29520	NWMO TCEA book 3	
479	USGS 58	2.271	4287	109.990	**-28.4**	**-29.3**	**2.41**	**2.44**	**2.454**			29521	NWMO TCEA book 3	
480	KGa-1 RT (atmos)	0.93	6128	89.087	**-57.0**	**-48.9**	**8.43**	**8.50**	**7.750**	**-50.25**	**1.00**	29522	NWMO TCEA book 3	
481	KGa-1 RT (atmos)	0.838	5425	88.971	**-57.0**	**-49.0**	**8.28**	**8.35**	**7.750**			29523	NWMO TCEA book 3	
482	KGa-1 RT (atmos)	0.973	6394	88.044	**-57.0**	**-49.9**	**8.40**	**8.48**	**7.750**			29524	NWMO TCEA book 3	
483	KGa-1 RT (atmos)	0.868	5659	87.200	**-57.0**	**-50.7**	**8.34**	**8.41**	**7.750**			29525	NWMO TCEA book 3	
484	KGa-1 RT (atmos)	0.998	6636	86.511	**-57.0**	**-51.3**	**8.50**	**8.58**	**7.750**			29526	NWMO TCEA book 3	
485	KGa-1 RT (atmos)	0.949	6157	87.321	**-57.0**	**-50.6**	**8.30**	**8.37**	**7.750**			29527	NWMO TCEA book 3	
486	KGa-1 RT (atmos)	0.86	5498	86.519	**-57.0**	**-51.3**	**8.18**	**8.25**	**7.750**			29528	NWMO TCEA book 3	
487	GBS biotite	3.41	4543	70.562	**-62.5**	**-66.3**	**1.70**	**1.72**	**1.940**			29529	NWMO TCEA book 3	

# of samples: 21
# of standards, duplicates, failed, blanks: 12,0,0,2

[Analysis-19]

Project: Kanik NWMO_TCEA-HM-H19-19 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: September 30, 2019 (FJL)

Date Analyzed: Sept 5, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 200C active vacuum oven for 4 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = breaking vac seal to AS= 34sec. and loading AS to closing AS= 1min: 15sec., total time = 1min. 49 sec., RH in lab 44%

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	41.02	-91.5
USGS 58	107.07	-28.4

slope:	0.95533
Intercept:	-130.68
r squared	0.999

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4553.50	2.438	5.98	USGS 58	muscovite
5473.50	3.403	7.26	USGS 57	biotite

Calculated equation: d2H = 0.955 *raw -130.7

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
170	USGS 57	3.278	5205	43.706	**-91.5**	**-88.9**	**2.11**	**2.09**	**2.135**	**-91.5**	**3.6**	29535	NWMO TCEA book 3	
171	USGS 58	2.402	4483	108.665	**-28.4**	**-26.9**	**2.48**	**2.45**	**2.454**	**-28.4**	**2.2**	29536	NWMO TCEA book 3	
172	SAz-1_K	1.372	3082	16.664	**?**	**-114.8**	**2.98**	**2.95**	**?**	**-118.5**	**3.6**	29537	NWMO TCEA book 3	
173	SAz-1_K	1.515	3500	12.453	**?**	**-118.8**	**3.07**	**3.03**	**?**			29538	NWMO TCEA book 3	
174	SAz-1_K	1.443	3238	9.149	**?**	**-121.9**	**2.98**	**2.95**	**?**			29539	NWMO TCEA book 3	
175	GBS biotite	3.443	4705	66.73	**-62.5**	**-66.9**	**1.81**	**1.80**	**1.940**	**-65.4**	**3.1**	29540	NWMO TCEA book 3	
176	SAz-1_Ca	1.554	4110	12.192	**?**	**-119.0**	**3.51**	**3.47**	**?**	**-121.3**	**2.4**	29541	NWMO TCEA book 3	
177	SAz-1_Ca	1.405	3515	11.07	**?**	**-120.1**	**3.32**	**3.29**	**?**			29542	NWMO TCEA book 3	
178	SAz-1_Ca	1.549	4199	9.538	**?**	**-121.6**	**3.60**	**3.56**	**?**			29543	NWMO TCEA book 3	
179	SAz-1_Ca	1.536	4101	6.351	**?**	**-124.6**	**3.54**	**3.51**	**?**			29544	NWMO TCEA book 3	
180	GBS biotite	3.55	4692	66.266	**-62.5**	**-67.4**	**1.75**	**1.74**	**?**			29545	NWMO TCEA book 3	
181	SAz-1_Na	1.491	3828	8.718	**?**	**-122.4**	**3.41**	**3.37**	**1.940**	**-125.9**	**2.5**	29546	NWMO TCEA book 3	
182	SAz-1_Na	1.498	3834	3.577	**?**	**-127.3**	**3.40**	**3.36**	**?**			29547	NWMO TCEA book 3	
183	SAz-1_Na	1.495	3805	4.779	**?**	**-126.1**	**3.38**	**3.34**	**?**			29548	NWMO TCEA book 3	
184	SAz-1_Na	1.526	3872	2.882	**?**	**-127.9**	**3.37**	**3.33**	**?**			29549	NWMO TCEA book 3	
185	USGS 57	3.527	5742	38.328	**-91.5**	**-94.1**	**2.16**	**2.14**	**2.135**			29550	NWMO TCEA book 3	
186	USGS 58	2.473	4624	105.47	**-28.4**	**-29.9**	**2.48**	**2.46**	**2.454**			29551	NWMO TCEA book 3	
187	GBS biotite	3.653	5097	72.027	**-62.5**	**-61.9**	**1.85**	**1.83**	**1.940**			29552	NWMO TCEA book 3	

# of samples: 13
# of standards, duplicates, failed, blanks: 7,0,0,2

[Analysis-20]

Project: Kanik NWMO_TCEA-HM-H19-20 (hydrous minerals)

Isotope(s): Hydrogen

Preparation: Nadine Kanik

Analyst: Nadine Kanik

Data Treatment and QA/QC: F. Longstaffe

Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS

Date Approved by Director: September 30, 2019 (FJL)

Date Analyzed: Sept 6, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 200C active vacuum oven for 4 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = breaking vac seal to AS= 31sec., waited to load until 4:00 min., closed AS at total of time = 4 min. 46 sec., RH in lab 41±1%

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	43.59	-91.5
USGS 58	111.76	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4568.50	2.509	6.16	USGS 58	muscovite
5406.50	3.410	7.28	USGS 57	biotite

slope:		0.92562		
Intercept:		-131.84		
r squared		0.999		
Calculated equation:	d2H =	0.926	*raw	-131.8

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
191	GBS biotite	3.612	4556	77.957	**-62.5**	**-59.7**	**1.70**	**1.70**	**1.940**	**-63.0**	**3.0**	29556	NWMO TCEA book 3	
192	GBS biotite	3.36	4504	76.559	**-62.5**	**-61.0**	**1.81**	**1.81**	**1.940**			29557	NWMO TCEA book 3	
193	USGS 57	3.243	5087	46.145	**-91.5**	**-89.1**	**2.11**	**2.11**	**2.135**	**-91.5**	**3.4**	29558	NWMO TCEA book 3	
194	USGS 58	2.594	4763	112.043	**-28.4**	**-28.1**	**2.47**	**2.47**	**2.454**	**-28.4**	**0.4**	29559	NWMO TCEA book 3	
195	SAz-1_K	1.531	3275	18.191	**?**	**-115.0**	**2.88**	**2.88**	**?**	**-118.0**	**2.6**	29560	NWMO TCEA book 3	
196	SAz-1_K	1.506	3241	13.258	**?**	**-119.6**	**2.90**	**2.90**	**?**			29561	NWMO TCEA book 3	
197	SAz-1_K	1.447	3090	13.265	**?**	**-119.6**	**2.88**	**2.88**	**?**			29562	NWMO TCEA book 3	
198	GBS biotite	3.406	4449	71.225	**-62.5**	**-65.9**	**1.76**	**1.76**	**1.940**			29563	NWMO TCEA book 3	
199	SAz-1_Ca	1.367	3238	22.094	**?**	**-111.4**	**3.19**	**3.19**	**?**	**-116.4**	**3.6**	29564	NWMO TCEA book 3	
200	SAz-1_Ca	1.501	3655	16.543	**?**	**-116.5**	**3.28**	**3.28**	**?**			29565	NWMO TCEA book 3	
201	SAz-1_Ca	1.517	3600	15.209	**?**	**-117.8**	**3.20**	**3.20**	**?**			29566	NWMO TCEA book 3	
202	SAz-1_Ca	1.529	3595	12.964	**?**	**-119.8**	**3.17**	**3.17**	**?**			29567	NWMO TCEA book 3	
203	GBS biotite	3.524	4978	70.804	**-62.5**	**-66.3**	**1.90**	**1.90**	**1.940**			29568	NWMO TCEA book 3	
204	SAz-1_Na	1.581	3781	10.113	**?**	**-122.5**	**3.22**	**3.22**	**?**	**-125.01**	**2.1**	29569	NWMO TCEA book 3	
205	SAz-1_Na	1.525	3484	8.15	**?**	**-124.3**	**3.08**	**3.08**	**?**			29570	NWMO TCEA book 3	
206	SAz-1_Na	1.547	3707	6.277	**?**	**-126.0**	**3.23**	**3.23**	**?**			29571	NWMO TCEA book 3	
207	SAz-1_Na	1.586	3704	4.995	**?**	**-127.2**	**3.14**	**3.15**	**?**			29572	NWMO TCEA book 3	
208	USGS 57	3.577	5726	41.025	**-91.5**	**-93.9**	**2.16**	**2.16**	**2.135**			29573	NWMO TCEA book 3	
209	USGS 58	2.423	4374	111.468	**-28.4**	**-28.7**	**2.43**	**2.43**	**2.454**			29574	NWMO TCEA book 3	
210	GBS biotite	3.628	4703	75.3	**-62.5**	**-62.1**	**1.75**	**1.75**	**1.940**			29575	NWMO TCEA book 3	

# of samples: 11

# of standards, duplicates, failed, blanks: 9,0,0,2

[Analysis-21]

Project: Kanik NWMO_TCEA-HM-H19-21 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaffe
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: September 30, 2019 (FJL)

Date Analyzed: Sept 6, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 200C active vacuum oven for 4 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = breaking vac seal to AS= 36sec., waited to load until 10:00 min., closed AS at total of time = 11 min. 10 sec., RH in lab 41±1%

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	45.01	-91.5
USGS 58	112.90	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4059.50	2.262	5.55	USGS 58	muscovite
5383.00	3.376	7.21	USGS 57	biotite

slope: 0.92954
Intercept: -133.34
r squared 0.999
Calculated equation: d2H = 0.930 *raw -133.3

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
214	GBS biotite	3.316	4560	79.379	**-62.5**	**-59.6**	**1.84**	**1.88**	**1.940**	**-63.8**	**3.3**	29579	NWMO TCEA book 3	
215	GBS biotite	3.516	4729	77.508	**-62.5**	**-61.3**	**1.80**	**1.84**	**1.940**			29580	NWMO TCEA book 3	
216	USGS 57	3.315	5249	46.661	**-91.5**	**-90.0**	**2.12**	**2.17**	**2.135**	**-91.5**	**2.2**	29581	NWMO TCEA book 3	
217	USGS 58	2.276	4057	113.843	**-28.4**	**-27.5**	**2.39**	**2.44**	**2.454**	**-28.4**	**1.2**	29582	NWMO TCEA book 3	
218	SAz-1_K	1.431	3145	22.109	**?**	**-112.8**	**2.94**	**3.01**	**?**	**-115.9**	**3.2**	29583	NWMO TCEA book 3	
219	SAz-1_K	1.42	3052	19.097	**?**	**-115.6**	**2.88**	**2.94**	**?**			29584	NWMO TCEA book 3	
220	SAz-1_K	1.481	3215	15.221	**?**	**-119.2**	**2.91**	**2.97**	**?**			29585	NWMO TCEA book 3	
221	GBS biotite	3.495	4455	72.474	**-62.5**	**-66.0**	**1.71**	**1.74**	**1.940**			29586	NWMO TCEA book 3	
222	SAz-1_Ca	1.522	4093	25.342	**?**	**-109.8**	**3.60**	**3.68**	**?**	**-112.5**	**2.4**	29587	NWMO TCEA book 3	
223	SAz-1_Ca	1.487	4171	23.154	**?**	**-111.8**	**3.76**	**3.84**	**?**			29588	NWMO TCEA book 3	
224	SAz-1_Ca	1.508	4244	22.133	**?**	**-112.8**	**3.77**	**3.85**	**?**			29589	NWMO TCEA book 3	
225	SAz-1_Ca	1.656	4509	19.075	**?**	**-115.6**	**3.65**	**3.72**	**?**			29590	NWMO TCEA book 3	
226	GBS biotite	3.462	4564	71.012	**-62.5**	**-67.3**	**1.77**	**1.80**	**1.940**			29591	NWMO TCEA book 3	
227	SAz-1_Na	1.568	3954	17.941	**?**	**-116.7**	**3.38**	**3.45**	**?**	**-118.63**	**1.7**	29592	NWMO TCEA book 3	
228	SAz-1_Na	1.429	3599	16.528	**?**	**-118.0**	**3.37**	**3.44**	**?**			29593	NWMO TCEA book 3	
229	SAz-1_Na	1.562	3952	13.745	**?**	**-120.6**	**3.39**	**3.46**	**?**			29594	NWMO TCEA book 3	
230	SAz-1_Na	1.418	3559	15.093	**?**	**-119.3**	**3.36**	**3.43**	**?**			29595	NWMO TCEA book 3	
231	USGS 57	3.437	5517	43.365	**-91.5**	**-93.0**	**2.15**	**2.19**	**2.135**			29596	NWMO TCEA book 3	
232	USGS 58	2.248	4062	111.949	**-28.4**	**-29.3**	**2.42**	**2.47**	**2.454**			29597	NWMO TCEA book 3	
233	GBS biotite	3.535	4689	73.652	**-62.5**	**-64.9**	**1.78**	**1.81**	**1.940**			29598	NWMO TCEA book 3	

# of samples: 11 (development project)
# of standards, duplicates, failed, blanks: 9,0,0,2

[Analysis-22]

Project: Kanik NWMO_TCEA-HM-H19-22 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: September 30, 2019 (FJL)

Date Analyzed: Sept 10, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 24 hours, and vac opened samples added to Al-tray and heated for 4 hours at 100C, and non-heated samples added in the analysis with both sets of heated samples, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = breaking vac seal to AS= 36sec. and loading AS to closing AS= 50sec., total time = 2min. 54 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value		
USGS 57	37.79	-91.5		
USGS 58	108.93	-28.4		
slope:		0.88690		
Intercept:		-125.01		
r squared		0.999		
Calculated equation:	d2H =	0.887	*raw	-125.0

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4911.50	2.593	6.36	USGS 58	muscovite
4927.50	2.867	6.12	USGS 57	biotite

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
237	GBS biotite	3.645	5475	67.469	**-62.5**	**-65.2**	**1.87**	**1.95**	**1.940**	**-65.1**	**0.4**	29622	NWMO TCEA book 3	
238	GBS biotite	3.65	5349	67.145	**-62.5**	**-65.5**	**1.82**	**1.90**	**1.940**			29623	NWMO TCEA book 3	
239	USGS 58	2.462	4904	108.148	**-28.4**	**-29.1**	**2.47**	**2.58**	**2.454**	**-28.4**	**1.0**	29624	NWMO TCEA book 3	
240	USGS 57	2.419	4198	38.848	**-91.5**	**-90.6**	**2.16**	**2.25**	**2.135**	**-91.5**	**1.3**	29625	NWMO TCEA book 3	
241	SWy-1_K (220C-24h)	1.821	4544	-15.32	**?**	**-138.6**	**3.10**	**3.23**	**?**	**-139.8**	**0.9**	29626	NWMO TCEA book 3	
242	SWy-1_K (220C-24h)	2.045	5113	-16.082	**?**	**-139.3**	**3.11**	**3.24**	**?**			29627	NWMO TCEA book 3	
243	SWy-1_K (220C-24h)	2.163	5467	-17.303	**?**	**-140.4**	**3.14**	**3.27**	**?**			29628	NWMO TCEA book 3	
244	SWy-1_K (220C-24h)	2.028	5060	-17.784	**?**	**-140.8**	**3.10**	**3.23**	**?**			29629	NWMO TCEA book 3	
245	SWy-1_K (220C-24h)	1.817	4511	-17.06	**?**	**-140.1**	**3.08**	**3.22**	**?**			29630	NWMO TCEA book 3	
246	SWy-1_Ca (220C-24h)	1.952	6197	-9.942	**?**	**-133.8**	**3.94**	**4.11**	**?**	**-133.6**	**0.4**	29631	NWMO TCEA book 3	
247	SWy-1_Ca (220C-24h)	1.899	6124	-9.837	**?**	**-133.7**	**4.01**	**4.18**	**?**			29632	NWMO TCEA book 3	
248	SWy-1_Ca (220C-24h)	1.839	5938	-9.147	**?**	**-133.1**	**4.01**	**4.18**	**?**			29633	NWMO TCEA book 3	
249	SWy-1_Na (220C-24h)	1.976	5706	-6.558	**?**	**-130.8**	**3.59**	**3.74**	**?**	**-130.0**	**0.9**	29634	NWMO TCEA book 3	
250	SWy-1_Na (220C-24h)	1.817	5140	-5.742	**?**	**-130.1**	**3.51**	**3.66**	**?**			29635	NWMO TCEA book 3	
251	SWy-1_Na (220C-24h)	1.938	5503	-4.62	**?**	**-129.1**	**3.53**	**3.68**	**?**			29636	NWMO TCEA book 3	
252	SWy-1_K (100C-4h)	1.912	4842	-14.663	**?**	**-138.0**	**3.15**	**3.28**	**?**	**-137.38**	**0.58**	29637	NWMO TCEA book 3	
253	SWy-1_K (100C-4h)	1.952	4988	-13.389	**?**	**-136.9**	**3.17**	**3.31**	**?**			29638	NWMO TCEA book 3	
254	SWy-1_K (100C-4h)	1.876	4763	-13.782	**?**	**-137.2**	**3.15**	**3.29**	**?**			29639	NWMO TCEA book 3	
255	SWy-1_Ca (100C-4h)	1.918	6875	-1.151	**?**	**-126.0**	**4.45**	**4.64**	**?**	**-125.04**	**1.95**	29640	NWMO TCEA book 3	
256	SWy-1_Ca (100C-4h)	1.9	6776	-1.442	**?**	**-126.3**	**4.43**	**4.62**	**?**			29641	NWMO TCEA book 3	
257	SWy-1_Ca (100C-4h)	1.884	6745	2.506	**?**	**-122.8**	**4.45**	**4.64**	**?**			29642	NWMO TCEA book 3	
258	SWy-1_Na (100C-4h)	1.745	4930	-6.693	**?**	**-130.9**	**3.51**	**3.66**	**?**	**-130.40**	**0.79**	29643	NWMO TCEA book 3	
259	SWy-1_Na (100C-4h)	1.761	4962	-5.054	**?**	**-129.5**	**3.50**	**3.65**	**?**			29644	NWMO TCEA book 3	
260	SWy-1_Na (100C-4h)	1.962	5580	-6.464	**?**	**-130.7**	**3.53**	**3.68**	**?**			29645	NWMO TCEA book 3	
261	SWy-1_K (atmos)	1.874	5504	-1.23	**?**	**-126.1**	**3.65**	**3.81**	**?**	**-127.23**	**1.10**	29646	NWMO TCEA book 3	
262	SWy-1_K (atmos)	1.804	5254	-2.577	**?**	**-127.3**	**3.62**	**3.77**	**?**			29647	NWMO TCEA book 3	
263	SWy-1_K (atmos)	1.943	5887	-3.711	**?**	**-128.3**	**3.76**	**3.93**	**?**			29648	NWMO TCEA book 3	
264	SWy-1_Ca (atmos)	1.817	10833	32.997	**?**	**-95.7**	**7.40**	**7.72**	**?**	**-95.42**	**1.32**	29649	NWMO TCEA book 3	
265	SWy-1_Ca (atmos)	1.943	11743	32.107	**?**	**-96.5**	**7.51**	**7.83**	**?**			29650	NWMO TCEA book 3	
266	SWy-1_Ca (atmos)	1.903	11405	35.004	**?**	**-94.0**	**7.44**	**7.76**	**?**			29651	NWMO TCEA book 3	
267	SWy-1_Na (atmos)	1.788	6295	8.038	**?**	**-117.9**	**4.37**	**4.56**	**?**	**-110.98**	**5.98**	29652	NWMO TCEA book 3	
268	SWy-1_Na (atmos)	1.862	7208	19.768	**?**	**-107.5**	**4.81**	**5.02**	**?**			29653	NWMO TCEA book 3	
269	SWy-1_Na (atmos)	1.878	7082	19.668	**?**	**-107.6**	**4.68**	**4.89**	**?**			29654	NWMO TCEA book 3	
270	USGS 57	3.314	5657	36.722	**-91.5**	**-92.4**	**2.12**	**2.21**	**2.135**			29655	NWMO TCEA book 3	
271	USGS 58	2.724	4919	109.715	**-28.4**	**-27.7**	**2.24**	**2.34**	**2.454**			29656	NWMO TCEA book 3	
272	GBS biotite	3.599	5314	68.138	**-62.5**	**-64.6**	**1.83**	**1.91**	**1.940**			29657	NWMO TCEA book 3	

# of samples: 29
# of standards, duplicates, failed, blanks: 7,0,0,2

[Analysis-23]

Project: Kanik NWMO_TCEA-HM-H19-23 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: October 1, 2019 (FJL)

Date Analyzed: Sept 10, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 4 hours, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = breaking vac seal to AS= 36sec., total time = 2min. 25 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	38.40	-91.5
USGS 58	110.22	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4662.00	2.509	6.16	USGS 58	muscovite
6050.50	3.537	7.55	USGS 57	biotite

slope: 0.87866
Intercept: -125.24
r squared 0.999
Calculated equation: d2H = 0.879 *raw -125.2

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
276	GBS biotite	3.451	5133	69.296	**-62.5**	**-64.4**	**1.86**	**1.96**	**1.940**	**-64.0**	**0.6**	29660	NWMO TCEA book 3	
277	GBS biotite	3.408	5087	69.393	**-62.5**	**-64.3**	**1.86**	**1.97**	**1.940**			29661	NWMO TCEA book 3	
278	USGS 58	2.511	4501	110.686	**-28.4**	**-28.0**	**2.24**	**2.37**	**2.454**	**-28.4**	**0.6**	29662	NWMO TCEA book 3	
279	USGS 57	3.408	5878	39.85	**-91.5**	**-90.2**	**2.15**	**2.28**	**2.135**	**-91.5**	**1.8**	29663	NWMO TCEA book 3	
280	SAz-1_Ca	1.599	4903	10.126	**?**	**-116.3**	**3.83**	**4.05**	**?**	**-118.7**	**1.6**	29664	NWMO TCEA book 3	
281	SAz-1_Ca	1.539	4529	6.454	**?**	**-119.6**	**3.67**	**3.89**	**?**			29665	NWMO TCEA book 3	
282	SAz-1_Ca	1.641	4981	5.554	**?**	**-120.4**	**3.79**	**4.01**	**?**			29666	NWMO TCEA book 3	
283	SAz-1_Ca	1.662	5211	8.186	**?**	**-118.1**	**3.91**	**4.14**	**?**			29667	NWMO TCEA book 3	
284	SAz-1_Ca	1.68	5067	6.771	**?**	**-119.3**	**3.76**	**3.98**	**?**			29668	NWMO TCEA book 3	
285	SWy-1_Ca	1.65	4629	-3.08	**?**	**-128.0**	**3.50**	**3.70**	**?**	**-129.2**	**0.8**	29669	NWMO TCEA book 3	
286	SWy-1_Ca	1.628	4353	-5.59	**?**	**-130.2**	**3.34**	**3.53**	**?**			29670	NWMO TCEA book 3	
287	SWy-1_Ca	1.639	4566	-4.219	**?**	**-129.0**	**3.48**	**3.68**	**?**			29671	NWMO TCEA book 3	
288	SWy-1_Ca	1.547	4311	-5	**?**	**-129.6**	**3.48**	**3.68**	**?**			29672	NWMO TCEA book 3	
289	SWy-1_Ca	1.561	4357	-4.793	**?**	**-129.5**	**3.48**	**3.69**	**?**			29673	NWMO TCEA book 3	
290	SapCa-1_Ca	1.768	5071	-4.264	**?**	**-129.0**	**3.58**	**3.79**	**?**	**-128.5**	**0.7**	29674	NWMO TCEA book 3	
291	SapCa-1_Ca	1.633	4775	-4.242	**?**	**-129.0**	**3.65**	**3.86**	**?**			29675	NWMO TCEA book 3	
292	SapCa-1_Ca	1.647	4926	-2.213	**?**	**-127.2**	**3.73**	**3.95**	**?**			29676	NWMO TCEA book 3	
293	SapCa-1_Ca	1.672	4840	-3.8	**?**	**-128.6**	**3.61**	**3.82**	**?**			29677	NWMO TCEA book 3	
294	SapCa-1_Ca	1.681	4664	-3.838	**?**	**-128.6**	**3.46**	**3.66**	**?**			29678	NWMO TCEA book 3	
295	STx-1_Ca	1.653	4559	39.426	**?**	**-90.6**	**3.44**	**3.64**	**?**	**-88.77**	**1.22**	29679	NWMO TCEA book 3	
296	STx-1_Ca	1.697	4638	43.036	**?**	**-87.4**	**3.41**	**3.61**	**?**			29680	NWMO TCEA book 3	
297	STx-1_Ca	1.531	4315	42.492	**?**	**-87.9**	**3.52**	**3.72**	**?**			29681	NWMO TCEA book 3	
298	STx-1_Ca	1.594	4320	41.25	**?**	**-89.0**	**3.38**	**3.58**	**?**			29682	NWMO TCEA book 3	
299	STx-1_Ca	1.6	4311	41.366	**?**	**-88.9**	**3.36**	**3.56**	**?**			29683	NWMO TCEA book 3	
300	SHCa-1_Ca	1.736	3744	7.897	**?**	**-118.3**	**2.69**	**2.85**	**?**	**-118.96**	**1.47**	29684	NWMO TCEA book 3	
301	SHCa-1_Ca	1.673	3506	4.737	**?**	**-121.1**	**2.62**	**2.77**	**?**			29685	NWMO TCEA book 3	
302	SHCa-1_Ca	1.654	3497	6.125	**?**	**-119.9**	**2.64**	**2.79**	**?**			29686	NWMO TCEA book 3	
303	SHCa-1_Ca	1.588	3365	8.155	**?**	**-118.1**	**2.64**	**2.80**	**?**			29687	NWMO TCEA book 3	
304	SHCa-1_Ca	1.686	3597	8.828	**?**	**-117.5**	**2.66**	**2.82**	**?**			29688	NWMO TCEA book 3	
305	SWa-1_Ca	1.654	4723	-25.751	**?**	**-147.9**	**3.56**	**3.77**	**?**	**-149.02**	**2.54**	29689	NWMO TCEA book 3	
306	SWa-1_Ca	1.568	4504	-23.046	**?**	**-145.5**	**3.58**	**3.79**	**?**			29690	NWMO TCEA book 3	
307	SWa-1_Ca	1.581	4456	-30.537	**?**	**-152.1**	**3.52**	**3.72**	**?**			29691	NWMO TCEA book 3	
308	SWa-1_Ca	1.587	4606	-27.025	**?**	**-149.0**	**3.62**	**3.83**	**?**			29692	NWMO TCEA book 3	
309	SWa-1_Ca	1.557	4420	-28.952	**?**	**-150.7**	**3.54**	**3.75**	**?**			29693	NWMO TCEA book 3	
310	USGS 57	3.665	6223	36.957	**-91.5**	**-92.8**	**2.12**	**2.24**	**2.135**			29694	NWMO TCEA book 3	
311	USGS 58	2.506	4823	109.748	**-28.4**	**-28.8**	**2.40**	**2.54**	**2.454**			29695	NWMO TCEA book 3	
312	GBS biotite	3.556	5147	70.468	**-62.5**	**-63.3**	**1.81**	**1.91**	**1.940**			29696		

# of samples: 30
# of standards, duplicates, failed, blanks: 7,0,0,2

[Analysis-24]

Project: Kanik NWMO_TCEA-HM-H19-24 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: October 1 , 2019 (FJL)

Date Analyzed: Sept 11, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 4 hours, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = breaking vac seal to AS= 25sec., total time = 2min. 05 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	40.64	-91.5
USGS 58	115.91	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4682.00	2.378	5.83	USGS 58	muscovite
6300.00	3.591	7.67	USGS 57	biotite

slope: 0.83836
Intercept: -125.57
r squared 0.999
Calculated equation: d2H = 0.838 *raw -125.6

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
316	GBS biotite	3.399	5062	76.716	-62.5	-61.3	1.81	1.86	1.940	-62.7	1.5	29705	NWMO TCEA book 3	
317	GBS biotite	3.533	5308	75.152	-62.5	-62.6	1.83	1.87	1.940			29706	NWMO TCEA book 3	
318	USGS 58	2.356	4711	116.732	-28.4	-27.7	2.43	2.49	2.454	-28.4	1.0	29707	NWMO TCEA book 3	
319	USGS 57	3.555	6243	43.761	-91.5	-88.9	2.14	2.19	2.135	-91.5	3.7	29708	NWMO TCEA book 3	
320	SAz-1_K	1.665	4091	14.404	?	-113.5	2.99	3.06	?	-114.0	0.8	29709	NWMO TCEA book 3	
321	SAz-1_K	1.672	4096	14.295	?	-113.6	2.98	3.05	?			29710	NWMO TCEA book 3	
322	SAz-1_K	1.683	4142	12.456	?	-115.1	3.00	3.07	?			29711	NWMO TCEA book 3	
323	SAz-1_K	1.62	4014	14.053	?	-113.8	3.02	3.09	?			29712	NWMO TCEA book 3	
325	SWy-1_K	1.827	4307	-11.357	?	-135.1	2.87	2.94	?	-134.6	0.9	29713	NWMO TCEA book 3	
326	SWy-1_K	1.6	3680	-9.11	?	-133.2	2.80	2.87	?			29714	NWMO TCEA book 3	
327	SWy-1_K	1.755	4125	-11.364	?	-135.1	2.86	2.93	?			29715	NWMO TCEA book 3	
328	SWy-1_K	1.834	4269	-11.371	?	-135.1	2.83	2.90	?			29716	NWMO TCEA book 3	
329	SapCa-1_K	1.716	3268	0.128	?	-125.5	2.32	2.37	?	-125.5	0.8	29717	NWMO TCEA book 3	
330	SapCa-1_K	1.751	3402	0.206	?	-125.4	2.36	2.42	?			29718	NWMO TCEA book 3	
331	SapCa-1_K	1.684	3233	1.23	?	-124.5	2.34	2.39	?			29719	NWMO TCEA book 3	
332	SapCa-1_K	1.693	3263	-1.081	?	-126.5	2.35	2.40	?			29720	NWMO TCEA book 3	
333	STx-1_K	1.748	4271	59.849	?	-75.4	2.97	3.04	?	-74.46	0.84	29721	NWMO TCEA book 3	
334	STx-1_K	1.62	4035	60.439	?	-74.9	3.03	3.10	?			29722	NWMO TCEA book 3	
335	STx-1_K	1.733	4302	61.598	?	-73.9	3.02	3.09	?			29723	NWMO TCEA book 3	
336	STx-1_K	1.622	3984	61.993	?	-73.6	2.99	3.06	?			29724	NWMO TCEA book 3	
337	SHCa-1_K	1.604	2076	17.312	?	-111.1	1.58	1.61	?	-110.53	0.89	29725	NWMO TCEA book 3	
338	SHCa-1_K	1.578	2103	17.245	?	-111.1	1.62	1.66	?			29726	NWMO TCEA book 3	
339	SHCa-1_K	1.689	2266	17.722	?	-110.7	1.63	1.67	?			29727	NWMO TCEA book 3	
340	SHCa-1_K	1.575	2099	19.513	?	-109.2	1.62	1.66	?			29728	NWMO TCEA book 3	
341	SWa-1_K	1.695	4035	-34.589	?	-154.6	2.90	2.97	?	-156.59	1.53	29729	NWMO TCEA book 3	
342	SWa-1_K	1.601	3917	-36.614	?	-156.3	2.98	3.05	?			29730	NWMO TCEA book 3	
343	SWa-1_K	1.724	4182	-38.576	?	-157.9	2.95	3.02	?			29731	NWMO TCEA book 3	
344	SWa-1_K	1.66	4020	-38.23	?	-157.6	2.95	3.02	?			29732	NWMO TCEA book 3	
345	USGS 57	3.627	6357	37.522	-91.5	-94.1	2.13	2.18	2.135			29733	NWMO TCEA book 3	
346	USGS 58	2.399	4653	115.083	-28.4	-29.1	2.36	2.42	2.454			29734	NWMO TCEA book 3	
312	GBS biotite	3.497	5188	73.163	-62.5	-64.2	1.81	1.85	1.940			29735		

# of samples: 24
# of standards, duplicates, failed, blanks: 7,0,0,2

[Analysis-25]

Project: Kanik NWMO_TCEA-HM-H19-25 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: October 2, 2019 (FJL)

Note: heated in 220C active vac indicates the total time samples were in active vac oven and includes the heating at 100C for 4 hours of 100C samples.

Date Analyzed: Sept 12, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 24 hours, and vac opened samples added to Al-tray and heated for 4 hours at 100C, and non-heated samples added in the analysis with both sets of heated samples, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = total loading time = 2min. 34 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	41.29	-91.5
USGS 58	114.46	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4704.00	2.459	6.03	USGS 58	muscovite
5745.00	3.442	7.35	USGS 57	biotite

slope: 0.86230
Intercept: -127.10
r squared 0.999
Calculated equation: d2H = 0.862 *raw -127.1

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
350	GBS biotite	3.474	5075	75.157	-62.5	-62.3	1.87	1.87	1.940	-63.5	1.7	29741	NWMO TCEA book 3	
351	GBS biotite	3.355	5019	74.6	-62.5	-62.8	1.91	1.92	1.940			29742	NWMO TCEA book 3	
352	USGS 58	2.434	4693	115.642	-28.4	-27.4	2.47	2.47	2.454	-28.4	1.4	29743	NWMO TCEA book 3	
353	USGS 57	3.528	5942	42.78	-91.5	-90.2	2.15	2.16	2.135	-91.5	1.8	29744	NWMO TCEA book 3	
354	SWa-1_K (220-24h)	1.634	4101	-31.695	?	-154.4	3.21	3.22	?	-153.6	1.5	29745	NWMO TCEA book 3	
355	SWa-1_K (220-24h)	1.778	4548	-30.278	?	-153.2	3.27	3.28	?			29746	NWMO TCEA book 3	
356	SWa-1_K (220-24h)	1.7	3838	-27.97	?	-151.2	2.89	2.90	?			29747	NWMO TCEA book 3	
357	SWa-1_K (220-24h)	1.653	4209	-32.125	?	-154.8	3.26	3.27	?			29748	NWMO TCEA book 3	
358	SWa-1_K (220-24h)	1.75	4384	-31.794	?	-154.5	3.20	3.21	?			29749	NWMO TCEA book 3	
359	SWa-1_Ca (220-24h)	1.615	4816	-17.11	?	-141.9	3.81	3.82	?	-141.0	2.0	29750	NWMO TCEA book 3	
360	SWa-1_Ca (220-24h)	1.723	5217	-18.907	?	-143.4	3.87	3.88	?			29751	NWMO TCEA book 3	
361	SWa-1_Ca (220-24h)	1.791	5464	-14.695	?	-139.8	3.90	3.91	?			29752	NWMO TCEA book 3	
362	SWa-1_Ca (220-24h)	1.747	5325	-13.736	?	-138.9	3.90	3.91	?			29753	NWMO TCEA book 3	
363	SWa-1_Na (220-24h)	1.63	4532	-25.191	?	-148.8	3.56	3.57	?	-148.7	0.8	29754	NWMO TCEA book 3	
364	SWa-1_Na (220-24h)	1.611	4473	-23.679	?	-147.5	3.55	3.56	?			29755	NWMO TCEA book 3	
365	SWa-1_Na (220-24h)	1.689	4700	-25.692	?	-149.3	3.56	3.57	?			29756	NWMO TCEA book 3	
366	SWa-1_Na (220-24h)	1.682	4726	-25.612	?	-149.2	3.59	3.60	?			29757	NWMO TCEA book 3	
367	SWa-1_K (100-4h)	1.677	4440	-29.862	?	-152.9	3.39	3.40	?	-154.32	1.15	29758	NWMO TCEA book 3	
368	SWa-1_K (100-4h)	1.784	4748	-33.09	?	-155.6	3.40	3.41	?			29759	NWMO TCEA book 3	
369	SWa-1_K (100-4h)	1.733	4626	-31.859	?	-154.6	3.41	3.42	?			29760	NWMO TCEA book 3	
370	SWa-1_K (100-4h)	1.761	4700	-31.43	?	-154.2	3.41	3.42	?			29761	NWMO TCEA book 3	
371	SWa-1_Ca (100-4h)	1.792	5955	-11.63	?	-137.1	4.25	4.26	?	-135.29	2.37	29762	NWMO TCEA book 3	
372	SWa-1_Ca (100-4h)	1.722	5719	-6.744	?	-132.9	4.25	4.26	?			29763	NWMO TCEA book 3	
373	SWa-1_Ca (100-4h)	1.765	5836	-12.083	?	-137.5	4.23	4.24	?			29764	NWMO TCEA book 3	
374	SWa-1_Ca (100-4h)	1.641	5350	-7.527	?	-133.6	4.17	4.18	?			29765	NWMO TCEA book 3	
375	SWa-1_Na (100-4h)	1.714	5068	-18.906	?	-143.4	3.78	3.79	?	-144.07	1.04	29766	NWMO TCEA book 3	
376	SWa-1_Na (100-4h)	1.734	5099	-19.594	?	-144.0	3.76	3.77	?			29767	NWMO TCEA book 3	
377	SWa-1_Na (100-4h)	1.648	4843	-18.818	?	-143.3	3.76	3.77	?			29768	NWMO TCEA book 3	
378	SWa-1_Na (100-4h)	1.731	4977	-21.417	?	-145.6	3.68	3.69	?			29769	NWMO TCEA book 3	
379	SWa-1_K (atmos)	1.683	4896	-19.436	?	-143.9	3.72	3.73	?	-142.28	1.75	29770	NWMO TCEA book 3	
380	SWa-1_K (atmos)	1.658	4725	-19.285	?	-143.7	3.65	3.66	?			29771	NWMO TCEA book 3	
381	SWa-1_K (atmos)	1.672	4840	-16.089	?	-141.0	3.70	3.71	?			29772	NWMO TCEA book 3	
382	SWa-1_K (atmos)	1.76	4909	-15.62	?	-140.6	3.57	3.58	?			29773	NWMO TCEA book 3	
383	SWa-1_Ca (atmos)	1.665	9617	31.72	?	-99.7	7.39	7.41	?	-93.14	4.65	29774	NWMO TCEA book 3	
384	SWa-1_Ca (atmos)	1.78	10691	43.439	?	-89.6	7.68	7.70	?			29775	NWMO TCEA book 3	
385	SWa-1_Ca (atmos)	1.707	9996	42.842	?	-90.2	7.49	7.51	?			29776	NWMO TCEA book 3	
386	SWa-1_Ca (atmos)	1.739	10117	39.544	?	-93.0	7.44	7.46	?			29777	NWMO TCEA book 3	
387	SWa-1_Na (atmos)	1.739	6600	13.223	?	-115.7	4.85	4.87	?	-120.74	5.75	29778	NWMO TCEA book 3	
388	SWa-1_Na (atmos)	1.624	6164	11.962	?	-116.8	4.86	4.87	?			29779	NWMO TCEA book 3	
389	SWa-1_Na (atmos)	1.707	6120	5.63	?	-122.2	4.59	4.60	?			29780	NWMO TCEA book 3	
390	SWa-1_Na (atmos)	1.652	5904	-1.301	?	-128.2	4.57	4.58	?			29781	NWMO TCEA book 3	
391	USGS 57	3.356	5548	39.792	-91.5	-92.8	2.11	2.12	2.135			29782	NWMO TCEA book 3	
392	USGS 58	2.483	4715	113.282	-28.4	-29.4	2.43	2.44	2.454			29783	NWMO TCEA book 3	
393	GBS biotite	3.615	5275	71.448	-62.5	-65.5	1.87	1.87	1.940			29784	NWMO TCEA book 3	

# of samples: 37
# of standards, duplicates, failed, blanks: 7,0,0,2

[Analysis-26]

Project: Kanik NWMO_TCEA-HM-H19-26 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: October 2, 2019 (FJL)

Note: heated in 220C active vac indicates the total time samples were in active vac oven and includes the heating at 100C for 4 hours of 100C samples.

Date Analyzed: Sept 13, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 24 hours, and vac opened samples added to Al-tray and heated for 4 hours at 100C, and non-heated samples added in the analysis with both sets of heated samples, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = total loading time = 2min. 10 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	38.57	-91.5
USGS 58	111.38	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
5005.50	2.518	6.18	USGS 58	muscovite
6246.50	3.581	7.65	USGS 57	biotite

slope: 0.86664
Intercept: -124.93
r squared 0.999
Calculated equation: d2H = 0.867 *raw -124.9

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
395	GBS biotite	3.675	5653	71.449	-62.5	-63.0	1.88	1.90	1.940	-63.3	0.4	29787	NWMO TCEA book 3	
396	USGS 58	2.644	5333	112.26	-28.4	-27.6	2.47	2.49	2.454	-28.4	1.1	29788	NWMO TCEA book 3	
397	USGS 57	3.659	6403	39.112	-91.5	-91.0	2.14	2.16	2.135	-91.5	0.7	29789	NWMO TCEA book 3	
398	SapCa-1_K (220-24h)	1.46	2925	0.644	?	-124.4	2.45	2.47	?	-126.4	1.3	29790	NWMO TCEA book 3	
399	SapCa-1_K (220-24h)	1.67	3219	-1.934	?	-126.6	2.36	2.38	?			29791	NWMO TCEA book 3	
400	SapCa-1_K (220-24h)	1.757	3458	-2.526	?	-127.1	2.41	2.43	?			29792	NWMO TCEA book 3	
401	SapCa-1_K (220-24h)	1.651	3186	-1.696	?	-126.4	2.36	2.38	?			29793	NWMO TCEA book 3	
402	SapCa-1_K (220-24h)	1.727	3496	-3.185	?	-127.7	2.48	2.50	?			29794	NWMO TCEA book 3	
403	SapCa-1_Ca (220-24h)	1.692	5799	5.317	?	-120.3	4.19	4.23	?	-122.7	1.6	29795	NWMO TCEA book 3	
404	SapCa-1_Ca (220-24h)	1.694	5557	1.711	?	-123.4	4.02	4.05	?			29796	NWMO TCEA book 3	
405	SapCa-1_Ca (220-24h)	1.765	5778	1.828	?	-123.3	4.01	4.04	?			29797	NWMO TCEA book 3	
406	SapCa-1_Ca (220-24h)	1.77	5983	1.503	?	-123.6	4.14	4.17	?			29798	NWMO TCEA book 3	
407	SapCa-1_Na (220-24h)	1.844	4326	-1.755	?	-126.5	2.87	2.90	?	-125.7	0.9	29799	NWMO TCEA book 3	
408	SapCa-1_Na (220-24h)	1.728	4079	0.601	?	-124.4	2.89	2.91	?			29800	NWMO TCEA book 3	
409	SapCa-1_Na (220-24h)	1.678	4001	-1.013	?	-125.8	2.92	2.94	?			29801	NWMO TCEA book 3	
410	SapCa-1_Na (220-24h)	1.611	3875	-1.358	?	-126.1	2.94	2.97	?			29802	NWMO TCEA book 3	
411	SapCa-1_K (100-4h)	1.65	3220	1.825	?	-123.3	2.39	2.41	?	-124.98	1.36	29803	NWMO TCEA book 3	
412	SapCa-1_K (100-4h)	1.711	3334	0.633	?	-124.4	2.38	2.41	?			29804	NWMO TCEA book 3	
413	SapCa-1_K (100-4h)	1.657	3225	-1.41	?	-126.2	2.38	2.40	?			29805	NWMO TCEA book 3	
414	SapCa-1_K (100-4h)	1.605	3047	-1.3	?	-126.1	2.32	2.34	?			29806	NWMO TCEA book 3	
415	SapCa-1_Ca (100-4h)	1.729	6306	6.756	?	-119.1	4.46	4.50	?	-121.09	2.28	29807	NWMO TCEA book 3	
416	SapCa-1_Ca (100-4h)	1.738	6425	5.843	?	-119.9	4.52	4.56	?			29808	NWMO TCEA book 3	
417	SapCa-1_Ca (100-4h)	1.735	6350	0.773	?	-124.3	4.48	4.52	?			29809	NWMO TCEA book 3	
418	SapCa-1_Ca (100-4h)	1.72	6204	4.337	?	-121.2	4.41	4.45	?			29810	NWMO TCEA book 3	
419	SapCa-1_Na (100-4h)	1.7	4244	5.404	?	-120.2	3.06	3.08	?	-120.25	0.43	29811	NWMO TCEA book 3	
420	SapCa-1_Na (100-4h)	1.649	4126	4.884	?	-120.7	3.06	3.09	?			29812	NWMO TCEA book 3	
421	SapCa-1_Na (100-4h)	1.774	4413	6.07	?	-119.7	3.04	3.07	?			29813	NWMO TCEA book 3	
422	SapCa-1_Na (100-4h)	1.675	3794	5.25	?	-120.4	2.77	2.80	?			29814	NWMO TCEA book 3	
423	SapCa-1_K (atmos)	1.71	3794	9.423	?	-116.8	2.72	2.74	?	-115.87	1.42	29815	NWMO TCEA book 3	
424	SapCa-1_K (atmos)	1.773	3864	9.901	?	-116.3	2.67	2.69	?			29816	NWMO TCEA book 3	
425	SapCa-1_K (atmos)	1.63	3473	9.585	?	-116.6	2.61	2.63	?			29817	NWMO TCEA book 3	
426	SapCa-1_K (atmos)	1.714	3943	12.888	?	-113.8	2.82	2.84	?			29818	NWMO TCEA book 3	
427	SapCa-1_Ca (atmos)	1.777	8007	44.418	?	-86.4	5.52	5.56	?	-90.74	3.23	29819	NWMO TCEA book 3	
428	SapCa-1_Ca (atmos)	1.767	8170	36.164	?	-93.6	5.66	5.71	?			29820	NWMO TCEA book 3	
429	SapCa-1_Ca (atmos)	1.694	7814	37.061	?	-92.8	5.65	5.69	?			29821	NWMO TCEA book 3	
430	SapCa-1_Ca (atmos)	1.709	7822	40.149	?	-90.1	5.60	5.65	?			29822	NWMO TCEA book 3	
431	SapCa-1_Na (atmos)	1.733	5623	29.158	?	-99.7	3.97	4.01	?	-103.59	3.90	29823	NWMO TCEA book 3	
432	SapCa-1_Na (atmos)	1.661	5103	23.686	?	-104.4	3.76	3.79	?			29824	NWMO TCEA book 3	
433	SapCa-1_Na (atmos)	1.632	5164	26.876	?	-101.6	3.87	3.91	?			29825	NWMO TCEA book 3	
434	SapCa-1_Na (atmos)	1.709	4872	18.769	?	-108.7	3.49	3.52	?			29826	NWMO TCEA book 3	
435	USGS 57	3.503	6090	38.036	-91.5	-92.0	2.13	2.15	2.135			29827	NWMO TCEA book 3	
436	USGS 58	2.392	4678	110.508	-28.4	-29.2	2.39	2.41	2.454			29828	NWMO TCEA book 3	
437	GBS biotite	3.596	5619	70.784	-62.5	-63.6	1.91	1.93	1.940			29829	NWMO TCEA book 3	

# of samples: 37 (development project)
# of standards, duplicates, failed, blanks: 6,0,0,0

[Analysis-27]

Project: Kanik NWMO_TCEA-HM-H19-27 (hydrous minerals)A1:O58

Isotope(s): Hydrogen

Preparation: Nadine Kanik Note: heated in 220C active vac indicates the total time samples were in active vac oven and includes the heating at 100C for 4 hours of 100C samples.

Analyst: Nadine Kanik

Data Treatment and QA/QC: F. Longstaff

Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS

Date Approved by Director: October 2, 2019 (FJL)

Date Analyzed: Sept 14, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 24 hours, and vac opened samples added to Al-tray and heated for 4 hours at 100C, and non-heated samples added in the analysis with both sets of heated samples, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = total loading time = 2min. 07 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	37.45	-91.5
USGS 58	113.97	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
5035.00	2.499	6.13	USGS 58	muscovite
6146.00	3.503	7.48	USGS 57	biotite

slope:		0.82463		
Intercept:		-122.38		
r squared		0.999		
Calculated equation:	d2H =	0.825	*raw	-122.4

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
439	GBS biotite	3.67	5556	73.508	-62.5	-61.8	1.84	1.84	1.940	-64.0	3.2	29831	NWMO TCEA book 3	
440	USGS 58	2.515	5086	115.471	-28.4	-27.2	2.46	2.46	2.454	-28.4	1.7	29832	NWMO TCEA book 3	
441	USGS 57	3.531	6143	37.296	-91.5	-91.6	2.12	2.12	2.135	-91.5	0.2	29833	NWMO TCEA book 3	
442	SAz-1_K (220-24h)	1.55	4229	3.146	?	-119.8	3.32	3.32	?	-117.9	1.5	29834	NWMO TCEA book 3	
443	SAz-1_K (220-24h)	1.561	4263	7.924	?	-115.8	3.32	3.33	?			29835	NWMO TCEA book 3	
444	SAz-1_K (220-24h)	1.61	4422	4.527	?	-118.7	3.34	3.34	?			29836	NWMO TCEA book 3	
445	SAz-1_K (220-24h)	1.662	4562	6.285	?	-117.2	3.34	3.34	?			29837	NWMO TCEA book 3	
446	SAz-1_K (220-24h)	1.607	4383	5.577	?	-117.8	3.32	3.32	?			29838	NWMO TCEA book 3	
447	SAz-1_Ca (220-24h)	1.566	5603	6.152	?	-117.3	4.35	4.36	?	-118.5	1.0	29839	NWMO TCEA book 3	
448	SAz-1_Ca (220-24h)	1.617	5364	3.59	?	-119.4	4.04	4.04	?			29840	NWMO TCEA book 3	
449	SAz-1_Ca (220-24h)	1.611	5850	5.27	?	-118.0	4.42	4.42	?			29841	NWMO TCEA book 3	
450	SAz-1_Ca (220-24h)	1.683	5917	3.87	?	-119.2	4.28	4.28	?			29842	NWMO TCEA book 3	
451	SAz-1_Na (220-24h)	1.616	4812	-0.269	?	-122.6	3.62	3.63	?	-121.1	1.1	29843	NWMO TCEA book 3	
452	SAz-1_Na (220-24h)	1.607	4884	1.739	?	-121.0	3.70	3.70	?			29844	NWMO TCEA book 3	
453	SAz-1_Na (220-24h)	1.661	5034	1.788	?	-120.9	3.69	3.69	?			29845	NWMO TCEA book 3	
454	SAz-1_Na (220-24h)	1.528	4594	2.9	?	-120.0	3.66	3.66	?			29846	NWMO TCEA book 3	
455	SAz-1_K (100-4h)	1.521	4292	12.755	?	-111.9	3.43	3.44	?	-114.34	1.71	29847	NWMO TCEA book 3	
456	SAz-1_K (100-4h)	1.522	4182	8.874	?	-115.1	3.34	3.35	?			29848	NWMO TCEA book 3	
457	SAz-1_K (100-4h)	1.585	4415	8.046	?	-115.7	3.39	3.39	?			29849	NWMO TCEA book 3	
458	SAz-1_K (100-4h)	1.528	4269	9.337	?	-114.7	3.40	3.40	?			29850	NWMO TCEA book 3	
459	SAz-1_Ca (100-4h)	1.625	6259	4.213	?	-118.9	4.69	4.69	?	-116.59	1.75	29851	NWMO TCEA book 3	
460	SAz-1_Ca (100-4h)	1.527	6177	9.22	?	-114.8	4.92	4.93	?			29852	NWMO TCEA book 3	
461	SAz-1_Ca (100-4h)	1.51	6464	6.835	?	-116.7	5.21	5.21	?			29853	NWMO TCEA book 3	
462	SAz-1_Ca (100-4h)	1.597	6636	7.861	?	-115.9	5.06	5.06	?			29854	NWMO TCEA book 3	
463	SAz-1_Na (100-4h)	1.568	5105	13.164	?	-111.5	3.96	3.96	?	-112.27	0.70	29855	NWMO TCEA book 3	
464	SAz-1_Na (100-4h)	1.446	4656	12.03	?	-112.5	3.92	3.92	?			29856	NWMO TCEA book 3	
465	SAz-1_Na (100-4h)	1.592	5189	11.192	?	-113.2	3.97	3.97	?			29857	NWMO TCEA book 3	
466	SAz-1_Na (100-4h)	1.661	5367	12.669	?	-111.9	3.93	3.93	?			29858	NWMO TCEA book 3	
467	SAz-1_K (atmos)	1.676	5366	27.468	?	-99.7	3.90	3.90	?	-99.25	0.99	29859	NWMO TCEA book 3	
468	SAz-1_K (atmos)	1.522	4817	29.633	?	-97.9	3.85	3.85	?			29860	NWMO TCEA book 3	
469	SAz-1_K (atmos)	1.628	5147	26.846	?	-100.2	3.85	3.85	?			29861	NWMO TCEA book 3	
470	SAz-1_K (atmos)	1.686	5382	28.246	?	-99.1	3.88	3.89	?			29862	NWMO TCEA book 3	
471	SAz-1_Ca (atmos)	1.583	11126	56.336	?	-75.9	8.55	8.56	?	-76.82	1.69	29863	NWMO TCEA book 3	
472	SAz-1_Ca (atmos)	1.587	11162	56.864	?	-75.5	8.56	8.56	?			29864	NWMO TCEA book 3	
473	SAz-1_Ca (atmos)	1.66	11439	52.284	?	-79.3	8.39	8.39	?			29865	NWMO TCEA book 3	
474	SAz-1_Ca (atmos)	1.543	10761	55.533	?	-76.6	8.49	8.49	?			29866	NWMO TCEA book 3	
475	SAz-1_Na (atmos)	1.507	7811	55.911	?	-76.3	6.31	6.31	?	-77.17	1.57	29867	NWMO TCEA book 3	
476	SAz-1_Na (atmos)	1.556	8052	56.625	?	-75.7	6.30	6.30	?			29868	NWMO TCEA book 3	
477	SAz-1_Na (atmos)	1.611	8059	54.488	?	-77.5	6.09	6.09	?			29869	NWMO TCEA book 3	
478	SAz-1_Na (atmos)	1.576	7886	52.314	?	-79.2	6.09	6.09	?			29870	NWMO TCEA book 3	
479	USGS 57	3.475	6149	37.609	-91.5	-91.4	2.15	2.15	2.135			29871	NWMO TCEA book 3	
480	USGS 58	2.482	4984	112.473	-28.4	-29.6	2.44	2.45	2.454			29872	NWMO TCEA book 3	
481	GBS biotite	3.529	5368	67.987	-62.5	-66.3	1.85	1.85	1.940			29873	NWMO TCEA book 3	

# of samples: 37 (development project)

# of standards, duplicates, failed, blanks: 6,0,0,0

[Analysis-28]

Project: Kanik NWMO_TCEA-HM-H19-28 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: , 2019 (FJL)

Date Analyzed: Sept 15, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 24 hours, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = total time = 2min. 26 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	38.38	-91.5
USGS 58	114.40	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4736.00	2.412	5.92	USGS 58	muscovite
5741.50	3.343	7.14	USGS 57	biotite

slope: 0.83001
Intercept: -123.35
r squared 0.999
Calculated equation: d2H = 0.830 *raw -123.4

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
483	GBS biotite	3.689	5415	69.57	**-62.5**	**-65.6**	**1.82**	**1.83**	**1.940**	**-66.0**	**0.6**	29878	NWMO TCEA book 3	
484	USGS 58	2.409	4828	114.882	**-28.4**	**-28.0**	**2.49**	**2.50**	**2.454**	**-28.4**	**0.6**	29879	NWMO TCEA book 3	
485	USGS 57	3.282	5633	39.103	**-91.5**	**-90.9**	**2.13**	**2.14**	**2.135**	**-91.5**	**0.9**	29880	NWMO TCEA book 3	
486	SAz-1_K	1.65	4211	5.845	**?**	**-118.5**	**3.17**	**3.19**	**?**	**-118.5**	**0.4**	29881	NWMO TCEA book 3	
487	SAz-1_K	1.698	4387	5.363	**?**	**-118.9**	**3.21**	**3.23**	**?**			29882	NWMO TCEA book 3	
488	SAz-1_K	1.59	4032	5.596	**?**	**-118.7**	**3.15**	**3.17**	**?**			29883	NWMO TCEA book 3	
489	SAz-1_K	1.732	4455	6.44	**?**	**-118.0**	**3.20**	**3.21**	**?**			29884	NWMO TCEA book 3	
490	SWy-1_K	1.728	3315	-14.884	**?**	**-135.7**	**2.38**	**2.40**	**?**	**-136.7**	**1.1**	29885	NWMO TCEA book 3	
491	SWy-1_K	1.704	3803	-15.284	**?**	**-136.0**	**2.77**	**2.79**	**?**			29886	NWMO TCEA book 3	
492	SWy-1_K	1.671	3912	-16.249	**?**	**-136.8**	**2.91**	**2.93**	**?**			29887	NWMO TCEA book 3	
493	SWy-1_K	1.702	3990	-17.965	**?**	**-138.3**	**2.91**	**2.93**	**?**			29888	NWMO TCEA book 3	
494	SapCa-1_K	1.713	3204	-3.057	**?**	**-125.9**	**2.32**	**2.34**	**?**	**-125.8**	**0.2**	29889	NWMO TCEA book 3	
495	SapCa-1_K	1.71	3251	-2.719	**?**	**-125.6**	**2.36**	**2.38**	**?**			29890	NWMO TCEA book 3	
496	SapCa-1_K	1.716	3158	-2.879	**?**	**-125.7**	**2.29**	**2.30**	**?**			29891	NWMO TCEA book 3	
497	SapCa-1_K	1.737	3214	-3.24	**?**	**-126.0**	**2.30**	**2.31**	**?**			29892	NWMO TCEA book 3	
498	STx-1_K	1.602	3997	52.944	**?**	**-79.4**	**3.10**	**3.12**	**?**	**-78.99**	**0.75**	29893	NWMO TCEA book 3	
499	STx-1_K	1.579	4083	54.544	**?**	**-78.1**	**3.21**	**3.23**	**?**			29894	NWMO TCEA book 3	
500	STx-1_K	1.569	3857	52.513	**?**	**-79.8**	**3.06**	**3.07**	**?**			29895	NWMO TCEA book 3	
501	STx-1_K	1.605	4005	53.803	**?**	**-78.7**	**3.10**	**3.12**	**?**			29896	NWMO TCEA book 3	
502	SHCa-1_K	1.647	2290	11.913	**?**	**-113.5**	**1.73**	**1.74**	**?**	**-113.64**	**1.09**	29897	NWMO TCEA book 3	
503	SHCa-1_K	1.67	2313	9.985	**?**	**-115.1**	**1.72**	**1.73**	**?**			29898	NWMO TCEA book 3	
504	SHCa-1_K	1.652	2293	11.712	**?**	**-113.6**	**1.73**	**1.73**	**?**			29899	NWMO TCEA book 3	
505	SHCa-1_K	1.585	2212	13.179	**?**	**-112.4**	**1.73**	**1.74**	**?**			29900	NWMO TCEA book 3	
506	SWa-1_K	1.635	4098	-36.604	**?**	**-153.7**	**3.12**	**3.13**	**?**	**-154.26**	**0.76**	29901	NWMO TCEA book 3	
507	SWa-1_K	1.645	4105	-37.52	**?**	**-154.5**	**3.10**	**3.12**	**?**			29902	NWMO TCEA book 3	
508	SWa-1_K	1.647	4108	-36.423	**?**	**-153.6**	**3.10**	**3.12**	**?**			29903	NWMO TCEA book 3	
509	SWa-1_K	1.748	4411	-38.402	**?**	**-155.2**	**3.14**	**3.15**	**?**			29904	NWMO TCEA book 3	
510	SCa-3_Cs	1.607	4308	33.338	**?**	**-95.7**	**3.33**	**3.35**	**?**	**-95.83**	**0.57**	29905	NWMO TCEA book 3	
511	SCa-3_Cs	1.73	4648	32.013	**?**	**-96.8**	**3.34**	**3.36**	**?**			29906	NWMO TCEA book 3	
512	SCa-3_Cs	1.607	4323	32.818	**?**	**-96.1**	**3.34**	**3.36**	**?**			29907	NWMO TCEA book 3	
513	SCa-3_Cs	1.637	4380	33.438	**?**	**-95.6**	**3.33**	**3.34**	**?**			29908	NWMO TCEA book 3	
514	SCa-3_Cs	1.696	4576	34.078	**?**	**-95.1**	**3.35**	**3.37**	**?**			29909	NWMO TCEA book 3	
515	SCa-3_Cs	1.627	4388	33.274	**?**	**-95.7**	**3.35**	**3.37**	**?**			29910	NWMO TCEA book 3	
516	GBS biotite	3.522	5025	68.511	**-62.5**	**-66.5**	**1.77**	**1.78**	**1.940**			29911	NWMO TCEA book 3	
517	USGS 57	3.403	5850	37.65	**-91.5**	**-92.1**	**2.14**	**2.15**	**2.135**			29912	NWMO TCEA book 3	
518	USGS 58	2.414	4736	113.917	**-28.4**	**-28.8**	**2.44**	**2.45**	**2.454**			29913	NWMO TCEA book 3	

# of samples: 36 (development project)
# of standards, duplicates, failed, blanks: 0,0,0,0

[Analysis-29]

Project: Kanik NWMO_TCEA-HM-H19-29 (hydrous minerals)
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Note: heated in 220C active vac indicates the total time samples were in active vac oven and includes the heating at 100C for 4 hours of 100C samples.
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: October 2, 2019 (FJL)

Date Analyzed: Sept 16, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 24 hours, and vac opened samples added to Al-tray and heated for 4 hours at 100C, and non-heated samples added in the analysis with both sets of heated samples, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = total loading time = 2min. 03 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	38.83	-91.5
USGS 58	111.73	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
5242.00	2.476	6.08	USGS 58	muscovite
6511.00	3.519	7.51	USGS 57	biotite

slope: 0.86563
Intercept: -125.11
r squared 0.999
Calculated equation: d2H = 0.866 *raw -125.1

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
520	GBS biotite	3.534	5750	70.043	-62.5	-64.5	1.88	1.89	1.940	-64.8	0.4	29915	NWMO TCEA book 3	
521	USGS 58	2.512	5382	111.701	-28.4	-28.4	2.47	2.48	2.454	-28.4	0.0	29916	NWMO TCEA book 3	
522	USGS 57	3.539	6604	40.322	-91.5	-90.2	2.15	2.16	2.135	-91.5	1.8	29917	NWMO TCEA book 3	
523	SHCa-1_K (220-24h)	1.697	2941	15.688	?	-111.5	2.00	2.01	?	-112.3	1.5	29918	NWMO TCEA book 3	
524	SHCa-1_K (220-24h)	1.692	2890	16.638	?	-110.7	1.97	1.98	?			29919	NWMO TCEA book 3	
525	SHCa-1_K (220-24h)	1.683	3201	15.782	?	-111.5	2.19	2.20	?			29920	NWMO TCEA book 3	
526	SHCa-1_K (220-24h)	1.698	2897	12.876	?	-114.0	1.97	1.98	?			29921	NWMO TCEA book 3	
527	SHCa-1_K (220-24h)	1.642	2813	13.241	?	-113.7	1.98	1.99	?			29922	NWMO TCEA book 3	
528	SHCa-1_Ca (220-24h)	1.801	5018	17.019	?	-110.4	3.21	3.23	?	-108.3	1.5	29923	NWMO TCEA book 3	
529	SHCa-1_Ca (220-24h)	1.612	4366	19.266	?	-108.4	3.12	3.14	?			29924	NWMO TCEA book 3	
530	SHCa-1_Ca (220-24h)	1.597	4294	20.552	?	-107.3	3.10	3.12	?			29925	NWMO TCEA book 3	
531	SHCa-1_Ca (220-24h)	1.698	4564	20.78	?	-107.1	3.10	3.12	?			29926	NWMO TCEA book 3	
532	SHCa-1_Na (220-24h)	1.709	3505	17.818	?	-109.7	2.37	2.38	?	-108.4	1.3	29927	NWMO TCEA book 3	
533	SHCa-1_Na (220-24h)	1.712	3581	18.71	?	-108.9	2.41	2.42	?			29928	NWMO TCEA book 3	
534	SHCa-1_Na (220-24h)	1.687	3531	21.37	?	-106.6	2.41	2.43	?			29929	NWMO TCEA book 3	
535	SHCa-1_Na (220-24h)	1.704	3524	19.281	?	-108.4	2.39	2.40	?			29930	NWMO TCEA book 3	
536	SHCa-1_K (100-4h)	1.763	3056	17.662	?	-109.8	2.00	2.01	?	-110.60	1.12	29931	NWMO TCEA book 3	
537	SHCa-1_K (100-4h)	1.711	3028	17.767	?	-109.7	2.04	2.05	?			29932	NWMO TCEA book 3	
538	SHCa-1_K (100-4h)	1.594	2755	16.661	?	-110.7	1.99	2.00	?			29933	NWMO TCEA book 3	
539	SHCa-1_K (100-4h)	1.693	2952	14.987	?	-112.1	2.01	2.02	?			29934	NWMO TCEA book 3	
540	SHCa-1_Ca (100-4h)	1.75	5751	20.852	?	-107.1	3.79	3.81	?	-104.65	1.91	29935	NWMO TCEA book 3	
541	SHCa-1_Ca (100-4h)	1.686	5641	25.78	?	-102.8	3.86	3.88	?			29936	NWMO TCEA book 3	
542	SHCa-1_Ca (100-4h)	1.677	5599	22.954	?	-105.2	3.85	3.87	?			29937	NWMO TCEA book 3	
543	SHCa-1_Ca (100-4h)	1.711	5613	24.962	?	-103.5	3.78	3.80	?			29938	NWMO TCEA book 3	
544	SHCa-1_Na (100-4h)	1.67	3636	23.933	?	-104.4	2.51	2.52	?	-104.15	0.68	29939	NWMO TCEA book 3	
545	SHCa-1_Na (100-4h)	1.654	3515	23.381	?	-104.9	2.45	2.46	?			29940	NWMO TCEA book 3	
546	SHCa-1_Na (100-4h)	1.619	3535	24.325	?	-104.1	2.52	2.53	?			29941	NWMO TCEA book 3	
547	SHCa-1_Na (100-4h)	1.775	3849	25.245	?	-103.3	2.50	2.51	?			29942	NWMO TCEA book 3	
548	SHCa-1_K (atmos)	1.701	3150	23.129	?	-105.1	2.14	2.15	?	-105.90	1.48	29943	NWMO TCEA book 3	
549	SHCa-1_K (atmos)	1.639	3261	19.666	?	-108.1	2.30	2.31	?			29944	NWMO TCEA book 3	
550	SHCa-1_K (atmos)	1.745	3498	22.67	?	-105.5	2.31	2.32	?			29945	NWMO TCEA book 3	
551	SHCa-1_K (atmos)	1.603	3191	23.332	?	-104.9	2.30	2.31	?			29946	NWMO TCEA book 3	
552	SHCa-1_Ca (atmos)	1.762	9055	58.663	?	-74.3	5.93	5.96	?	-72.79	1.19	29947	NWMO TCEA book 3	
553	SHCa-1_Ca (atmos)	1.775	9065	60.416	?	-72.8	5.89	5.92	?			29948	NWMO TCEA book 3	
554	SHCa-1_Ca (atmos)	1.761	8883	60.687	?	-72.6	5.82	5.85	?			29949	NWMO TCEA book 3	
555	SHCa-1_Ca (atmos)	1.688	8633	62.011	?	-71.4	5.90	5.93	?			29950	NWMO TCEA book 3	
556	SHCa-1_Na (atmos)	1.694	4784	55.368	?	-77.2	3.26	3.27	?	-85.70	9.30	29951	NWMO TCEA book 3	
557	SHCa-1_Na (atmos)	1.734	5082	54.12	?	-78.3	3.38	3.40	?			29952	NWMO TCEA book 3	
558	SHCa-1_Na (atmos)	1.706	4628	34.624	?	-95.1	3.13	3.14	?			29953	NWMO TCEA book 3	
559	SHCa-1_Na (atmos)	1.678	4481	38.014	?	-92.2	3.08	3.10	?			29954	NWMO TCEA book 3	
560	USGS 57	3.498	6418	37.343	-91.5	-92.8	2.12	2.13	2.135			29955	NWMO TCEA book 3	
561	USGS 58	2.44	5102	111.754	-28.4	-28.4	2.41	2.42	2.454			29956	NWMO TCEA book 3	
562	GBS biotite	3.496	5239	69.318	-62.5	-65.1	1.73	1.74	1.940			29957	NWMO TCEA book 3	

# of samples: 37
# of standards, duplicates, failed, blanks: 6,0,0,0

[Analysis-30]

Project: Kanik NWMO_TCEA-HM-H19-30 (hydrous minerals)A1:O69

Isotope(s): Hydrogen

Preparation: Nadine Kanik

Note: heated in 220C active vac indicates the total time samples were in active vac oven and includes the heating at 100C for 4 hours of 100C samples.

Analyst: Nadine Kanik

Data Treatment and QA/QC: F. Longstaff

Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS

Date Approved by Director: October 2, 2019 (FJL)

Date Analyzed: Sept 17, 2019

Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 24 hours, and vac opened samples added to Al-tray and heated for 4 hours at 100C, and non-heated samples added in the analysis with both sets of heated samples, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = total loading time = 1min. 59 sec.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	38.19	-91.5
USGS 58	111.13	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
4997.00	2.377	5.83	USGS 58	muscovite
6193.00	3.330	7.11	USGS 57	biotite

slope:	0.86504
Intercept:	-124.53
r squared	0.999

Calculated equation: d2H = 0.865 *raw -124.5

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
564	GBS biotite	3.562	5688	69.561	-62.5	-64.4	1.83	1.86	1.940	-64.4	0.0	29961	NWMO TCEA book 3	
565	USGS 58	2.335	4954	111.887	-28.4	-27.7	2.44	2.48	2.454	-28.4	0.9	29962	NWMO TCEA book 3	
566	USGS 57	3.417	6424	37.981	-91.5	-91.7	2.16	2.19	2.135	-91.5	0.3	29963	NWMO TCEA book 3	
567	STx-1_K (220-24h)	1.547	4340	54.745	?	-77.2	3.22	3.27	?	-78.0	0.9	29964	NWMO TCEA book 3	
568	STx-1_K (220-24h)	1.515	4321	54.938	?	-77.0	3.27	3.33	?			29965	NWMO TCEA book 3	
569	STx-1_K (220-24h)	1.634	4638	54.036	?	-77.8	3.26	3.31	?			29966	NWMO TCEA book 3	
570	STx-1_K (220-24h)	1.699	4910	52.538	?	-79.1	3.32	3.37	?			29967	NWMO TCEA book 3	
571	STx-1_K (220-24h)	1.515	4158	52.945	?	-78.7	3.15	3.20	?			29968	NWMO TCEA book 3	
572	STx-1_Ca (220-24h)	1.536	4918	40.376	?	-89.6	3.68	3.74	?	-89.9	0.5	29969	NWMO TCEA book 3	
573	STx-1_Ca (220-24h)	1.576	5014	40.788	?	-89.3	3.65	3.71	?			29970	NWMO TCEA book 3	
574	STx-1_Ca (220-24h)	1.569	5026	39.371	?	-90.5	3.68	3.74	?			29971	NWMO TCEA book 3	
575	STx-1_Ca (220-24h)	1.583	5016	39.815	?	-90.1	3.64	3.70	?			29972	NWMO TCEA book 3	
576	STx-1_Na (220-24h)	1.501	4582	41.734	?	-88.4	3.50	3.56	?	-88.2	0.9	29973	NWMO TCEA book 3	
577	STx-1_Na (220-24h)	1.585	4908	43.582	?	-86.8	3.55	3.61	?			29974	NWMO TCEA book 3	
578	STx-1_Na (220-24h)	1.58	4859	41.422	?	-88.7	3.53	3.59	?			29975	NWMO TCEA book 3	
579	STx-1_Na (220-24h)	1.568	4847	41.287	?	-88.8	3.55	3.61	?			29976	NWMO TCEA book 3	
580	STx-1_K (100-4h)	1.618	4721	56.576	?	-75.6	3.35	3.41	?	-74.36	1.07	29977	NWMO TCEA book 3	
581	STx-1_K (100-4h)	1.614	4607	57.495	?	-74.8	3.28	3.33	?			29978	NWMO TCEA book 3	
582	STx-1_K (100-4h)	1.67	4761	59.42	?	-73.1	3.27	3.33	?			29979	NWMO TCEA book 3	
583	STx-1_K (100-4h)	1.549	4530	58.504	?	-73.9	3.36	3.41	?			29980	NWMO TCEA book 3	
584	STx-1_Ca (100-4h)	1.676	6355	41.413	?	-88.7	4.35	4.43	?	-87.75	2.01	29981	NWMO TCEA book 3	
585	STx-1_Ca (100-4h)	1.525	5977	44.722	?	-85.8	4.50	4.58	?			29982	NWMO TCEA book 3	
586	STx-1_Ca (100-4h)	1.554	5673	39.783	?	-90.1	4.19	4.26	?			29983	NWMO TCEA book 3	
587	STx-1_Ca (100-4h)	1.58	6039	44.157	?	-86.3	4.39	4.46	?			29984	NWMO TCEA book 3	
588	STx-1_Na (100-4h)	1.593	5022	49.913	?	-81.4	3.62	3.68	?	-81.14	0.62	29985	NWMO TCEA book 3	
589	STx-1_Na (100-4h)	1.536	4851	50.829	?	-80.6	3.63	3.69	?			29986	NWMO TCEA book 3	
590	STx-1_Na (100-4h)	1.583	4959	49.28	?	-81.9	3.60	3.66	?			29987	NWMO TCEA book 3	
591	STx-1_Na (100-4h)	1.571	4912	50.646	?	-80.7	3.59	3.65	?			29988	NWMO TCEA book 3	
592	STx-1_K (atmos)	1.624	5073	63.446	?	-69.7	3.59	3.65	?	-70.33	0.75	29989	NWMO TCEA book 3	
593	STx-1_K (atmos)	1.503	4803	62.755	?	-70.2	3.67	3.73	?			29990	NWMO TCEA book 3	
594	STx-1_K (atmos)	1.617	5276	63.024	?	-70.0	3.75	3.81	?			29991	NWMO TCEA book 3	
595	STx-1_K (atmos)	1.581	5002	61.429	?	-71.4	3.63	3.69	?			29992	NWMO TCEA book 3	
596	STx-1_Ca (atmos)	1.587	8542	64.464	?	-68.8	6.18	6.28	?	-64.52	2.91	29993	NWMO TCEA book 3	
597	STx-1_Ca (atmos)	1.656	8001	70.567	?	-63.5	5.55	5.64	?			29994	NWMO TCEA book 3	
598	STx-1_Ca (atmos)	1.521	7496	70.402	?	-63.6	5.66	5.75	?			29995	NWMO TCEA book 3	
599	STx-1_Ca (atmos)	1.591	8203	72.071	?	-62.2	5.92	6.02	?			29996	NWMO TCEA book 3	
600	STx-1_Na (atmos)	1.509	5569	59.762	?	-72.8	4.24	4.31	?	-68.80	2.88	29997	NWMO TCEA book 3	
601	STx-1_Na (atmos)	1.535	5542	65.371	?	-68.0	4.14	4.21	?			29998	NWMO TCEA book 3	
602	STx-1_Na (atmos)	1.525	5726	64.925	?	-68.4	4.31	4.38	?			29999	NWMO TCEA book 3	
603	STx-1_Na (atmos)	1.542	5764	67.64	?	-66.0	4.29	4.36	?			30000	NWMO TCEA book 3	
604	USGS 57	3.242	5962	38.395	-91.5	-91.3	2.11	2.15	2.135			30001	NWMO TCEA book 3	
605	USGS 58	2.419	5040	110.379	-28.4	-29.1	2.39	2.43	2.454			30002	NWMO TCEA book 3	
606	GBS biotite	3.588	5448	69.533	-62.5	-64.4	1.74	1.77	1.940			30003	NWMO TCEA book 3	

# of samples: 37

# of standards, duplicates, failed, blanks: 6,0,0,0

[Analysis-31]

Project: Kanik NWMO_TCEA-HM-H19-31 (hydrous minerals)A1:O44
Isotope(s): Hydrogen
Preparation: Nadine Kanik
Analyst: Nadine Kanik
Data Treatment and QA/QC: F. Longstaff
Instrument(s): TCEA with glassy carbon reactor and Delta XL Plus (Light) IRMS
Date Approved by Director: October 2, 2019 (FJL)

Date Analyzed: Sept 17, 2019
Conditions: He flow rate= 90ml/min, GC operating temp.= 120C, Reactor operating temp.= 1450C, Pre-treatment= heated in 220C active vacuum oven for 4 hours, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed. Loading time with Al-tray and operator = total time = 2min. 05 sec.
Calibrated reference gas: -124.69

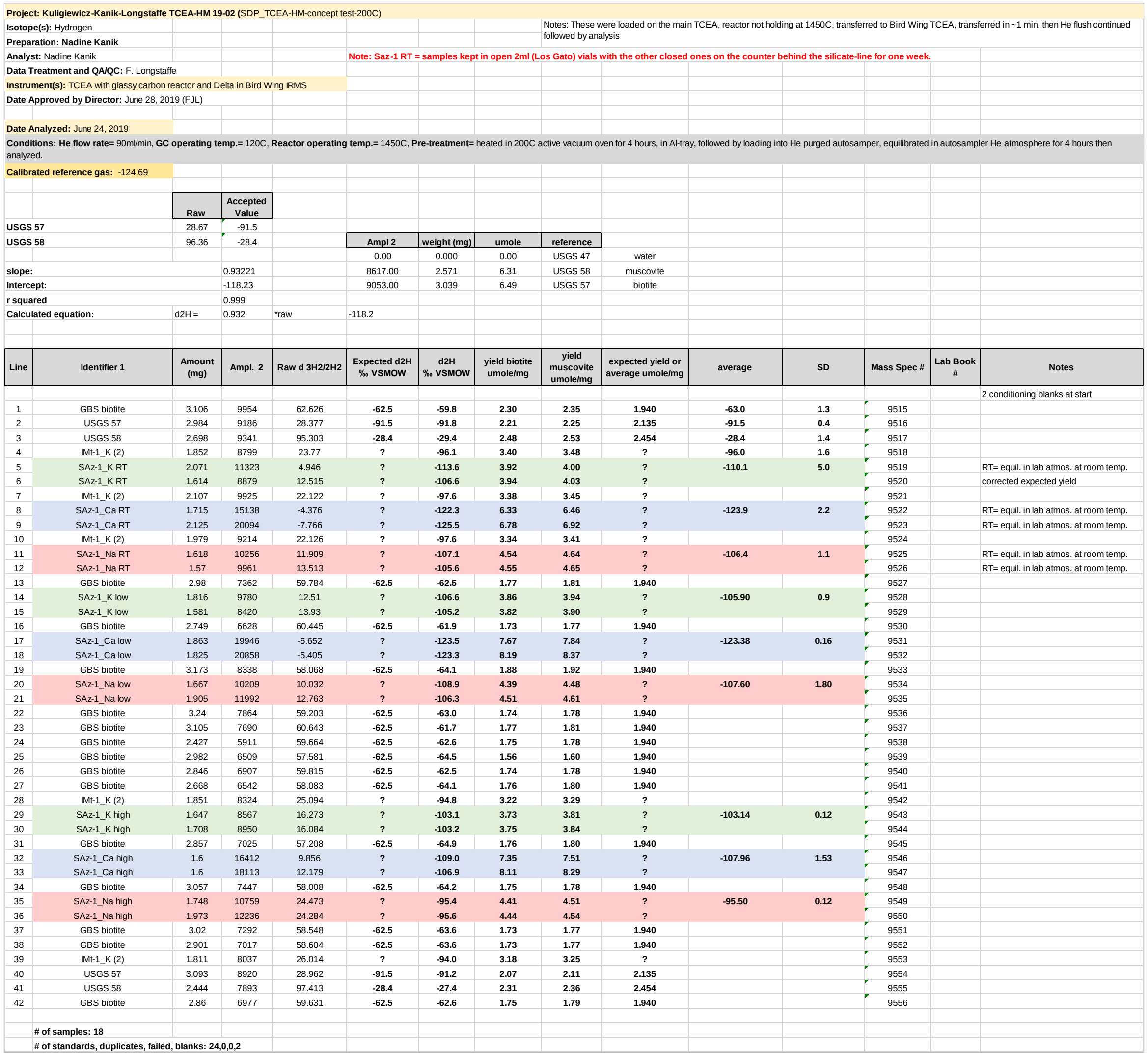
		Raw	Accepted Value	
USGS 57		38.05	-91.5	
USGS 58		111.16	-28.4	
slope:			0.86310	
Intercept:			-124.34	
r squared			0.999	
Calculated equation:		d2H =	0.863	*raw -124.3

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
5201.00	2.552	6.26	USGS 58	muscovite
6352.00	3.513	7.50	USGS 57	biotite

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
608	GBS biotite	3.547	5658	69.579	-62.5	-64.3	1.88	1.92	1.940	-64.7	0.5	30005	NWMO TCEA book 3	
609	GBS biotite	3.567	5613	69.259	-62.5	-64.6	1.86	1.89	1.940			30006		
610	USGS 58	2.519	5134	111.834	-28.4	-27.8	2.41	2.45	2.454	-28.4	0.8	30007	NWMO TCEA book 3	
611	USGS 57	3.586	6557	38.376	-91.5	-91.2	2.16	2.20	2.135	-91.5	0.4	30008	NWMO TCEA book 3	
612	SAz-1_Na	1.767	5188	3.501	?	-121.3	3.47	3.53	?	-121.0	0.6	30009	NWMO TCEA book 3	
613	SAz-1_Na	1.568	4570	4.698	?	-120.3	3.44	3.51	?			30010	NWMO TCEA book 3	
614	SAz-1_Na	1.628	4742	4.163	?	-120.7	3.44	3.51	?			30011	NWMO TCEA book 3	
615	SAz-1_Na	1.64	4722	3.086	?	-121.7	3.40	3.47	?			30012	NWMO TCEA book 3	
616	SWy-1_Na	1.715	4689	-4.139	?	-127.9	3.23	3.29	?	-129.5	1.2	30013	NWMO TCEA book 3	
617	SWy-1_Na	1.65	4491	-5.771	?	-129.3	3.21	3.28	?			30014	NWMO TCEA book 3	
618	SWy-1_Na	1.672	4531	-6.883	?	-130.3	3.20	3.26	?			30015	NWMO TCEA book 3	
619	SWy-1_Na	1.657	4461	-7.091	?	-130.5	3.18	3.24	?			30016	NWMO TCEA book 3	
620	SapCa-1_Na	1.702	3523	-0.778	?	-125.0	2.44	2.49	?	-126.4	1.7	30017	NWMO TCEA book 3	
621	SapCa-1_Na	1.686	3661	-0.686	?	-124.9	2.56	2.61	?			30018	NWMO TCEA book 3	
622	SapCa-1_Na	1.77	3774	-3.983	?	-127.8	2.52	2.57	?			30019	NWMO TCEA book 3	
623	SapCa-1_Na	1.785	3984	-4.156	?	-127.9	2.64	2.69	?			30020	NWMO TCEA book 3	
624	STx-1_Na	1.613	4643	43.399	?	-86.9	3.40	3.47	?	-87.47	0.57	30021	NWMO TCEA book 3	
625	STx-1_Na	1.558	4416	42.693	?	-87.5	3.35	3.41	?			30022	NWMO TCEA book 3	
626	STx-1_Na	1.697	4902	42.082	?	-88.0	3.41	3.48	?			30023	NWMO TCEA book 3	
627	STx-1_Na	1.65	4734	143.288	?	-0.7	3.39	3.45	?			30024	NWMO TCEA book 3	anomalous value, reason unclear excluded from calcs
628	SHCa-1_Na	1.733	2942	14.185	?	-112.1	2.00	2.04	?	-111.18	0.80	30025	NWMO TCEA book 3	
629	SHCa-1_Na	1.683	2952	165.961	?	18.9	2.07	2.11	?			30026	NWMO TCEA book 3	anomalous value, reason unclear excluded from calcs
630	SHCa-1_Na	1.644	2836	15.689	?	-110.8	2.04	2.08	?			30027	NWMO TCEA book 3	
631	SHCa-1_Na	1.661	2803	15.869	?	-110.6	1.99	2.03	?			30028	NWMO TCEA book 3	
632	SWa-1_Na	1.581	4450	-30.515	?	-150.7	3.32	3.39	?	-152.31	1.17	30029	NWMO TCEA book 3	
633	SWa-1_Na	1.553	4255	-33.096	?	-152.9	3.23	3.30	?			30030	NWMO TCEA book 3	
634	SWa-1_Na	1.609	4502	-33.619	?	-153.4	3.30	3.37	?			30031	NWMO TCEA book 3	
635	SWa-1_Na	1.675	4747	-32.374	?	-152.3	3.35	3.41	?			30032	NWMO TCEA book 3	
636	SCa-3_Cs	1.728	4677	33.927	?	-95.1	3.20	3.26	?	-75.10	41.99	30033	NWMO TCEA book 3	
637	SCa-3_Cs	1.718	4706	36.834	?	-92.6	3.23	3.30	?			30034	NWMO TCEA book 3	
638	SCa-3_Cs	1.627	4324	34.856	?	-94.3	3.14	3.20	?			30035	NWMO TCEA book 3	
639	SCa-3_Cs	1.714	4624	35.602	?	-93.6	3.19	3.25	?			30036	NWMO TCEA book 3	
640	USGS 57	3.439	6147	37.728	-91.5	-91.8	2.11	2.15	2.135			30037	NWMO TCEA book 3	
641	USGS 58	2.584	5268	110.487	-28.4	-29.0	2.41	2.45	2.454			30038	NWMO TCEA book 3	
642	GBS biotite	3.667	5704	68.422	-62.5	-65.3	1.84	1.87	1.940			30039	NWMO TCEA book 3	

# of samples: 26
# of standards, duplicates, failed, blanks: 7,0,0,2

[Analysis-Supplemental 1]



Project: Kuligiewicz-Kanik-Longstaffe TCEA-HM 19-02 (SDP_TCEA-HM-concept test-200C)

Isotope(s): Hydrogen

Preparation: Nadine Kanik

Analyst: Nadine Kanik

Data Treatment and QA/QC: F. Longstaffe

Instrument(s): TCEA with glassy carbon reactor and Delta in Bird Wing IRMS

Date Approved by Director: June 28, 2019 (FJL)

Notes: These were loaded on the main TCEA, reactor not holding at 1450C, transferred to Bird Wing TCEA, transferred in ~1 min, then He flush continued followed by analysis

Note: Saz-1 RT = samples kept in open 2ml (Los Gato) vials with the other closed ones on the counter behind the silicate-line for one week.

Date Analyzed: June 24, 2019

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 200C active vacuum oven for 4 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	28.67	-91.5
USGS 58	96.36	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
8617.00	2.571	6.31	USGS 58	muscovite
9053.00	3.039	6.49	USGS 57	biotite

slope:		0.93221		
Intercept:		-118.23		
r squared		0.999		
Calculated equation:	d2H =	0.932	*raw	-118.2

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
1	GBS biotite	3.106	9954	62.626	-62.5	-59.8	2.30	2.35	1.940	-63.0	1.3	9515		
2	USGS 57	2.984	9186	28.377	-91.5	-91.8	2.21	2.25	2.135	-91.5	0.4	9516		
3	USGS 58	2.698	9341	95.303	-28.4	-29.4	2.48	2.53	2.454	-28.4	1.4	9517		
4	IMt-1_K (2)	1.852	8799	23.77	?	-96.1	3.40	3.48	?	-96.0	1.6	9518		
5	SAz-1_K RT	2.071	11323	4.946	?	-113.6	3.92	4.00	?	-110.1	5.0	9519		RT= equil. in lab atmos. at room temp.
6	SAz-1_K RT	1.614	8879	12.515	?	-106.6	3.94	4.03	?			9520		corrected expected yield
7	IMt-1_K (2)	2.107	9925	22.122	?	-97.6	3.38	3.45	?			9521		
8	SAz-1_Ca RT	1.715	15138	-4.376	?	-122.3	6.33	6.46	?	-123.9	2.2	9522		RT= equil. in lab atmos. at room temp.
9	SAz-1_Ca RT	2.125	20094	-7.766	?	-125.5	6.78	6.92	?			9523		RT= equil. in lab atmos. at room temp.
10	IMt-1_K (2)	1.979	9214	22.126	?	-97.6	3.34	3.41	?			9524		
11	SAz-1_Na RT	1.618	10256	11.909	?	-107.1	4.54	4.64	?	-106.4	1.1	9525		RT= equil. in lab atmos. at room temp.
12	SAz-1_Na RT	1.57	9961	13.513	?	-105.6	4.55	4.65	?			9526		RT= equil. in lab atmos. at room temp.
13	GBS biotite	2.98	7362	59.784	-62.5	-62.5	1.77	1.81	1.940			9527		
14	SAz-1_K low	1.816	9780	12.51	?	-106.6	3.86	3.94	?	-105.90	0.9	9528		
15	SAz-1_K low	1.581	8420	13.93	?	-105.2	3.82	3.90	?			9529		
16	GBS biotite	2.749	6628	60.445	-62.5	-61.9	1.73	1.77	1.940			9530		
17	SAz-1_Ca low	1.863	19946	-5.652	?	-123.5	7.67	7.84	?	-123.38	0.16	9531		
18	SAz-1_Ca low	1.825	20858	-5.405	?	-123.3	8.19	8.37	?			9532		
19	GBS biotite	3.173	8338	58.068	-62.5	-64.1	1.88	1.92	1.940			9533		
20	SAz-1_Na low	1.667	10209	10.032	?	-108.9	4.39	4.48	?	-107.60	1.80	9534		
21	SAz-1_Na low	1.905	11992	12.763	?	-106.3	4.51	4.61	?			9535		
22	GBS biotite	3.24	7864	59.203	-62.5	-63.0	1.74	1.78	1.940			9536		
23	GBS biotite	3.105	7690	60.643	-62.5	-61.7	1.77	1.81	1.940			9537		
24	GBS biotite	2.427	5911	59.664	-62.5	-62.6	1.75	1.78	1.940			9538		
25	GBS biotite	2.982	6509	57.581	-62.5	-64.5	1.56	1.60	1.940			9539		
26	GBS biotite	2.846	6907	59.815	-62.5	-62.5	1.74	1.78	1.940			9540		
27	GBS biotite	2.668	6542	58.083	-62.5	-64.1	1.76	1.80	1.940			9541		
28	IMt-1_K (2)	1.851	8324	25.094	?	-94.8	3.22	3.29	?			9542		
29	SAz-1_K high	1.647	8567	16.273	?	-103.1	3.73	3.81	?	-103.14	0.12	9543		
30	SAz-1_K high	1.708	8950	16.084	?	-103.2	3.75	3.84	?			9544		
31	GBS biotite	2.857	7025	57.208	-62.5	-64.9	1.76	1.80	1.940			9545		
32	SAz-1_Ca high	1.6	16412	9.856	?	-109.0	7.35	7.51	?	-107.96	1.53	9546		
33	SAz-1_Ca high	1.6	18113	12.179	?	-106.9	8.11	8.29	?			9547		
34	GBS biotite	3.057	7447	58.008	-62.5	-64.2	1.75	1.78	1.940			9548		
35	SAz-1_Na high	1.748	10759	24.473	?	-95.4	4.41	4.51	?	-95.50	0.12	9549		
36	SAz-1_Na high	1.973	12236	24.284	?	-95.6	4.44	4.54	?			9550		
37	GBS biotite	3.02	7292	58.548	-62.5	-63.6	1.73	1.77	1.940			9551		
38	GBS biotite	2.901	7017	58.604	-62.5	-63.6	1.73	1.77	1.940			9552		
39	IMt-1_K (2)	1.811	8037	26.014	?	-94.0	3.18	3.25	?			9553		
40	USGS 57	3.093	8920	28.962	-91.5	-91.2	2.07	2.11	2.135			9554		
41	USGS 58	2.444	7893	97.413	-28.4	-27.4	2.31	2.36	2.454			9555		
42	GBS biotite	2.86	6977	59.631	-62.5	-62.6	1.75	1.79	1.940			9556		

# of samples: 18

# of standards, duplicates, failed, blanks: 24,0,0,2

[Analysis-Supplemental 2]

Project: Kuligiewicz-Kanik-Longstaffe TCEA-HM 19-01 (SDP_TCEA-HM-concept test-150C)

Isotope(s): Hydrogen

Preparation: Nadine Kanik

Analyst: Nadine Kanik

Data Treatment and QA/QC: F. Longstaffe

Instrument(s): TCEA with glassy carbon reactor and Delta in Bird Wing IRMS

Date Approved by Director: June 28, 2019 (FJL)

Notes: main TCEA undergoing repairs, reactor not holding at 1450C, samples analized on Bird Wing TCEA with Delta V IRMS

Date Analyzed: June 25, 2019

Conditions: He flow rate= 90ml/min, **GC operating temp.=** 120C, **Reactor operating temp.=** 1450C, **Pre-treatment=** heated in 150C active vacuum oven for 4 hours, in Al-tray, followed by loading into He purged autosamper, equilibrated in autosampler He atmosphere for 4 hours then analyzed.

Calibrated reference gas: -124.69

	Raw	Accepted Value
USGS 57	31.30	-91.5
USGS 58	98.07	-28.4

Ampl 2	weight (mg)	umole	reference	
0.00	0.000	0.00	USGS 47	water
8658.00	2.707	6.64	USGS 58	muscovite
8626.00	3.040	6.49	USGS 57	biotite

slope:		0.94506		
Intercept:		-121.08		
r squared		0.999		
Calculated equation:	d2H =	0.945	*raw	-121.1

Line	Identifier 1	Amount (mg)	Ampl. 2	Raw d 3H2/2H2	Expected d2H ‰ VSMOW	d2H ‰ VSMOW	yield biotite umole/mg	yield muscovite umole/mg	expected yield or average umole/mg	average	SD	Mass Spec #	Lab Book #	Notes
														2 conditioning blanks at start
46	GBS biotite	3.168	7212	62.126	**-62.5**	**-62.4**	**1.71**	**1.75**	**1.940**	**-63.5**	**1.9**	9562		
47	GBS biotite	2.972	7018	62.915	**-62.5**	**-61.6**	**1.78**	**1.81**	**1.940**			9563		
48	GBS biotite	2.907	6732	63.39	**-62.5**	**-61.2**	**1.74**	**1.78**	**1.940**			9564		
49	IMt-1_K (2)	1.573	6604	26.372	**?**	**-96.2**	**3.16**	**3.22**	**?**	**-96.3**	**2.2**	9565		
50	USGS 57	3.038	8596	31.762	**-91.5**	**-91.1**	**2.13**	**2.17**	**2.135**	**-91.5**	**0.6**	9566		
51	USGS 58	2.603	8241	98.62	**-28.4**	**-27.9**	**2.38**	**2.43**	**2.454**	**-28.4**	**0.7**	9567		
52	IMt-1_K (2)	1.537	6458	29.022	**?**	**-93.7**	**3.16**	**3.22**	**?**			9568		
53	SAz-1_K low	1.577	7173	13.996	**?**	**-107.9**	**3.42**	**3.49**	**?**	**-109.0**	**1.6**	9569		low= equil. with d2H -161‰ water (LSD)
54	SAz-1_K low	1.609	7352	11.559	**?**	**-110.2**	**3.44**	**3.51**	**?**			9570		low= equil. with d2H -161‰ water (LSD)
55	GBS biotite	2.764	6220	59.421	**-62.5**	**-64.9**	**1.69**	**1.73**	**1.940**			9571		
56	SAz-1_Ca low	1.605	14017	-0.641	**?**	**-121.7**	**6.57**	**6.70**	**?**	**-123.1**	**1.9**	9572		low= equil. with d2H -161‰ water (LSD)
57	SAz-1_Ca low	1.701	14344	-3.538	**?**	**-124.4**	**6.34**	**6.47**	**?**			9573		low= equil. with d2H -161‰ water (LSD)
58	GBS biotite	2.789	6983	58.13	**-62.5**	**-66.1**	**1.88**	**1.92**	**1.940**			9574		
59	SAz-1_Na low	1.704	9565	13.739	**?**	**-108.1**	**4.22**	**4.31**	**?**	**-111.00**	**4.1**	9575		low= equil. with d2H -161‰ water (LSD)
60	SAz-1_Na low	2.121	12078	7.607	**?**	**-113.9**	**4.28**	**4.37**	**?**			9576		low= equil. with d2H -161‰ water (LSD)
61	GBS biotite	2.61	6187	58.863	**-62.5**	**-65.5**	**1.78**	**1.82**	**1.940**			9577		
62	USGS 57	2.638	7371	29.348	**-91.5**	**-93.3**	**2.10**	**2.14**	**2.135**			9578		
63	USGS 58	2.438	7740	98.77	**-28.4**	**-27.7**	**2.39**	**2.44**	**2.454**			9579		
64	IMt-1_K (2)	1.59	6593	26.088	**?**	**-96.4**	**3.12**	**3.18**	**?**			9580		
65	SAz-1_K high	1.516	6909	15.239	**?**	**-106.7**	**3.43**	**3.50**	**?**	**-107.59**	**1.28**	9581		high= equil. with d2H +88‰ water (Heaven)
66	SAz-1_K high	1.743	8042	13.319	**?**	**-108.5**	**3.47**	**3.54**	**?**			9582		high= equil. with d2H +88‰ water (Heaven)
67	GBS biotite	2.755	6087	59.917	**-62.5**	**-64.5**	**1.66**	**1.70**	**1.940**			9583		
68	SAz-1_Ca high	1.535	13767	12.609	**?**	**-109.2**	**6.75**	**6.88**	**?**	**-106.36**	**3.97**	9584		high= equil. with d2H +88‰ water (Heaven)
69	SAz-1_Ca high	1.928	19902	18.544	**?**	**-103.6**	**7.77**	**7.92**	**?**			9585		high= equil. with d2H +88‰ water (Heaven)
70	GBS biotite	2.805	6450	60.414	**-62.5**	**-64.0**	**1.73**	**1.76**	**1.940**			9586		
71	SAz-1_Na high	1.67	9257	23.357	**?**	**-99.0**	**4.17**	**4.25**	**?**	**-98.95**	**0.09**	9587		high= equil. with d2H +88‰ water (Heaven)
72	SAz-1_Na high	1.599	8720	23.491	**?**	**-98.9**	**4.10**	**4.18**	**?**			9588		high= equil. with d2H +88‰ water (Heaven)
73	GBS biotite	2.467	5587	60.697	**-62.5**	**-63.7**	**1.70**	**1.74**	**1.940**			9589		
74	IMt-1_K (2)	1.66	6947	23.32	**?**	**-99.0**	**3.15**	**3.21**	**?**			9590		
75	USGS 57	3.042	8656	30.843	**-91.5**	**-91.9**	**2.14**	**2.18**	**2.135**			9591		
76	USGS 58	2.811	9075	97.522	**-28.4**	**-28.9**	**2.43**	**2.48**	**2.454**			9592		
77	GBS biotite	2.536	5559	63.927	**-62.5**	**-60.7**	**1.65**	**1.68**	**1.940**			9593		

# of samples: 12

# of standards, duplicates, failed, blanks: 20,0,0,2

Appendix 2 - Open versus Closed Capsule Tests

The first several analytical sessions (Appendix 1, Analyses 1 to 17) were primarily devoted to method development; these tests included ensuring that the analytical equipment was working properly, and developing best practices for equipment maintenance. As a result, data from Analyses 1 to 17 are not considered completely reliable or fully comparable to data obtained from Analyses 18 to 31. The latter group of analyses were performed using a standard protocol. That protocol was the product of the many adjustments and modifications made to the equipment and method in order to accommodate the unique challenges of analyzing hydrous minerals using the TCEA-CF-IRMS method.

The development phase (Analyses 1-17) nonetheless provided the opportunity to test the idea proposed by VanDeVelde and Bowen (2013) regarding possible changes in smectite δ^2H resulting from incomplete degassing of samples wrapped in silver foil capsules. To test this possibility, samples from Analyses 12 were analyzed in open capsules, under the same pretreatment (degassing) conditions as samples contained in closed capsules (Table A2.1). For the batches testing degassing in open capsules, the samples were weighed into silver capsules, and the middle of the capsules was then pinched with precision tweezers (Fig. A2.1).

Appendix 2 (cont'd)- Open versus Closed Capsule Tests

Table A2.1. Summary for δ^2H of samples degassed with open and with closed silver capsules.

Sample	Average δ^2H_{VSMOW} (‰)	SD	*n*
Open Capsules			
Analysis 12 [degassed 24 hours at 200°C in Al-tray]			
SWy-1_K	–140.8	1.4	3
SapCa-1_K	–128.9	1.3	3
Closed capsules			
Analysis 8 [degassed 24 hours at 200°C in glass vials]			
SWy-1_K	–141.6	1.7	3
SapCa-1_K	–130.5	1.4	3
Analysis 13 [degassed 24 hours at 200°C in Al-tray]			
SWy-1_K	–143.4	0.5	2
SapCa-1_K	–131.2	1.4	2
Analysis 14 [degassed 24 hours at 200°C in Al-tray]			
SWy-1_K	–140.4	0.6	2
SapCa-1_K	–129.0	2.4	2

SD= standard deviation

This left two large openings on each side of the capsule to facilitate unhindered degassing while still providing containment for the sample material. The samples were then placed in the Al-tray and degassed in a vacuum oven as described in section 3.2. Following degassing, the samples were removed from the vacuum oven, quickly pinched shut with tweezers, and placed in the autosampler for TCEA-CF-IRMS measurement as per section 3.3. There were minimal or no appreciable differences in δ^2H for samples degassed in open (Appendix 1, Analysis 12) versus closed capsules (Appendix 1, Analyses 8, 13, 14).

Appendix 2 (cont’d)- Open versus Closed Capsule Tests

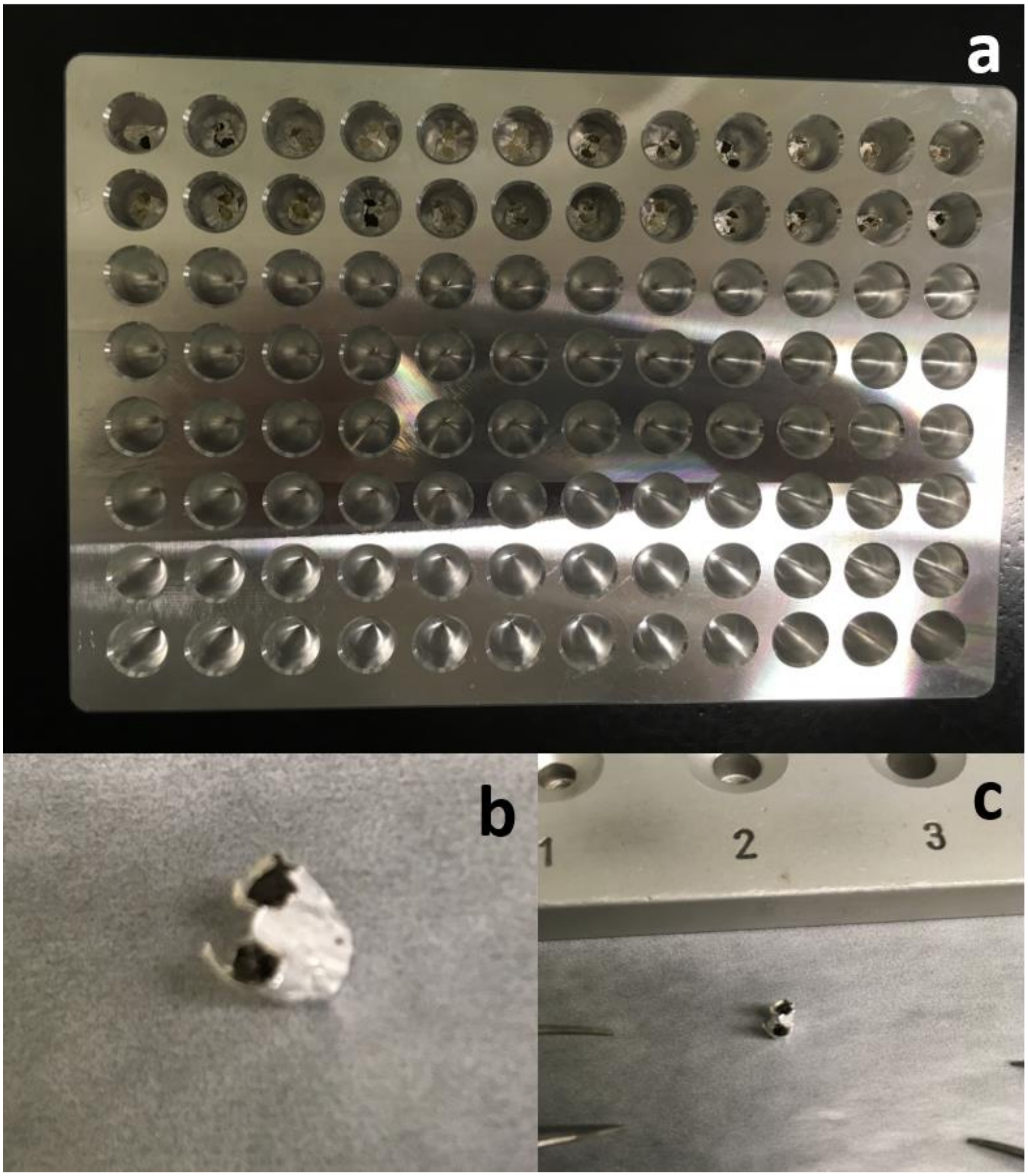


Figure A2.1. (a) Al-tray containing 24 partially closed silver capsules containing smectite samples; (b) close up of partially closed silver capsule, and (c) silver capsule shown in relation to tweezer tips and a metal sample holder.

Appendix 3 – Kaolinite Triple Temperature Test

The CMS Source Clay Repository kaolinite, KGa-1 RT (RT denotes it was stored in LSIS at room temperature) was analyzed using a similar procedure to the triple temperature test for smectites (see section 4.2.3). The only difference in pretreatment (degassing) was that the kaolinite was degassed at 220˚C for 25 hours and at 100˚C for 5 hours, compared to 24 and 4 hours, respectively for the smectites.

The results of this test are summarized in Table A3.1, with all results given in Appendix 1 (Analysis 18). While 1:1 clay minerals were not the focus of this study and are not expected to experience the same rehydration effects as expandable 2:1 clay minerals, a shift to lower δ^2H was observed for the kaolinite heated for the longer time at a higher temperature. Because of this variation, and as a result of autosampler space constraints KGa-1 RT was excluded as an in-house TCEA-CF-IRMS standard for Analyses 19-31.

Appendix 3 (cont’d)- Kaolinite Triple Temperature Test

Table A3.1. δ^2H of KGa-1 RT after different pretreatments (degassing) (220°C, 25 h; 100°C, 5 h; laboratory atmosphere).

Sample	δ^2H_{VSMOW} (‰)	Average δ^2H_{VSMOW} (‰)	H_2 yield (μmol/mg)	Average H_2 yield (μmol/mg)
KGa-1 RT (220°C-25h)	–61.0	–62.5	8.53	8.40
KGa-1 RT (220°C-25h)	–61.8		8.38	
KGa-1 RT (220°C-25h)	–61.9		8.27	
KGa-1 RT (220°C-25h)	–63.2		8.44	
KGa-1 RT (220°C-25h)	–63.0		8.47	
KGa-1 RT (220°C-25h)	–63.6		8.40	
KGa-1 RT (220°C-25h)	–62.8		8.34	
KGa-1 RT (100°C-5h)	–50.0	–51.9	8.42	8.34
KGa-1 RT (100°C-5h)	–51.2		8.29	
KGa-1 RT (100°C-5h)	–52.2		8.25	
KGa-1 RT (100°C-5h)	–52.4		8.30	
KGa-1 RT (100°C-5h)	–52.3		8.39	
KGa-1 RT (100°C-5h)	–52.7		8.39	
KGa-1 RT (100°C-5h)	–52.8		8.36	
KGa-1 RT (atmos)	–48.9	–50.2	8.43	8.35
KGa-1 RT (atmos)	–49.0		8.28	
KGa-1 RT (atmos)	–49.8		8.40	
KGa-1 RT (atmos)	–50.6		8.34	
KGa-1 RT (atmos)	–51.3		8.50	
KGa-1 RT (atmos)	–50.5		8.30	
KGa-1 RT (atmos)	–51.3		8.18	

Appendix 4 – Smectite Exchange with Isotopically Labeled Waters

Tests were performed using SAz-1 smectite in K-, Ca- and Na-saturated forms of SAz-1 to determine if and to what extent the δ^2H of smectite bound water hydrogen and possibly hydroxyl hydrogen would change when exchanged with water of known isotopic composition, depending on cation saturation (Table A4.1). Aliquots of each cation saturation of SAz-1 labelled “low” were exchanged with a laboratory water standard (LSD) having δ^2H = −161 ‰, while aliquots labelled “high” were equilibrated with a laboratory water standard (Heaven) having δ^2H = +88 ‰, and those labelled “RT” were wrapped in silver foil and left open to laboratory atmosphere for the same time period. Detailed results are reported in Appendix 1 [Analysis-Supplemental 1 & 2].

Exchange was performed in a 2 ml gas tight, glass vial (Fig. A4.1). Approximately 2 mg of SAz-1 was folded into silver capsules. Variously colored strings, each color denoting one of the three cation-saturated forms, were tied with tweezers around each silver-wrapped sample. Approximately 1 ml of isotopically labeled water was added to each vial. One of each cation-saturated form was suspended by the string over the labeled water for a total of three samples per vial. The seal and screw cap were then placed on the vial, sealing it and securing the strings holding the samples in place above the water. The samples in the vials were left on the laboratory bench (22°C) to exchange for one week. The vials were then opened, the string removed, and the samples were pretreated (degassed) at either 200°C or 150°C (Table A4.1) for four hours, and then analyzed by TCEA CF-IRMS. The samples degassed at 220°C for which results are reported in Table A4.1 were exposed for ~ 4 minutes longer to the laboratory atmosphere because of equipment failure. These samples were analyzed as quickly as possible using the laboratory’s other TCEA, which is connected in continuous flow mode to a Delta V IRMS. This system is otherwise identical to the instrumentation used to produce the data listed in Appendix 1, Analysis 1 to 31.

Appendix 4 (cont'd)- Smectite Exchange with Isotopically Labeled Waters

A summary of the results is presented in Table A4.1 below, which shows a systematic difference in the δ^2H of samples equilibrated with 'low' versus 'high' waters. Interestingly exchange was noticed between clay minerals exchanged with both high and low waters with trends appearing for each different cation form. The degassing temperature appeared to have a small effect as δ^2H was slightly lower for samples degassed at 200°C than those at 150°C (Table A4.1). The δ^2H of the clay minerals decreased when exchanged with the light water, with the largest decreases occurring for the cation forms in the order K < Na < Ca (Table A4.1). The same was also true for the clay minerals exchanged with the high water, whereby the δ^2H of the clay minerals increased toward the δ^2H of the water in the same order Ca > Na > K. This followed the pattern, previously observed in this study, for the different cation saturations in relation to hydrogen yield excess. The excess bound water remaining on the clay minerals, post degassing, shifted the δ^2H of the smectite toward the δ^2H of the water, with the effect increasing in the order of cation bound water retention K < Na < Ca (Table A4.1). This is interesting and has implications for how the δ^2H of bound water in clays can be altered by the water/water vapour with which it is in contact. Further investigations of this aspect were beyond the scope of the present study, but will be pursued in a future study.

Appendix 4 (cont'd)- Smectite Exchange with Isotopically Labeled Waters

Table A4.1. δ^2H and H_2 yield of the SAz-1 clay exchanged with 'high' and 'low' labelled waters of known isotopic composition and degassed at 150-200°C for 4 hours.

Sample	δ^2H_{VSMOW} (‰)	H_2 yield (μmol/mg)
Degassed at 150°C for 4 hours		
SAz-1_K low	–107.9	3.42
SAz-1_K low	–110.2	3.44
SAz-1_Ca low	–121.7	6.57
SAz-1_Ca low	–124.4	6.34
SAz-1_Na low	–108.1	4.22
SAz-1_Na low	–113.9	4.28
SAz-1_K high	–106.7	3.43
SAz-1_K high	–108.5	3.47
SAz-1_Ca high	–109.2	6.75
SAz-1_Ca high	–103.6	7.77
SAz-1_Na high	–99.0	4.17
SAz-1_Na high	–98.9	4.10
Degassed at 200°C for 4 hours		
SAz-1_K RT	–113.6	3.92
SAz-1_K RT	–106.6	3.94
SAz-1_Ca RT	–122.3	6.33
SAz-1_Ca RT	–125.5	6.78
SAz-1_Na RT	–107.1	4.54
SAz-1_Na RT	–105.6	4.55
SAz-1_K low	–106.6	3.86
SAz-1_K low	–105.2	3.82
SAz-1_Ca low	–123.5	7.67
SAz-1_Ca low	–123.3	8.19
SAz-1_Na low	–108.9	4.39
SAz-1_Na low	–106.3	4.51
SAz-1_K high	–103.1	3.73
SAz-1_K high	–103.2	3.75
SAz-1_Ca high	–109.0	7.35
SAz-1_Ca high	–106.9	8.11
SAz-1_Na high	–95.4	4.41
SAz-1_Na high	–95.6	4.44

Appendix 4 (cont'd)- Smectite Exchange with Isotopically Labeled Waters

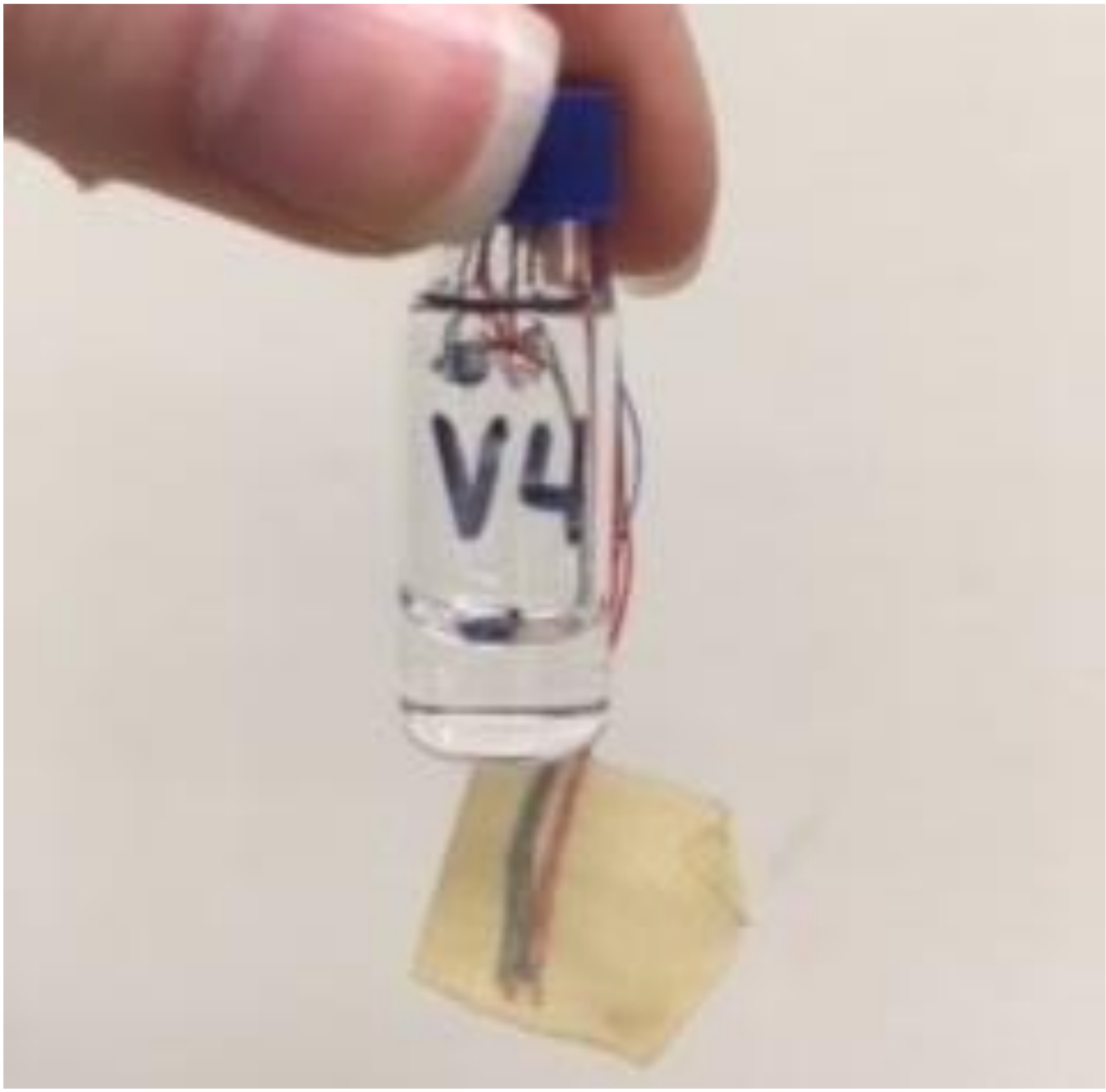


Figure A4.1 Silver-wrapped samples in sealed vial suspended above water of 'high' or 'low' δ^2H.

Curriculum Vitae

Name:	Nadine J. Kanik
Post-secondary Education and Degrees:	University of Winnipeg Winnipeg, Manitoba, Canada 2013-2017 Honours B.Sc. Physical Geography The University of Western Ontario London, Ontario, Canada 2017-2020 M.Sc. Geology
Honours and Awards:	Clay Minerals Society Travel Award 2020 Queen Elizabeth II Graduate Scholarship in Science and Technology 2019-2020 Dean's Honour List-Student of Distinction 2015&2016 Brian Evans Memorial Scholarship in Geography 2015&2016
Related Work Experience	Graduate Teaching Assistant The University of Western Ontario 2017-2019 Project Manager for Research Audit The University of Western Ontario Apr.2018-Oct.2018 Contract Lab Instructor University of Winnipeg, Department of Geography Dec.2016-Apr.2017 Undergraduate Teaching Assistant University of Winnipeg, Department of Geography 2013-2016
Publications and Presentations:	The Clay Minerals Society Conference, October 2020, Richland, WA, United States of America. "Impact of interlayer cation composition on smectite δ^2H". **Nadine J. Kanik**, Fred J. Longstaffe, and Arkadiusz Derkowski. [Oral Presentation] The 2019 Nuclear Waste Management Organization Geoscience Seminar, June 2019, Toronto, Ontario, Canada. "TC-EA

measurement of clay δ^2H and implications for porewater isotopic compositions in shales”. **Nadine J. Kanik** and Fred J. Longstaffe.
[Poster Presentation]

The 2018 Nuclear Waste Management Organization Geoscience Seminar, June 2018, Toronto, Ontario, Canada. “Investigation of the H- and O-isotope discrimination and exchange among smectite-group clay minerals and associated bound and mobile water in fine-grained mudstones and shales”. **Nadine J. Kanik** and Fred J. Longstaffe.
[Poster Presentation]

Chinique de Armas, Y., Roksandic, M., Nikitović, D., Rodríguez Suárez, R., Smith, D., **Kanik, N**., ... & Buhay, W. M. (2017). Isotopic reconstruction of the weaning process in the archaeological population of Canímar Abajo, Cuba: A Bayesian probability mixing model approach. *PloS one, 12*(5), e0176065.
[Publication]