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NOTE

HYDROGEN-ISOTOPE EXCHANGE IN HALLOYSITE: INSIGHT FROM ROOM-TEMPERATURE EXPERIMENTS

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INTRODUCTION

Halloysite is a common pedogenic clay mineral, often found in young soils developed on volcanic deposits (Dixon, 1989). It is a member of the kaolin group of clays with the same ideal stoichiometric composition as kaolinite [$Al_2Si_2O_5(OH)_4$]. Halloysite, however, often contains water of hydration (*i.e.*, $Al_2Si_2O_5(OH)_4 \cdot nH_2O$), and is commonly found with a tubular morphology. This "rolling" of halloysite has received a great deal of study because there is no generally agreed upon mechanism for the process and there is no corresponding phenomenon in natural kaolinite (*e.g.*, Bates *et al.*, 1950; Bailey, 1989; Singh, 1996; Singh and Mackinnon, 1996). The crystal structure of halloysite often shows stacking disorder. This property, combined with a rolled morphology, makes identification by X-ray diffraction (XRD) difficult. The XRD peaks at 7.5, 4.4, and 3.6 Å are often asymmetric with a large width at half peak height (Bailey, 1989).

Oxygen-isotope systematics of halloysite are thought to be similar to kaolinite (Savin and Epstein, 1970), but a recent review suggested a small fractionation (~1‰) between the two minerals (Sheppard and Gilg, 1996). Hydrogen-isotope systematics of halloysite have not been investigated in great detail, but preliminary measurements (Lawrence and Taylor, 1972) suggested that H in halloysite is easily exchangeable at room temperature. Hsieh (1997) used selective dissolution, centrifugation, and XRD techniques to extract and identify pedogenic halloysite from some Hawaiian soils for measurement of $\delta^{18}O$ values. These isotopic analyses produced low oxygen yields and $\delta^{18}O$ values which differed from those expected for a mineral with isotopic characteristics similar to kaolinite. Small amounts of two of these purified halloysite samples remained from the work of Hsieh. We report the results of hydrogen isotope exchange experiments at 22°C followed by dehydroxylation experiments *in vacuo* at 250°C that were performed on these remaining samples. The results are discussed in terms of: (a) the fraction of the total H in hydroxyl that was isotopically exchanged at 22°C and (b) possible implications of the dehydroxylation experiments for oxygen isotopic analysis of pedogenic halloysite.

EXPERIMENTAL METHODS

Hydrogen-isotope exchange experiments were performed with a high-vacuum apparatus described in Yapp (1983) and following the procedure in Yapp and Poths (1995) for exchange experiments with goethite samples. Briefly, the procedure was as follows: halloysite was weighed into a silica glass boat and both sample and boat were loaded into a horizontal silica glass dehydration chamber. The sample chamber was connected to a multi-coil trap, but separated with a stopcock. Halloysite was initially heated ("outgassed") at 100°C for 60 min in vacuum, and the evolved water and CO_2 were immediately frozen in a trap cooled by liquid nitrogen ("open" system conditions). The entire sample chamber was then cooled to room temperature. Water for exchange with halloysite was introduced into both the sample chamber and multi-coil trap, and the entire volume closed. After the prescribed exchange time (ranging from ~59 to 118 h) at room temperature (~22°C), an aliquot of water vapor was sampled by closing the stopcock between the multi-coil trap and dehydration chamber and collecting the water vapor in the trap (called the "trap vapor" aliquot). The exchange experiment was then "quenched" by immediately freezing the remainder of the water vapor, followed by heating the sample at 100°C to remove water adsorbed on the halloysite. The desorbed water was combined with the "quenched" vapor to form a single aggregate sample (called the "vapor + 100°C" aliquot). Halloysite was then sub-

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Table 1. Data from hydrogen isotope exchange experiments at 22°C.

Sample		Initial exchange water		22°C exch. time (min)	After exchange: Trap vapor		Vapor + 100°C		Halloysite: 250°C			850°C		Total (250°C + 850°C)		
MHD #	Mass (mg)[1]	(μmol)	δD		Yield (μmol)	δD	Yield (μmol)	δD	Yield (μmol)	δD	Time (min)	Yield (μmol)	δD	H_2O wt. %	δD	Apparent $\alpha_{min\text{-}vap}$[2]
Halloysite 1[3]																
1742	58.2	339	−2	3572	23	−42	304	−24	112	−4	60	362	−24	14.7	−19	1.024
1747	53.7	339	−184	3610	23	−152	298	−169	105	−56	60	334	−52	14.7	−53	1.117
1819	59.4	356	−256	5784	18	−173	325	−203	123	−84	60	374	−61	15.0	−67	1.128
1834	52.3	372	−105	3943	25	−78	329	−98	103	−30	60	315	−40	14.4	−38	1.043
1945	43.6	256	−2	6575	23	−35	220	−27	86	−5	60	200	−27	14.4	−19	1.017
1945					(second 250°C fraction)				15	−12[4]	120					
1945					(third 250°C fraction)				12		225					
1945					(fourth 250°C fraction)				23		910					
Halloysite 2[3]																
1947	31.1	228	−256	7070	21	−180	196	−198	37	−78	60	151	−68	10.8	−70	1.134
1950	32.7	228	−2	7065	21	—	203	−41	38	−10	60	125	−24	10.8	−24	—
1950					(second 250°C fraction)				32	−35	625					

[1] After initial outgassing at 100°C.
[2] Apparent mineral-vapor hydrogen isotope fractionation factor [see Equation (2) in text].
[3] Halloysite 1: initial δD = −37‰; 14.4 wt. % structural water. Halloysite 2: 10.8 wt. % structural water.
[4] δD of combined second, third, and fourth 250°C fractions.

jected to open system dehydration in vacuum at 250°C and then 850°C for 60 min each. As water evolved during each dehydration step, it was frozen into a multi-coil trap cooled by liquid nitrogen. For some experiments (MHD-1945 and MHD-1950), several successive dehydration steps were performed *in vacuo* at 250°C.

In summary, the sequence of recovery of water after exchange was as follows: a) an aliquot of the vapor after ~59 to 118 h of exchange at 22°C was sequestered (*i.e.,* the trap vapor); b) the remainder of the exchanged vapor and the water outgassed from halloysite *in vacuo* at 100°C were collected and combined (*i.e.,* the vapor + 100°C water); c) water was collected from the dehydroxylation steps *in vacuo* at 250°C (*i.e.,* the 250°C water); and d) the balance of the H in the halloysite hydroxyl was recovered from dehydroxylation *in vacuo* at 850°C (*i.e.,* 850°C water).

Water evolved during each heating step was cryogenically separated from CO_2 (analyzed, but not discussed here), and the recovered water was quantitatively converted to hydrogen gas over hot uranium (800°C) for yield and D/H determinations. Hydrogen gas yields were measured manometrically with an analytical precision of about ±0.5 μmol. D/H ratios were measured on a Finnigan MAT-252 mass spectrometer and are reported as δD values, where

$$\delta D = \left[\frac{R_{sample}}{R_{standard}} - 1\right] \times 1000‰. \quad (1)$$

For R = D/H, the standard is V-SMOW. The analytical precision of δD measurements is better than ±4‰ for these halloysite samples.

The water introduced for exchange was added from sealed capillary tubes ("capillary water"). The initial amounts based on the measured mass of water in the capillary varied from 228 to 394 μmol depending on the experiment. Four different waters were used in the experiments. Their initial δD values (with an uncertainty of ±2‰) are listed in Table 1 and range from −2‰ to −256‰.

The amount of water presumed to be adsorbed on halloysite during exchange can be calculated from the following information: a) the measured amount of water vapor in the "trap vapor" aliquot, b) the amount of "total exchange water" (trap vapor and vapor + 100°C aliquots), c) the known volumes for the multi-coil trap and sample chamber, and d) an assumption that the pressure of water vapor was the same in all parts of the exchange system.

Two different samples designated halloysite 1 and halloysite 2 were available in sufficient quantity for the D/H experiments. Both samples were from soils on the Kohala peninsula on the island of Hawaii. Halloysite 1 was from a soil (elevation: 185 m, sea level datum) which receives 18 cm of annual precipitation, whereas halloysite 2 was separated from a soil (elevation: 674 m) which receives 57 cm of annual precipitation. The measured δD value of halloysite 1 prior to exchange and the weight percent of structural water are given in Table 1. δD values were measured after outgassing at 100°C for 60 min in vacuum. Weight percent of structural water was determined (after outgassing at 100°C) from the total yield of hydrogen (250°C + 850°C heating steps). For halloysite 2, there was insufficient material to measure the δD value of

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Table 2. Parameters calculated from exchange experiments.

Sample MHD #	Outgassed water[1] (μmol)	Ads. exch. water[2] (μmol)	RH[3]
1742	125	163	0.53
1747	141	157	0.53
1819	213	206	0.45
1834	169	163	0.62
1945	90	68	0.57
1947	82	57	0.52
1950	86	64	0.52

[1] Amount of water recovered from *initial* outgassing at 100°C prior to exchange.
[2] Calculated amount of water adsorbed onto halloysite during exchange (see text).
[3] Relative humidity in sample chamber during exchange (see text).

an aliquot that had not been exchanged with waters of extreme δD values.

XRD analyses (Hsieh, 1997) indicate that the only crystalline phase present is halloysite (without water of hydration). For halloysite 1, the water content of the mineral (after outgassing at 100°C) is somewhat higher (Table 1) than the 14.0 wt. % expected for the ideal stoichiometry $[Al_2Si_2O_5(OH)_4]$ (Dixon, 1989). These results suggest that outgassing in vacuum for 60 min at 100°C does not remove all adsorbed water. However, even the highest yield (MHD-1819) is only a factor of 1.07 greater than stoichiometric, and the quantity of nonstoichiometric water does not account for the D/H exchange results. At present, we have no explanation for the lower yields from halloysite 2.

RESULTS

The δD value of the total system (capillary water plus halloysite) before exchange was calculated by mass balance for each experiment by using the amount of "stoichiometric" water in halloysite and its initial δD value and the amount of capillary water and its initial δD value. The δD value of the total system after exchange was calculated with the measured total amount and weighted δD value of the "exchanged" capillary water and the δD value of the total stoichiometric water in halloysite (250 and 850°C). The amount of water ("trap vapor" and "vapor + 100°C") recovered from the system upon termination of the exchange process was ~95–98% of the initial amount of capillary water. For all experiments using halloysite 1, the difference between the δD of the total system before and after exchange was no greater than 5‰. These results suggest that the closed-system condition (for capillary water plus halloysite) was met in each experiment. For those experiments using halloysite 2 (MHD-1947 and MHD-1950), closed-system conditions were assumed. Because the results of these two experiments (MHD-1947 and MHD-1950) generally followed the trends of others (presented below), this assumption is probably valid.

The results of exchange experiments between halloysite and water vapor at ~22°C are presented in Table 1. The δD values of halloysite (weighted average of 250 and 850°C fractions) after the exchange experiments are shifted compared to the original values (Table 1). The magnitude and direction of the change differ depending on the water used in the exchange. Experiments using halloysite 1 and exchange water with an initial δD value of −2‰ changed the δD value of the halloysite in a positive direction from −37 to −19‰ (MHD-1742 and MHD-1945), whereas an exchange experiment (MHD-1819) using water with more negative δD value shifted the halloysite δD to a more negative value. These results support the conclusion of Lawrence and Taylor (1972) that hydrogen isotopes in halloysite are measurably exchangeable with water vapor at room temperature on relatively short time scales (59–118 h).

Various parameters calculated from the exchange experiments are presented in Table 2. Relative humidities (RH) in the exchange systems were determined by first calculating the μmol of water vapor that are expected in the chamber if the vapor is in equilibrium with *liquid* water at 22°C. Then, the RH in the chamber was calculated by normalizing the measured amount of water vapor to the calculated equilibrium amount of water vapor.

Quantities of water calculated to have been adsorbed on halloysite during the exchange experiments are not correlated with the mass of the halloysite or with the amount of capillary water introduced into the system. In contrast, the calculated μmol of water vapor adsorbed on halloysite during exchange and the μmol of water recovered during the initial outgassing at 100°C prior to exchange *are* well correlated (Figure 1a). The ratio of the calculated amount of water adsorbed on halloysite during exchange to the amount of water recovered during the initial outgassing at 100°C is plotted against the RH value in Figure 1b. The strong correlation in Figure 1a and lack of correlation in Figure 1b suggest that the quantity of exchange water adsorbed on halloysite was determined by the number of adsorption sites vacated when the mineral was originally outgassed at 100°C. The correlation is not controlled by the vapor pressure in the system.

Heating the samples for 60 min at 250°C *in vacuo* (with continuous removal of evolved water by freezing it in a multi-coiled trap cooled by liquid nitrogen) removed ~20–26% of the total amount of stoichiometric H in halloysite in all experiments (Table 1). Continued heating at 250°C resulted in additional loss of water. Figure 2 shows the mole fraction of hydrogen $[X_S(H_2)]$ remaining in the sample *vs.* the cumulative time of heating for MHD-1945 and MHD-1950. About 40% of the stoichiometric water in halloysite 1 was re-

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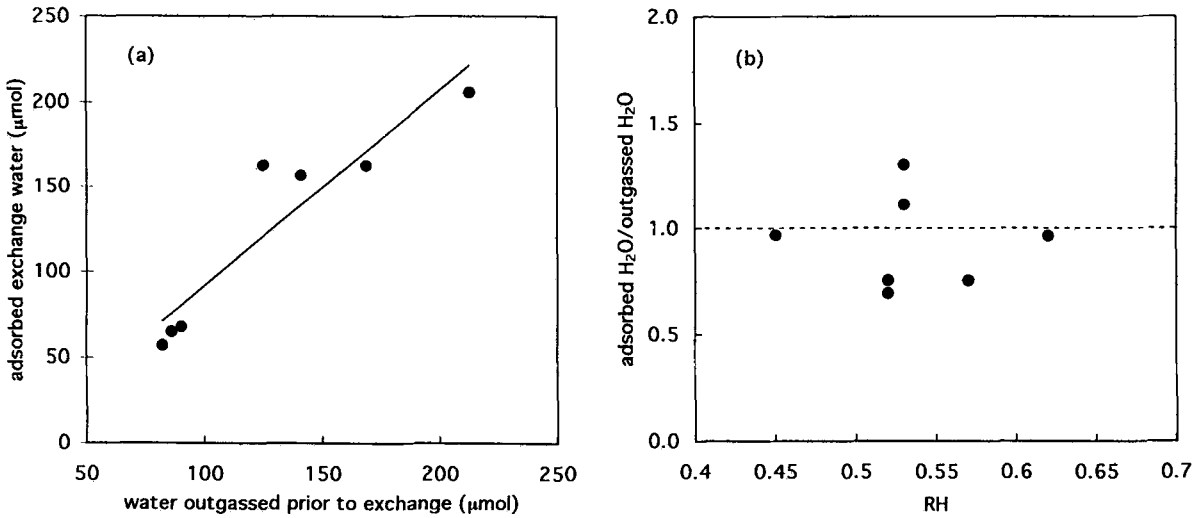


Figure 1. (a) The calculated amount of water adsorbed on halloysite during exchange plotted against water removed during the initial outgassing at 100°C prior to exchange. The slope of the linear regression (solid line) is 1.15, the intercept is −24, and the R^2 value is 0.87. (b) The ratio of the amount of water adsorbed on halloysite during exchange relative to water removed during outgassing at 100°C prior to exchange plotted against the "relative humidity" in the sample chamber. The dotted line represents a reference ratio of unity.

moved when the sample was heated for a total of ~1300 min at 250°C *in vacuo* (Figure 2), and the rate of water loss decreased significantly after 180 min. Despite a lower water content in halloysite 2, a similar proportion (36%) of the water was lost after ~685 min of heating at 250°C (Figure 2).

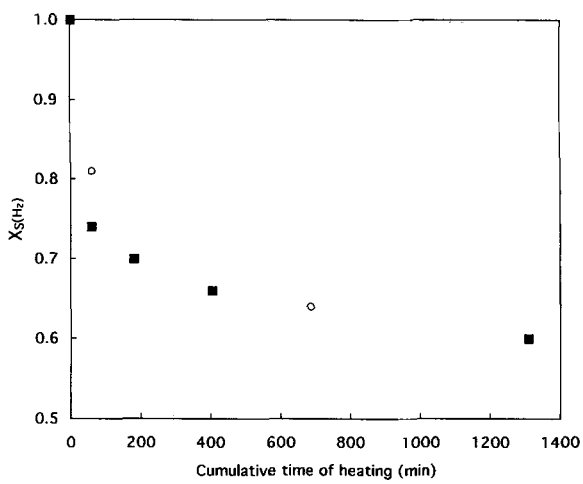


Figure 2. The fraction of hydrogen, $X_S(H_2)$, remaining in the sample plotted against the cumulative time of heating (at 250°C) for halloysite 1, experiment MHD-1945 (■) and for halloysite 2, experiment MHD-1950 (○). The rate of H loss (evolved as water) decreases with time. Despite different total water contents (see footnote to Table 1), between 36–40% of the structural hydrogen of the OH group (reported as water) is lost from both samples after ~685 min of heating at 250°C *in vacuo*.

DISCUSSION

The two exchange experiments using halloysite 1 and water with an initial δD of −2‰ (MHD-1742 and MHD-1945, Table 1) gave final halloysite δD values that were equal (−19‰). This apparent agreement, despite significantly different times of exchange, suggests that equilibrium was approached in the exchange process. Furthermore, MHD-1742 and MHD-1945 show δD values for the final trap vapor which are in reasonable agreement (see Table 1). If all of the exchange experiments did approach equilibrium, the final hydrogen isotopic fractionation between the mineral and vapor should be the same for all samples. An apparent $\alpha_{min\text{-}vap}$ was calculated for all samples (Table 1), where

$$\alpha_{min\text{-}vap} = \frac{(D/H)_{mineral}}{(D/H)_{vapor}} \quad (2)$$

The range of apparent α values is from 1.017 to 1.134. The variation in apparent fractionation factors for the samples (Table 1) is much larger than is expected simply from the propagation of analytical errors. Therefore, in contrast to the conclusion drawn from experiments MHD-1742 and MHD-1945, these disparate α values suggest that hydrogen-isotope exchange equilibrium between halloysite and water vapor was not attained in all experiments. These contrasting conclusions might be reconciled if only a portion of the H in halloysite-hydroxyl groups is involved in isotopic exchange at room temperature on the time scales of the experiments. If so, a simple mass balance model

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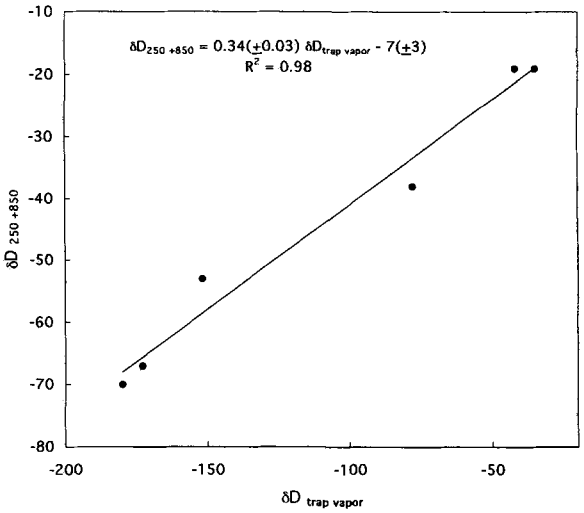


Figure 3. The δD value for structural hydrogen of the OH group in halloysite ($\delta D_{250+850}$) after exchange with water vapor at 22°C plotted against the δD value of the final exchanged water vapor (*i.e.*, trap vapor, see text). The solid line represents a linear regression fitted through the data. The equation for the regression is shown.

for hydrogen-isotope exchange in halloysite at 22°C may be applicable.

The following assumptions are used in this model: 1) from the standpoint of D/H exchange, there are two fractions of structural hydrogen, one that is non-exchangeable on laboratory time scales at 22°C and one that rapidly approaches isotopic equilibrium with ambient water vapor; and 2) the isotopically exchangeable H in halloysite exhibits an isotopic fractionation relative to water vapor that is the same for all samples. The following mass-balance equation (see Yapp and Poths, 1995) results from these assumptions:

$$\delta D_t = X_e \delta D_e + (1 - X_e)\delta D_s, \quad (3)$$

where, δD_t = measured δD value of the total stoichiometric H extracted from halloysite (*i.e.*, weighted average of 250 and 850°C steps); δD_e = δD value of the exchangeable H in halloysite; δD_s = δD value of the non-exchangeable H in halloysite, and X_e = the exchangeable H as a mole fraction of total stoichiometric H in halloysite.

The second assumption suggests that δD_e is related to the final δD value of the exchange vapor (δD_v) by an equilibrium-fractionation factor. Thus,

$$\delta D_e = \alpha_{e-v}(1000 + \delta D_v) - 1000, \quad (4)$$

where α_{e-v} is the equilibrium-fractionation factor between the exchangeable H in halloysite and water vapor at ~22°C. A combination of Equations (3) and (4) yields the following:

$$\delta D_t = \alpha_{e-v} X_e(\delta D_v) + [\delta D_s(1 - X_e) + 1000X_e(\alpha_{e-v} - 1)]. \quad (5)$$

Let

$$m = \alpha_{e-v} X_e, \quad (6)$$

$$b = [\delta D_s(1 - X_e) + 1000X_e(\alpha_{e-v} - 1)], \quad \text{and} \quad (7)$$

$$\delta D_t = m\delta D_v + b. \quad (8)$$

If α_e, X_e, and δD_s are constant for all samples, then m and b are constant, and a plot of δD_t *vs.* δD_v is linear.

For most materials, the values of equilibrium fractionation factors are very close to unity. Thus, if $\alpha_{e-v} \approx 1$, then $m \approx X_e$. Figure 3 presents a plot of δD_t *vs.* δD_v for the exchange experiments (where δD_v is the δD of the trap vapor). Despite some scatter, the data define a linear relationship with a slope of 0.34 ± 0.03, an intercept of −7 ± 3, and an R^2 value of 0.98. This suggests that X_e has a value of ~0.34 for halloysite.

During the first hour of heating *in vacuo* at 250°C, 20–26% of the total stoichiometric H was removed for all samples. Upon further heating for as long as 1315 min at 250°C (sample MHD-1945), ≤40% of the total stoichiometric H was removed from halloysite (Figure 2). This fraction is somewhat larger than the X_e value deduced from the room temperature exchange experiments. The thermal breakdown characteristics of pedogenic halloysite at 250°C *in vacuo* may not be precisely relevant to the hydrogen-isotope exchange properties of halloysite at 22°C for the time scales of these exchange experiments, but both sets of data indicate the presence of some relatively weakly bound H in hydroxyl groups.

Differential thermal analysis (DTA) of halloysite (*e.g.*, Johnson *et al.*, 1990) indicates that, in terms of thermal response, there is only one type of H in structural hydroxyl in halloysite. The D/H exchange experiments discussed herein suggest that only about one third of the H in these pedogenic halloysites is rapidly exchanged at 22°C. These different results might be reconciled, if the exchangeable H in the pedogenic halloysites is related to the effective surface area of the sample. However, this possibility can not be evaluated with our present data.

There may be an isotopic fractionation between oxygen atoms of the OH groups lost upon heating at 250°C and the remaining (non-hydroxyl) oxygen atoms. Such a fractionation has been observed for other clays (*e.g.*, Bechtel and Hoernes, 1990; Girard and Savin, 1996). Incremental heating experiments *in vacuo* on kaolinite show no significant weight loss until temperatures above 350°C (Girard and Savin, 1996). Thus, the kaolinite structure does not decompose until those temperatures. Kaolinites are routinely outgassed for 60 min at 200–250°C *in vacuo* prior to reaction with BrF_5 for oxygen isotopic analysis. This outgas-

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sing removes water adsorbed on mineral surfaces, and Savin (1967) noted that removal of adsorbed water does not affect the $\delta^{18}O$ value of structural oxygen in kaolinite. The loss of stoichiometric water from halloysite at 250°C *in vacuo* suggests that the kaolinite outgassing procedure may not be appropriate for pedogenic halloysite. Based on the total hydrogen yield for halloysite 1 (*i.e.,* ~14.4 wt. % as H_2O), the outgassing at 100°C used in these halloysite-exchange experiments does not seem to remove any structural H. Therefore, routine analyses for the $\delta^{18}O$ value of halloysite should probably not include outgassing *in vacuo* at temperatures much higher than ~100°C. However, the results of this work do not indicate an optimal time interval for outgassing.

CONCLUSIONS

Results of the hydrogen-isotope exchange experiments suggest that ~34% of the total H in pedogenic halloysite can be exchanged at ~22°C in a few days (59–118 h in these experiments). The question of the time scale for isotopic exchange at low temperature of the remaining H remains unresolved. This reinforces the observation of Lawrence and Taylor (1972) that H in halloysite rapidly exchanges isotopes with ambient H_2O at room temperature.

The thermal-breakdown behavior of pedogenic halloysite *in vacuo* is different from kaolinite, despite having the same ideal chemical composition. Kaolinite does not undergo significant loss of stoichiometric H until ~350°C, while halloysite loses ~40% of its stoichiometric hydrogen over 1315 min of heating at 250°C.

Kaolinites are routinely outgassed at 200–250°C for oxygen isotopic analyses. Routine analyses of halloysite should probably include outgassing at lower temperatures (~100°C) because of the loss of stoichiometric hydroxyl (lost as water) at higher temperatures. An optimal outgassing time and temperature remain to be determined. Loss of stoichiometric hydrogen from OH groups in halloysite would imply that both δD and $\delta^{18}O$ measurements of halloysite which had been outgassed at ~250°C would not be the correct values for the undisturbed structure.

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