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 \[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\]. Halloysite, however, often contains water of hydration (i.e., \[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4.n\text{H}_2\text{O}\]), 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 \(\delta^{18}\text{O}\) values. These isotopic analyses produced low oxygen yields and \(\delta^{18}\text{O}\) 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-
Table 1. Data from hydrogen isotope exchange experiments at 22°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial exchange water Mass (mg)</th>
<th>Initial exchange water (μmol)</th>
<th>22°C exchange time (min)</th>
<th>Trap vapor Yield (μmol)</th>
<th>δD</th>
<th>Vapor + 100°C Yield (μmol)</th>
<th>δD</th>
<th>250°C Yield (μmol)</th>
<th>δD</th>
<th>Time (min)</th>
<th>δD</th>
<th>850°C Yield (μmol)</th>
<th>δD</th>
<th>H₂O wt. %</th>
<th>δD</th>
<th>Apparent δH₂O,ppx</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halloysite 1</td>
<td>1742</td>
<td>58.2</td>
<td>339</td>
<td>-2</td>
<td>3572</td>
<td>23</td>
<td>-42</td>
<td>304</td>
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<td>112</td>
<td>-4</td>
<td>60</td>
<td>362</td>
<td>-24</td>
<td>14.7</td>
<td>-19</td>
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<tr>
<td></td>
<td>1747</td>
<td>53.7</td>
<td>339</td>
<td>-184</td>
<td>3610</td>
<td>23</td>
<td>-152</td>
<td>325</td>
<td>-203</td>
<td>123</td>
<td>-84</td>
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<td>374</td>
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<td></td>
<td>1819</td>
<td>59.4</td>
<td>356</td>
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<td>5784</td>
<td>18</td>
<td>-173</td>
<td>329</td>
<td>-98</td>
<td>103</td>
<td>-30</td>
<td>60</td>
<td>315</td>
<td>-40</td>
<td>14.4</td>
<td>-38</td>
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<tr>
<td></td>
<td>1834</td>
<td>52.3</td>
<td>372</td>
<td>-105</td>
<td>3943</td>
<td>25</td>
<td>-78</td>
<td>329</td>
<td>-98</td>
<td>103</td>
<td>-30</td>
<td>60</td>
<td>315</td>
<td>-40</td>
<td>14.4</td>
<td>-38</td>
</tr>
<tr>
<td></td>
<td>1945</td>
<td>43.6</td>
<td>256</td>
<td>-2</td>
<td>6575</td>
<td>23</td>
<td>-35</td>
<td>220</td>
<td>-27</td>
<td>86</td>
<td>-5</td>
<td>60</td>
<td>200</td>
<td>-27</td>
<td>14.4</td>
<td>-19</td>
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<tr>
<td></td>
<td>1945 (second 250°C action)</td>
<td></td>
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<td>1945 (third 250°C action)</td>
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<tr>
<td></td>
<td>1945 (fourth 250°C action)</td>
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<tr>
<td>Halloysite 2</td>
<td>1947</td>
<td>31.1</td>
<td>228</td>
<td>-256</td>
<td>7070</td>
<td>21</td>
<td>-180</td>
<td>196</td>
<td>-198</td>
<td>37</td>
<td>-78</td>
<td>60</td>
<td>151</td>
<td>-68</td>
<td>10.8</td>
<td>-70</td>
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<td></td>
<td>1950</td>
<td>32.7</td>
<td>228</td>
<td>-2</td>
<td>7065</td>
<td>21</td>
<td>—</td>
<td>203</td>
<td>-41</td>
<td>38</td>
<td>-10</td>
<td>60</td>
<td>125</td>
<td>-24</td>
<td>10.8</td>
<td>-24</td>
</tr>
<tr>
<td></td>
<td>1950 (second 250°C action)</td>
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</table>

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.

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...
Table 2. Parameters calculated from exchange experiments.

<table>
<thead>
<tr>
<th>Sample MHD #</th>
<th>Outgassed water$^1$ (μmol)</th>
<th>Ads. excl. water$^2$ (μmol)</th>
<th>RH$^3$</th>
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</thead>
<tbody>
<tr>
<td>1742</td>
<td>125</td>
<td>163</td>
<td>0.53</td>
</tr>
<tr>
<td>1747</td>
<td>141</td>
<td>157</td>
<td>0.53</td>
</tr>
<tr>
<td>1819</td>
<td>213</td>
<td>206</td>
<td>0.45</td>
</tr>
<tr>
<td>1834</td>
<td>169</td>
<td>163</td>
<td>0.62</td>
</tr>
<tr>
<td>1945</td>
<td>90</td>
<td>68</td>
<td>0.57</td>
</tr>
<tr>
<td>1947</td>
<td>82</td>
<td>57</td>
<td>0.52</td>
</tr>
<tr>
<td>1950</td>
<td>86</td>
<td>64</td>
<td>0.52</td>
</tr>
</tbody>
</table>

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 [Al₂Si₂O₅(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 [Xₘ(H₂)] 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-
moved when the sample was heated for a total of \( \sim 1300 \) min at \( 250^\circ C \) 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 \( \sim 685 \) min of heating at \( 250^\circ C \) (Figure 2).

**DISCUSSION**

The two exchange experiments using halloysite 1 and water with an initial \( \delta D \) of \(-2\%\) (MHD-1742 and MHD-1945, Table 1) gave final halloysite \( \delta D \) 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 \( \delta D \) 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 \( \alpha_{\text{min-vap}} \) was calculated for all samples (Table 1), where

\[
\alpha_{\text{min-vap}} = \frac{(D/H)_{\text{mineral}}}{(D/H)_{\text{vapor}}}
\]

The range of apparent \( \alpha \) 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 \( \alpha \) 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
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:

\[ \delta D_t = X_e \delta D_e + (1 - X_e) \delta D_n, \]  

where, \( \delta D_t \) = measured \( \delta D \) value of the total stoichiometric H extracted from halloysite (i.e., weighted average of 250 and 850°C steps); \( \delta D_e \) = \( \delta D \) value of the exchangeable H in halloysite; \( \delta D_n \) = \( \delta D \) 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 \( \delta D_e \) is related to the final \( \delta D \) value of the exchange vapor (\( \delta D_v \)) by an equilibrium-fractionation factor. Thus,

\[ \delta D_e = \alpha_{e-v} (1000 + \delta D_v) - 1000, \]

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

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

Let

\[ m = \alpha_{e-v} X_e, \]

\[ b = [\delta D_v (1 - X_e) + 1000X_e(\alpha_{e-v} - 1)], \]  

and

\[ \delta D_v = m \delta D_e + b. \]

If \( \alpha_{e-v}, X_e \), and \( \delta D_v \) are constant for all samples, then \( m \) and \( b \) are constant, and a plot of \( \delta D_v \) vs. \( \delta D_t \) 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 \( \delta D_v \) vs. \( \delta D_t \) for the exchange experiments (where \( \delta D_t \) is the \( \delta D \) of the trap vapor). Despite some scatter, the data define a linear relationship with a slope of 0.34 ± 0.03, an intercept of \( \sim 7 \pm 3 \), and an \( R^2 \) value of 0.98. This suggests that \( X_e \) has a value of \( \sim 0.34 \) 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), \( \leq 40% \) 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.
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$_2$O), 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$_2$O 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 $\delta$D 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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**REFERENCES**


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