**$^{18}\text{O}/^{16}\text{O}$ In CO_2 Evolved From Goethite During Some Unusually Rapid Solid State
 $\alpha\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$ Phase Transitions: Test of an Exchange Model For Possible
Use In Oxygen Isotope Analyses Of Goethite**

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ABSTRACT

The initial ~ 60% of an isothermal vacuum dehydration of goethite can commonly be approximated by first order kinetics. Also, natural goethites contain small amounts of an Fe(CO₃)OH component in apparent solid solution. The ¹⁸O/¹⁶O of CO₂ evolved from the Fe(CO₃)OH during isothermal vacuum dehydrations is related to the ¹⁸O/¹⁶O of the goethite by an apparent fractionation factor (α_{app}) that is, in turn, correlated with a first order rate constant, $|m|$. A kinetic exchange model predicts that α_{app} should decrease as $|m|$ increases for a range of $|m|$ that corresponds to relatively slow rates of dehydration. This pattern has been observed in published results. In contrast, for rapid rates of dehydration, α_{app} is predicted to increase with increasing $|m|$. Isothermal vacuum dehydrations of two natural goethites had unusually large values of $|m|$ and provided serendipitous tests of this rapid-rate prediction. For these experiments, the measured values of α_{app} were consistent with patterns of variation predicted by the model. This allowed an estimate of the activation energy (E_2) of a model parameter, K_2 , which is the rate constant for oxygen isotope exchange between CO₂ and H₂O during the solid-state goethite to hematite phase transition. The estimated value of E_2 is only ~ 9 kJ/mol. Heterogeneous catalysis tends to decrease the activation energies of gas reactions. Consequently, the inferred value of E_2 suggests that goethite and/or hematite catalyze oxygen isotope exchange between CO₂ and H₂O during the solid-state phase change.

Yield, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values are routinely measured for increments of CO₂ evolved from the Fe(CO₃)OH component during isothermal vacuum dehydration of goethite. Model-predicted values of α_{app} can be combined with plateau $\delta^{18}\text{O}$ values of the evolved CO₂ to estimate the $\delta^{18}\text{O}$ of the goethite with a less than optimal, but potentially useful, precision of about $\pm 0.8\text{‰}$. Therefore, a single analytical procedure (incremental dehydration) applied to one aliquot of a sample could provide not only $\delta^{13}\text{C}$ and mole fractions (X) of the Fe(CO₃)OH component, but also hydrogen yield, δD , and the approximate $\delta^{18}\text{O}$ value of the goethite. Recovery of multiple types of geochemical data from a single aliquot would be particularly useful if the amount of sample available for analysis were limited. Also, the method could be used to estimate the $\delta^{18}\text{O}$ value of goethite in mixtures of minerals not amenable to selective dissolution – e.g., goethite admixed with hematite.

1. INTRODUCTION

The mineral goethite (α -FeOOH) is a common product of chemical weathering in wet, oxidizing environments (e.g., Garrels and Christ, 1965; Schwertmann, 1988). Because of this environmental selectivity, the stable isotope composition of structural oxygen in goethite can be an important source of information on surface and near-surface paleotemperatures as well as the isotopic characteristics of ancient meteoric waters (Bird et al, 1992, 1993; Hein et al., 1994; Girard et al., 1997, 2000, 2002; Bao et al., 2000; Pack et al., 2000; Poage et al., 2000; Sjostrom et al., 2004; Tabor et al., 2004a; Fifarek and Rye, 2005; Seidel et al, 2005; Tabor and Yapp, 2005a; Hren et al., 2006; Grosz et al, 2006; Dideriksen et al., 2010; Yapp, 1987a, 1991, 1993a, 1993b, 1997, 1998, 2000, 2008; Yapp and Shuster, 2011; Gulbranson et al., 2015).

One or more fine-grained oxygen-bearing substances such as silica, aluminosilicates, Al-oxides/hydroxides, carbonates, phosphates, etc., are associated with goethites in most natural occurrences, and the goethite is not generally separable from these mixtures by physical methods. The BrF₅ fluorination technique of Clayton and Mayeda (1963) is commonly used to extract oxygen from goethite for isotopic analysis, but it also extracts the oxygen from the admixed minerals, thus producing a gas whose $\delta^{18}\text{O}$ value represents the mixture rather than the $\delta^{18}\text{O}$ value of the end-member FeOOH that might have been targeted for paleoenvironmental interpretation. Studies of oxygen isotopes in natural goethites have dealt with this problem by combining various selective dissolution methods with chemical analyses, isotopic measurements, and mass balance calculations to determine the $\delta^{18}\text{O}$ values of the FeOOH. Selective dissolution techniques are reliable if the admixed minerals have significantly different degrees of solubility in the NaOH, CBD, and HCl solutions that are commonly employed in the method (e.g., Kampf and Schwertmann, 1982; Yapp, 1991, Bird et al., 1992; Girard et al., 2000).

However, there is an important limitation in these selective dissolution methods. Goethite in natural systems is often intimately mixed with hematite (e.g., Bird et al, 1992; Yapp, 1993a; Girard et al., 2002; Ramanaidou et al., 2003), and the solubilities are similar enough that current selective dissolution techniques are not useful in the determination of their respective $\delta^{18}\text{O}$ values. Girard et al. (2000) worked on a deposit

that could be effectively microsampled, but even then they noted that, in some samples, cross contamination of a few percent was unavoidable (although it was not expected to have a significant effect on measured $\delta^{18}\text{O}$ values). Thus, another analytical method for determining the $\delta^{18}\text{O}$ of goethite would be of value. Such a method may derive from an unusual aspect of the geochemistry of goethite.

Stoichiometric oxygen is not the only reservoir of oxygen in goethite crystals. Russell et al. (1975) showed that ambient CO_2 is adsorbed on goethite when the carbon atom in a CO_2 molecule binds weakly to a structural oxygen atom (possibly in channels on the surfaces of goethite crystals) to form an asymmetric carbonate molecule. Because the structural oxygen atom on the goethite surface is bound in turn to an Fe atom in the crystal, a de facto Fe(III) carbonate is formed. During crystal growth, this weakly chemisorbed CO_2 is presumably occluded in the goethite structure as an $\text{Fe}(\text{CO}_3)\text{OH}$ component in solid solution (Yapp, 1987b), and infrared spectroscopy has affirmed the existence of such a component (Yapp and Poths, 1990; Boily et al., 2006). Therefore, the formula for goethite may be written as $\text{Fe}[\text{O}_{(1-X)}(\text{CO}_3)_X]\text{OH}$, where $0 \leq X \ll 1$.

During incremental isothermal vacuum dehydration (dehydroxylation) of goethite to hematite, there is a correlated loss of CO_2 and H_2O , and the overall reaction for the phase transition can be represented as:

“Plateau” $\delta^{13}\text{C}$ values and hydrogen-normalized amounts of the evolved CO_2 are, respectively, measures of the $\delta^{13}\text{C}$ and mole fraction (X) of the $\text{Fe}(\text{CO}_3)\text{OH}$ component in goethite (e.g., Yapp and Poths, 1991, 1993; Hsieh and Yapp, 1999; Tabor et al., 2004b). For natural goethites analyzed thus far, values of X have commonly been on the order of 0.01 or less, with none greater than 0.022 (Yapp, 2001, 2002; Tabor et al., 2004b, Tabor and Yapp, 2005b; Feng and Yapp, 2009; Gulbranson et al., 2011).

Under open system conditions in an incremental isothermal dehydroxylation, the early steps (i.e., the first ~ 60 % of dehydration) can often be approximated by first order kinetics (Criado et al., 1984; Goss, 1987; Yapp, 2003) as follows.

$$\frac{d[X_s(H_2)]}{dt} = -m[X_s(H_2)] \quad (1)$$

Now, let $|m|$ = the absolute value of the phenomenological first order slope determined from dehydration data plotted as “ $\ln X_S(H_2)$ ” vs. “ t ”. See the appendix for additional definitions of terms.

Successive increments of CO_2 evolved from the $Fe(CO_3)OH$ component during isothermal, open system vacuum dehydration may exhibit “plateau” $\delta^{18}O$ values. Such plateau values are related to the $\delta^{18}O$ of the $FeOOH$ by an apparent fractionation factor ($^{18}\alpha_{app}$). A relationship between $^{18}\alpha_{app}$ and $|m|$ is predicted by a simple kinetic model in which isothermal vacuum dehydration proceeds via a migrating, intermediate, “transition state” volume (Yapp, 2003). During breakdown of goethite, oxygen isotope exchange is assumed to occur only among chemical species within those successive volumes. The overall dehydration reaction sequence is summarized as follows:

Some x-ray diffraction (XRD) studies of solid-state, synthetic goethite to hematite phase transitions suggest the presence (at *ca.* 230 °C) of an intermediate “protohematite” that retains significant hydroxyl (e.g., Wolska and Schwertmann, 1989; Gualtieri and Venturelli, 1999). Those experiments were carried out in air at ambient room pressures. At a total system pressure of ~ 0.2 bar of O_2 , the rate of isothermal breakdown of goethite to hematite at 230 °C is substantially slower than the rate in vacuum (Yapp, 1983). This suggests that protohematite might have been a significant intermediate phase in those XRD/dehydration experiments, in part, because loss of hydroxyl was retarded by the presence of ambient air. On the other hand, Prasad et al (2006) concluded from in situ FTIR studies of the dehydration of natural and synthetic goethite that there was no evidence for the presence of intermediate proto-hematite during the solid-state phase transition.

The possible existence of proto-hematite as a transitional species during the solid-state goethite to hematite phase change suggests that the simple formula ($Fe_2O_3^*$) in Eq. 2 might not be an exact representation of the composition of the transition state solid. Nevertheless, to the extent that the kinetic exchange model accounts for the oxygen isotope effects observed in isothermal vacuum dehydrations of natural goethite, the formulation in Eq. 2 could be considered a useful first approximation, and the postulate

of a small transition volume that migrates with the reaction front remains an important aspect of the model.

The relevant reactions for single-atom oxygen isotope exchange are assumed to be:

The preceding exchange reactions and considerations of flux balance during pseudo-first order isothermal dehydration of goethite to hematite led to the following model equation (Yapp, 2003):

$$^{18}\alpha_{app} = \alpha_{CO_2-V} \frac{\left\{ \frac{|m|}{2\Phi K_1 \alpha_{G-V}} + \frac{1}{Y_H} \right\}}{\left\{ \frac{|m|}{2\Phi K_1} + \frac{Y_V}{Y_H} + \alpha_{H-V} \right\}} \left\{ 1 - e^{-\left[\frac{2\Phi K_2}{|m|} \right]} \right\} + \alpha_0 e^{-\left[\frac{2\Phi K_2}{|m|} \right]} \quad (5)$$

Terms are defined in the appendix. As seen in Eq. 5, the modeled relationship between $^{18}\alpha_{app}$ and $|m|$ depends, among other things, on the relative magnitudes of the forward rate constants (K_1 and K_2) of exchange reactions 3 and 4.

Eq. 5 was used to calculate a family of curves (Fig. 1) that depict predicted relationships between $^{18}\alpha_{app}$ and $|m|$ at a dehydration temperature of 215 °C for different choices of the ratio K_2/K_1 . Relevant values of the various model parameters used in the calculations, including fractionation factors (α) and $2\phi K_1$, were taken from Yapp (2003) and references therein.

For each model curve of Fig. 1, there is a predicted minimum in the value of $^{18}\alpha_{app}$. The magnitude of $^{18}\alpha_{app}$ at each minimum and the corresponding value of $|m|$ at that minimum are different for different choices of K_2/K_1 at 215 °C. For $K_2/K_1 = 1000$, the minimum in $^{18}\alpha_{app}$ occurs at a value of $|m|$ outside the range for which the curves in Fig. 1 were calculated. Let $|m|_0$ = the value of $|m|$ at a minimum in $^{18}\alpha_{app}$. For any particular isothermal model curve, “slow-rate” dehydrations are defined in this work to be those for which $|m| < |m|_0$, whereas “rapid-rate” dehydrations are those for which $|m| > |m|_0$.

In slow-rate goethite dehydration experiments, values of $^{18}\alpha_{\text{app}}$ are predicted to decrease as $|m|$ increases, whereas $^{18}\alpha_{\text{app}}$ is expected to increase with increasing $|m|$ for rapid-rate dehydrations.

Experimentally determined values of $^{18}\alpha_{\text{app}}$ and $|m|$ for vacuum dehydrations of natural goethites were reported by Yapp (2003). For reference, those results are listed in Table 1 and plotted in Fig. 1. With the exception of a kaolinite-rich sample (MSwitz-1 in Table 1; open diamond in Fig. 1), those data constitute a generally coherent array for which increasing values of $|m|$ correspond to decreasing values of $^{18}\alpha_{\text{app}}$. This pattern is consistent with the slow-rate predictions of model curves for which $K_2/K_1 \geq \sim 15$ (Fig. 1). There is some scatter in the slow-rate data array of Fig. 1, but the scatter is related, in part, to the temperature of dehydration, which facilitated a model-based estimate of the temperature dependence of $2\Phi K_1$ (Yapp, 2003).

Measured, first order dehydration rates and the kinetic exchange model described above could be used to estimate oxygen isotope fractionation factors between CO_2 evolved from the $\text{Fe}(\text{CO}_3)\text{OH}$ component and structural oxygen in FeOOH . These fractionation factors could then be used in conjunction with measured plateau $\delta^{18}\text{O}$ values of the evolved CO_2 (if such plateaus are present) to estimate a $\delta^{18}\text{O}$ value of goethite in mixtures of goethite and hematite. However, for the method to be considered credible, additional predictions of the model need to be tested, most notably the prediction that there are minima in the model curves. This prediction could be tested with results from rapid-rate dehydrations of goethite at $T \leq 230^\circ\text{C}$. The constraint of an upper temperature limit of 230°C is imposed for these tests, because the identification of any new dehydration experiments as inherently rapid-rate is accomplished by comparison with the slow-rate data of Table 1 for which $T \leq 230^\circ\text{C}$ and $|m| \leq 0.0124 \text{ min}^{-1}$. If the existence of minima in the curves is supported by rapid rate data, the results would further constrain the magnitude of K_2/K_1 .

This paper presents previously unpublished oxygen isotope results from incremental vacuum dehydrations of two natural goethite samples. In these experiments, variously performed at temperatures from 173 to 215°C , early rates of dehydration were unusually rapid. The implications of these serendipitous results for the kinetic exchange model and its use in the analysis of $\delta^{18}\text{O}$ values of goethite are discussed.

2. SAMPLES AND EXPERIMENTAL METHODS

2.1. Samples

The natural goethite sample, Ax-2, was provided by Dr. Hope Jahren and is from Axel Heiberg Island in the Canadian Arctic (Jahren and Sternberg, 2002; Jahren et al., 2009). A description of the sample can be found in Yapp and Shuster (2011). As noted therein, XRD analysis detected no substitution of Al for Fe in the goethite, and there was no XRD-detectable gibbsite. Thus, there is no contamination from CO₂ occluded in gibbsite (e.g., Schroeder and Melear, 1999; Tabor and Yapp, 2005c). Minor amounts of XRD-detectable lepidocrocite (γ -FeOOH) and hematite are present in Ax-2, but the amounts appear to be too small to be of analytical significance (Yapp and Shuster, 2011).

Sample ICAlas-1 (chemical analysis in Yapp, 2000) was from gossan associated with the Illinois Creek ore prospect in the Kaiyah Mts. of Alaska, USA, and was provided by Dr. Virginia Gillerman. The sample was dominated by goethite pseudomorphed after siderite. It also contained accessory quartz and an unidentified ~ 10 Å mineral, but had no XRD-detectable gibbsite.

2.2. Stable isotope analysis

Analytical methods used in the vacuum dehydration experiments have been discussed elsewhere (Yapp and Poths, 1991; 1993; Hsieh and Yapp, 1999; Yapp 2003). However, a brief summary is provided here. The goethite samples were powdered under reagent-grade acetone and passed through a 63-micron brass sieve. Powders were treated for 16 h at room temperature with 0.5 to 1.0 M reagent-grade HCl, then repeatedly rinsed with aliquots of deionized water until the pH of the rinse water remained at its initial value after 10 minutes of contact with the sample. The rinse water was decanted, and samples were treated at room temperature with successive aliquots of 30% H₂O₂ solution over a period of 30 days to remove easily oxidized organic matter. After decanting the final H₂O₂ solution, the samples were dried under vacuum at room temperature. These samples were termed “cleaned”.

For each incremental dehydration experiment (Table 2), the cleaned goethite sample was outgassed, first at ~ 22 °C and then at 100°C, under open system conditions in vacuum for a specified time to remove adsorbed H₂O and CO₂ (step 1). The second dehydration increment (step 2) in each experiment was performed under closed system

conditions in ~ 0.16 bar of pure O_2 for specified times and temperatures (Table 2). The system was closed in the sense that the evolved H_2O and CO_2 gases were not removed from the dehydration chamber until the end of the specified time, when they were then frozen into a liquid-nitrogen-cooled, multiple-coil trap, and O_2 was pumped away. Successive, timed, open system dehydration steps (Table 2) were then performed in vacuum ($\sim 2 \times 10^{-6}$ bar). The “open system” descriptor refers to the fact that as the H_2O and CO_2 egressed from the goethite, the gases were immediately removed from the dehydration chamber by freezing into a liquid-nitrogen-cooled, multiple-coil trap. In each experiment, a final dehydration step was performed at $850^\circ C$ under closed system conditions in ~ 0.16 bar of O_2 to recover any hydrogen (as H_2O) and carbon (as CO_2) that remained in the sample.

After each timed dehydration step, the increments of evolved CO_2 and H_2O frozen in the multiple-coil trap were separated cryogenically using a dry ice-methanol slush to sublimate the CO_2 . Note: for oxygen isotope applications, the frozen mixture of CO_2 and H_2O should *not* be thawed and refrozen in the multiple-coil trap prior to cryogenic separation. The amount of CO_2 recovered from a step was measured with a mercury manometer that resolved differences of about $0.1 \mu mol$. Oxygen and carbon isotope ratios of increments of CO_2 were measured on a Finnigan multi-collector, gas-source, isotope-ratio mass spectrometer. The isotope ratios are reported in the standard “ δ ” notation:

$$\delta^{18}O \text{ or } \delta^{13}C = \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right] \times 1000\text{‰}$$

$R = {}^{18}O/{}^{16}O$ or ${}^{13}C/{}^{12}C$ depending upon which element is represented. For oxygen, the standard is V-SMOW; for carbon it is V-PDB. Hereafter, the standards are referred to as SMOW and PDB, respectively. The overall analytical precision of $\delta^{18}O$ and $\delta^{13}C$ measurements was $\pm 0.2\text{‰}$. Each evolved increment of H_2O was quantitatively converted to H_2 gas over depleted uranium metal at $760^\circ C$. A Toepler pump was used to measure yields of H_2 with a precision of $\pm 1 \mu mol$.

3. RESULTS

Results from the incremental dehydrations of two aliquots of Ax-2 (Experiments 1 and 2) are in Table 2 and include the duration of each step, the amount and

isotopic composition of evolved CO₂ and the corresponding amount of H₂O (measured as H₂). Table 2 also includes results from ICA_{Las}-1, for which there was sufficient material to perform a stepwise dehydration experiment. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of increments of evolved CO₂ are plotted against $X_V(\text{H}_2)$ in Fig. 2 for all three experiments. $X_V(\text{H}_2)$ is the cumulative hydrogen in the evolved water as a mole fraction of the total hydrogen in the sample and is calculated exclusive of the respective step 1 values. $X_V(\text{H}_2) = 1.00$ when the sample has been completely dehydrated.

3.1. HTN water

3.1.1 HTN water in Ax-2

After first outgassing the sample at $\sim 22^\circ\text{C}$ and then 100°C in vacuum, Yapp and Shuster (2011) used isotope exchange experiments at room temperature (22°C) to demonstrate that a very high proportion ($\sim 47\%$) of the hydrogen in the outgassed Ax-2 goethite was present in “high temperature nonstoichiometric” (HTN) water (Yapp and Poths, 1995). By comparison, 49% [$X_V(\text{H}_2) = 0.49$] of the total hydrogen in an outgassed aliquot of Ax-2 (i.e., exclusive of hydrogen from step 1) was removed at 215°C in step 2 of dehydration Experiment 1 (Table 2). Unless it is accidental, the similarity of the $X_V(\text{H}_2)$ value (0.49) to the fraction of HTN hydrogen (0.47) suggests that most, or all, of the hydrogen recovered from step 2 in Experiment 1 originated as HTN water.

The preceding supposition is generally supported by the infrared results of Boily et al. (2006), which indicate that nonstoichiometric water is evolved from goethite at *ca.* 200°C prior to the loss of structural hydroxyl. Moreover, loss of structural hydroxyl hydrogen from goethite is suppressed when a dehydration step (e.g., step 2 in Table 2) is performed in the presence of ~ 0.16 bar O₂ under closed system conditions (Yapp, 1983). Thus, the hydrogen recovered from Ax-2 in closed system step 2 of Experiment 1 appears to have been derived overwhelmingly from HTN water.

For closed system step 2 in Experiment 2, the temperature was only 180°C , and $X_V(\text{H}_2)$ for that Ax-2 aliquot was only 0.23 (Table 2). However, the H₂O subsequently recovered in the non-isothermal ($155 - 175^\circ\text{C}$) open system vacuum dehydration of step 3 brought the value of $X_V(\text{H}_2)$ to 0.44, which is comparable to the value of 0.47 for HTN hydrogen in Ax-2 goethite. This suggests that, in Experiment 2, the hydrogen recovered from steps 2 and 3 originated predominantly in HTN water.

3.1.2. HTN water in ICAlas-1

If it is assumed that the small amounts of Al and Mn in ICAlas-1 occur as minor substituents (~ 1.7 and ~ 2.6 mol %, respectively) for Fe in the goethite structure, the chemical analyses reported by Yapp (2000) indicate that about 16% of the total water recovered from ICAlas-1 is “excess” water (i.e., HTN water). The incremental dehydration data for ICAlas-1 in Table 2 show that, exclusive of step 1, about 11% of the total hydrogen (as H_2O) was recovered in closed-system step 2 at 200 °C. Over the temperature interval from ~ 130 °C to 200 °C, infrared spectroscopy suggests that the water evolved from progressive heating of synthetic goethite (at a rate of 12 °C/min) is primarily nonstoichiometric (Boily et al., 2006). This observation supports an assumption that the hydrogen recovered in step 2 of the ICAlas-1 dehydration was derived primarily from HTN water. If so, the hydrogen recovered in subsequent open-system vacuum dehydration steps (Table 2) was derived overwhelmingly from structural hydroxyl in ICAlas-1.

3.1.3. Summary for HTN water

As a working hypothesis, it is assumed that hydrogen data representing loss of structural, stoichiometric hydroxyl from Ax-2 goethite begin with step 3 in Experiment 1 and with step 4 in Experiment 2. For ICAlas-1, data for evolved stoichiometric hydrogen are presumed to begin with step 3 (see Table 2).

The kinetic data for the ICAlas-1 and Ax-2 dehydration experiments are listed in Table 3, wherein $X_S(\text{H}_2)$ is the hydrogen remaining in the sample after each step as a mole fraction of the “total hydrogen”. For reasons stated above, the total hydrogen in Ax-2 Experiment 1 excludes hydrogen recovered in steps 1 and 2. In Ax-2 Experiment 2, hydrogen from steps 1, 2, and 3 was excluded from the total. For ICAlas-1, hydrogen from steps 1 and 2 was excluded from the calculation of $X_S(\text{H}_2)$.

3.2. Dehydration rates

3.2.1. Ax-2 dehydration rates

For Experiment 1, 30 minutes of open system vacuum dehydration at 215 °C in step 3 removed 66% of the Ax-2 hydrogen [i.e., $X_S(\text{H}_2) = 0.34$]. For Experiment 2, 30 minutes of open system dehydration at 173 °C in step 4 removed 52% of the Ax-2 hydrogen [i.e., $X_S(\text{H}_2) = 0.48$].

If the rate of goethite dehydration can be approximated as first order in $X_S(H_2)$ (Eq. 1), plots of $\ln X_S(H_2)$ against time should be linear. Values of $\ln X_S(H_2)$ from Table 3 are plotted against cumulative elapsed time in Fig. 3A.

The data of Fig. 3A suggest that an approximation of first order kinetics for the Ax-2 dehydrations must be limited to step 3 in Experiment 1 and step 4 in Experiment 2, because of the large extents of reaction attained in those 30-minute steps. Use of increments shorter than 30 minutes to increase the number of data points in the early part of the dehydration experiments was not practicable, because 25 to 30 minutes was about the minimum time required to: (1) separate H_2O and CO_2 recovered from a single step and (2) convert the H_2O to H_2 . While these recovered gases were being processed, the volatiles from the next timed step were accumulating in a multiple-coil cold trap, but they could not be processed until the work on the H_2O and CO_2 from the preceding step had been completed. Therefore, the rapidity of the initial rates of breakdown limited the number of quasi-first order increments in each Ax-2 experiment to one (step 3 in Experiment 1; step 4 in Experiment 2).

The slopes of the quasi-first order portions of the Ax-2 dehydration data are shown in Fig. 3A. In each case, the slope was determined for a two-point line that passed through the origin and the relevant experimental data point. For Experiment 1 at 215 °C, $|m| = 0.036 \text{ min}^{-1}$. For Experiment 2 at 173 °C, $|m| = 0.024 \text{ min}^{-1}$. The values of $|m|$ for Ax-2 are plotted in the histogram of Fig. 4, which also contains values of $|m|$ for the goethites of Table 1 (the latter represent dehydration temperatures from 200 to 230 °C). As seen in Fig. 4, the quasi-first order rates of dehydration for Ax-2 are substantially larger than those of the other natural goethites, irrespective of the specific dehydration temperature (for $173 \text{ °C} \leq T \leq 230 \text{ °C}$).

Wolska and Schwertmann (1989) observed that, when heated in air, synthetic goethites with larger amounts of “excess” water exhibited lower goethite-to-hematite phase transition temperatures. This observation suggests that the large proportion of excess water (i.e., HTN hydrogen) in Ax-2 might be similarly related to the unusual rapidity of its goethite-to-hematite phase transition (at both 173 °C and 215 °C). An investigation of the underlying cause of that rapidity is beyond the scope of this work. However, at the current level of development, the rapid-rate oxygen isotope predictions

of the kinetic exchange model can be tested against the experimental results from Ax-2 without a specific explanation for the rapidity of the solid-state phase change in this sample.

3.2.2. ICAlas-1 dehydration rate

The kinetic data for the isothermal vacuum dehydration of ICAlas-1 are listed in Table 3 and plotted as $\ln X_S(H_2)$ vs. time in Fig. 3B. Of the total hydrogen in ICAlas-1, 54% was evolved as H_2O over a 30 minute interval at 200 °C in a single step (step 3, Table 3). By the same arguments put forth for Ax-2, the data in Fig. 3B suggest that step 3 best approximates first order kinetics for the dehydration of ICAlas-1. A straight line from the origin through the data point of step 3 (Fig. 3B) yields a first order slope $|m|$ of 0.026 min^{-1} . As seen in Fig.4, this value of $|m|$ for ICAlas-1 is larger than any value of $|m|$ reported for the goethite samples of Yapp (2003).

3.3. Oxygen isotopes in evolved CO_2

3.3.1. Ax-2 – CO_2 oxygen isotopes

The speed with which Ax-2 broke down to hematite precluded collection of CO_2 increments sufficiently resolved to reveal definitive plateau values of F and $\delta^{13}C$. However, Yapp and Shuster (2011) concluded that the CO_2 recovered from the initial *isothermal* vacuum dehydration steps in each of the experiments was from the $Fe(CO_3)OH$ component in the goethite. Their conclusion was based on two considerations: (1) In each experiment the initial isothermal, open system step in vacuum represented the breakdown of more than 50% of the goethite and therefore should have dominantly interrogated the $Fe(CO_3)OH$ component. Moreover, the rate of dehydration during that step was so rapid that the contribution of CO_2 from slow oxidation (by the $Fe(III)$ oxide) of any small amounts of residual, refractory organic carbon should have been negligible. The very positive $\delta^{13}C$ values of the evolved CO_2 support this supposition (i.e., 6.8‰ for step 3 in Experiment 1 and 6.5‰ for step 4 in Experiment 2; Table 2). (2) Within analytical uncertainty, the $\delta^{13}C$ values of the CO_2 in those steps were the same for the two experiments even though the vacuum dehydrations were performed at different temperatures. This result is expected if the CO_2 originated overwhelmingly from the $Fe(CO_3)OH$ component, which only breaks down at these temperatures when the confining, local goethite structure breaks down (Yapp and Poths,

1991). At the same time, the $\delta^{18}\text{O}$ value of the CO_2 from Ax-2 Experiment 1 differs from that of Ax-2 Experiment 2. For step 3 in Experiment 1 at 215 °C, $\delta^{18}\text{O} = 10.1\text{‰}$, whereas for step 4 in Experiment 2 at 173 °C, $\delta^{18}\text{O} = 12.3\text{‰}$ (Table 2). This difference in $\delta^{18}\text{O}$ is consistent with temperature-dependent patterns of oxygen isotope variation observed in other experiments (Yapp, 2003).

Thus, it is assumed that the oxygen isotope data from step 3 in Ax-2 Experiment 1 and step 4 in Ax-2 Experiment 2 (Table 2) reflect processes in the solid-state goethite to hematite phase transition at 215 °C and 173 °C, respectively, that can be approximated with first order reaction kinetics (Fig. 3A). If so, the relatively high values of $|m|$ for Ax-2 (Fig. 4) suggest that the associated oxygen isotope data could be used to evaluate the previously untested rapid-rate predictions of the kinetic exchange model (Eq. 5).

3.3.2. ICAlas-1 – CO_2 oxygen isotopes

As noted, the dehydration characteristics of Ax-2 served as a basis for the interpretation of the data from ICAlas-1. For ICAlas-1, the data of step 3 are presumed to approximate a first order rate of dehydration (Table 3 and Fig. 3B). The CO_2 evolved from the $\text{Fe}(\text{CO}_3)\text{OH}$ component in this step has a $\delta^{18}\text{O}$ value of +6.0‰. The $\delta^{18}\text{O}$ value of the CO_2 , the goethite $\delta^{18}\text{O}$ value of -13.2‰ and a value for $|m|$ of 0.026 min^{-1} , are included in the test of the rapid-rate predictions of the exchange model.

4. DISCUSSION

4.1. Rapid-rate data and model predictions

Values of $^{18}\alpha_{\text{app}}$ and $|m|$ for Ax-2 and ICAlas-1 (derived from the results in Tables 2 and 3) are listed in Table 4 and plotted in Fig. 5. For comparison, the published values of $^{18}\alpha_{\text{app}}$ and $|m|$ from the goethites of Table 1 are also plotted in Fig. 5. The Ax-2 and ICAlas-1 $^{18}\alpha_{\text{app}}$ values are higher than would be expected if the monotonic decline observed in the published data array were simply to continue in that manner. Thus, the new $^{18}\alpha_{\text{app}}$ data are shifted in a direction that is qualitatively consistent with the rapid-rate predictions of the kinetic exchange model. Therefore, the new data might be used to constrain model-derived values of K_2/K_1 at the measured temperatures of dehydration.

To calculate the necessary model curves, values for the temperature-dependent parameters in Eq. 5 were taken from various sources. Values for $\alpha_{\text{CO}_2-\text{V}}$ were calculated

by combining values of $\alpha_{\text{CO}_2\text{-L}}$ from Friedman and O'Neil (1977) with values of $\alpha_{\text{L-V}}$ from Majoube (1971) and Horita and Wesolowski (1994). Values for $\alpha_{\text{H-V}}$ were determined by combining the results for $\alpha_{\text{H-L}}$ in Zheng (1991) with the results for $\alpha_{\text{L-V}}$ in Majoube (1971) and Horita and Wesolowski (1994). The relevant values for $2\phi K_1$ were calculated from the results in Yapp (2003). At all temperatures, a value of 1.0349 was used for α_0 (Yapp, 2003), and a value of 1.0069 was used for $\alpha_{\text{G-Gv}}$ (Yapp, 1990). Stoichiometric constraints imply that $Y_V = 0.25$ and $Y_H = 0.75$. The rationale for these choices is discussed in Yapp (2003).

Families of model curves representing a wide range of values for K_2/K_1 were calculated for dehydration temperatures of 215 °C, 173 °C, and 200 °C. The curves are plotted in Figs. 6A, 6B, and 6C, together with the experimental data from the relevant rapid-rate goethite dehydration experiments. The ratio K_2/K_1 is an adjustable parameter in the calculation of the model curves. For any particular dehydration temperature, each choice of K_2/K_1 yields its own distinct curve. Thus, the value of K_2/K_1 is constrained if the corresponding model curve passes through a data point from a rapid-rate dehydration experiment. This experimental constraint implies that the inferred magnitude of K_2/K_1 could have physical significance. Values of K_2/K_1 deduced in this manner for the three rapid-rate experiments are listed in Table 4 and suggest that K_2/K_1 decreases as temperature increases.

An Arrhenius relation appears to be applicable to K_1 (Yapp, 2003), and if the values of K_1 and K_2 are separately dependent on temperature, there is an additional implication in the data of Table 4. The following Arrhenius formulations (e.g., Atkins, 1982) are assumed for K_1 and K_2 (terms are defined in the appendix):

$$\ln K_1 = \ln A_1 - \frac{E_1}{RT} \quad (6)$$

$$\ln K_2 = \ln A_2 - \frac{E_2}{RT} \quad (7)$$

Subtracting Eq. 6 from Eq. 7 yields

$$\ln \frac{K_2}{K_1} = \ln \frac{A_2}{A_1} - \left[\frac{E_2 - E_1}{R} \right] \frac{1}{T} \quad (8)$$

If $E_2 \neq E_1$, Eq. 8 predicts that $\ln(K_2/K_1)$ should be a linear function of the reciprocal of the temperature (Kelvin scale). Values of $\ln(K_2/K_1)$ calculated from the data in Table 4 are plotted against $1000/T$ in Fig. 7A. In this instance, the temperature of interest is the open system isothermal dehydration temperature. A linear regression of the three data points of Fig. 7A yields the following equation:

$$\ln(K_2/K_1) = 2230_{(\pm 2000)}/T - 1.9_{(\pm 4.3)} \quad (9)$$

The r^2 value for the regression is 0.99 and applies only to the three nominal values of $\ln(K_2/K_1)$. As deduced from Equations 8 and 9,

$$E_2 - E_1 \approx -19_{(\pm 17)} \text{ kJ/mol} \quad (10)$$

Although there is a large uncertainty in the value of $E_2 - E_1$ arising from the uncertainties in the values of $\ln(K_2/K_1)$, some additional discussion of the activation energies may be useful. It has been estimated that $E_1 \approx 28_{(\pm 11)} \text{ kJ/mol}$ (Yapp, 2003). This value, in combination with Eq. 10, implies that $E_2 \approx 9_{(+28, -9)} \text{ kJ/mol}$ – a very low activation energy.

The conclusions that can be drawn from the result for E_2 are limited by the substantial uncertainty in its estimated value. However, in general, heterogeneous catalysis lowers activation energies of reactions among gas phase species (e.g., Atkins, 1982). Thus, the nominal value of E_2 points to the possibility that heterogeneous catalysis, involving the local mineral surface, facilitates oxygen isotope exchange between co-evolved CO_2 and H_2O vapor during the solid-state goethite to hematite phase transition.

4.2. Possible implications for oxygen isotope analysis of goethite

The temperature dependence deduced for $\ln(K_2/K_1)$ (Eq. 9; Fig. 7A) was used in Eq. 5, together with previously discussed values for other parameters, to calculate a series of model curves that represent the current best estimate of the expected variation of α_{app} with $|m|$ for dehydration temperatures ranging from 170 °C to 230 °C. The calculated curves are in Fig. 7B. For comparison, the slow-rate experimental data of Yapp (2003) and the rapid-rate results of this work are also plotted in Fig. 7B. There is scatter evident in the comparison of measured and modeled results in Fig. 7B. The extent of the scatter can be illustrated with the parameter “ Δ ”, defined for this work as follows:

$$\Delta = 1000 \ln \alpha_{\text{app}}(\text{measured}) - 1000 \ln \alpha_{\text{app}}(\text{model}).$$

Thus, if $\Delta = 0.0$, there is exact agreement between measured and modeled α_{app} values.

Values of Δ are plotted against $|m|$ in Fig. 8. The average value of Δ for all 21 results in Fig. 8 is $0.4 (\pm 1.1; \text{one s.d.})$ with more scatter at smaller values of $|m|$. Smaller values of $|m|$ imply longer residence times for H_2O in the transition volume (Yapp, 2003). Longer residence times would increase the chance of enough oxygen isotope exchange with accessory minerals to measurably perturb the $\delta^{18}\text{O}$ of the evolved H_2O (and thus the CO_2). However, nominally anhydrous accessory minerals such as hematite (not in the transition state form) and quartz [even as the fused SiO_2 (“quartz”) glass of the dehydration chamber] are notably resistant to solid-state oxygen isotope exchange at the temperatures and time scales of these experiments (Becker and Clayton, 1976; Yapp, 1990; Fayek and Kyser, 2000). Moreover, XRD-detectable, hydroxyl-bearing gibbsite and/or boehmite were absent from the samples of this study. Ax-2 contained a small amount of XRD-detectable lepidocrocite ($\gamma\text{-FeOOH}$), but the oxygen isotope characteristics of lepidocrocite are not expected to be substantially different from goethite. Also, lepidocrocite is present in such small amounts that its effects, if any, on Ax-2 would be minor (Yapp and Shuster, 2011).

For the Δ values of Fig. 8, the three largest departures from zero are exhibited by samples containing accessory phyllosilicates. MSwitz-1 is of special note as an outlier. It has: (a) the largest Δ value ($+3.8$) in Fig. 8; (b) a small $|m|$ of 0.0028 min^{-1} ; (c) admixed kaolinite; and (d) accessory minerals with a composite $\delta^{18}\text{O}$ value of 18.5‰ (Yapp, 1998) that contain a high proportion of the total oxygen in the sample (28 mol % in kaolinite + quartz; Yapp, 2003). This combination of conditions suggests that the measured α_{app} of MSwitz-1 might have been shifted to a higher value by some degree of oxygen isotope exchange between accessory kaolinite and the water that evolved from goethite as it transformed to hematite.

If MSwitz-1 is excluded, the remaining 20 samples of Fig. 8 have an average Δ value of $0.2 (\pm 0.8; \text{one s.d.})$. The lower degree of scatter with respect to the model curves seems to support an assumption that, for those 20 samples, the types and amounts of accessory minerals have a limited effect on the oxygen isotope variation of evolved CO_2 among goethites undergoing isothermal vacuum dehydration at $T \leq 230^\circ\text{C}$.

The preceding discussion supports the use of the kinetic exchange model in conjunction with plateau $\delta^{18}\text{O}$ values of CO_2 evolved from the $\text{Fe}(\text{CO}_3)\text{OH}$ component to

determine $\delta^{18}\text{O}$ values of goethite, especially when selective dissolution of admixed minerals is not practicable – e.g., mixtures with hematite.

5. CONCLUSIONS

Isothermal dehydration of goethite can commonly be approximated by first order kinetics for extents of reaction of $\sim 60\%$. A kinetic exchange model predicts that α_{app} should decrease as the absolute value of the first order slope, $|m|$, increases for a range of $|m|$ that corresponds to relatively slow rates of dehydration. This pattern has been observed in published results. In contrast, for rapid rates of dehydration, α_{app} is predicted to increase with increasing $|m|$. A test of this prediction was provided by vacuum dehydrations of two natural goethites with unusually large values of $|m|$. The measured values of α_{app} for these rapid-rate experiments were consistent with patterns of variation predicted by the model, which then constrained the temperature dependence of the model parameter, K_2 – a rate constant for oxygen isotope exchange between CO_2 and H_2O during the solid-state goethite to hematite phase transition.

These results indicate that K_2 has an activation energy (E_2) of only ~ 9 kJ/mol. Heterogeneous catalysis tends to decrease the activation energies of gas reactions (Atkins, 1982). Consequently, the inferred value of E_2 is consistent with the idea that goethite and/or hematite catalyze oxygen isotope exchange between CO_2 and H_2O during the solid-state phase change.

If the rate of an incremental isothermal vacuum dehydration of goethite is well approximated by first order kinetics, the temperature of dehydration and the measured value of $|m|$ determine a model-predicted value of α_{app} . Increments of CO_2 evolved from the $\text{Fe}(\text{CO}_3)\text{OH}$ component during such a dehydration are routinely measured for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. If plateau $\delta^{18}\text{O}$ values are present in the incremental dehydration spectrum, that $\delta^{18}\text{O}$ value can be combined with model values of α_{app} to estimate the $\delta^{18}\text{O}$ of the goethite with a precision of about $\pm 0.8\%$. The estimated precision is less than optimal, but the method could have utility. For example, mixtures of goethite and hematite are common, but existing selective dissolution methods are ineffective for determining their respective $\delta^{18}\text{O}$ values. In such instances, plateau $\delta^{18}\text{O}$ data from incrementally evolved CO_2 could be an important source of information on the $\delta^{18}\text{O}$ value of the goethite.

For many goethite-bearing samples, a single analytical procedure (incremental dehydration) applied to one aliquot of the sample could provide not only $\delta^{13}\text{C}$ and mole fractions (X) of the $\text{Fe}(\text{CO}_3)\text{OH}$ component, but also hydrogen yield, δD , and the approximate $\delta^{18}\text{O}$ value of the goethite. Recovery of multiple types of geochemical data from a single aliquot would be particularly useful if the amount of sample available for analysis were limited – as an extreme example: goethite on Mars (Klingelhöfer et al., 2005).

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- 747

FIGURE CAPTIONS

Figure 1. From Eq. 5, a family of model curves depicting predicted relationships between $^{18}\alpha_{\text{app}}$ and $|m|$ at a goethite vacuum dehydration temperature of 215 °C for different choices of the ratio K_2/K_1 . Relevant values of various model parameters used in the calculations were taken from Yapp (2003) and references therein. See text for discussion.

Figure 2. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of increments of evolved CO_2 are plotted against $X_V(\text{H}_2)$ for the three rapid-rate goethite dehydration experiments. $X_V(\text{H}_2)$ is the cumulative hydrogen in the evolved water as a mole fraction of the total hydrogen in the sample and is calculated exclusive of the respective step 1 values for evolved hydrogen (see Table 2). $X_V(\text{H}_2) = 1.00$ when the sample has been completely dehydrated. (A) Ax-2 (Experiment 1). (B) Ax-2 (Experiment 2). (C) ICAIas-1. See text for discussion.

Figure 3. Values of $\ln X_S(\text{H}_2)$ from Table 3 are plotted against cumulative elapsed time for the isotherm vacuum dehydration of goethite. (A) Results from Ax-1 (Experiment 1 at 215 °C and Experiment 2 at 173 °C). (B) Results from ICAIas-1 at 200 °C. The portions of the data that are thought to approximate first order dehydration kinetics in each experiment define the linear regressions shown in the figures. See text for discussion.

Figure 4. Values of $|m|$ for Ax-2 (Experiments 1 and 2) and ICAIas-1 are plotted in the histogram together with values of $|m|$ for the goethites of Table 1 (the latter represent dehydration temperatures from 200 to 230 °C).

Figure 5. Values of $^{18}\alpha_{\text{app}}$ plotted against $|m|$ for the Ax-2 and ICAIas-1 results in Table 4. For comparison, the published values of $^{18}\alpha_{\text{app}}$ and $|m|$ from the goethites of Table 1 are also plotted. The Ax-2 and ICAIas-1 experiments exhibit higher values of α_{app} than would be expected from a simple extrapolation of the monotonic decline observed in the published data array. See text for discussion.

Figure 6. Families of model curves calculated for three dehydration temperatures: (A) 215 °C, (B) 173 °C, and (C) 200 °C. The curves are plotted together with the experimental data from the relevant rapid-rate goethite dehydration experiment: (A)

Ax-2 (Experiment 1); (B) Ax-2 (Experiment 2); (C) ICAlas-1. The ratio K_2/K_1 is an adjustable parameter in the calculation of the model curves, and for any particular dehydration temperature, each choice of K_2/K_1 yields its own distinct curve.

Figure 7. (A) Values of $\ln(K_2/K_1)$ calculated from the data in Table 4 are plotted against $1000/T$. The temperature of interest is the open system isothermal dehydration temperature. See text for discussion. (B) A series of model curves that represent the best estimate of the expected variation of α_{app} with $|m|$ for dehydration temperatures ranging from 170 °C to 230 °C. The slow-rate experimental data of Yapp (2003) and the rapid-rate results of this work are also plotted. The open diamond represents data from a sample (MSwitz-1) that contained accessory kaolinite (see Table 1).

Figure 8. Δ is plotted against $|m|$, where $\Delta = 1000\ln\alpha_{\text{app}}(\text{measured}) - 1000\ln\alpha_{\text{app}}(\text{model})$. The average value of Δ for all 21 results is $0.4 (\pm 1.1)$. If MSwitz-1 is excluded, the remaining 20 samples have an average Δ value of $0.2 (\pm 0.8; \text{one s.d.})$. See text for discussion.

Table 1. Published results from incremental dehydration experiments. Data are from Yapp (2003).

Goethite Samples	Minor minerals	Goethite $\delta^{18}\text{O}_{\text{SMOW}}$	T °C	CO ₂ from Fe(CO ₃)OH		$ m $ (min ⁻¹)	¹⁸ α_{app}
				X _C	$\delta^{18}\text{O}_{\text{SMOW}}$		
PPColo-1	qtz	-4.5	200	0.0165	20.5	0.0017	1.0251
NMx-2	qtz	-1.6	200	0.0125	19.9	0.0038	1.0215
MHWis-1	qtz	-2.8	200	0.0041	22.2	0.0016	1.0251
MPCUtah-1	qtz	-11.3	200	0.0105	8.2	0.0091	1.0197
SConn-2	qtz	-4.0	200	0.0151	21.1	0.0014	1.0252
BCMrylnd-1	qtz	-2.2	200	0.0182	17.1	0.0113	1.0193
Roraima Ter	qtz	-2.2	210	0.0080	20.1	0.0024	1.0223
BAla-1	qtz	0.2	220	0.0020	20.5	0.0051	1.0203
SConn-1	qtz	-4.1	220	0.0052	15.1	0.0088	1.0193
SLab-1	qtz	-5.3	220	0.0015	15.5	0.0057	1.0209
IRMWis-1*	ill + qtz	-1.0	230	0.0065	25.0	0.0017	1.0260
IRMWis-1*	ill + qtz	-1.0	230	0.0065	23.3	0.0021	1.0243
OPWis-6*	ill + qtz	-1.0	230	0.0048	24.3	0.0019	1.0253
OPWis-G-1*	ill + qtz	-1.0	230	0.0042	21.6	0.0029	1.0226
OPWis-9*	ill + qtz	-1.0	230	0.0054	17.2	0.0124	1.0182
OPWis-5*	ill + qtz	-1.0	230	0.0055	18.2	0.0101	1.0192
MSwitz-1*	kao + qtz	1.7	230	0.0113	28.1	0.0028	1.0263
CBraz-1	ana + rut	1.2	230	0.0108	23.8	0.0035	1.0226

* For the indicated samples, the particular value of $|m|$ reported here differs from the *measured* value reported in Yapp (2003), because that measured value has been adjusted to account for the hydrogen present in admixed phyllosilicates. qtz = quartz; ill = illite; kao = kaolinite; ana = anatase; rut = rutile. T = the temperature of isothermal vacuum dehydration under “open system” conditions (Yapp, 1983). X_C = the mole fraction of the Fe(CO₃)OH component in solid solution in the goethite. See the text and appendix for further definitions/explanations of the parameters.

Table 2. Data from relatively rapid, incremental vacuum dehydrations of natural goethites. $\delta^{18}\text{O}$ values for the evolved CO_2 are newly reported here. For Ax-2, the $\delta^{18}\text{O}$ value of -9.6‰ for structural oxygen is from Yapp and Shuster (2011). For ICAlas-1, the structural oxygen $\delta^{18}\text{O}$ value of -13.2‰ is from Yapp (2000).

Step	Time (min)	T (°C)	H ₂ (μmol)	CO ₂		X _V (H ₂)	F	
				(μmol)	$\delta^{13}\text{C}_{\text{PDB}}$			$\delta^{18}\text{O}_{\text{SMOW}}$
Ax-2: [Experiment 1; initial mass = 257.9 mg; $\delta^{18}\text{O}$ of structural oxygen = -9.6‰]								
1	55	22 and 100	928	6.0	1.8	35.6	-	-
2	30*	215*	686	54.5	-5.5	12.0	0.49	0.0794
3	30	215	462	11.6	6.8	10.1	0.83	0.0251
4	30	215	28	0.9	2.1	1.4	0.85	0.0321
5	60	215	23	0.7	-0.6	0.2	0.86	0.0304
6	30*	850*	192	29.5	4.5	6.2	1.00	0.1536
Ax-2: [Experiment 2; initial mass = 206.1 mg; $\delta^{18}\text{O}$ of structural oxygen = -9.6‰]								
1	111	23 and 100	845	6.2	3.8	40.6	-	-
2	30*	180*	204	33.0	-6.7	22.4	0.23	0.1618
3	21	155-175	199	3.2	-1.7	19.9	0.44	0.0161
4	30	173	261	5.8	6.5	12.3	0.73	0.0222
5	30	173	43	1.3	5.8	6.1	0.78	0.0302
6	60	173	22	0.7	1.2	4.0	0.80	0.0318
7	120	173	16	0.7	-1.9	2.9	0.82	0.0438
8	31*	850*	161	23.0	1.9	10.0	1.00	0.1429
ICAlas-1: [initial mass = 138.4 mg; $\delta^{18}\text{O}$ of structural oxygen = -13.2‰]								
1	60	100	197	-	-	-	-	-
2	30*	200*	86	0.8	-23.0	12.7	0.11	0.0091
3	30	200	371	2.0	-3.8	6.0	0.59	0.0054
4	30	200	69	0.8	-2.3	5.9	0.68	0.0116
5	120	200	123	1.9	-1.7	4.1	0.84	0.0154
6	300	200	49	1.1	-2.4	6.4	0.90	0.0224
7	30*	850*	74	5.1	-7.4	8.0	1.00	0.0689

*Closed system step in ~ 0.16 bar O_2 . All other increments: “open system” steps in vacuum (e.g., Yapp and Pothe, 1991, 1993; Hsieh and Yapp, 1999). The initial mass of a sample is the mass in open air before outgassing at 100°C. The $\delta^{18}\text{O}$ values in bold italics are considered to be those of CO_2 evolved from the $\text{Fe}(\text{CO}_3)\text{OH}$ component in goethite at dehydration rates that mimic first order kinetics (Eqn. 5). Because of the rapidity of breakdown, there is only one such increment in each experiment. See the appendix for definitions of $X_V(\text{H}_2)$ and F.

Table 3. Kinetic data for isothermal vacuum dehydrations of Ax-2 and ICAlas-1 goethite (after first outgassing at 100 °C).

Step	T(°C)	Cumulative time (min)	X _S (H ₂)	lnX _S (H ₂)
Ax-2: Experiment 1				
	—	0	^a 1.00	0.000
3	215	30	0.34	-1.079
4	215	60	0.30	-1.204
5	215	120	0.27	-1.309
Ax-2: Experiment 2				
	—	0	^b 1.00	0.000
4	173	30	0.48	-0.734
5	173	60	0.40	-0.916
6	173	120	0.35	-1.050
7	173	240	0.32	-1.139
ICA las-1				
	—	0	^c 1.00	0.00
3	200	30	0.46	-0.78
4	200	60	0.36	-1.03
5	200	180	0.18	-1.72
6	200	480	0.11	-2.23

^aValues of X_S(H₂) for Ax-2 in Experiment 1 were calculated exclusive of the hydrogen from steps 1 and 2 (see text and Table 2).

^bValues of X_S(H₂) for Ax-2 in Experiment 2 were calculated exclusive of the hydrogen from steps 1, 2, and 3 (see text and Table 2).

^cValues of X_S(H₂) for ICA las-1 were calculated exclusive of the hydrogen from steps 1 and 2 (see text and Table 2).

Table 4. Values of $|m|$, $^{18}\alpha_{\text{app}}$ and model-derived K_2/K_1 for the rapid-rate dehydrations

Goethite Samples	Minor minerals	Goethite $\delta^{18}\text{O}$	T $^{\circ}\text{C}$	CO_2 from $\text{Fe}(\text{CO}_3)\text{OH}$ $\delta^{18}\text{O}_{\text{SMOW}}$	$ m $ (min^{-1})	$^{18}\alpha_{\text{app}}$	Model derived K_2/K_1
Ax-2	hm, lp	-9.6	215	10.1	0.036	1.0199	14.5
Ax-2	hm, lp	-9.6	173	12.3	0.024	1.0221	22.5
ICAlas-1	qtz, phy	-13.2	200	6.0	0.026	1.0195	17.6

hm = hematite; lp = lepidocrocite; qtz = quartz; phy = 10 Å accessory mineral. T = the temperature of isothermal vacuum dehydration under “open system” conditions (Yapp, 1983). See the text and appendix for other definitions.

Figure 1

Figure 2a

Figure 2b

Figure 2c

Figure 3a

Figure 3b

Figure 4

Figure 5

Figure 6a

Figure 6b

Figure 6c

Figure 7a

Figure 7b

Figure 8