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## A model for $^{18}\text{O}/^{16}\text{O}$ variations in $\text{CO}_2$ evolved from goethite during the solid-state $\alpha\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$ phase transition

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**Abstract**—“Plateau”  $\delta^{18}\text{O}$  values of  $\text{CO}_2$  that evolved from the  $\text{Fe}(\text{CO}_3)\text{OH}$  component during isothermal vacuum dehydrations (200–230 °C) of 18 natural goethites range from 8.2 to 28.1‰. In contrast, the measured  $\delta^{18}\text{O}$  values of the goethite structural oxygen range from –11.3 to 1.7‰. The results of this study indicate that the apparent oxygen isotope fractionation factor ( $^{18}\alpha_{\text{app}}$ ) between plateau  $\text{CO}_2$  and initial goethite is systematically related to the rate of isothermal vacuum dehydration. The nonlinear correlation and the magnitudes of the  $^{18}\alpha_{\text{app}}$  values are predicted by a relatively simple mass balance model with the following assumptions: (1) the rate of isothermal vacuum dehydration of goethite (for the interval from 0 to ~60 to 80% loss of structural hydroxyl hydrogen) can be reasonably well represented by first-order kinetics and (2) isotopic exchange between evolving  $\text{H}_2\text{O}$  vapor and solid occurs only in successive, local transition states. The generally good correspondence between the model predictions and the experimental data seems to validate these assumptions. Thus, the  $^{18}\text{O}/^{16}\text{O}$  ratios of the evolved  $\text{CO}_2$  can act as probes into the transient processes operating at the molecular level during the solid-state goethite-to-hematite phase transition. For example, the activation energy for the rate constant associated with the transition state, oxygen isotopic exchange between solid and  $\text{H}_2\text{O}$  vapor, is tentatively estimated as  $28 \pm 11$  KJ/mol. Such knowledge may be of consequence in understanding the significance of  $^{18}\text{O}/^{16}\text{O}$  ratios in hematites from some natural environments (e.g., Mars?).

Kinetic data and  $\delta^{18}\text{O}$  values of  $\text{CO}_2$  are routinely obtained in the course of measurements of the abundance and  $\delta^{13}\text{C}$  values of the  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite. The observed correlation between  $^{18}\alpha_{\text{app}}$  and dehydration rates suggests that plateau  $\delta^{18}\text{O}$  values of evolved  $\text{CO}_2$  may provide complementary estimates of the  $\delta^{18}\text{O}$  values of total goethite structural oxygen (O, OH,  $\text{CO}_2$ ) with an overall precision of about  $\pm 1\%$ . However, because of isotopic exchange during the dehydration process,  $\delta^{18}\text{O}$  values of the evolved  $\text{CO}_2$  do not reflect the original  $\delta^{18}\text{O}$  values of the  $\text{CO}_2$  that was occluded as  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite. Copyright © 2003 Elsevier Science Ltd

### 1. INTRODUCTION

In goethite, formation of an Fe(III) carbonate component occurs as a consequence of a surface reaction between the carbon atom in a neutral  $\text{CO}_2$  molecule and a structural  $\text{O}^{2-}$  ion that is present in channels parallel to the goethite crystallographic c-axis (Russell et al., 1975; Yapp, 1987a). This  $\text{O}^{2-}$  ion is, in turn, bound to a sixfold coordinated Fe(III) ion in goethite, which suggests the local formation of  $\text{Fe}(\text{CO}_3)\text{OH}$ .



If this proposed reaction between  $\text{CO}_2$  and structural oxygen occurs during growth of goethite crystals, the  $\text{Fe}(\text{CO}_3)\text{OH}$  is occluded in the structure as a component in apparent solid solution (Yapp, 1987a; Yapp and Poths, 1990). Thus, the chemical formula for goethite might be expressed as  $\text{Fe}[\text{O}_{(1-x)}, (\text{CO}_3)_x]\text{OH}$ . Although the Fe(III) carbonate is unstable, it only breaks down to release  $\text{CO}_2$  upon breakdown of the local, confining goethite structure (Yapp and Poths, 1993). Such breakdown occurs upon solid-state, topotactic transformation of goethite to hematite during dehydration at temperatures of ~200 °C in vacuum and results in the correlated loss of  $\text{CO}_2$  and structural hydrogen (as  $\text{H}_2\text{O}$ ) from goethite.



Controlled, isothermal, incremental vacuum dehydration of goethite allows the determination of the abundance and carbon isotope composition of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component. “Plateau” values of  $\delta^{13}\text{C}$  and the molar ratios (F) of incrementally evolved  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are presumed to represent those of the  $\text{Fe}(\text{CO}_3)\text{OH}$  component in the goethite (Yapp and Poths, 1993). The mole fraction (X) of the  $\text{Fe}(\text{CO}_3)\text{OH}$  in goethite is equal to one half of the plateau value of F (Yapp and Poths, 1993). For natural goethites analyzed thus far,  $X < 0.02$ , while  $\delta^{13}\text{C}$  values range from –21.7 to 3.3‰ (Yapp, 2001). These values of X and  $\delta^{13}\text{C}$  for the  $\text{Fe}(\text{CO}_3)\text{OH}$  component have provided information on partial pressures of ancient atmospheric  $\text{CO}_2$ , paleosol productivity, and mixing processes of aqueous carbonates in oxidizing surficial environments (Yapp and Poths, 1992, 1996, and references therein; Hsieh and Yapp, 1999; Yapp, 1997, 2001).

The value of this mineral system as a source of information on processes in the ancient surficial carbon cycle suggests that the  $^{18}\text{O}/^{16}\text{O}$  ratios of the evolved  $\text{CO}_2$  might also contain paleoenvironmental information. If so, it may complement information contained in the  $^{18}\text{O}/^{16}\text{O}$  ratios of goethite structural oxygen (Yapp, 1987b, 1993a, 1993b, 1998, 2000; Bird et al., 1992, 1993; Hein et al., 1994; Girard et al., 1997, 2000; Bao et al., 2000; Pack et al., 2000; Poage et al., 2000).

Measurements of  $^{18}\text{O}/^{16}\text{O}$  ratios of  $\text{CO}_2$  evolved incremen-

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Table 1. Data for structural oxygen (O + OH + CO<sub>2</sub> in goethite) and open system isothermal dehydration of goethites in vacuum. “|m|” and “<sup>18</sup>α<sub>app</sub>” defined in the text.

Sample	Accessory Minerals	Y(O)	Structural oxygen δ <sup>18</sup> O <sub>SMOW</sub>	Sample mass (mg)	Open system isothermal dehydration in vacuum				
					Open system T(°C)	X	CO <sub>2</sub> from Fe(CO <sub>3</sub> )OH *δ <sup>18</sup> O <sub>SMOW</sub>	Apparent 1 <sup>st</sup> order  m  (min <sup>-1</sup> )	<sup>18</sup> α <sub>app</sub>
PPColo-1	qtz	0.05	-4.5	285.6	200	0.0165	20.5	0.0017	1.0251
NMx-2	qtz	0.04	-1.6	260.2	200	0.0125	19.9	0.0038	1.0215
MHWis-1	qtz	0.04	-2.8	223.6	200	0.0041	22.2	0.0016	1.0251
MPCUtah-1	qtz	0.07	-11.3	265.8	200	0.0105	8.2	0.0091	1.0197
SConn-2	qtz	0.02	-4.0	218.4	200	0.0151	21.1	0.0014	1.0252
BCMrylnd-1	qtz	0.03	-2.2	163.2	200	0.0182	17.1	0.0113	1.0193
Roraima Terr.	qtz	0.04	-2.2	353.3	210	0.0080	20.1	0.0024	1.0223
BAla-1	qtz	0.03	0.2	186.2	220	0.0020	20.5	0.0051	1.0203
SConn-1	qtz	0.07	-4.1	256.5	220	0.0052	15.1	0.0088	1.0193
SLab-1	qtz	0.05	-5.3	189.6	220	0.0015	15.5	0.0057	1.0209
IRMWis-1	ill+qtz	0.18	-1.0	224.2	230	0.0065	25.0	0.0013	1.0260
IRMWis-1	ill+qtz	0.18	-1.0	200.5	230	0.0065	23.3	0.0016	1.0243
OPWis-6	ill+qtz	0.18	-1.0	246.0	230	0.0048	24.3	0.0014	1.0253
OPWis-G-1	ill+qtz	0.24	-1.0	347.8	230	0.0042	21.6	0.0022	1.0226
OPWis-9	ill+qtz	0.19	-1.0	215.2	230	0.0054	17.2	0.0093	1.0182
OPWis-5	ill+qtz	0.21	-1.0	233.4	230	0.0055	18.2	0.0076	1.0192
MSwitz-1	kao+qtz	0.28	1.7	215.8	230	0.0113	28.1	0.0021	1.0263
CBraz-1	ana+rut	0.25	1.2	160.6	230	0.0108	23.8	0.0035	1.0226

Structural oxygen δ<sup>18</sup>O data are from Yapp (2000). Y(O) is oxygen in the accessory mineral as a mole fraction of sample oxygen (Yapp, 1991, 1997, 1998). X is the mole fraction of Fe(CO<sub>3</sub>)OH in goethite (Yapp, 2001).

qtz = quartz. ill = illite. kao = kaolinite. ana = anatase. rut = rutile. \* Based on plateau values for δ<sup>13</sup>C.

tally from goethite during vacuum dehydration-decarbonation are reported here. Oxygen isotope fractionations measured between plateau δ<sup>18</sup>O values of evolved CO<sub>2</sub> and the structural oxygen (O, OH, CO<sub>2</sub>) in the initial goethite are discussed in relation to the rate of the solid-state transformation from goethite to hematite. Mathematical terms used in the model developed for this study are defined in the Appendix.

## 2. SAMPLES AND EXPERIMENTAL METHODS

All of the goethites used in this study are from natural occurrences and had previously been analyzed to determine the δ<sup>18</sup>O value of the structural oxygen (Table 1). Sample descriptions can be found elsewhere (Yapp and Poths, 1996; Yapp, 2000, and references therein). Goethite samples were powdered to particle sizes of < 63 μm and chemically cleaned, first with 0.5-mol/L HCl, then with 30% H<sub>2</sub>O<sub>2</sub> solution at room temperature (Yapp, 1998). After outgassing in vacuum at 100 °C for 60 min, the chemically cleaned samples were heated at the assigned dehydration temperature under closed-system conditions in ~0.16 bar of pure O<sub>2</sub> for 30 min to remove additional organic matter. At this O<sub>2</sub> pressure (and temperatures of ~230 °C), the rate of breakdown of goethite is suppressed, but additional organic matter, which might otherwise be easily oxidized by goethite at the temperatures of subsequent vacuum dehydration steps, is removed before those steps. Each sample was then incrementally dehydrated-decarbonated under isothermal open-system conditions in vacuum at a specified temperature in the range from 200 to 230 ±3 °C. The foregoing procedures follow published methods (Yapp and Poths, 1996; Hsieh and Yapp, 1999, and references therein). For all the natural goethite samples of this study, the mole fraction of CO<sub>2</sub> (as Fe(CO<sub>3</sub>)OH) was < 0.02 (see Table 1).

Additional vacuum dehydration experiments were performed on two aliquots of goethite sample PPColo-1 such that the successive open-system steps were run at progressively higher temperatures (Table 2). Before each incremental step in these non-isothermal experiments, PPColo-1 was removed to the room temperature portion of the evacuated dehydration chamber while the furnace temperature was raised to the next specified value.

Oxygen isotope values are reported in the conventional δ<sup>18</sup>O notation with respect to SMOW (Gonfiantini, 1978). Repetition of δ<sup>18</sup>O measurements of selected aliquots of CO<sub>2</sub> gas extracted from the Fe(CO<sub>3</sub>)OH suggested a precision of about ±0.3‰ on the smallest extracts (~0.2 μmol).

The rates of isothermal dehydration were routinely determined by measurement of the amounts of hydrogen recovered from the goethite in each timed step of the various vacuum dehydration experiments. Incremental hydrogen yields were measured by quantitative conversion of H<sub>2</sub>O to H<sub>2</sub> over a depleted uranium furnace at ~800 °C. Amounts of the resultant H<sub>2</sub> were measured manometrically (with a Toepler pump) to a precision of ±1 μmol.

The extent of substitution of Al for Fe in goethite was determined by the X-ray diffraction (XRD) method of Schulze (1984) with a precision of ±3 mol.%. None of the Al (as AlOOH) was in excess of 9 mol.% in the FeOOH-AlOOH solid solution. XRD analyses did not detect any gibbsite in the samples used in this study, and no contributions of CO<sub>2</sub> were expected from this source (Schroeder and Melear, 1999).

Chemical analyses of the samples are reported elsewhere (Yapp, 1987b, 1991, 1993a, 1997, 1998). No natural goethites with admixed silicate oxygen in excess of 29 mol.% were included in this study. Ten of the 18 samples shown in Table 1

Table 2. Incremental, non-isothermal dehydration data for aliquots of PPColo-1.

T(°C)	Time (minutes)	Cumulative time (min)	CO <sub>2</sub> μmoles	CO <sub>2</sub> δ <sup>18</sup> O <sub>SMOW</sub>	H <sub>2</sub> μmoles	10 <sup>6</sup> /T <sup>2</sup>	1000ln <sup>18</sup> α <sub>app</sub>	<sup>18</sup> α <sub>app</sub>
(Aliquot #1) no closed system step in O <sub>2</sub> at beginning of dehydration								
160	30	30	1.50	22.1	128	5.3	26.4	1.0267
160	30	60	0.75	20.0	64	5.3	24.3	1.0246
180	30	90	1.25	18.8	134	4.9	23.1	1.0234
200	30	120	4.50	17.4	307	4.5	21.8	1.0220
220	30	150	9.75	15.0	362	4.1	19.4	1.0196
230	30	180	8.25	14.0	231	4.0	18.4	1.0186
240	30	210	4.00	12.5	119	3.8	16.9	1.0171
260	30	240	1.75	10.2	55	3.5	14.7	1.0148
300	1020	1260	2.00	6.5	64	3.0	11.0	1.0110
850*	30*	1290	16.75		69			
(Aliquot #2) excludes data from 200°C closed system step in O <sub>2</sub>								
200	60	60	2.50	16.3	377	4.5	20.7	1.0209
210	60	120	5.25	16.5	294	4.3	20.9	1.0211
220	60	180	8.75	16.9	297	4.1	21.3	1.0215
230	60	240	8.25	15.8	233	4.0	20.2	1.0204
240	60	300	2.75	13.9	92	3.8	18.3	1.0185
260	60	360	1.25	11.4	56	3.5	15.8	1.0160
280	60	420	0.50	9.0	24	3.3	13.5	1.0136
320	60	480	1.00	7.2	32	2.8	11.7	1.0118
360	60	540	1.25	4.6	31	2.5	9.1	1.0091
400	60	600	1.25	2.3	22	2.2	6.8	1.0068
850*	30*	630	13.50		32			

\* Closed system in O<sub>2</sub>. All other increments open system in vacuum.

contained < 8 mol.% silicate oxygen, whereas silicate (or Ti-oxide) oxygen in the remaining samples ranged from 18 to 28 mol.%.

### 3. RESULTS

Two isothermal, incremental, vacuum dehydration-decarboxylation spectra depicting the δ<sup>18</sup>O value of the CO<sub>2</sub> evolved from goethite as a function of reaction progress are shown in Fig. 1 for goethite samples MSwitz-1 and SConn-1. X<sub>v</sub>(H<sub>2</sub>) is the progress variable. X<sub>v</sub>(H<sub>2</sub>) = 0.0 when there has been no dehydration of goethite, whereas X<sub>v</sub>(H<sub>2</sub>) = 1.0 when the goethite has been completely converted to hematite. There is evidence of the attainment of an approximate plateau of δ<sup>18</sup>O values for the CO<sub>2</sub> evolved from some goethites (Fig. 1). Identification of the increments that correspond to CO<sub>2</sub> evolved from the Fe(CO<sub>3</sub>)OH component is based on plateau values for δ<sup>13</sup>C (Table 3). Subsequent discussion of the oxygen isotope results will refer to the respective average δ<sup>18</sup>O values of these plateaus. If there was no attainment of an oxygen isotope plateau at least as credible as the examples in Fig. 1, the results from such an anomalous experiment were not included here. Such anomalous experiments represented only 18% of 22 dehydration experiments performed for this work. The origins of the anomalous behavior are not known at present. Table 1 lists the plateau δ<sup>18</sup>O values measured for CO<sub>2</sub> recovered from 18 natural goethite samples. These δ<sup>18</sup>O values range from 8.2 to 28.1‰. Elapsed times of individual dehydration steps ranged up to 1560 min. Total elapsed times for isothermal dehydrations ranged from 420 to 3900 min among the samples of Table 1. As examples, the kinetic data obtained for two natural goethites (MSwitz-1 and SConn-1) are listed in Table 3.

Table 2 contains the results from the non-isothermal dehydration-decarboxylation experiments performed on two aliquots

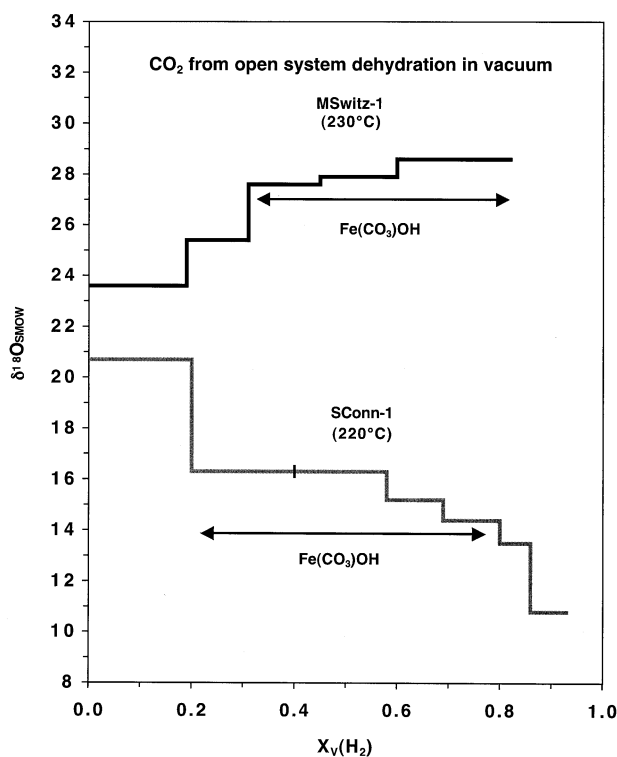


Fig. 1. δ<sup>18</sup>O values of CO<sub>2</sub> incrementally evolved from goethites MSwitz-1 and SConn-1 during isothermal vacuum dehydration. X<sub>v</sub>(H<sub>2</sub>) is a progress variable. X<sub>v</sub>(H<sub>2</sub>) = 0.0 when no goethite has been dehydrated. X<sub>v</sub>(H<sub>2</sub>) = 1.0 when the goethite has been completely converted to hematite (see text). Identification of the increments corresponding to plateau δ<sup>18</sup>O values of CO<sub>2</sub> from the Fe(CO<sub>3</sub>)OH component is based on plateau values for δ<sup>13</sup>C (see Table 3).

Table 3.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of evolved  $\text{CO}_2$  and kinetic data for isothermal vacuum dehydration of two natural goethites.

Sample	Open system T (°C)	Evolved $\text{CO}_2$ $\delta^{13}\text{C}_{\text{PDB}}$	Evolved $\text{CO}_2$ $\delta^{18}\text{O}_{\text{SMOW}}$	Cumulative time (min)	$X_{\text{S}}(\text{H}_2)$	$\ln X_{\text{S}}(\text{H}_2)$
SConn-1				0	1.00	0.00
SConn-1	220	-11.1	20.7	10	0.80	-0.22
SConn-1	220	-11.1	16.3	40	0.60	-0.51
SConn-1	220	-10.5	16.3	70	0.42	-0.87
SConn-1	220	-11.3	15.2	100	0.31	-1.17
SConn-1	220	-12.3	14.4	160	0.20	-1.61
SConn-1	220	-14.3	13.5	220	0.14	-1.97
SConn-1	220	-21.5	10.8	1180	0.07	-2.66
MSwitz-1				0	1.00	0.00
MSwitz-1	230	-8.4	23.6	60	0.81	-0.21
MSwitz-1	230	-15.7	25.4	150	0.69	-0.37
MSwitz-1	230	-17.6	27.6	270	0.55	-0.60
MSwitz-1	230	-17.4	27.9	450	0.38	-0.96
MSwitz-1	230	-16.9	28.6	1410	0.16	-1.80

of PPColo-1. Temperatures of the various increments of vacuum dehydration ranged from 160 to 400 °C. No plateaus of  $\delta^{18}\text{O}$  values were observed among the increments of  $\text{CO}_2$  evolved during these experiments. In fact, the  $\delta^{18}\text{O}$  values of increments of  $\text{CO}_2$  evolved from a goethite sample under non-isothermal vacuum dehydration conditions systematically decrease with increasing temperature (Table 2).

#### 4. DISCUSSION

##### 4.1. Reaction Kinetics and Patterns of Oxygen Isotope Variation

An apparent oxygen isotope fractionation factor ( $1000\ln^{18}\alpha_{\text{app}}$ ) between each increment of evolved  $\text{CO}_2$  and the initial goethite structural oxygen is plotted against  $10^6/T^2$  in Fig. 2 for two aliquots of PPColo-1. Terms are defined in the Appendix. The initial  $\delta^{18}\text{O}$  value of the PPColo-1 goethite is a constant—i.e.,  $\delta^{18}\text{O}_{\text{G}} = -4.5\text{‰}$ . Therefore, the systematic decrease of  $1000\ln^{18}\alpha_{\text{app}}$  with increasing temperature for PPColo-1 in Fig. 2 is caused entirely by the decrease in the  $\delta^{18}\text{O}$  value of the incrementally evolved  $\text{CO}_2$ .

The coherent arrays of the non-isothermal data for the two aliquots of PPColo-1 (Fig. 2) suggest that values of  $1000\ln^{18}\alpha_{\text{app}}$  calculated for plateau values of the various isothermal experiments of Table 1 might coincide with these PPColo-1 arrays at corresponding temperatures. Values of  $1000\ln^{18}\alpha_{\text{app}}$  for the samples of Table 1 are plotted against  $10^6/T^2$  in Fig. 2. Within experimental error, nine of the 18 isothermal results are coincident with the non-isothermal PPColo-1 arrays. Of the nine remaining samples, seven plot above the non-isothermal data array, while two are below. This scatter of the isothermal results indicates that factors in addition to temperature must affect the values of  $1000\ln^{18}\alpha_{\text{app}}$ .

Girard and Savin (1996) observed that thermal dehydroxylation of coarse-grained ( $> 1 \mu\text{m}$ ) kaolinite and dickite samples yielded oxygen isotope fractionations between the products (residual mineral and evolved  $\text{H}_2\text{O}$ ) that depended on the temperature of the process. They suggested that the temperature dependence might be a result of isotopic exchange associated with the diffusion of evolved  $\text{H}_2\text{O}$  through the coarser-grained particles. This suggestion implies that rates of dehydroxylation could be related to the magnitude of observed oxygen isotope

fractionations. If so, such a relationship might explain the aforementioned range of  $1000\ln^{18}\alpha_{\text{app}}$  values observed for different isothermally dehydrated goethite samples (e.g., 230 °C, Fig. 2).

Hancock and Sharp (1972) and Goss (1987) discussed the complexities involved in assigning reaction mechanisms to the solid-state phase transitions associated with dehydration (i.e., dehydroxylation) reactions. In particular, Goss (1987) discussed the kinetics and reaction mechanisms that seem to apply to the solid-state goethite to hematite transformation and concluded that the process is controlled primarily by a two-dimensional phase boundary. However, for at least the initial 60% of the reaction progress, a number of mathematical expressions for rates of mineral dehydration (Hancock and Sharp, 1972; Goss, 1987) provide reasonable empirical fits to experimental data (Criado et al., 1984). Therefore, as a first approximation, the rates of isothermal vacuum dehydrations of the goethite samples are represented by first-order kinetics.

$$\frac{dX_{\text{S}}(\text{H}_2)}{dt} = -kX_{\text{S}}(\text{H}_2) \quad (3a)$$

$$\ln X_{\text{S}}(\text{H}_2) = -kt = mt \quad (3b)$$

As examples of the kinetic data obtained for the isothermal dehydrations of the natural goethites of this study, results from samples MSwitz-1 and SConn-1 are plotted in Fig. 3 as  $\ln X_{\text{S}}(\text{H}_2)$  vs.  $t$ . For values of  $X_{\text{S}}(\text{H}_2) > \sim 0.15$  to 0.20, the data are highly linear with  $r^2$  values of 0.98 (SConn-1) and 0.99 (MSwitz-1). Absolute values  $|m|$  of the slopes, as determined from linear regressions of  $\ln X_{\text{S}}(\text{H}_2)$  vs.  $t$ , are listed in Table 1 for each of the 18 goethite samples. All of these linear regressions exhibited  $r^2$  values  $\geq 0.94$ .

The apparent fractionation factors ( $^{18}\alpha_{\text{app}}$ ) are plotted against corresponding values of  $|m|$  in Fig. 4. There is a general pattern of decreasing values of  $^{18}\alpha_{\text{app}}$  with increasing values of  $|m|$ . The shape of the data array in Fig. 4 seems to be concave up with greater changes of the  $^{18}\alpha_{\text{app}}$  values at lower values of  $|m|$ . A model of the isotopically significant processes that operate during the dehydration-decarbonation reaction must account for the geometry of the data array and the magnitudes of the  $^{18}\alpha_{\text{app}}$  values in Fig. 4. It should be noted that there is no correlation between  $^{18}\alpha_{\text{app}}$  and the mole fraction of

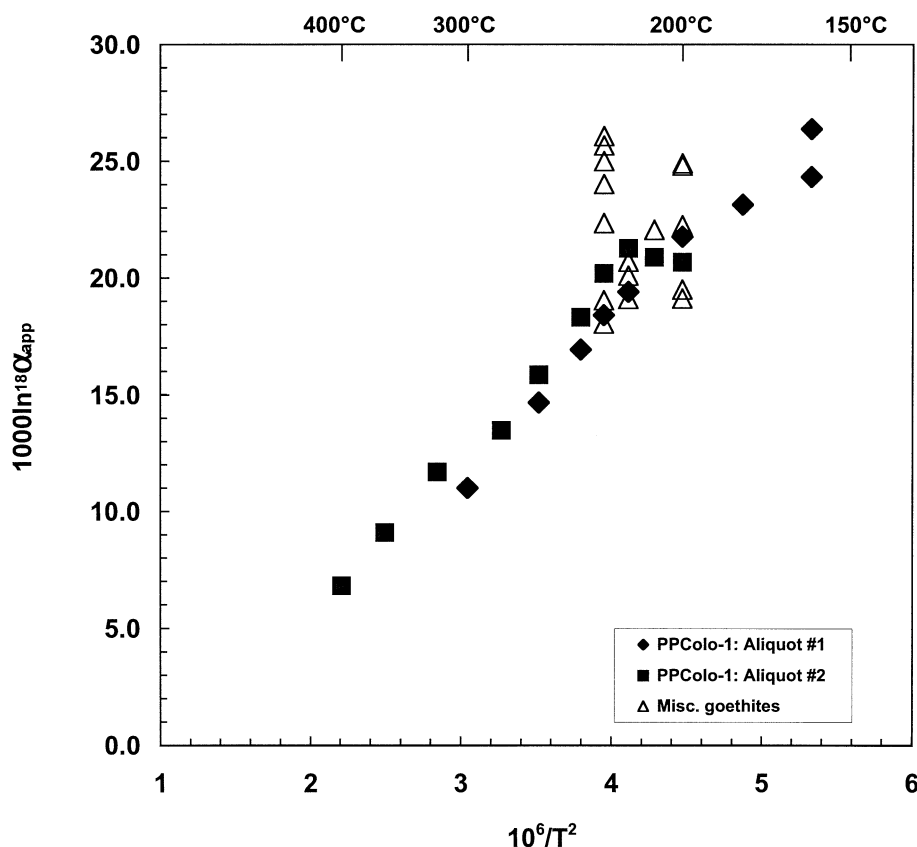


Fig. 2.  $1000\ln^{18}\alpha_{app}$  vs.  $10^6/T^2$  for non-isothermal incremental vacuum dehydration of two aliquots of goethite sample PPColo-1 (filled squares and diamonds). Also shown are the values of  $1000\ln^{18}\alpha_{app}$  determined at different temperatures for the 18 goethite samples dehydrated under isothermal conditions (see text).

Fe(CO<sub>3</sub>)OH in the goethite. Furthermore, there is no correlation between  $^{18}\alpha_{app}$  and Y(O), where Y(O) is the oxygen in accessory minerals as a mole fraction of the total sample oxygen (Table 1). This suggests that, with the possible exception of MSwitz-1 (Table 1, Fig. 4), the oxygen in the accessory minerals did not significantly influence the isotopic composition of the evolved CO<sub>2</sub>.

The extent to which high proportions of phyllosilicates in some goethites contribute to the scatter in the data of Fig. 4 needs to be established. For example, kaolinite does not dehydroxylate at 230 °C but does break down at 450 °C (Girard and Savin, 1996). If kaolinite were admixed with goethite, and the amount of hydrogen in the refractory silicate hydroxyl were not taken into account, apparent values of  $X_S(H_2)$  calculated for the goethite would be too high, and the inferred value of  $|m|$  would be too low. This is illustrated by the values of  $|m|$  for the samples in Table 1 that contain either kaolinite or illite. About 13% of the hydrogen in the illite-bearing samples is not in the goethite (Yapp, 1993a). Chemical analyses of the kaolinite-bearing sample (MSwitz-1), as reported in Yapp (1998), were used to determine that 15% of the total hydrogen in the sample was in kaolinite with the remainder in goethite. The similarities in the amounts of phyllosilicate hydrogen (13 and 15%) indicate that the proportional effects of this excess H on the measured values of  $|m|$  should be essentially the same in the illite- and kaolinite-bearing samples.

Therefore, for 15% of total sample H in these phyllosilicates, it is calculated that the measured slope,  $|m|$ , is 25% lower than the actual value of the slope. Open triangles in Fig. 4 represent the adjusted values of the slope for goethites from the phyllosilicate-bearing samples. The largest shifts in the calculated values of  $|m|$  are at the higher values of  $|m|$ , because the effect on slope is a proportional effect (i.e., multiplicative). Even after these calculated adjustments, the overall pattern of variation of  $^{18}\alpha_{app}$  with  $|m|$  remains the same.

The effects, if any, of varying degrees of Al substitution for Fe in the goethite structure are unknown at this time. The maximum concentration of substituted Al in the goethite samples of Table 1 is 9 mol.% (CBraz-1). There is no obvious effect of this extent of Al substitution on the pattern of variation of the data of Fig. 4.

#### 4.2. Model for Oxygen Isotope Variation of CO<sub>2</sub> Evolved from Goethite

Neither goethite nor hematite readily exchange structural oxygen isotopes with water (Becker and Clayton, 1976; Yapp, 1991). Therefore, the rapid mineral-vapor oxygen isotope exchange observed during solid-state transformation of synthetic goethite to hematite (Yapp, 1990b) probably occurred only in successive local microenvironments as each local domain actually underwent the phase transformation. This supposition is

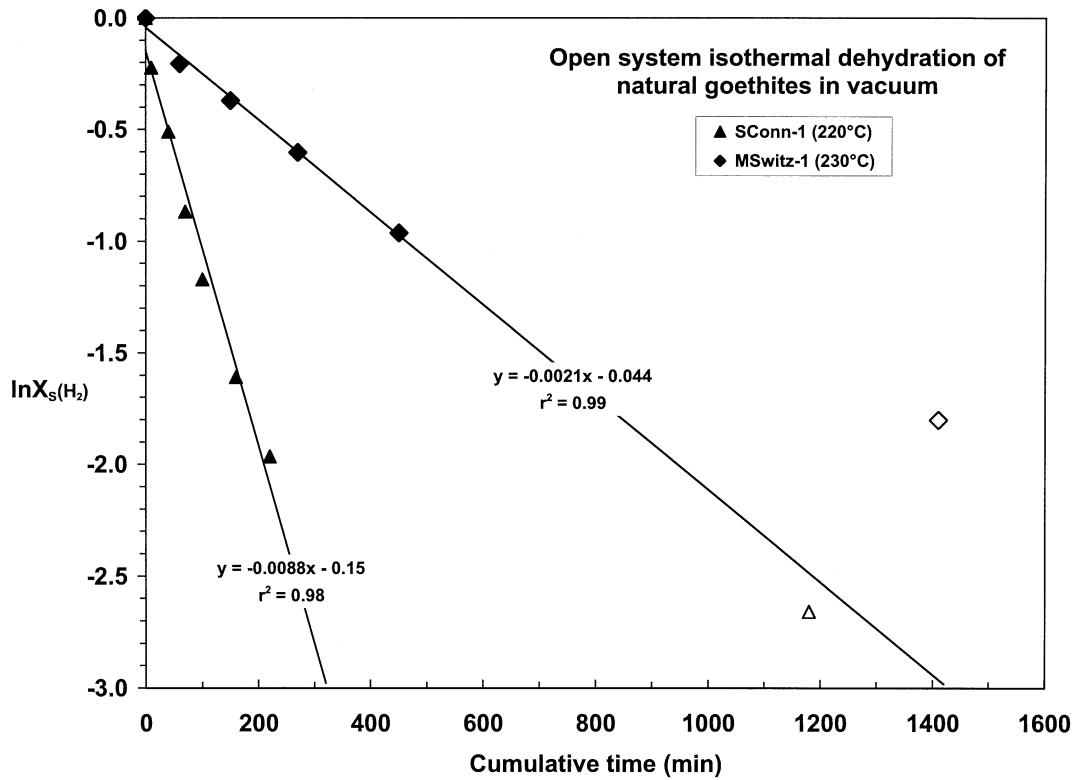
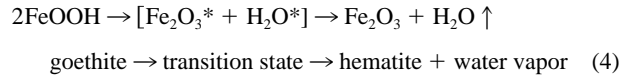


Fig. 3.  $\ln X_s(H_2)$  vs. cumulative dehydration time for isothermal incremental vacuum dehydration of goethite samples MSwitz-1 and SConn-1. The solid lines represent linear regressions of the data depicted by the filled symbols of each array (see text). The open triangle and the open diamond represent the final incremental dehydration steps for SConn-1 and MSwitz-1, respectively. These two “late-stage” data points lie well off of the linear trends defined by the “early-stage” data of their respective samples.

generally consistent with the observation of Goss (1987) that, as the reaction front progresses into the goethite crystal,  $H_2O$  vapor egresses through microfractures developed in the product hematite.

The development of a model that accounts for the oxygen isotope data of Fig. 4 initially neglects  $CO_2$ , because this component is present in relatively small proportions. It is assumed in this model that (1) an intermediate transition state exists during the solid-state goethite-to-hematite reaction; (2) this transition state is present only at the reaction front and therefore can be thought of as migrating with the front; (3) the transition state is characterized by a transition volume; (4) the only oxygen isotope exchange that occurs between mineral and  $H_2O$  vapor occurs in the immediate volume of the transition state; (5) upon local emergence of the products—hematite and  $H_2O$  vapor—from the transition state, the  $\delta^{18}O$  value of the hematite is the same as that of the immediate precursor transition-state species ( $Fe_2O_3^*$ ), similarly for  $H_2O$  in relation to  $H_2O^*$ ; (6) the  $H_2O$  vapor is immediately removed (under external vacuum conditions) from the mineral system via the microfractures; and (7) upon emergence from the transition state, the local crystal environment is permanently converted to the hematite product—i.e., the reaction does not reverse and does not develop another local transition volume. This overall process is summarized with the following reaction:



With the foregoing assumptions, the following mathematical expression is proposed as a representation of the rate at which goethite breaks down to hematite:

$$\frac{dn_G}{dt} = -V_{ts}K_G(C_{eq} - C_v^*) = -K_G\left(\frac{C_{eq}}{C_v^*} - 1\right)n_v^* \quad (5)$$

Eqn. 5 derives from modification of a more general expression for reaction rate as formulated in transition-state theory (e.g., Lasaga, 1981), with an assumption that the exponents on the concentrations in Eqn. 5 are unity. If  $C_v^* = C_{eq}$  (i.e., equilibrium), Eqn. 5 indicates that goethite will not break down. Define  $n_v^*/n_G = \Phi$ , then

$$\frac{d\ln X_s(H_2)}{dt} = -\Phi K_G\left(\frac{C_{eq}}{C_v^*} - 1\right) \quad (6)$$

But,

$$\frac{d\ln X_s(H_2)}{dt} = m \text{ (see Eqn. 3b)}$$

Therefore,

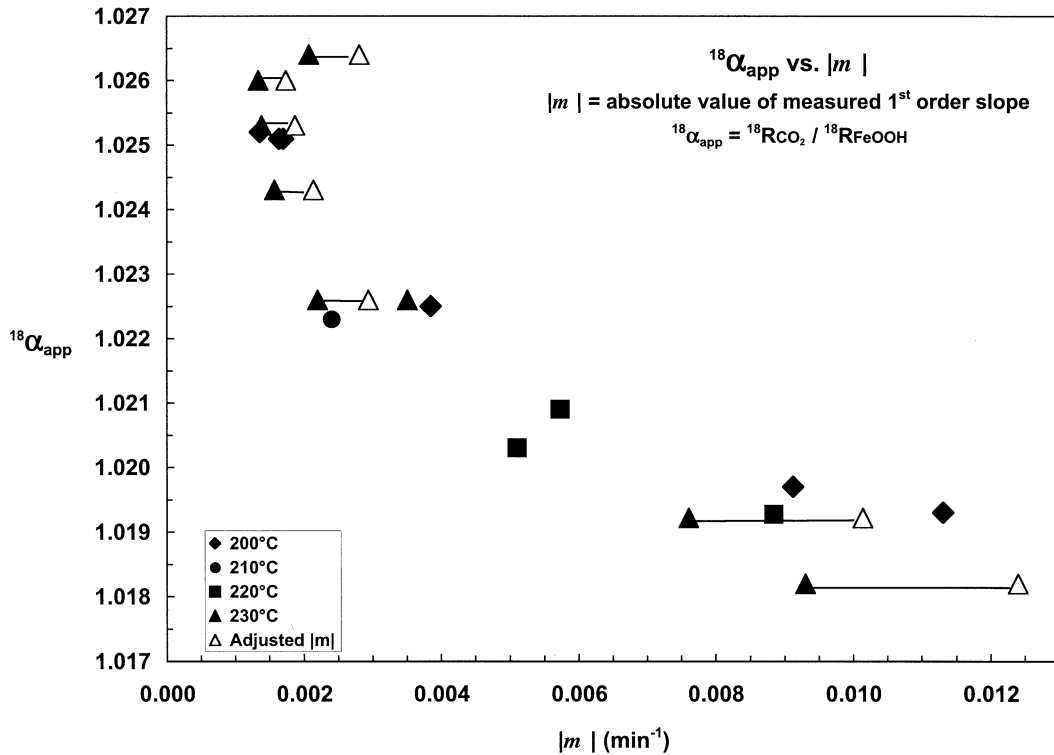


Fig. 4.  $^{18}\alpha_{app}$  vs.  $|m|$  for the 18 goethite samples of Table 1.  $^{18}\alpha_{app}$  and  $|m|$  are defined in the text. The nonlinear, concave-up geometry of the correlation and the magnitudes of the  $^{18}\alpha_{app}$  values are predicted by a simple model of the dehydration process (see text). The open triangles show the calculated shifts in  $|m|$  for the samples of Table 1 with phyllosilicate impurities (see text). Tie lines connect the data points representing corresponding unmodified and adjusted values of  $|m|$ .

$$m = -\Phi K_G \left( \frac{C_{eq}}{C_V^*} - 1 \right) \quad (7)$$

The relatively high degree of linearity (for  $X_S(H_2) > \sim 0.20$ ) of the data arrays in Fig. 3 indicates that “ $m$ ” in each case is essentially constant (Eqn. 3b). At a particular temperature,  $C_{eq}$  is expected to be constant (e.g., Denbigh, 1981). This implies that  $C_V^*$  and  $\Phi$  are also constant in each experiment (Eqn. 7). Constant values of  $C_V^*$  are presumed to represent steady-state values ( $C_{V,ss}^*$ ). The assumption that  $\Phi$  is approximately constant during the first 60 to 80% of a dehydration is problematic but is adopted as a working hypothesis.

If the local transition volume at each instant is envisaged as a reservoir with input ( $F_{in}$ ) of H<sub>2</sub>O from local breakdown of the goethite and output ( $F_{out}$ ) of H<sub>2</sub>O via microfractures as the transition-state species Fe<sub>2</sub>O<sub>3</sub>\* becomes hematite, the rate of change of the amount of H<sub>2</sub>O\* in the transition volume may be expressed as follows:

$$\frac{dn_V^*}{dt} = F_{in} - F_{out} \quad (8)$$

$$F_{in} = \frac{1}{2} V_{ts} K_G [C_{eq} - C_V^*] \quad (9)$$

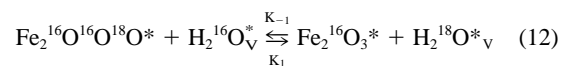
$$F_{out} = V_{ts} K_V C_V^* \quad (10)$$

The factor of 1/2 arises in Eqn. 9 because, upon breakdown of

goethite, 2 moles of FeOOH are lost for every mole of H<sub>2</sub>O produced (see Eqn. 2 and 4). Eqn. 10 reflects an assumption that the rate of loss of H<sub>2</sub>O\* from the transition volume at each instant is a linear function of the concentration of the vapor in that volume. This assumption has not been validated but is made to facilitate discussion. The validity of this assumption and others may be assessed to some extent by the ability of the resultant model equation to explain the data. Substitution of Eqn. 9 and 10 into Eqn. 8 yields:

$$\frac{dn_V^*}{dt} = \frac{1}{2} V_{ts} K_G [C_{eq} - C_V^*] - V_{ts} K_V C_V^* \quad (11)$$

An analogous expression can be formulated for the H<sub>2</sub><sup>18</sup>O molecule in the transition volume. However, in this instance, the model assumptions require consideration of the oxygen isotope exchange between the transition-state vapor and the Fe<sub>2</sub>O<sub>3</sub>\* species:



It is assumed that a “pseudo first-order” rate process (e.g., Criss et al., 1987) is applicable to the isotopic exchange between Fe<sub>2</sub>O<sub>3</sub>\* and H<sub>2</sub>O\* in the transition volume. Furthermore, the oxygen isotope exchange in each successive transition-state volume is assumed to occur under local closed-system condi-

tions with respect to any other portion of the mineral system. Then, for isotopic exchange in the transition state, coupled with mass transfer into and out of the transition volume,

$$n_v^* \frac{dR_v}{dt} + R_v \frac{dn_v^*}{dt} = \frac{1}{2} V_{ts} R_{Gv} K_G [C_{eq} - C_v^*] - \alpha_K V_{ts} K_v R_v C_v^* + K_1 [R_H - \alpha_{H-v} R_v] V_{ts} C_v^* \quad (13)$$

The value of  $\alpha_K$  is not known but will be assumed to be unity for this discussion (i.e., "viscous" transport of H<sub>2</sub>O out of the mineral system).

For local, closed-system isotopic exchange between Fe<sub>2</sub>O<sub>3</sub>\* and H<sub>2</sub>O\* in each successive transition-state volume,

$$R_G = Y_H R_H + Y_V R_V \quad (14)$$

$$Y_H + Y_V = 1 \quad (14a)$$

$$R_H = \frac{1}{Y_H} R_G - \frac{Y_V}{Y_H} R_V \quad (14b)$$

For stoichiometric goethite,  $Y_H = 0.75$ , while  $Y_V = 0.25$  (see Eqn. 4).

The existence of approximate plateau values of  $\delta^{18}\text{O}$  for the CO<sub>2</sub> evolved from goethite during solid-state dehydration reactions (Fig. 1) suggests that H<sub>2</sub>O\* vapor may reach, or closely approach, isotopic steady state. Substitution of Eqn. 11 and 14b into Eqn. 13, with an assumption that  $R_v$  is at steady-state, yields:

$$\frac{1}{2} K_G R_{Vss} \left( \frac{C_{eq}}{C_v^*} - 1 \right) = \frac{1}{2} R_{Gv} K_G \left( \frac{C_{eq}}{C_v^*} - 1 \right) + K_1 \left( \frac{1}{Y_H} R_G - \frac{Y_V}{Y_H} R_{Vss} - \alpha_{H-v} R_{Vss} \right) \quad (15)$$

It is assumed that there is a systematic relationship between the values of  $R_G$  and  $R_{Gv}$  that can be expressed with a fractionation factor  $\alpha_{G-Gv}$ . Also, as noted previously, it is assumed that  $C_v^*$  quickly reaches a steady-state value ( $C_{Vss}^*$ ) for any particular dehydration experiment. With relevant substitutions, grouping of similar terms, and rearrangement of Eqn. 15, the resultant expression is:

$$\frac{R_{Vss}}{R_G} = \frac{\left\{ \frac{1}{2} K_G \alpha_{G-Gv} \left( \frac{C_{eq}}{C_{Vss}^*} - 1 \right) + \frac{1}{Y_H} \right\}}{\left\{ \frac{1}{2} K_1 \left( \frac{C_{eq}}{C_{Vss}^*} - 1 \right) + \frac{Y_V}{Y_H} + \alpha_{H-v} \right\}} \quad (16)$$

From Eqn. 7,

$$\left( \frac{C_{eq}}{C_{Vss}^*} - 1 \right) = \frac{-m}{\Phi K_G}$$

Therefore,

$$\frac{R_{Vss}}{R_G} = \frac{\left\{ \frac{(-m)}{2\Phi K_1 \alpha_{G-Gv}} + \frac{1}{Y_H} \right\}}{\left\{ \frac{(-m)}{2\Phi K_1} + \frac{Y_V}{Y_H} + \alpha_{H-v} \right\}} \quad (17)$$

Use of the data in Table 1 to test the possible validity of the model represented by Eqn. 17 depends on the successful de-

velopment of an expression for the relationship between the  $\delta^{18}\text{O}$  of the H<sub>2</sub>O\* vapor and the measured plateau  $\delta^{18}\text{O}$  of the CO<sub>2</sub> evolved from goethite. The rate of oxygen isotope exchange between CO<sub>2</sub> and the steady-state H<sub>2</sub>O\* vapor is assumed to be reasonably well represented by a pseudo first-order equation of the following form (e.g., Criss et al., 1987):

$$\frac{dR_{CO_2}}{dt} = K_2 [\alpha_{CO_2-v} R_{Vss} - R_{CO_2}] \quad (18)$$

If the number of moles of oxygen in each increment of evolved H<sub>2</sub>O is much greater than the number of moles of oxygen in co-evolved CO<sub>2</sub> (a reasonable assumption for the samples of this study), the solution to Eqn. 18 is:

$$R_{CO_2} = \alpha_{CO_2-v} R_{Vss} - (\alpha_{CO_2-v} R_{Vss} - R_0) e^{-K_2 t} \quad (19)$$

Rearranging Eqn. 19 to solve for  $R_{Vss}$ ,

$$R_{Vss} = \frac{R_{CO_2} - R_0 e^{-K_2 t}}{\alpha_{CO_2-v} (1 - e^{-K_2 t})} \quad (20)$$

Substitution of Eqn. 20 into Eqn. 17 yields:

$${}^{18}\alpha_{app} = \alpha_{CO_2-v} \frac{\left\{ \frac{|m|}{2\Phi K_1 \alpha_{G-Gv}} + \frac{1}{Y_H} \right\}}{\left\{ \frac{|m|}{2\Phi K_1} + \frac{Y_V}{Y_H} + \alpha_{H-v} \right\}} [1 - e^{-K_2 t}] + \alpha_o e^{-K_2 t} \quad (21)$$

Since  $-m > 0$ , it is represented as the absolute value,  $|m|$ , in Eqn. 21. Eqn. 21 predicts that  ${}^{18}\alpha_{app}$  should be related to the rate of dehydration as represented by  $|m|$ . This assumes that  $\Phi$ ,  $K_1$ ,  $K_2$ , and the various  $\alpha$  terms on the right-hand-side of Eqn. 21 have the same respective values in experiments performed at the same temperature.

One of the principal difficulties in the use of Eqn. 21 to predict values of  ${}^{18}\alpha_{app}$  as a function of  $|m|$  is assignment of an appropriate value for  $t$ . One approach to this problem is the use of a steady-state residence time ( $\tau_{ss}$ ) for the vapor in the transition state. Define  $\tau_{ss}$  as follows:

$$\tau_{ss} = \frac{V_{ts} C_{Vss}^*}{F_{in}} = \left\{ \frac{V_{ts} C_{Vss}^*}{\frac{1}{2} V_{ts} K_G (C_{eq} - C_{Vss}^*)} \right\} = \frac{2}{K_G \left( \frac{C_{eq}}{C_{Vss}^*} - 1 \right)} \quad (22)$$

But, from Eqn. 7

$$\frac{|m|}{\Phi} = K_G \left( \frac{C_{eq}}{C_{Vss}^*} - 1 \right)$$

Thus,

$$\tau_{ss} = \frac{2\Phi}{|m|} \quad (23)$$

Substitution of  $\tau_{ss}$  from Eqn. 23 for  $t$  in Eqn. 21 yields,



$$^{18}\alpha_{\text{app}} = \alpha_{\text{CO}_2\text{-v}} \frac{\left\{ \frac{|m|}{2\Phi K_1 \alpha_{\text{G-Gv}}} + \frac{1}{Y_{\text{H}}} \right\}}{\left\{ \frac{|m|}{2\Phi K_1} + \frac{Y_{\text{V}}}{Y_{\text{H}}} + \alpha_{\text{H-v}} \right\}} \left[ 1 - e^{-\left[ \frac{2\Phi K_2}{|m|} \right]} \right] + \alpha_{\text{O}} e^{-\left[ \frac{2\Phi K_2}{|m|} \right]} \quad (24)$$

If values for  $\alpha_{\text{H-v}}$ ,  $\alpha_{\text{G-Gv}}$ ,  $\alpha_{\text{CO}_2\text{-v}}$ , and  $\alpha_{\text{O}}$  can be established, along with the previously discussed values for  $Y_{\text{H}}$  and  $Y_{\text{V}}$ , Eqn. 24 can be used to calculate values of  $^{18}\alpha_{\text{app}}$  as a function of specified values of  $|m|/(2\Phi K_1)$  for different choices of the ratio  $K_2/K_1$ .

It is assumed that values for oxygen isotope partitioning between  $\text{Fe}_2\text{O}_3^*$  and  $\text{H}_2\text{O}^*$  ( $\alpha_{\text{H-v}}$ ) as a function of temperature are approximated by hematite-water vapor fractionation factors. There are a number of published hematite-liquid water fractionation curves (e.g., Yapp, 1990a; Zheng, 1991; Bao et al., 2000). The curves of Yapp (1990a) and Bao et al. (2000) are based on experiments in which hematite was precipitated from aqueous solutions. The Zheng (1991) results for hematite-liquid  $\text{H}_2\text{O}$  oxygen isotope exchange were calculated with a semi-empirical method. It is not apparent which of these curves might best be used to estimate the oxygen isotope fractionation represented by  $\alpha_{\text{H-v}}$  in the current experiments, but the hematite that formed in these dehydration reactions did not precipitate from aqueous solutions. As a basis for discussion, the hematite-liquid water curve ( $\alpha_{\text{H-L}}$ ) of Zheng (1991) was used in combination with the oxygen isotope fractionation factors for liquid  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  vapor ( $\alpha_{\text{L-v}}$ ) (Majoube, 1971; Horita and Wesolowski, 1994) to estimate values of  $\alpha_{\text{H-v}}$ .

A value of 1.0069 was used for  $\alpha_{\text{G-Gv}}$  at all temperatures (open-system dehydration of synthetic goethite, Yapp, 1990b). Values of  $\alpha_{\text{CO}_2\text{-v}}$  were determined by combining the fractionation factors for liquid  $\text{H}_2\text{O}$ - $\text{H}_2\text{O}$  vapor ( $\alpha_{\text{L-v}}$ ) with values for  $\text{CO}_2$  gas-liquid  $\text{H}_2\text{O}$  ( $\alpha_{\text{CO}_2\text{-L}}$ ) presented in Friedman and O'Neil (1977). The value of  $\alpha_{\text{O}}$  was calculated from the value of  $\alpha_{\text{CO}_2\text{-L}}$  at 25 °C (1.0412) and the goethite-liquid  $\text{H}_2\text{O}$  fractionation factor ( $\alpha_{\text{G-L}}$ ) of Yapp (1990a) at 25 °C (1.0061). The temperature of 25 °C was chosen as a representation of the "sedimentary" temperatures at which goethite commonly crystallizes (e.g., Langmuir, 1971). The value of  $\alpha_{\text{O}}$  at 25 °C is 1.0349.

For a particular goethite sample,  $\delta^{18}\text{O}$  values of  $\text{H}_2\text{O}$  vapor evolved during dehydration are more positive if there is a high degree of isotopic exchange with the  $\text{Fe}_2\text{O}_3^*$  and more negative if there is little or no such isotopic exchange (Yapp, 1990b). The extent of mineral-vapor exchange is related to the residence time of the  $\text{H}_2\text{O}^*$  in the transition volume, which is, in turn, related to the value of  $|m|$  (see Eqn. 23). Longer residence times (smaller values of  $|m|$ ) should result in more positive  $\delta^{18}\text{O}$  values of the evolved  $\text{H}_2\text{O}$  vapor up to the equilibrium limit. Depending on relative rates of the  $\text{CO}_2$ - $\text{H}_2\text{O}^*$  and  $\text{Fe}_2\text{O}_3^*$ - $\text{H}_2\text{O}^*$  exchange reactions,  $\delta^{18}\text{O}$  values of evolved  $\text{CO}_2$  may or may not reflect the patterns of isotopic variation in the  $\text{H}_2\text{O}$ . A series of calculations for  $^{18}\alpha_{\text{app}}$  (Eqn. 24) were performed for a dehydration temperature of 200 °C. At this temperature,  $\alpha_{\text{H-v}} = 0.9911$ , while  $\alpha_{\text{CO}_2\text{-v}} = 1.0225$ . Calculated values of  $^{18}\alpha_{\text{app}}$  are presented in Fig. 5 for values of  $|m|/(2\Phi K_1)$  that range from 0 to 100.

The competitive effects (on the value of  $^{18}\alpha_{\text{app}}$ ) of the rates of isotopic exchange with respect to the rate of dehydration are illustrated by the calculated curves of Fig. 5. For higher values of  $K_2/K_1$ , local minima of  $^{18}\alpha_{\text{app}}$  are predicted at progressively higher values of  $|m|/(2\Phi K_1)$ . In contrast, for  $K_2/K_1 \ll 1$ , no local minima are indicated and  $^{18}\alpha_{\text{app}}$  rapidly increases to its maximum value as  $|m|/(2\Phi K_1)$  increases. This maximum value of  $^{18}\alpha_{\text{app}}$  corresponds to the  $\delta^{18}\text{O}$  value of the  $\text{CO}_2$  at the time it was incorporated into the goethite structure. In other words, if the rate of  $\text{CO}_2$  removal from the goethite were much faster than the rate at which  $\text{CO}_2$  exchanges with the evolved  $\text{H}_2\text{O}$  vapor, the  $\text{CO}_2$  would retain its original  $\delta^{18}\text{O}$  value. The calculated value of  $^{18}\alpha_{\text{app}}$  as  $|m| \rightarrow 0$  (i.e.,  $\tau \rightarrow \infty$ ) corresponds to isotopic exchange equilibrium among the  $\text{Fe}_2\text{O}_3^*$ ,  $\text{H}_2\text{O}^*$ , and  $\text{CO}_2$  at the temperature of dehydration.

Measured  $^{18}\alpha_{\text{app}}$  values of Table 1 and Fig. 4 range from 1.0182 to 1.0263, decrease with increasing  $|m|$ , and exhibit no obvious local minima. The curves of Fig. 5 predict the observed  $^{18}\alpha_{\text{app}}$  values, a decrease of  $^{18}\alpha_{\text{app}}$  with increasing values of  $|m|$ , and an absence of minima in the data if  $|m|/(2\Phi K_1) < \sim 5$  and  $K_2/K_1 \geq \sim 25$ . Thus, if the model represented by Eqn. 24 is applicable to the data of Fig. 4, the rate constant ( $K_2$ ) for oxygen isotope exchange between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapor at  $\sim 200$  °C is much larger than the rate constant ( $K_1$ ) for isotopic exchange between  $\text{Fe}_2\text{O}_3^*$  and  $\text{H}_2\text{O}^*$  vapor at 200 °C. This interpretation implies that, as a consequence of exchange processes operating during the solid-state goethite to hematite transition, none of the  $\text{CO}_2$  from the experiments of Table 1 retains the  $\delta^{18}\text{O}$  value it possessed at the time of incorporation into the goethite structure.

### 4.3. Model-Derived Parameters

The inset in Fig. 5 displays model curves with values of  $^{18}\alpha_{\text{app}}$  calculated for  $|m|/(2\Phi K_1) \leq 5$  and  $K_2/K_1 = 25$ . The upper curve in the inset corresponds to a dehydration temperature of 200 °C while the lower represents 230 °C. It should be noted that for the specified range of  $|m|/(2\Phi K_1)$ , any choice of  $K_2/K_1 > 25$  would yield calculated curves at 200 and 230 °C, which would be effectively coincident with the corresponding isothermal curves shown in the inset.

Calculated values of  $^{18}\alpha_{\text{app}}$  and their variation with a model-derived parameter involving  $|m|$  (curves in Fig. 5, inset) are notably similar to measured values and the pattern of variation of  $^{18}\alpha_{\text{app}}$  in Fig. 4. This similarity suggests that the model may reasonably approximate the processes that operate during isothermal vacuum dehydration of goethite. If so, a value for  $2\Phi K_1$  may be calculated from the model (Eqn. 24) and measured values of  $^{18}\alpha_{\text{app}}$  and  $|m|$ . A value of  $0.0030 \text{ min}^{-1}$  for  $2\Phi K_1$  at 200 °C was calculated for the isothermal dehydration of MPCUtah-1 (Table 1). All other values of  $|m|$  in Table 1 were then divided by this value of  $0.0030 \text{ min}^{-1}$  to obtain model-derived values of  $|m|/(2\Phi K_1)$ . Measured values of  $^{18}\alpha_{\text{app}}$  are plotted against these proportionally adjusted values of  $|m|$  (i.e.,  $|m|/[2\Phi K_1]$ ) in the inset of Fig. 5.

With one exception (MSwitz-1), these adjusted data of Table 1 scatter between the 200 and 230 °C curves of Fig. 5 (inset). Much of this scatter reflects the scatter in Fig. 4. However, some of the scatter in Fig. 5 may also indicate that information is lost when adjustment of measured values of  $|m|$  is performed

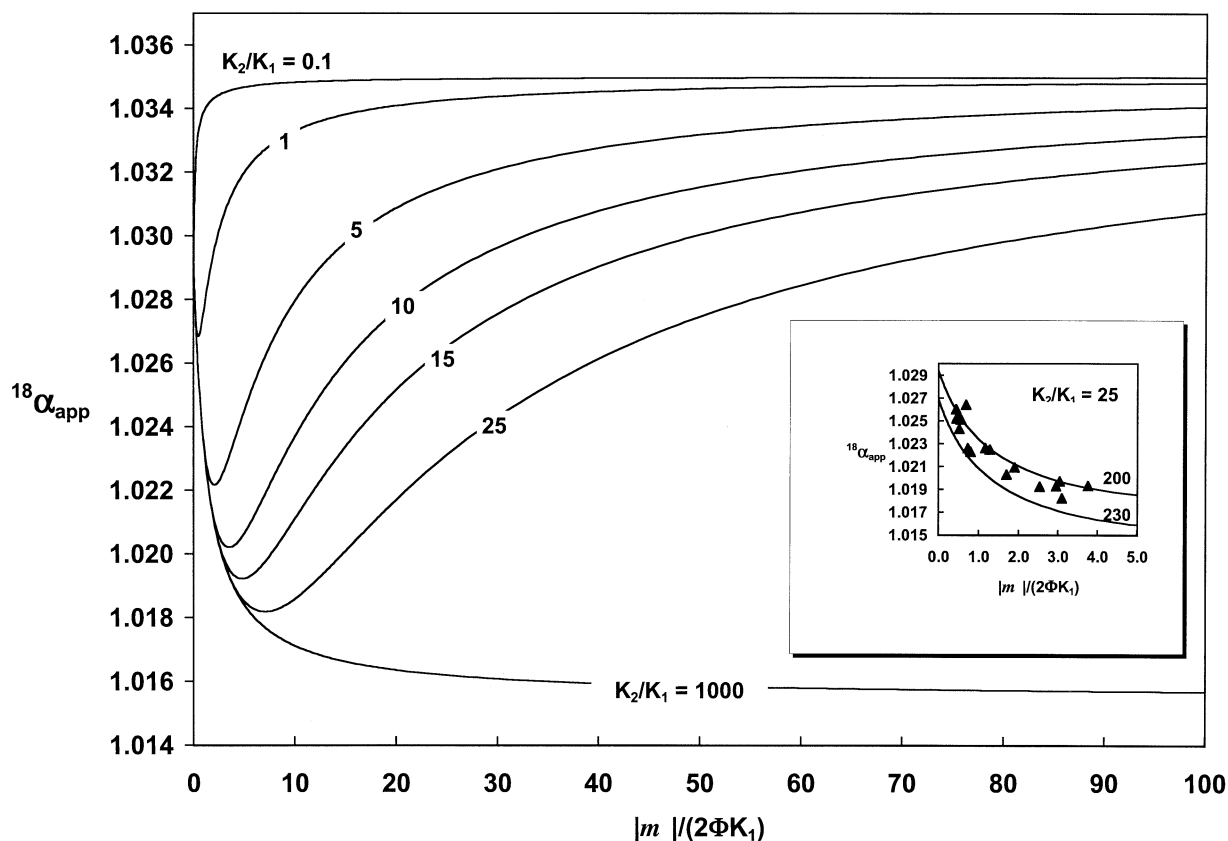


Fig. 5. Curves depicting the variation of  $^{18}\alpha_{\text{app}}$  with  $|m|/(2\Phi K_1)$  as predicted by a model for oxygen isotope variation of  $\text{CO}_2$  evolved from goethite during isothermal dehydration. The pattern of variation is sensitive to the relative magnitudes of  $K_1$  and  $K_2$ .  $K_1$  is the rate constant for oxygen isotope exchange between  $\text{Fe}_2\text{O}_3^*$  and  $\text{H}_2\text{O}^*$ , and  $K_2$  is the rate constant for oxygen isotope exchange between evolving  $\text{CO}_2$  and  $\text{H}_2\text{O}^*$ . See text and Appendix for definitions. The inset depicts calculated curves of  $^{18}\alpha_{\text{app}}$  vs.  $|m|/(2\Phi K_1)$  at 200 °C (upper curve) and 230 °C (lower curve) for  $K_2/K_1 = 25$  and values of  $|m|/(2\Phi K_1)$  between 0 and 5. The data points in the inset are from Table 1 with proportional adjustment of the measured values of  $|m|$  (see text).

with a single value for  $2\Phi K_1$ . For example, the measured values of  $|m|$  and  $^{18}\alpha_{\text{app}}$  for OPWis-9, which was dehydrated at 230 °C (Table 1), yield a calculated value of  $0.0043 \text{ min}^{-1}$  for  $2\Phi K_1$ —i.e., almost 50% larger than the value calculated from the 200 °C data of MPCUtah-1. Even if these values for  $2\Phi K_1$  are reasonably accurate, they are probably significantly smaller than  $K_1$ . This supposition is based on the fact that  $\Phi$  is defined as  $n_v^*/n_G$ , and it is likely that  $n_v^* \ll n_G$ . Thus,  $\Phi \ll 1$ .

Eqn. 24 (for  $K_2/K_1 = 25$ ) and measured values of  $^{18}\alpha_{\text{app}}$  in Table 1 were used to calculate values for  $W$  at the nominal dehydration temperatures, where

$$W = |m|/(2\Phi K_1) \quad (25)$$

Values of  $W$  are plotted against corresponding measured values of  $|m|$  in Fig. 6. There is scatter in the “isothermal” data of Fig. 6 that may arise if, during dehydration, the actual temperature of a sample differed (e.g.,  $\sim 10$  °C) in some instances from the nominal furnace temperatures (e.g., Hancock and Sharp, 1972). However, notwithstanding the scatter, the 200 and 230 °C data of Fig. 6 appear to define distinctly separate arrays.

If the assumptions of the model are generally valid, isothermal arrays of  $W$  vs.  $|m|$  should be linear with slopes equal to

$1/(2\Phi K_1)$  and intercepts of zero (Eqn. 25). There are sufficient data for the 200 and 230 °C dehydration experiments to perform linear regressions of each, which were forced through the origin. The equations of these regressions and the associated lines are displayed in Fig. 6. The slopes are  $323 \pm 9 \text{ min}$  at 200 °C and  $212 \pm 20 \text{ min}$  at 230 °C. Values of  $r^2$  are 0.99 and 0.93, respectively.

Only three of the dehydration experiments of Table 1 were performed at 220 °C, and  $|m|$  was  $\geq 0.0051 \text{ min}^{-1}$  for each of these experiments. Nevertheless, with the assumption that Eqn. 25 is applicable, a linear regression of the 220 °C data points of Fig. 6 was forced through the origin and yielded a slope of 236 min. The standard error of the slope of the 220 °C line is not shown in Fig. 6 because of the small number of data. It is assumed that the standard error of the slope for the 220 °C data is identical to that of the slope for the 230 °C data (i.e.,  $\pm 20$  min). The single data point representing the 210 °C experiment is not discussed here.

The reciprocals of the slopes determined from the linear regressions should approximate values of  $2\Phi K_1$ . These inferred “average” values for  $2\Phi K_1$ , with estimated uncertainties based on standard errors of the slopes of the lines in Fig. 6, are 0.0031

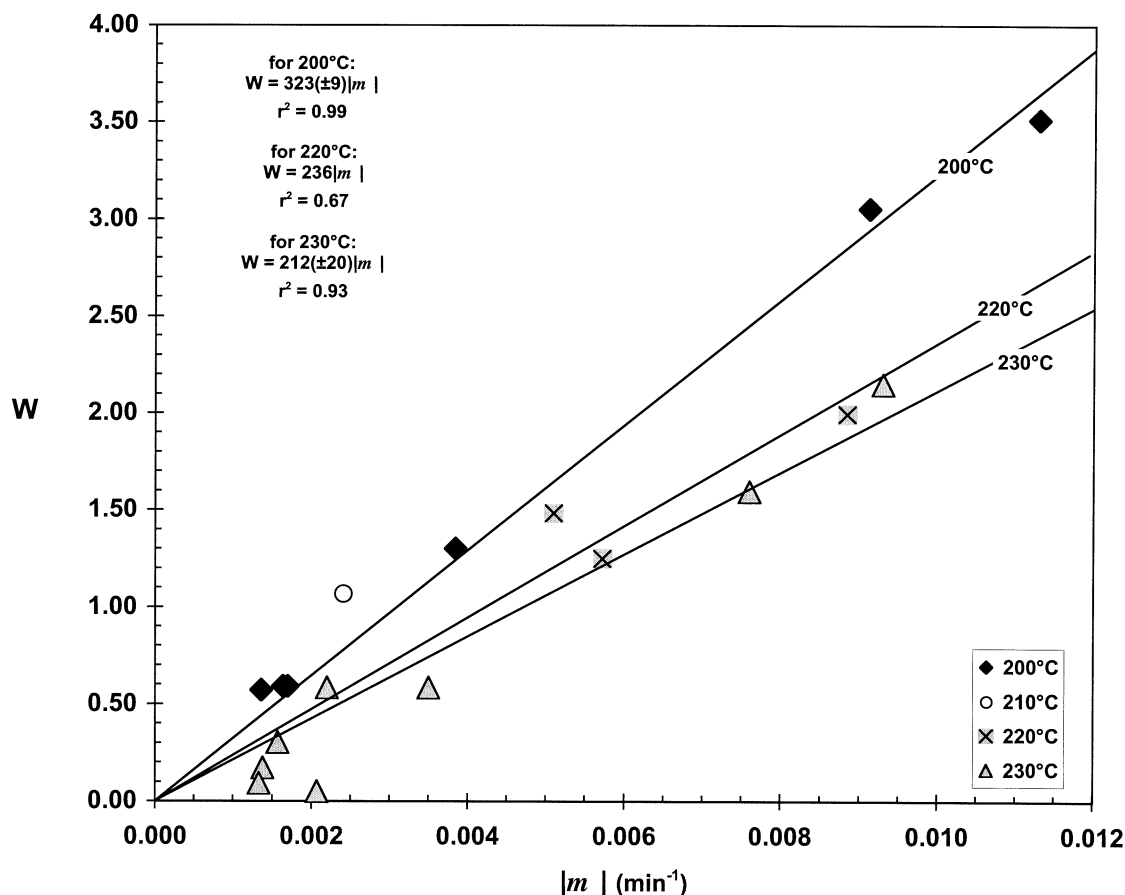


Fig. 6.  $W$  vs.  $|m|$  for the goethite samples of Table 1.  $W = |m|/(2\Phi K_1)$ . Values of  $W$  were calculated at the nominal dehydration temperatures of the samples of Table 1 using Eqn. 24 and the measured values of  $^{18}\alpha_{\text{app}}$ . The solid lines represent linear regressions (and associated equations) for the dehydrations at 200, 220, and 230 °C (see text).

$\pm 0.0001 \text{ min}^{-1}$  (200 °C);  $0.0042 \pm 0.0005 \text{ min}^{-1}$  (220 °C); and  $0.0047 \pm 0.0005 \text{ min}^{-1}$  (230 °C). As mentioned previously, the assumption of an approximately constant value for  $\Phi$  is problematic for any single dehydration experiment and even more problematic if  $\Phi$  is assumed to be constant among different experiments. However, unless they are accidental, the reasonably high degrees of coherence of the 200 and 230 °C arrays in Fig. 6 seem to support the assumption of constant  $\Phi$  as a first approximation.

If the differences among the values of  $2\Phi K_1$  for the three temperatures of dehydration are primarily a consequence of variations of  $K_1$  with temperature, a linear relationship might be expected on an Arrhenius-type plot of  $\ln(2\Phi K_1)$  vs.  $1/T$ . This is depicted in Fig. 7. There are only three points and the uncertainties are large, but the values of  $\ln(2\Phi K_1)$  appear to vary systematically with  $1/T$ . A linear regression of the data of Fig. 7 has a slope of  $-3392 \text{ K}$ . For Arrhenius-type behavior, this slope is equal to  $-E_a/R$ , where  $E_a$  is the activation energy, and  $R$  (8.314 J/K/mol) is the gas constant (Atkins, 1982). Therefore,  $E_a$  may have a value of  $28 \pm 11 \text{ KJ/mol}$ . An  $E_a$  value of 28 KJ/mol is at the low end of the range of values tabulated by Cole and Ohmoto (1986). The large number of assumptions inherent in the derivation of this putative value of

$E_a$  and the analytical uncertainties preclude speculation about its significance.

Kinetic data and plateau  $\delta^{18}\text{O}$  values of evolved CO<sub>2</sub> are routinely obtained in the course of measurements of the abundance and  $\delta^{13}\text{C}$  values of the Fe(CO<sub>3</sub>)OH in goethite. Therefore, these plateau  $\delta^{18}\text{O}$  data could provide useful complementary information on the approximate  $\delta^{18}\text{O}$  value of the goethite structural oxygen (O, OH, CO<sub>2</sub>). However,  $\delta^{18}\text{O}$  values of the goethite structural oxygen estimated in this manner are likely to be accurate to only about  $\pm 1\%$ . Moreover, the somewhat anomalous behavior of MSwitz-1 suggests that significant amounts of admixed kaolinite may affect the oxygen isotope composition of the CO<sub>2</sub> evolved from goethite.

## 5. CONCLUSIONS

Plateau  $\delta^{18}\text{O}$  values of CO<sub>2</sub> evolved during isothermal vacuum dehydration of goethite do not reflect the original  $\delta^{18}\text{O}$  value of the CO<sub>2</sub> occluded as Fe(CO<sub>3</sub>)OH in the mineral structure. However, the apparent oxygen isotope fractionation ( $^{18}\alpha_{\text{app}}$ ) between evolved plateau CO<sub>2</sub> and initial goethite exhibits a correlation with the rate of goethite dehydration. This nonlinear correlation and the magnitudes of the  $^{18}\alpha_{\text{app}}$  values can be explained with a relatively simple quantitative model, if

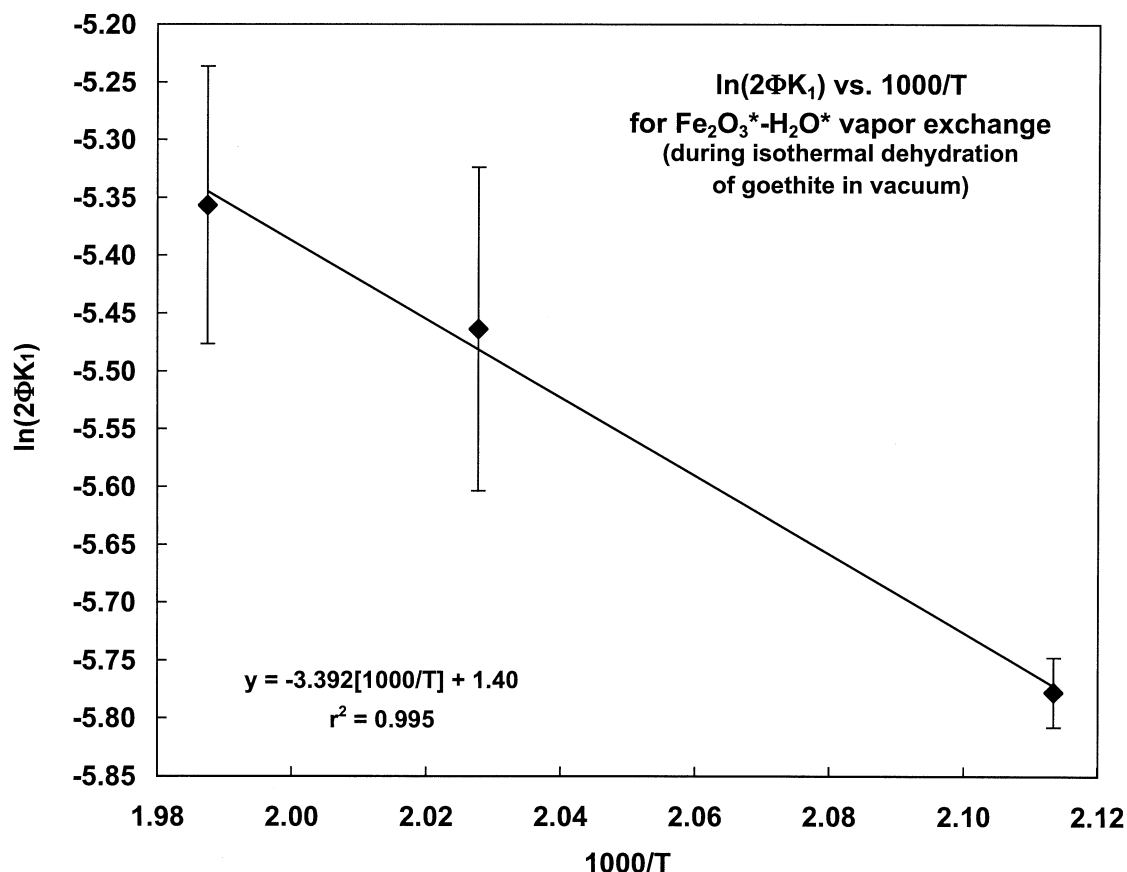


Fig. 7. Values of  $\ln(2\Phi K_1)$  vs.  $1/T$ . Values of  $\ln(2\Phi K_1)$  were calculated from the slopes of the linear regressions in Fig. 6. Error bars reflect the standard errors of the slopes in Fig. 6 (see text). The slope of the regression line shown here (with the attendant equation) may approximate  $-E_a/R$  for  $K_1$  with an inferred value for  $E_a$  of  $28 \pm 11$  KJ/mol (see text).

it is assumed that isotopic exchange between evolving  $H_2O$  vapor and residual solid occurs only in successive, local transition states and that the rate of isothermal vacuum dehydration of goethite is adequately represented by first-order kinetics. Model curves calculated for isothermal dehydrations in the range 200 to 230 °C largely encompass the experimental data. The rate constant for oxygen isotope exchange between the transition-state species  $Fe_2O_3^*$  and  $H_2O^*$  has an estimated activation energy of  $28 \pm 11$  KJ/mol.

The postulated existence of exchangeable  $Fe_2O_3^*$  and  $H_2O^*$  species in successive transition-state volumes is not proven, but the similarities of the measured results and model predictions support the hypothesis. Interestingly, Özdemir and Dunlop (2000) have suggested that small amounts of an intermediate magnetite ( $Fe_3O_4$ ) phase are formed (along with the dominant hematite) during dehydration of goethite. The isotopic implications of their suggestion are not known at present.

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## APPENDIX

### DEFINITIONS OF TERMS

$$^{18}\alpha_{\text{app}} = R_{\text{CO}_2}/R_{\text{G}}$$

$\alpha_{\text{CO}_2\text{-v}} = R_{\text{CO}_2}/R_{\text{H}_2\text{O v}} =$  the equilibrium oxygen isotope fractionation factor between CO<sub>2</sub> gas and H<sub>2</sub>O vapor

$$\alpha_{\text{G-Gv}} = R_{\text{G}}/R_{\text{Gv}}$$

$\alpha_{\text{H-v}} = R_{\text{H}}/R_{\text{v}} = K_{-1}/K_1 =$  the equilibrium fractionation factor between Fe<sub>2</sub>O<sub>3</sub>\* and H<sub>2</sub>O\* vapor in the transition state for the reaction as written (Eqn. 12)

$$\alpha_{\text{K}} = ^{18}\text{K}_{\text{v}}/\text{K}_{\text{v}}$$

$\alpha_{\text{O}} = R_{\text{O}}/R_{\text{G}} =$  the value (at the time of goethite crystallization) of the <sup>18</sup>O/<sup>16</sup>O fractionation factor between CO<sub>2</sub> incorporated in the crystal structure and the structural FeOOH

$C_{\text{eq}} =$  the concentration (mol/L) of H<sub>2</sub>O vapor in the transition volume if the vapor were in equilibrium with the goethite

$C_{\text{v}}^* = n_{\text{v}}^*/V_{\text{ts}} =$  the concentration (mol/L) of H<sub>2</sub>O vapor in the transition volume at each instant

$C_{\text{vss}}^* =$  steady-state value of  $C_{\text{v}}^*$

$k =$  the overall rate constant for phenomenological first-order dehydration kinetics of goethite

$K_{\text{G}} =$  rate constant (min<sup>-1</sup>) for the breakdown of goethite in the transition-state model

$K_{\text{v}} =$  rate constant (min<sup>-1</sup>) for the removal of H<sub>2</sub>O vapor from the transition volume

$^{18}\text{K}_{\text{v}} =$  rate constant for removal of H<sub>2</sub><sup>18</sup>O vapor from the transition volume

$K_1 =$  the forward rate constant of the exchange reaction of Eqn. 12

$K_{-1} =$  the rate constant for the reverse reaction of Eqn. 12

$K_2 =$  the rate constant for isotopic exchange between CO<sub>2</sub> gas and H<sub>2</sub>O\* vapor (Eqn. 18)

$m = -k$  (i.e., the measured slope of the line in plots of lnX<sub>S</sub>(H<sub>2</sub>) vs. t)

$n_{\text{G}} =$  moles of goethite (FeOOH) that remain at each instant of a dehydration reaction

$n_{\text{v}}^* =$  moles of H<sub>2</sub>O\* (at each instant in the successive transition volumes)

$$\Phi = n_v/n_G$$

$R_{CO_2}$  =  $^{18}O/^{16}O$  ratio of the evolved  $CO_2$  at each instant

$R_G$  = the  $^{18}O/^{16}O$  ratio of the structural oxygen in initial and residual goethite (assumed to remain constant throughout the dehydration process)

$R_{Gv}$  =  $^{18}O/^{16}O$  ratio of the water vapor at the moment of its formation upon the local breakdown of goethite (i.e., input vapor to successive transition volumes)

$R_H$  = the  $^{18}O/^{16}O$  ratio of the  $Fe_2O_3^*$  species in the transition volume

$R_0$  =  $^{18}O/^{16}O$  ratio of the  $CO_2$  at  $t = 0$ . This corresponds to the  $\delta^{18}O$  value of the  $CO_2$  at the time of its incorporation as  $Fe(CO_3)OH$  in the goethite structure

$R_v$  = the  $^{18}O/^{16}O$  ratio of the water vapor ( $H_2O^*$ ) in the transition volume at each instant

$R_{vss}$  = steady-state value of  $R_v$

$t$  = total elapsed dehydration time

$T$  = temperature; Kelvin (K) scale unless indicated otherwise

$V_{ts}$  = the instantaneous volume of each successive transition state

$$W = |m|/(2\Phi K_1)$$

$X_S(H_2)$  = hydrogen remaining in goethite as a mole fraction of the total initial hydrogen in the goethite

$X_v(H_2)$  = cumulative hydrogen evolved from goethite as a mole fraction of the total initial hydrogen in goethite

$Y_H$  = the oxygen in  $Fe_2O_3^*$  as a mole fraction of the total oxygen in each successive transition volume

$Y_v$  = the oxygen in  $H_2O^*$  vapor as a mole fraction of the total oxygen in each successive transition volume