

OXYGEN-ISOTOPE FRACTIONATION BETWEEN ALUMINUM-HYDROXIDE PHASES AND WATER AT <60°C: RESULTS OF DECADE-LONG SYNTHESIS EXPERIMENTS

FRÉDÉRIC VITALI,¹ FRED J. LONGSTAFFE,¹ MICHAEL I. BIRD,² AND W. GLEN E. CALDWELL¹

¹ Department of Earth Sciences, The University of Western Ontario, London, Ontario N6A 5B7 Canada

² Research School of Earth Sciences, The Australian National University, Canberra, A.C.T. 0200, Australia

Abstract—Oxygen-isotope data were obtained for synthetic aluminum-hydroxide phases precipitated over 65–125 mo and have been compared to results from similar experiments conducted for 3–56 mo. The Al(OH)₃ polymorphs, gibbsite, nordstrandite, and bayerite, were synthesized, but gibbsite was dominant in most samples, and commonly the only phase present. Using pure gibbsite samples, the following oxygen-isotope fractionation factors, $\alpha_{\text{gibbsite-H}_2\text{O}}$, were obtained: 1.0167 ± 0.0003 ($9 \pm 1^\circ\text{C}$), 1.0147 ± 0.0007 ($24 \pm 2^\circ\text{C}$), 1.0120 ± 0.0003 ($51 \pm 2^\circ\text{C}$). These values, and the associated equation for an oxygen-isotope geothermometer for the interval 0–60°C, $10^3 \ln \alpha_{\text{gibbsite-H}_2\text{O}} = 2.04 \times 10^6/T^2 - 3.61 \times 10^3/T + 3.65$ (T in K), are not significantly different from those obtained from experiments of much shorter duration. These results, and the good agreement with $\alpha_{\text{gibbsite-H}_2\text{O}}$ values obtained for well-constrained natural systems, suggest that the experimentally determined fractionation factors describe equilibrium conditions for gibbsite that has precipitated directly from solution.

As also proposed by others using a modified-increment calculation, our synthesis experiments suggest that $\alpha_{\text{Al(OH)}_3\text{-H}_2\text{O}}$ is polymorph-dependent at low temperatures and that a significant temperature-dependent trend exists in the values of $\alpha_{\text{Al(OH)}_3\text{-H}_2\text{O}}$. However, previously calculated fractionation factors obtained using the modified-increment method are higher than those obtained from the experiments, with this discrepancy becoming larger as temperature decreases.

Key Words—Aluminum Hydroxides, Fractionation Factor, Gibbsite, Oxygen Isotope, Synthesis.

INTRODUCTION

Aluminum-hydroxide phases are widely distributed at the surface of the earth, most commonly as gibbsite in soils and bauxite deposits (see Hsu, 1989, for a review). The two other Al(OH)₃ polymorphs, bayerite and nordstrandite, are rare but not unknown in nature (Hattaway and Schlanger, 1962; Wall *et al.*, 1962; Gross and Heller, 1963; Goldbery and Loughnan, 1970; Davis and Hill, 1974). The oxygen-isotope composition of aluminum-hydroxide phases has the potential to provide information about the conditions prevailing during the formation of soils and bauxites (Lawrence and Taylor, 1971, 1972; Bernard *et al.*, 1976; Bernard, 1978; Chen *et al.*, 1988, 1990; Bird *et al.*, 1989, 1990, 1992, 1994; Yapp, 1993). However, interpretation of such data requires high accuracy for the aluminum hydroxide-H₂O fractionation factors at low temperatures.

The oxygen-isotope fractionation factor (α) between a phase and H₂O is defined as:

$$\alpha_{\text{phase-H}_2\text{O}} = (\delta^{18}\text{O}_{\text{phase}} + 1000)/(\delta^{18}\text{O}_{\text{H}_2\text{O}} + 1000). \quad (1)$$

Fractionation factors are commonly determined by: (1) examination of natural assemblages, (2) calculations based on theoretical or semi-empirical models, or (3) experimental synthesis.

Several estimates of the gibbsite-H₂O fractionation factor at surficial temperatures were made using naturally occurring samples (Lawrence and Taylor, 1971,

1972; Chen *et al.*, 1988, 1990; Bird *et al.*, 1989, 1992, 1994). In these studies, crystallization temperatures and the oxygen-isotopic composition of coexisting water were estimated by considering the climatic conditions that likely prevailed during gibbsite formation. However, the reliability of fractionation factors obtained in this manner can be lowered by (1) incorrect assumptions about past climatic conditions, (2) possible contaminants such as kaolinite or amorphous material in natural samples, and (3) the potential for gibbsite formation by mechanisms other than neoformation. Bird *et al.* (1994) also calculated $\alpha_{\text{gibbsite-H}_2\text{O}}$ using the $\delta^{18}\text{O}$ values of coexisting gibbsite and kaolinite from a single sample or, at least, the same bauxite deposit. They assumed that the kaolinite-H₂O fractionation curve for oxygen isotopes is well defined and that the kaolinite and gibbsite formed from water of the same isotopic composition at the same temperature. Owing to the large variation of age and provenance of the samples, the latter assumption may not always be correct.

Semi-empirical models for the calculation of oxygen-isotope mineral-H₂O fractionation factors have become increasingly useful in recent years, especially for low-temperature systems (*e.g.*, Savin and Lee, 1988; Zheng, 1998). Recently, Zheng (1998) used a modified-increment calculation to produce oxygen-isotope geothermometers for the aluminum hydroxide-H₂O system. These results also predicted different nord-

trandite-H₂O, bayerite-H₂O, and gibbsite-H₂O oxygen-isotope fractionations for these minerals formed under similar conditions.

Previous experimental determinations of the gibbsite-H₂O oxygen-isotope fractionation factor are based on the analysis of synthetic aluminum-hydroxide phases precipitated over 3–56 mo (Bird *et al.*, 1994). In this paper, we report on a continuation of the experiments of Bird *et al.*, (1994) for an additional 65–121 mo. We have three main objectives: (1) to compare the values of the fractionation factors obtained between the shorter and longer experiments as a measure of the approach to isotopic equilibrium achieved; (2) to compare the experimentally derived oxygen-isotope geothermometer for the gibbsite-H₂O system at low temperatures (<60°C) with those obtained from previous natural, experimental, and theoretical studies; and (3) to investigate experimentally the possibility that $\alpha_{\text{Al(OH)}_3\text{-H}_2\text{O}}$ values differ at low temperatures for gibbsite, bayerite, and nordstrandite.

METHODS

Aluminum-hydroxide synthesis

The syntheses of aluminum-hydroxide precipitates were conducted in full, sealed 500-mL Nalgene bottles at 9 ± 1 , 24 ± 2 , and $51 \pm 2^\circ\text{C}$, as described by Bird *et al.* (1994), and generally follow the procedures of McHardy and Thomson (1971) and Hsu (1966). Briefly, three approaches were used: Method A—Synthesis from aging hydroxy-aluminum solutions; NaOH solution was added dropwise to a solution of AlCl₃ to produce a concentration of 0.02 M for Al and an OH/Al ratio of 2.2–2.4. Method B—Synthesis by hydrolysis: (i) An aluminum foil was degreased in acetone and amalgamated by dipping in a solution of HgCl₂ (dissolved in acetone with a concentration of 1% HgCl₂, 99% acetone) for 5–10 s. Excess solution was removed by rinsing in water, and the foil placed in a 0.003 or 0.006 M solution of acetic acid. (ii) Alternatively, to retard the hydrolysis reaction, HgCl₂ was omitted in some cases, and instead, aluminum turnings were etched for 30 s in 6 N HCl, rinsed in water, and placed in 0.003 or 0.006 M acetic acid. Method C—Synthesis by aging of an amorphous aluminous precipitate: An amorphous aluminous precipitate was formed on aluminum bars at 25°C. The precipitate was removed and bottled in the same water, or washed and bottled using distilled water.

The precipitates of aluminum hydroxide formed from each of the above methods were sampled after 3–56 mo, and then the oxygen-isotope results were reported by Bird *et al.* (1994). These experiments were then allowed to continue, and the additional results provide the basis for this paper. Samples G-19B, G-20A, G-20B, G-21A, and G-21B, maintained at $8 \pm 2^\circ\text{C}$ for 24 mo for the study of Bird *et al.* (1994), were

maintained at a similar temperature (9°C) for an additional 67 mo. Nine solutions (G-3A, G-3B, G-3C, G-5A, G-5B, G-10B, G-11A, G-12A, G-16A), maintained at 22–25°C for 3–56 mo for the study of Bird *et al.* (1994), were maintained at 24°C for an additional 65–121 mo. Solutions G-13B and G-14B, maintained at 51°C for 24 mo for the study of Bird *et al.* (1994), were placed at 24°C for an additional 65 mo. Solution G-12B, which was originally sampled by Bird *et al.* (1994) after 7 mo at 51°C, was subsequently maintained at 24°C for 46 mo, all precipitate then removed, and the remaining solution allowed to stand for an additional 65 mo at 24°C prior to sampling for this study. For each solution, the pH was measured, and then an aliquot of precipitate extracted by centrifugation using capped and sealed centrifuge tubes. The precipitate was washed four times and then freeze-dried for mineralogical and oxygen-isotopic analysis. Supernatant water was retained for oxygen-isotopic analysis.

Mineralogical and isotopic analyses

A Rigaku rotating-anode X-ray diffractometer, equipped with a curved-crystal monochromator and utilizing CoK α radiation, was used to identify the solid phases produced by syntheses and to estimate the relative abundances. All samples were examined using a Philips CM10 transmission electron microscope (TEM), operated at an accelerating voltage of 80 or 100 kV and with an objective aperture size of 30 μm . Selected samples were sputter-coated with 20–30 nm of gold, and examined using a Hitachi S-4500 field-emission scanning electron microscope (FE-SEM) using a 5 kV electron beam and a working distance of 15 mm.

The oxygen-isotope results for water and solids are reported using the standard delta (δ) notation in parts per thousand (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) (Coplen, 1994). The $\delta^{18}\text{O}$ values of water samples were determined using the CO₂-H₂O equilibration method (Epstein and Mayeda, 1953). Prior to analysis, aluminum-hydroxide samples were degassed under vacuum at 90°C for 13 h. Oxygen for isotopic analysis was liberated quantitatively from dried (8–10 mg) samples by reaction with bromine pentafluoride at 580–600°C, and converted to CO₂ by reaction with an incandescent carbon rod (Clayton and Mayeda, 1963). All isotopic measurements were performed using a VG-Optima dual-inlet, triple-collecting, stable-isotope ratio mass spectrometer. An average value of $-7.30 \pm 0.07\text{‰}$ was obtained for a VSMOW-Standard Light Antarctic Precipitation (SLAP) normalized internal water standard (accepted value, -7.27‰). An average $\delta^{18}\text{O}$ value of $11.52 \pm 0.19\text{‰}$ was obtained for an internal quartz standard (accepted value, 11.5‰), which corresponds to a value of 9.6‰ for National Bu-

Table 1. Mineralogical, chemical, and oxygen-isotope results for aluminum-hydroxide syntheses.

Sample	Method (see text)	Total months elapsed ¹	Mineralogy ²	Temp. (°C)	pH (final) ³	$\delta^{18}\text{O}_{\text{minerals}}$ (‰)	$\delta^{18}\text{O}_{\text{water}}$ (‰)	$\alpha_{\text{m-w}}$ (± 0.0005)
G-3A	A	114 (49)	G	24	3.9 (3.6)	8.9	-6.5	1.0155
G-3B	A	114 (49)	G	24	3.8 (3.5)	7.8	-6.2, -6.2	1.0140
G-3C	A	114 (49)	G	24	3.9 (3.6)	8.5	-5.9	1.0144
G-5A	B(i)	125 (4)	G	24	3.9 (3.8)	8.2	-6.7	1.0151
G-5B	B(i)	125 (6)	G	24	3.8 (3.8)	9.0	-6.1, -6.5	1.0154
G-10B	B(ii) ⁴	121 (56)	N + B	24	8.7 (8.5)	19.5	6.1	1.0133
G-11A	B(ii)	118 (53)	G(d) + B(m)	24	6.8 (5.1)	7.1	-7.1	1.0144
G-12A	B(ii)	118 (53)	G(d) + B(t)	24	4.7 (4.6)	7.0	-6.9	1.0140
G-12B	B(ii)	65 ⁵	B(d) + G(m) + amorph.	24 ⁵	4.2 (4.3)	7.1	-6.9	1.0141
G-13B	C	89 (24)	G	51 ⁶	3.6 (3.6)	5.3	-6.8	1.0122
G-14B	C	89 (24)	G	51 ⁶	3.6 (3.6)	5.0	-6.8	1.0118
G-16A	C	114 (3)	B + N?/G? + amorph.	24	4.2 (n.m.)	9.8	-7.2	1.0172
G-19B	B(ii)	91 (24)	G	9	6.7 (5.7)	8.7	-7.7	1.0165
G-20A	B(i)	91 (24)	G	9	6.7 (5.6)	9.0, 8.8	-7.4	1.0164
G-20A T3%	B(i) ⁷	91 (24)	G	9	6.7 (5.6)	9.1	-7.4	1.0167
G-20A T5%	B(i) ⁷	91 (24)	G	9	6.7 (5.6)	9.1	-7.4	1.0166
G-20B	B(i)	91 (24)	G	9	6.8 (5.6)	8.6	-7.6	1.0164
G-21A	B(i)	91 (24)	G(d) + B(t)	9	4.2 (4.4)	9.4	-7.4	1.0169
G-21B	B(i)	91 (24)	G(d) + B(t)	9	4.2 (4.4)	9.3	-7.5, -7.5	1.0169

¹ Total months elapsed: time since the beginning of the synthesis; the values in parentheses are time elapsed prior to the earlier sampling by Bird *et al.* (1994).

² Mineralogy: G = gibbsite; B = bayerite; N = nordstrandite; amorph = amorphous material; d = dominant, m = minor, t = trace.

³ Values listed in parentheses were obtained at the time of sampling by Bird *et al.* (1994); n.m. = not measured.

⁴ Tank water used rather than distilled water.

⁵ This sample was incubated initially at 51°C; all precipitate was removed after 7 mo, and the temperature then lowered to 24°C. The precipitate formed during the next 46 mo was also discarded. Only solids formed during the subsequent 65 mo were analyzed in this study.

⁶ These samples were incubated at 51°C for 24 mo, after which the temperature was lowered to 24°C for the remainder of the experiment (65 mo).

⁷ Sample G-20A treated with 3% and 5% Na₂CO₃, respectively.

reau of Standards NBS-28. Reproducibility was better than $\pm 0.2\%$ for all synthesis solids and water samples.

RESULTS

Mineralogy

The X-ray diffraction (XRD) results show that gibbsite is the main product of the syntheses performed under acidic conditions (Table 1; Figure 1a), whereas nordstrandite and bayerite are abundant only in experiments under alkaline conditions (sample G-10B, Table 1; Figure 1b). Similar results were reported by Hsu (1989). Six samples contain both gibbsite and bayerite, although in two cases (G-21A, G-21B) the amount of bayerite is low and detectable only by TEM. XRD and TEM observations showed that samples G-12B and G-16A also contain amorphous material, in addition to well-crystallized aluminum hydroxides.

SEM photomicrographs, typical of the aluminum-hydroxide phases, are shown in Figures 2 and 3. Gibbsite occurs typically as thin, platy crystals with a diameter of $<0.4 \mu\text{m}$ (G-19B, Figure 2). Mixtures of nordstrandite and bayerite show a different mode of aggregation, which is characterized by thicker plates without a distinct habit and with diameters of $\leq 0.8 \mu\text{m}$, mixed with numerous smaller and thinner crystals

(G-10B, Figure 3). By TEM, the gibbsite generally appears as well-crystallized, hexagonal plates varying in diameter from 0.1 to 0.3 μm (G-11A, Figure 4), although larger particles ($\leq 0.7 \mu\text{m}$) were observed in some samples (G-12B, Figure 5a). Schoen and Roberson (1970) and McHardy and Thomson (1971) used TEM to show that bayerite was morphologically distinct from gibbsite. Such differences are observed here, with bayerite occurring as cone-shaped crystals (G-16A, Figure 5b) or in the shape of an hour glass (G-21B, Figure 5c).

Oxygen isotopes

The $\delta^{18}\text{O}$ values of the aluminum-hydroxide solids and coexisting H₂O, and resulting fractionation factors, are listed in Table 1. Bird *et al.* (1994) calculated $\alpha_{\text{gibbsite-H}_2\text{O}}$ using an average of the initial and final $\delta^{18}\text{O}$ values for the water used in the syntheses. In our calculations, the $\delta^{18}\text{O}$ value measured for the water at the end of the experiment was utilized. The two procedures produced very little difference in the calculated value of $\alpha_{\text{gibbsite-H}_2\text{O}}$ for oxygen isotopes. However, hydrogen-isotope results (Vitali *et al.*, unpubl. data) for the same samples indicate that the latter approach describes hydrogen-isotope equilibrium best, especially at very low temperatures.

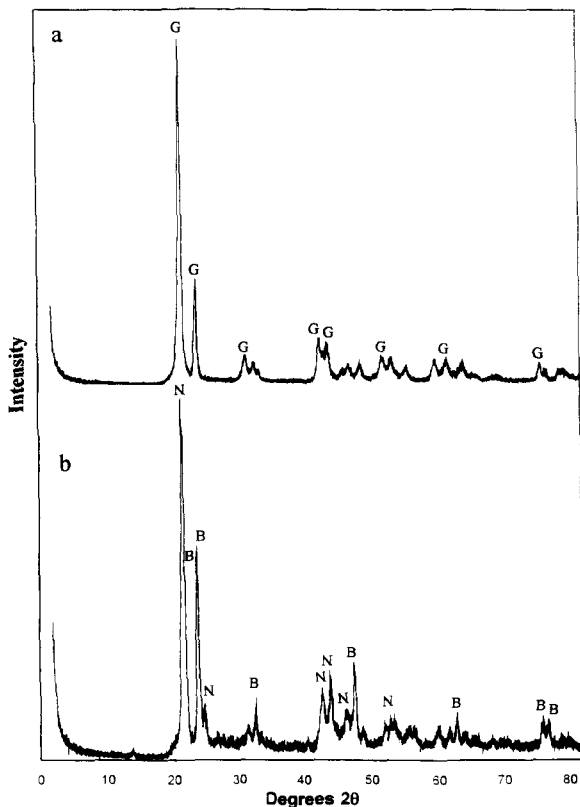


Figure 1. Characteristic X-ray diffractograms for the synthesis products: (a) gibbsite (G), sample G-20A; (b) bayerite (B) and nordstrandite (N), sample G-10B.

One feature of note is that $\alpha_{\text{gibbsite-H}_2\text{O}}$ for samples G-13B (1.0122) and G-14B (1.0118) did not change significantly after 65 mo at 24°C from the value obtained by Bird *et al.* (1994) at 51°C (1.0116 and 1.0122). Thus, Al(OH)₃ crystallization by Method C was completed in the first 24 mo and retrograde oxygen-isotopic exchange was insignificant during the subse-

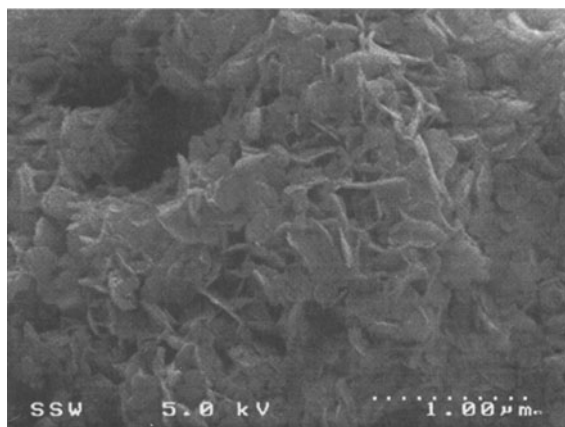


Figure 2. SEM photomicrograph of gibbsite (sample G-19B).

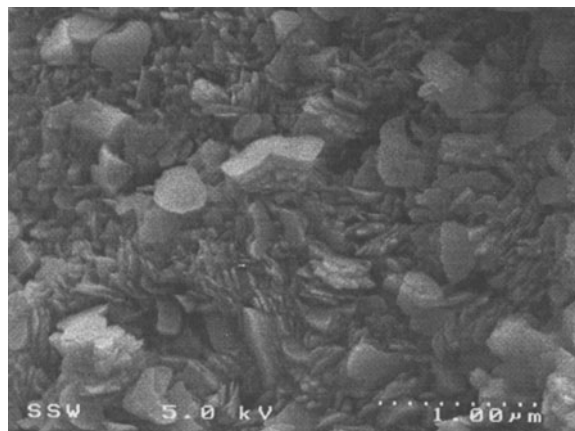


Figure 3. SEM photomicrograph of bayerite and nordstrandite mixture (sample G-10B).

quent period at a lower temperature. Accordingly, the data for these samples remain a good measure of $\alpha_{\text{gibbsite-H}_2\text{O}}$ at 51°C. By comparison, the value of $\alpha_{\text{gibbsite-H}_2\text{O}}$ for sample G-12B, which also was synthesized at 51°C for 7 mo, but using Method B (ii) rather than Method C, changed considerably from 1.0118 (Bird *et al.*, 1994) to 1.0141 after the temperature was lowered to 24°C. The latter value is within the range obtained for the other experiments conducted at 24°C. This sample precipitated aluminum hydroxide following the change in temperature; moreover, the solids produced during the final 65 mo of the experiment carried little, if any, memory of the higher-temperature history of the initial solution. The high-temperature signal probably was eliminated by the earlier extraction of all precipitate after 46 mo at 24°C (see Methods).

The values of $\delta^{18}\text{O}$ for the aluminum-hydroxide phases and coexisting H₂O are correlated to temperature and show the following ranges (excepting sample G-10B, which was synthesized using ¹⁸O-enriched water): 9°C (8.6 to 9.4‰; -7.7 to -7.4‰); 24°C (7.1 to

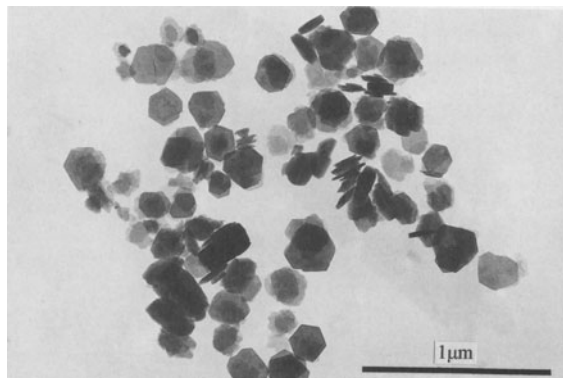


Figure 4. TEM photomicrograph of gibbsite particles (sample G-11A).

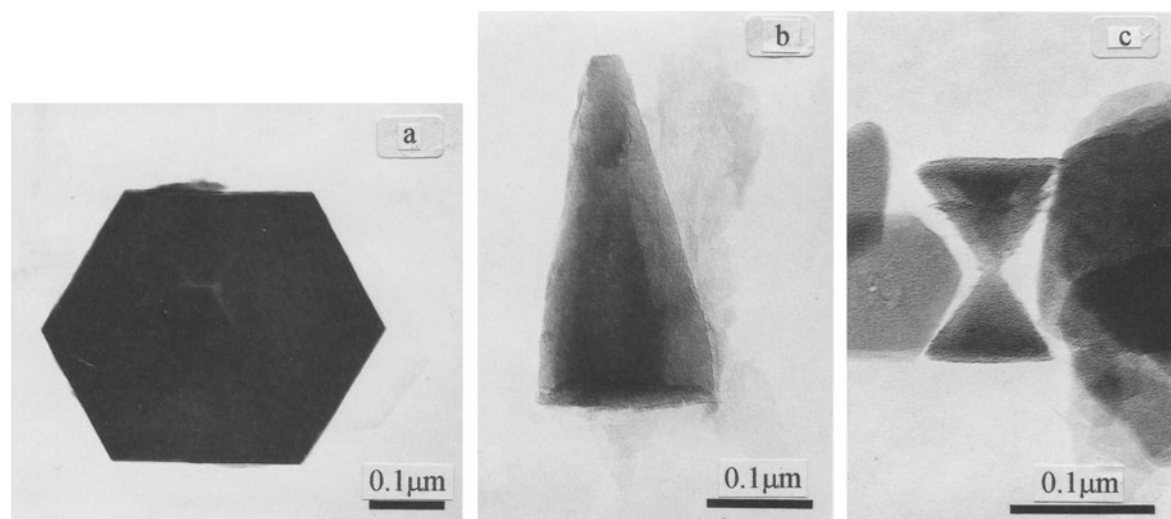


Figure 5. Characteristic morphology of $\text{Al}(\text{OH})_3$ polymorphs observed in TEM photomicrographs: (a) hexagonal plate of well-crystallized gibbsite (sample G-12B); (b) cone-shaped bayerite (sample G-16A); (c) triangular duplex of bayerite (hour-glass habit) (sample G-21B).

7.8‰; -7.2 to -5.9 ‰), and 51°C (5.0 to 5.3‰; -6.8 ‰). Such data are often more difficult to interpret because of the presence of precipitate containing amorphous aluminum hydroxide. For example, partial dehydroxylation of amorphous material during *in vacuo* heating of the samples prior to fluorination can cause the remaining solid to become enriched in ^{18}O (Bird *et al.*, 1994). Thus, amorphous material is commonly removed by overnight dissolution in a 5% Na_2CO_3 solution at room temperature (Jackson, 1975). Prior to isotopic analysis, Bird *et al.* (1994) followed this procedure to prepare samples. However, using that procedure, we observed significant dissolution of crystalline $\text{Al}(\text{OH})_3$, even at Na_2CO_3 concentrations as low as 3% (Figure 6). Partial dissolution did not affect the oxygen-isotope composition of the well-crystallized test sample (G-20A), which was free of amorphous material (Table 1). Nevertheless, given the small

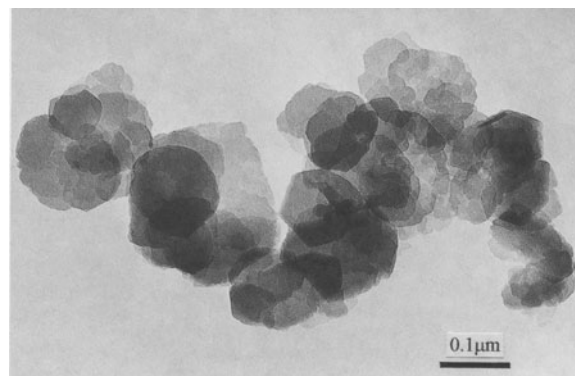


Figure 6. TEM photomicrograph of gibbsite partially dissolved by treatment with 5% Na_2CO_3 (sample G-20A T5%).

amount of material available for most samples, we did not continue to use this chemical treatment. Instead, samples were examined using TEM and XRD, and only those that contained abundant, well-crystallized $\text{Al}(\text{OH})_3$ were retained for oxygen-isotopic analysis. Two samples contained some amorphous material (G-16A \gg G-12B, Table 1). These samples were excluded from the determination of the fractionation factor at 24°C .

The aluminum-hydroxide phases in sample G-16A were synthesized using an amorphous precipitate initially formed at 25°C in water enriched in ^{18}O by ~ 12 ‰ relative to the G-16A solution (Bird *et al.*, 1994). After 3 mo, the solids that crystallized from amorphous material had exchanged ~ 40 – 50 % of the oxygen with the new solution (Bird *et al.*, 1994). The $\delta^{18}\text{O}$ value reported here for the G-16A synthesis after a total of 114 mo indicates that the percentage of exchange has increased to at least 80–85%. The true amount of exchange is probably even higher; the G-16A solids analyzed here included some dehydrated amorphous material, which is expected to have a higher oxygen-isotope value than the hydrated equivalent.

DISCUSSION

Oxygen-isotope fractionation factors for synthetic gibbsite and H_2O

The following average fractionation factors were calculated (Table 1) for well-crystallized Al-hydroxide samples containing ≥ 95 % gibbsite: 1.0167 ± 0.0003 ($9 \pm 1^\circ\text{C}$), 1.0147 ± 0.0007 ($24 \pm 2^\circ\text{C}$), 1.0120 ± 0.0003 ($51 \pm 2^\circ\text{C}$). From these data, the following oxygen-isotope geothermometer was obtained, which is valid for temperatures $< 60^\circ\text{C}$:

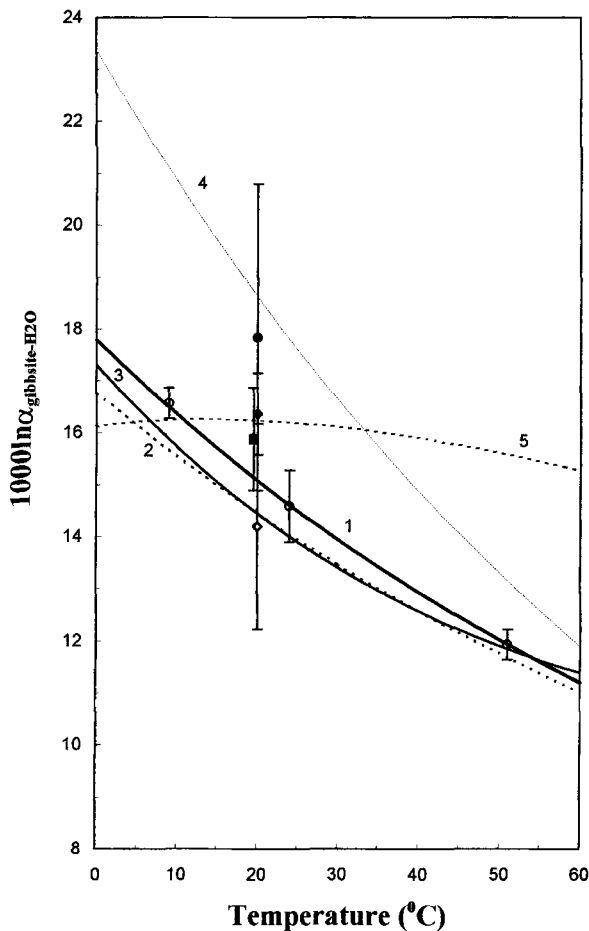


Figure 7. Oxygen-isotope fractionation in the gibbsite-H₂O system from 0 to 60°C as determined from synthesis experiments, bond-type and modified-increment calculations, and natural systems. Curve 1 = synthesis, this study (fractionation factors and associated errors at 9, 24, and 51°C are shown); curve 2 = synthesis, Bird *et al.* (1994); curve 3 = synthesis, recalculated from Bird *et al.* (1994); curve 4 = modified-increment calculation, Zheng (1998); curve 5 = bond-type calculation, Savin and Lee (1988). Fractionation factors from natural low-temperature settings: (●) Lawrence and Taylor (1972); (◆) Bernard (1978). (■) Chen *et al.* (1988), (◇) Bird *et al.* (1989).

$$10^3 \ln \alpha_{\text{gibbsite-H}_2\text{O}} = 2.04 \times 10^6/T^2 - 3.61 \times 10^3/T + 3.65 \quad (2)$$

where temperature, T, is in K. This equation represents a variation in $\alpha_{\text{gibbsite-H}_2\text{O}}$ from 1.0180 at 0°C to 1.0113 at 60°C.

Using the results for synthesis products formed after 3–56 mo, Bird *et al.* (1994) obtained the following linear expression for the oxygen-isotope fractionation between crystalline aluminum-hydroxide phases (mostly gibbsite, but including some samples dominated by nordstrandite or bayerite) and H₂O:

$$10^3 \ln \alpha_{\text{gibbsite-H}_2\text{O}} = 1.31 \times 10^6/T^2 - 0.78 \quad (3)$$

where temperature, T, is in K. We recalculated this equation to produce the following polynomial expression,

$$10^3 \ln \alpha_{\text{gibbsite-H}_2\text{O}} = 5.99 \times 10^6/T^2 - 30.95 \times 10^3/T + 50.3 \quad (4)$$

where temperature, T, is in K. Equation (4) allows for closer comparison with Equation (2).

Figure 7 illustrates that there are only small differences between the geothermometer obtained in the current study [Equation (2)] and that calculated from the data of Bird *et al.* (1994) [Equation (4)]. This result suggests that the use of the 5% Na₂CO₃ pretreatment by Bird *et al.* (1994) did not significantly affect the oxygen-isotope composition of the crystalline reaction products. Moreover, fractionation factors obtained after additional synthesis periods of 65–121 mo were not significantly different from those measured after 3–56 mo. Thus, these results suggest that a close approach to oxygen-isotope equilibrium was attained as the crystalline solids precipitated. The results discussed earlier for samples G-13B and G-14B also demonstrate the robust preservation of the oxygen-isotopic signature acquired by well-crystallized aluminum-hydroxide phases in low-temperature systems.

Nordstrandite-bayerite effects?

Although gibbsite was the only aluminum-hydroxide phase formed in many experiments, and the dominant phase in most, nordstrandite and bayerite were present in major, minor, or trace amounts in some samples. On the basis of the data available to them, Bird *et al.* (1994) suggested that the $\alpha_{\text{Al(OH)}_3\text{-H}_2\text{O}}$ value did not vary significantly with polymorph. On a theoretical basis, however, Zheng (1998) used the modified-increment method to calculate oxygen-isotope geothermometers for each aluminum-hydroxide polymorph. At 24°C, the values of Zheng (1998) for $1000 \ln \alpha_{\text{nordstrandite-H}_2\text{O}}$ and $1000 \ln \alpha_{\text{bayerite-H}_2\text{O}}$ produce results that are ~1 and ~2‰ lower, respectively, than those obtained using $1000 \ln \alpha_{\text{gibbsite-H}_2\text{O}}$. Consistent with this theoretical prediction, the value of $1000 \ln \alpha_{\text{Al(OH)}_3\text{-H}_2\text{O}}$ measured for the sample consisting of a mixture of nordstrandite and bayerite (G-10B) is ~1.5‰ lower than the average for the gibbsite samples formed at 24°C (Table 1). Reexamination of the data of Bird *et al.* (1994) shows similar results for some samples produced at ≤25°C. Polymorph-dependent fractionation may possibly explain why the average value of $\alpha_{\text{gibbsite-H}_2\text{O}}$ obtained at 22°C by Bird *et al.* (1994) was slightly lower than expected. Likewise, the small deviation at lower temperatures between Equations (2) and (4) may in part be a general consequence of this effect. However, no polymorph dependency of $\alpha_{\text{Al(OH)}_3\text{-H}_2\text{O}}$ is evident in the data of Bird *et al.* (1994) for syntheses conducted at 51°C. Additional experiments are needed to resolve these conflicting observa-

Table 2. Oxygen-isotope geothermometers and fractionation factors for gibbsite-H₂O.

Proposed geothermometers		Reference
$10^3 \ln \alpha_{\text{gibbsite-H}_2\text{O}} = 2.04 \times 10^6/T^2 - 3.61 \times 10^3/T + 3.65$		(This study)
$10^3 \ln \alpha_{\text{gibbsite-H}_2\text{O}} = 3.89 \times 10^6/T^2 - 8.52 \times 10^3/T + 2.42$		(Zheng, 1998)
$10^3 \ln \alpha_{\text{gibbsite-H}_2\text{O}} = 1.31 \times 10^6/T^2 - 0.78$		(Bird <i>et al.</i> , 1994)
$10^3 \ln \alpha_{\text{gibbsite-H}_2\text{O}} = 5.99 \times 10^6/T^2 - 30.95 \times 10^3/T + 50.3$		(Bird <i>et al.</i> , 1994, recalculated)
$10^3 \ln \alpha_{\text{AlOH-H}_2\text{O}} = -4.25 \times 10^6/T^2 + 29.6 \times 10^3/T - 35.28$		(Savin and Lee, 1988)
$\alpha_{\text{gibbsite-H}_2\text{O}}$	Temp. (°C)	
1.0173 ± 0.002^1	Surficial	(Bird <i>et al.</i> , 1994)
1.0163 ± 0.002^2	Surficial	(Bird <i>et al.</i> , 1994)
1.0143 ± 0.002	Surficial	(Bird <i>et al.</i> , 1989)
1.016 ± 0.001	19–20°C	(Chen <i>et al.</i> , 1988, 1990)
1.0165 ± 0.0008	Surficial	(Bernard, 1978)
1.018 ± 0.003	Surficial	(Lawrence and Taylor, 1972)

¹ Fractionation factor for gibbsite-H₂O calculated from the isotopic composition of pure kaolinite and gibbsite.

² Fractionation factor for gibbsite-H₂O assuming equilibrium between pure gibbsite and modern water.

tions. However, the possibility of a polymorph-dependent, oxygen-isotope fractionation effect in the aluminum hydroxide-H₂O system cannot be ignored, especially at low temperatures.

Comparison with other estimates of $\alpha_{\text{Al(OH)}_3\text{-H}_2\text{O}}$

The fractionation factors derived from synthesis experiments are compared to those obtained using samples from soils and bauxite deposits (Lawrence and Taylor, 1972; Bernard, 1978; Chen *et al.*, 1988; Bird *et al.*, 1989, 1994) in Table 2 and Figure 7. Studies of natural samples are often limited by the purity of the mineral separate obtained, and by assumptions of both temperature and oxygen-isotope composition of the water during gibbsite formation. The $\alpha_{\text{gibbsite-H}_2\text{O}}$ value (1.016) determined by Chen *et al.* (1988) is therefore particularly useful, because the gibbsite crystallization temperature of 19–20°C is well justified and the oxygen-isotopic composition of coexisting groundwater is known. A crystallization temperature of 20°C was assumed for the samples described by Lawrence and Taylor (1972), Bernard (1978), and Bird *et al.* (1989).

Most data plot near to the value of $\alpha_{\text{gibbsite-H}_2\text{O}}$ of 1.0152 predicted by Equation (2) for 20°C; an accurate value likely lies in the range 1.015–1.016. Bird *et al.* (1994) obtained a comparable average value of 1.0163 using the $\delta^{18}\text{O}$ values of 21 samples of gibbsite and modern meteoric water (Table 2). The value reported by Lawrence and Taylor (1972) is furthest from the other results and has the largest error, which suggests an impure sample and/or an incorrect assumption for the $\delta^{18}\text{O}$ value of coexisting meteoric water. Although these latter difficulties make the result suspect, Bird *et al.* (1994) noted that variations in $\alpha_{\text{gibbsite-H}_2\text{O}}$ are possible at low temperatures, arguing that: a) the $\delta^{18}\text{O}$ value of gibbsite may be partly determined by the chemistry of the solution (*e.g.*, dissolved sulphate concentration) and the complexes in which aluminum is transported to the site of precipitation, as previously

demonstrated by Bird *et al.* (1993) for titanium-oxide minerals, and b) gibbsite may inherit part or all of its oxygen by desilication of kaolinite, as opposed to direct precipitation from solution. A reliable, independent means of distinguishing between “primary” gibbsite formed from the desilication of clay minerals and “secondary” gibbsite formed by the translocation and reprecipitation of aluminum from solution must be developed to resolve such issues.

Figure 7 and Table 2 also provide a comparison between experimentally derived (this study, Bird *et al.*, 1994) and calculated gibbsite-H₂O geothermometers (Savin and Lee, 1988; Zheng, 1998). The geothermometer of Savin and Lee (1988) was calculated from the bond-type approach, where the isotopic behavior of oxygen in a mineral depends mostly on the atoms to which the oxygen is bonded. The resulting geothermometer is largely insensitive to temperature at <60°C, with $\alpha_{\text{gibbsite-H}_2\text{O}}$ changing from 1.0163 at 0°C to 1.0154 at 60°C. As noted by Bird *et al.* (1994), this result differs from the synthesis results, which range from 1.0180 to 1.0113 over the same temperature range. Only at ~10°C do both methods produce a similar fractionation factor.

In contrast, Zheng (1998) used a modified-increment method to calculate $\alpha_{\text{gibbsite-H}_2\text{O}}$. This approach is an attempt to integrate the isotopic effects from vibrational frequency and reduced mass with those from crystal chemistry and structure. The resulting gibbsite-H₂O geothermometer follows a similar trend to that obtained from the synthesis experiments. However, the calculated variation in $\alpha_{\text{gibbsite-H}_2\text{O}}$ from 0°C (1.0236) to 60°C (1.0120) is larger than that obtained from experiment, and it becomes increasingly so with decreasing temperature. For example, the calculated value at 20°C (1.0188) is larger than any other average result shown in Figure 7 and Table 2 for natural or synthetic samples. Zheng (1998) noted that such a discrepancy may indicate unreliable (non-equilibrium) results in the

syntheses, or some error in the modified-increment method that affects minerals containing hydrogen bonds. The similarity between the fractionation factors obtained in shorter (Bird *et al.*, 1994) versus longer syntheses (this study) suggests that a further modification to the increment method is needed to model accurately oxygen-isotope fractionation in aluminum-hydroxide phases at low temperatures.

ACKNOWLEDGMENTS

We acknowledge thoughtful reviews of the manuscript by S. Guggenheim, S. Chaudhuri, and Y. Shieh. We thank R. Davidson, K. Law, P. Middlestead, and R. Smith for assistance in the laboratory. Financial support for this research was provided by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

- Bernard, C. (1978) Composition isotopique des minéraux secondaires des bauxites. Problèmes de genèse. Ph.D thesis, Université Paris VII, France, 272 pp.
- Bernard, C., Bocquier, G., and Javoy, M. (1976) Détermination des rapports isotopiques ¹⁸O/¹⁶O de la gibbsite et de la boehmite présentes dans différentes bauxites. *Comptes Rendus Académie Sciences Paris*, **282**, 1089–1092.
- Bird, M.I., Chivas, A.R., and Andrew, A.S. (1989) A stable-isotope study of lateritic bauxites. *Geochimica et Cosmochimica Acta*, **53**, 1411–1420.
- Bird, M.I., Chivas, A.R., and Andrew, A.S. (1990) Reply to Comment by C.H. Chen, Liu K.K., and Y.N. Shieh on "A stable-isotope study of lateritic bauxites". *Geochimica et Cosmochimica Acta*, **54**, 1485–1486.
- Bird, M.I., Longstaffe, F.J., Fyfe, W.S., and Bildgen, P. (1992) Oxygen-isotope systematics in a multiphase weathering system in Haiti. *Geochimica et Cosmochimica Acta*, **56**, 2831–2838.
- Bird, M.I., Longstaffe, F.J., Fyfe, W.S., and Bildgen, P. (1993) Oxygen-isotope fractionation in titanium oxide minerals at low temperature. *Geochimica et Cosmochimica Acta*, **57**, 3083–3087.
- Bird, M.I., Longstaffe, F.J., Fyfe, W.S., Tazaki, K., and Chivas, A.R. (1994) Oxygen-isotope fractionation in gibbsite: Synthesis experiments versus natural samples. *Geochimica et Cosmochimica Acta*, **58**, 5267–5277.
- Chen, C.H., Liu, K.K., and Shieh, Y.N. (1988) Geochemical and isotopic studies of bauxitisation in the Tatun volcanic area, Northern Taiwan. *Chemical Geology*, **68**, 41–56.
- Chen, C.H., Liu, K.K., and Shieh, Y.N. (1990) Comment on "A stable-isotope study of lateritic bauxite" by M.I. Bird, A.R. Chivas, and A.S. Andrew. *Geochimica et Cosmochimica Acta*, **54**, 1483–1484.
- Clayton, R.N. and Mayeda, T.K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta*, **27**, 43–52.
- Coplen, T.B. (1994) Reporting of stable hydrogen, carbon, and oxygen isotopic abundances (Technical Report). *Pure and Applied Chemistry*, **66**, 273–276.
- Davis, C.E. and Hill, V.G. (1974) Occurrence of nordstrandite and its possible significance in Jamaica bauxite. *Travaux Commission Internationale Etude Bauxites Alumine Alum. ICSOBA*, **11**, 61–70.
- Epstein, S. and Mayeda, T. (1953) Variations in the ¹⁸O/¹⁶O ratio in natural waters. *Geochimica et Cosmochimica Acta*, **4**, 213–224.
- Goldbery, R. and Loughnan, F.C. (1970) Dawsonite and nordstrandite in the Permian Berry Formation of the Sydney Basin, New South Wales. *American Mineralogist*, **55**, 477–490.
- Gross, S. and Heller, L. (1963) A natural occurrence of bayerite. *Mineralogical Magazine*, **33**, 723–724.
- Hathaway, J.C. and Schlanger, S.O. (1962) Nordstrandite from Guam. *Nature*, **196**, 265–266.
- Hsu, P.H. (1966) Formation of gibbsite from aging hydroxy-aluminum solutions. *Soil Science Society of America Proceedings*, **30**, 173–176.
- Hsu, P.H. (1989) Aluminum hydroxides and oxhydroxides. In *Minerals in Soil Environments*, 2nd edition, J.B. Dixon and S.B. Weed, eds., Soil Science Society of America, Madison, Wisconsin, 331–378.
- Jackson, M.L. (1975) *Soil Chemical Analysis Advanced Course*, 2nd edition. Published by the Author, Madison, Wisconsin, 895 pp.
- Lawrence, J.R. and Taylor, H.P., Jr. (1971) Deuterium and oxygen-18 correlation: Clay minerals and hydroxides in Quaternary soils compared to meteoric waters. *Geochimica et Cosmochimica Acta*, **35**, 993–1003.
- Lawrence, J.R. and Taylor, H.P., Jr. (1972) Hydrogen and oxygen isotope systematics in weathering profiles. *Geochimica et Cosmochimica Acta*, **36**, 1377–1393.
- McHardy, W.J. and Thomson, A.P. (1971) Conditions for the formation of bayerite and gibbsite. *Mineralogical Magazine*, **38**, 358–368.
- Savin, S.M. and Lee, M. (1988) Isotopic studies of phyllosilicates. In *Hydrous Phyllosilicates (Exclusive of Micas)*, *Reviews in Mineralogy*, Volume 19, S. W. Bailey, ed., Mineral Society of America, Washington, D.C., 189–223.
- Schoen, R. and Roberson, C.E. (1970) Structures of aluminum hydroxides and geochemical implications. *American Mineralogist*, **55**, 43–77.
- Wall, J.R.D., Wolfenden, E.B., Beard, E.H., and Deans, T. (1962) Nordstrandite in soil from west Sarawak, Borneo. *Nature*, **196**, 264–265.
- Yapp, C.J., (1993) The stable isotope geochemistry of low temperature Fe(III) and Al oxides with implications for continental paleoclimates. In *Climate Change in Continental Isotopic Records*, P.K. Swart, K.C. Lohmann, J. McKenzie, and S. Savin, eds., American Geophysical Union Monograph 78, Washington, D.C., 285–294.
- Zheng, Y.F. (1998) Oxygen isotope fractionation between hydroxide minerals and water. *Physics and Chemistry of Minerals*, **25**, 213–221.

E-mail of corresponding author: fvitali@julian.uwo.ca

(Received 29 July 1999; accepted 19 November 1999; Ms. 367; A.E. Sam Chaudhuri)