

## METASTABILITY IN NEAR-SURFACE ROCKS OF MINERALS IN THE SYSTEM $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}^1$

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**Abstract**—Gibbs free energies for phases in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  have been calculated from reversed experiments in order to correct earlier values and to calculate a phase diagram consistent with more recent experiments. An internally consistent diagram could not be calculated that agreed with all published experiments, and choices of preferred data were made. The following Gibbs free energies, relative to the elements at STP (298.15 K, 1 bar), have been derived:

$\Delta G_f^\circ(\text{diaspore}) = -921.19$ kJ/mole	$\Delta G_f^\circ(\text{pyrophyllite}) = -5266.47$ kJ/mole
$\Delta G_f^\circ(\text{kaolinite}) = -3800.18$ kJ/mole	$\Delta G_f^\circ(\text{andalusite}) = -2442.04$ kJ/mole
$\Delta G_f^\circ(\text{kyanite}) = -2443.66$ kJ/mole	$\Delta G_f^\circ(\text{sillimanite}) = -2439.63$ kJ/mole
$\Delta G_f^\circ(\text{gibbsite}) = -1154.9$ kJ/mole	$\Delta G_f^\circ(\text{bayerite}) = -1153.0$ kJ/mole
$\Delta G_f^\circ(\text{boehmite}) = -918.4$ kJ/mole	$\Delta G_f^\circ(\text{nordstrandite}) = -1154.1$ kJ/mole
$\Delta G_f^\circ(\text{halloysite}) = -3783.2$ kJ/mole	$\Delta G_f^\circ(\text{dickite}) = -3798.8$ kJ/mole

The above values were calculated assuming literature values for corundum, quartz, and  $\text{H}_2\text{O}$  (v).

Examination of available thermodynamic, experimental, and observational data on the aluminum hydroxides gibbsite, boehmite, bayerite, and nordstrandite suggests that these minerals are metastable with respect to diaspore + water at STP and at higher temperatures. Similarly, halloysite and dickite are metastable with respect to kaolinite at these conditions. The occurrence of these minerals in soils must therefore be ascribed to nonequilibrium processes, and the use of equilibrium phase diagrams to explain their occurrence is inappropriate.

**Key Words**—Aluminum hydroxide, Dickite, Gibbs free energy, Halloysite, Kaolinite, Metastability, Phase equilibria, Pyrophyllite.

### INTRODUCTION

The mere existence of a phase in surface or near-surface rocks does not imply that it is stable. Ostwald's step-rule shows that, especially in a low-temperature environment, phases may commonly be found that in a strict thermodynamic sense are metastable. Several phase diagrams in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  (e.g., Chesworth, 1972, 1975, 1980a, 1980b) imply that the phases nordstrandite, bayerite, boehmite, and gibbsite are stable phases in soils. In this paper available thermodynamic and phase equilibrium data are examined and used to derive thermodynamic data and phase relations for the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ . The results, which take into account additional experimental and thermodynamic data (Hemley *et al.*, 1980; Haas *et al.*, 1981; Hemingway and Sposito, 1990), and which correct errors in the earlier work of Perkins *et al.* (1979),

show that diaspore is the only stable aluminum hydroxide phase at near-surface conditions on the earth.

### THERMODYNAMIC PROPERTIES

Fifteen phases in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  have been considered: kyanite, andalusite, sillimanite, diaspore, kaolinite, pyrophyllite, corundum, gibbsite, bayerite, nordstrandite, boehmite, dickite, halloysite, quartz, and water. Thermodynamic properties of these phases have been derived from several sources (Table 1). Molar volumes for all phases except pyrophyllite were taken from Robie *et al.* (1979). The molar volume of pyrophyllite was calculated from unit-cell refinement (Lee and Guggenheim, 1981) on a sample from Ibitara, Brazil. This sample contained about 3% solid solution of Na, Mg, and Fe, which required a small linear volume correction in order to derive the volume of end-member pyrophyllite.

Entropy values for quartz, corundum, and pyrophyllite were taken from Robie *et al.* (1979). The high-temperature heat capacities and standard entropies of

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Table 1. Thermodynamic values for minerals in the system  $Al_2O_3$ - $SiO_2$ - $H_2O$ .<sup>1</sup>

Phase	Formula	Abbr	$V_m^{298}$ (cm <sup>3</sup> /mole)	$S_m^{298}$ (J/mole·K)	Coefficients for Cp equation				Source <sup>1</sup>
					A	B	C	D	
Quartz	SiO <sub>2</sub>	Oz	22.688 (1)	41.46 (20)	44.876	37.648	-0.057	-9.941	(1)
Corundum	Al <sub>2</sub> O <sub>3</sub>	Cor	25.57 (1)	50.92 (8)	153.489	1.956	-9.023	-20.267	(1)
Diaspore	AlO(OH)	Ds	17.76 (13)	35.34 (10)	250.963	-59.493	-34.684	18.696	(1)
Pyrophyllite	Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	Py	127.93 (15)	239.40 (40)	694.299	-7.230	-67.546	-6.454	(1)
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Ka	99.52 (26)	203.05 (125)	589.486	-19.893	-58.351	0.284	(1)
Andalusite	Al <sub>2</sub> SiO <sub>5</sub>	And	51.53 (4)	91.39 (14)	196.969	19.156	5.577	-42.705	(1)
Kyanite	Al <sub>2</sub> SiO <sub>5</sub>	Sil	44.09 (7)	82.30 (13)	181.138	27.067	-2.278	-48.565	(1)
Sillimanite	Al <sub>2</sub> SiO <sub>5</sub>	Ky	49.90 (4)	95.79 (14)	164.471	33.575	-0.010	-46.069	(1)
Bayelite	Al(OH) <sub>3</sub>	By	31.14 (9)	79.4 (45*)		**			(2), (3), (4)
Gibbsite	Al(OH) <sub>3</sub>	Gb	31.96 (8)	68.45 (38)	236.703	47.715	-29.022	7.916	(4), (5), (9)
Nordstrandite	Al(OH) <sub>3</sub>	Nrd	31.96 (9)	68.45 (63)		**			(4), (6), (7)
Boehmite	AlO(OH)	Bm	19.53 (5)	37.19 (21)	187.804	12.358	-22.898	5.820	(8), (9)
Halloysite	Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>	Hi	99.4 (13)	203.3 (32)	619.573	-35.829	-63.856	5.201	(9)
Dickite	Al <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>4</sub>	Dk	99.30 (18)	197.0 (32)	695.690	-60.181	-79.213	18.103	(9)

$C_p = A + 10^{-3}B \cdot T + 10^2 C \cdot T^{-1/2} + 10^4 D \cdot T^{-2}$  (J/mole·K).

\*Estimated uncertainty, none given.

\*\*No data available.

<sup>1</sup> Sources: (1) See text for sources of data; (2) Rothbauer *et al.* (1967); (3) Hemingway *et al.* (1978); (4) Apps *et al.* (1989); (5) Haas *et al.* (1981); Perkins *et al.* (1979); (6) Estimated entropy (Fyfe *et al.*, 1958); (7) Hathaway and Schlanger (1965); Bosmans (1970); (8) Hemingway and Sposito (1990); (9) Robinson *et al.* (1982).

Table 2. Gibbs energies and sources of data for reactions.<sup>1</sup>

Reaction	$\Delta G_{298}^\circ$ (kJ/mole)	Sources of data
(1) $2 \text{Ds} = \text{Cor} + \text{H}_2\text{O}(\text{v})$	$31.45 \pm 0.49$	Fyfe and Hollander (1964), Haas (1972)
(2) $\text{Py} = \text{And} + 3 \text{Qz} + \text{H}_2\text{O}(\text{v})$	$26.90 \pm 0.46$	Haas and Holdaway (1973)
(3) $\text{Py} + 6 \text{Ds} = 4 \text{And} + 4 \text{H}_2\text{O}(\text{v})$	$109.04 \pm 2.99$	Haas and Holdaway (1973), Hemley <i>et al.</i> (1980)
(4) $\text{Ka} + 2 \text{Qz} = \text{Py} + \text{H}_2\text{O}(\text{v})$	$17.04 \pm 0.83$	Reed and Hemley (1966), Hemley <i>et al.</i> (1980)
(5) $2 \text{Ka} = 2 \text{Ds} + \text{Py} + 2 \text{H}_2\text{O}(\text{v})$	$33.61 \pm 2.03$	$2(\text{reaction 4}) + (4/3)(\text{reaction 2}) - (1/3)(\text{reaction 3})$ ; Hemley <i>et al.</i> (1980)
(6) $\text{Py} = \text{Ky} + 3 \text{Qz} + 3 \text{H}_2\text{O}(\text{v})$	$25.21 \pm 0.46$	(reaction 2) - (reaction 8)
(7) $\text{Py} + 6 \text{Ds} = 4 \text{Ky} + 4 \text{H}_2\text{O}(\text{v})$	$102.28 \pm 3.01$	(reaction 3) - $4(\text{reaction 8})$
(8) $\text{Ky} = \text{And}$	$1.62 \pm 0.18$	Holdaway (1971)
(9) $\text{Ky} = \text{Si}$	$4.03 \pm 0.24$	Holdaway (1971)
(10) $\text{And} = \text{Si}$	$2.41 \pm 0.06$	Holdaway (1971)

<sup>1</sup>  $\Delta G_{298}^\circ$  values for reactions (5), (6), and (7) calculated from values for reactions (2), (3), (4), and (8).

andalusite, kyanite, and sillimanite came from Robinson *et al.* (1982) and Robie and Hemingway (1984). The calorimetric measurements of Perkins *et al.* (1979) were used to calculate the entropy of diaspore. As these measurements only extend to 520 K, the heat capacity was plotted against  $1/T$  and extrapolated graphically to 800 K in order to calculate entropy for higher temperature calculations. The entropy of kaolinite was estimated from the following relation using 1 atm values:  $S_{\text{T}}^\circ - S_{298}^\circ(\text{kaolinite}) = S_{\text{T}}^\circ - S_{298}^\circ(\text{serpentine}) + S_{\text{T}}^\circ - S_{298}^\circ(\text{pyrophyllite}) - S_{\text{T}}^\circ - S_{298}^\circ(\text{talc})$ . The entropy data for serpentine and talc were taken from Robie *et al.* (1979).

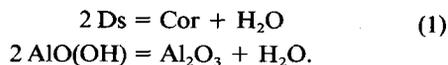
Thermal expansion data for  $\alpha$ -quartz and corundum were taken from Skinner (in Clark, 1966), and expansion data for the  $\text{Al}_2\text{SiO}_5$  polymorphs were from Winter and Ghose (1979). The thermal expansivity of kaolinite was assumed to be equal to that of pyrophyllite (Taylor and Bell, 1969), and the thermal expansion and compressibility of diaspore were assumed equal to those of corundum. Compressibilities of kyanite, andalusite, and sillimanite were measured by Brace *et al.* (1969); those for corundum and  $\alpha$ -quartz were listed by Birch (in Clark, 1966); the compressibilities of kaolinite and pyrophyllite were assumed to be equal to that of talc (Vaidya *et al.*, 1973).

The thermodynamic calculations in the present paper were made using the program THERMO (Perkins *et al.*, 1987), which is similar to the programs EQUILI (unpublished; developed by Wall and Essene) and PTX (Slaughter *et al.*, 1976). All calculations involved a second-order approximation in which it was assumed that 1 atm expansivities applied at higher pressures, and that 298 K compressibilities applied at higher temperatures. Modified Redlich-Kwong expressions (Kerrick and Jacobs, 1981) were used to calculate the thermodynamic properties of  $\text{H}_2\text{O}(\text{v}) > 400^\circ\text{C}$ ;  $< 400^\circ\text{C}$ , the data of Burnham *et al.* (1969) were used. Calculations by THERMO, using the data summarized above, were compared with experimental studies on selected reactions in order to derive values of  $\Delta G_{298}^\circ$  for the reactions.

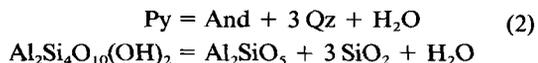
#### Evaluation of experimental data in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

Perkins *et al.* (1979) published a table of Gibbs energies for stable reactions in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ . They derived the values by fitting curves to experimental reversals and calculating the  $\Delta G_{298}^\circ$  for the reactions that were consistent with their fits. Attempts to recalculate their phase diagrams from these data, however, show that some errors are present in their tabulation of Gibbs energies. Because new thermodynamic and experimental data have become available that place tighter constraints on phase equilibria in this system, the calculations of Perkins *et al.* (1979) were repeated to obtain a set of thermodynamic parameters consistent with available reversed phase equilibrium experiments and thermophysical data (Table 2). The results of experimental studies that relied solely on synthesis from noncrystalline starting materials were not considered.

Fyfe and Hollander (1964), Haas (1972), and Hemley *et al.* (1980) studied the following reaction at pressures  $< 10$  kbar:



A calculated curve is consistent with all reversals except one of Hemley *et al.* (1980) (Figure 1). The inconsistency is well within the error of the data. A high-pressure extrapolation of this curve is consistent with the piston-cylinder experiments of Matushima *et al.* (1967). The reaction:



was studied experimentally by Kerrick (1968), Velde and Kornprobst (1969), Haas and Holdaway (1973), and Hemley *et al.* (1980) (Figure 1). The few experiments of Velde and Kornprobst (1969) on reaction (2) that tightly constrain the equilibrium, relied on the identification of very small amounts of pyrophyllite in run products. Inasmuch as these results disagree with

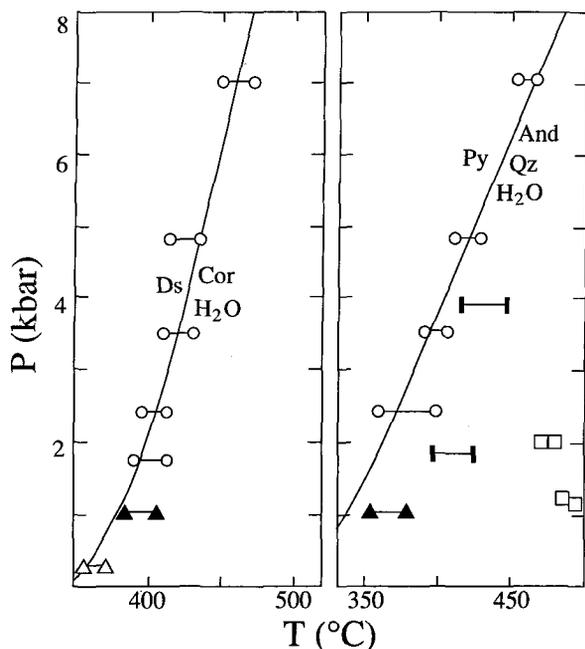
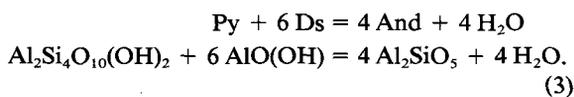


Figure 1. Experimental reversals of reaction (1)  $2\text{Ds} = \text{Cor} + \text{H}_2\text{O}$ , and of reaction (2)  $\text{Py} = \text{And} + 3\text{Qz} + \text{H}_2\text{O}$  compared to calculated curves (solid lines). In this and the next figure experimental reversals are indicated by open circles (Haas, 1972), solid triangles (Hemley *et al.*, 1980), open triangles (Fyfe and Hollander, 1964), vertical bars (Kerrick, 1968), solid circles (Haas and Holdaway, 1973), open squares (Velde and Kornprobst, 1969), solid squares (Thompson, 1970), and double lines at ends of bars (Reed and Hemley, 1966). Abbreviations defined in Table 1.

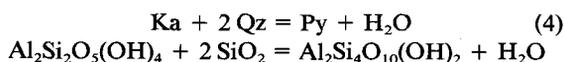
all other data, they have been discarded. The remaining data fit a calculated curve to within  $\pm 10^\circ\text{C}$ , except for the 1.8-kbar data of Kerrick (1968), which disagree by about  $30^\circ\text{C}$ . At high pressure (15–30 kbar), the calculated curve (after correcting for kyanite instead of andalusite) lies 10–20 $^\circ\text{C}$  below reversal temperatures obtained by Matushima *et al.* (1967).

Haas and Holdaway (1973) and Hemley *et al.* (1980) studied reaction (3):



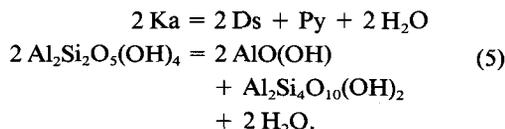
Their data agree with a curve calculated from Gibbs energies for pyrophyllite and diaspore calculated from reactions (1) and (2) (Figure 2).

Reaction (4):



was studied experimentally by several authors (Reed and Hemley, 1966; Velde and Kornprobst, 1969; Thompson, 1970; Hemley *et al.*, 1980). Unfortunately, these data are not internally consistent (Figure 2), and some decision as to which should be accepted was

therefore necessary. The data of Velde and Kornprobst (1969) are largely unreversed and have therefore been discarded. The data of Hemley *et al.* (1980,  $273 \pm 10^\circ\text{C}$ , 1 kbar) are consistent with the data of Reed and Hemley (1966,  $<300^\circ\text{C}$ , 1 kbar), but disagree with those of Thompson (1970). Some insight into this disagreement can be found by considering an experimental study (Hemley *et al.* 1980) of the reaction:



If Thompson's (1970) experiments are valid, reaction (4) is metastable with respect to the one reversal of Hemley *et al.* (1980) on reaction (5) at  $300 \pm 10^\circ\text{C}$ , 1 kbar. Because the results of Hemley *et al.* (1980) appear to be internally consistent, they are accepted here for both reaction (4) and (5); the results of Thompson (1970) have been ignored. Robinson *et al.* (1982) reached the same conclusions about the data of Kerrick (1968), Velde and Kornprobst (1969), and Thompson (1970).

#### *Self-consistent set of Gibbs energies and phase relations*

The triple point and reactions relating andalusite, kyanite, and sillimanite were derived from the data of Essene *et al.* (in preparation) and are consistent with the triple point reported by Holdaway (1971). If these values are combined with the values of the Gibbs energies at STP for reactions (1)–(4) calculated in the present study (Table 2), a consistent set of free energies for the individual phases can be derived. Values for the free energies of  $\text{H}_2\text{O}(\text{v})$ , corundum, and  $\alpha$ -quartz were assumed (Robinson *et al.*, 1982) in order to solve for the Gibbs energies of the remaining phases. The uncertainties in the Gibbs energies of reactions (1)–(4), determined from the widths of the reversal brackets, and in the Gibbs energies of formation of andalusite, diaspore, kaolinite, and pyrophyllite are given in Tables 2 and 3. Because the Gibbs energies of corundum, quartz, and water are assumed values in this study, the uncertainties in these values have not been included in the calculation of uncertainties for andalusite, diaspore, kaolinite, and pyrophyllite. Addition of these values increases the quoted standard deviations by 800–900 J/mole. All of these values are, however, highly correlated. Thus, the uncertainty in the Gibbs energy of a reaction calculated from the data given here is probably closer to the largest standard deviation of any of the phases involved, rather than the sum of the squares of the standard deviations of all of the phases in the reaction.

The resulting Gibbs energies are compared in Table 3 with previous compilations (Helgeson *et al.*, 1978; Robie *et al.*, 1979; Robinson *et al.*, 1982; Berman, 1988). The data in Helgeson *et al.* (1978) are consis-

tently less negative than the others, and can be traced to the value they assumed for corundum, which is about 12 kJ/mole less negative than those in the other compilations. The values obtained in the present study are in good agreement with those of Robie *et al.* (1979), Robinson *et al.* (1982), and Berman (1988). The small discrepancies do not seriously affect calculations involving dehydration reactions, but calculations of the few solid-solid reactions in the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system (e.g.,  $\text{Py} = \text{Ds} + \text{Qz}$ ) still have large uncertainties.

Our value for the Gibbs energy of kaolinite at STP ( $-3800$  kJ/mole), as well as those of the other published data bases, is only in fair agreement with results obtained from low-temperature solubility studies ( $-3776$  to  $-3783$  kJ/mole, Polzer and Hem, 1965; Kittrick, 1966, 1970). Hemingway (1982) pointed out that such studies often yield incorrect values due to slow reaction rates and the presence of fine particulates and metastable phases. The Gibbs energy obtained may therefore be systematically less stable than equilibrium values, as is observed, and we have therefore ignored the low-temperature solubility data.

*Metastability of boehmite, gibbsite, bayerite, and nordstrandite*

Chesworth (1978) criticized Day's (1976) conclusion that gibbsite and boehmite were metastable at *all* pressure and temperature conditions. Nevertheless, Perkins *et al.* (1979) also concluded that boehmite is metastable relative to diaspore or corundum +  $\text{H}_2\text{O}$  for all geological pressures and temperatures (i.e.,  $P > 1$  bar,  $T > 273$  K). Chesworth (1978) pointed out that large standard errors exist in tabulations of Gibbs energies of aluminum hydrates, consistent with the possibility that gibbsite and boehmite are stable near STP. He further argued that the occurrence of gibbsite and boehmite to the exclusion of diaspore in rocks formed at the earth's surface is a strong indication of their stability. It is important to evaluate these arguments, because they imply the existence of large errors in current experimental and thermodynamic data for the aluminum hydroxides. Chesworth (1972, 1975, 1980a, 1980b) presented several phase diagrams showing boehmite and gibbsite to be stable at STP without considering the possibility that diaspore is more stable. Thermodynamic and experimental data, however, show that gibbsite, boehmite, and bayerite are always metastable relative to diaspore and water at STP and that boehmite is metastable relative to diaspore at STP even if the uncertainties in the thermodynamic data are considered (Table 3).

Contrary to Chesworth's (1978) assertion, the occurrence of authigenic diaspore has been reported (Kraus, 1968; Shah, 1976; Hsu, 1977; Volochaev *et al.*, 1978). Many other geologically relevant systems exist in which stable assemblages are not formed at the surface of the Earth. For example, thermodynamic data

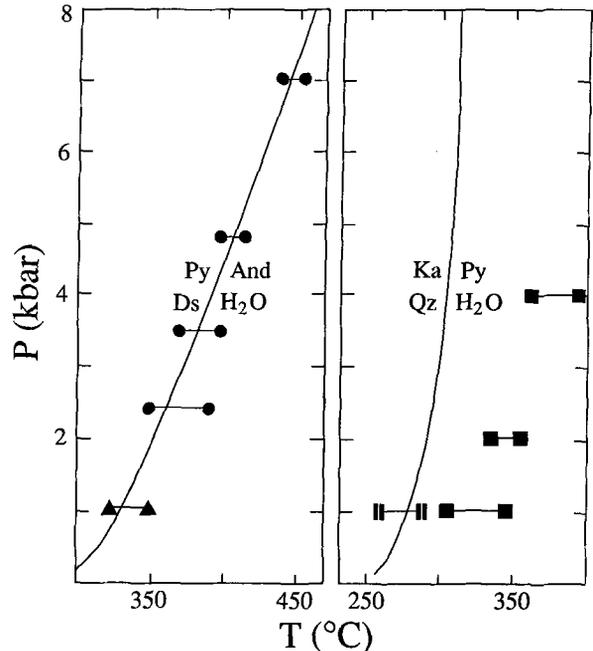


Figure 2. Experimental reversals of reaction (3)  $\text{Py} + 6 \text{Ds} = 4 \text{And} + 4 \text{H}_2\text{O}$ , and of reaction (4)  $\text{Ka} + \text{Qz} = \text{Py} + \text{H}_2\text{O}$ , compared to calculated curves. Symbols as in Figure 1. Abbreviations defined in Table 1.

for the system  $\text{MgO-CO}_2\text{-H}_2\text{O}$  (Robie and Hemingway, 1973; Hemingway and Robie, 1973) clearly show the stable phase assemblage to be brucite + magnesite +  $\text{H}_2\text{O(l)}$  rather than hydromagnesite, nesquehonite, or artinite, yet the latter minerals are widespread and the former assemblage is unknown in surface rocks so far as we can ascertain. Similarly, anatase is a  $\text{TiO}_2$  polymorph commonly found in diagenetic, hydrothermal, and altered rocks, yet it is clearly metastable relative to rutile (Jamieson and Olinger, 1969; Mitsuhashi and Kleppa, 1979; Robinson *et al.*, 1982). In addition, Jiang *et al.* (1990) presented evidence that illite (and smectite) are metastable relative to micas + pyrophyllite for all geological conditions.

Consider the consequences of accepting boehmite as the stable  $\text{AlO(OH)}$  polymorph at STP. Inasmuch as it has a higher entropy ( $37.2$  J/mole·K) than diaspore ( $35.3$  J/mole·K), it can never be transformed to diaspore by increasing temperature unless the entropy of the transformation changes sign at higher temperatures. As high-temperature ( $>273$  K) entropies can be reasonably modeled from oxide compositions of the phases (cf. Fyfe *et al.*, 1958), and as these phases are isochemical, it is unlikely that such a sign change occurs. In addition, a change in the sign of the entropy of reaction would imply that one of the assemblages is stable both at low and at high temperatures, but not over some intermediate temperature range—a very unusual reaction topology.

The volume difference between boehmite and dia-

Table 3. Gibbs energies of formation from the elements (kJ/mole) of H<sub>2</sub>O(v) and minerals in the system Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O.

Phase	Helgeson <i>et al.</i> (1978)	Robie <i>et al.</i> (1979)	Robinson <i>et al.</i> (1982)	Berman (1988)	This study <sup>1</sup>
H <sub>2</sub> O(v)	-228.59	-228.57	-228.61	-228.54	[-228.61 (8)]
H <sub>2</sub> O(l)	-237.18	-237.14	-237.16	-237.13	[-237.14 (8)]
Quartz	-856.24	-856.28	-856.31	-856.29	[-856.31 (110)]
Corundum	-1568.26	-1582.23	-1582.33	-1582.19	[-1582.33 (39)]
Diaspore	-913.79	-922.00	-921.43	-920.81	-921.19 (25)
Pyrophyllite	-5255.09	-5265.88	-5268.26	-5266.86	-5266.47 (128)
Kaolinite	-3789.09	-3799.36	-3802.50	-3799.77	-3800.18 (153)
Andalusite	-2429.18	-2439.89	-2444.56	-2441.81	[-2442.04 (48)]
Kyanite	-2430.72	-2441.28	-2445.58	-2443.37	[-2443.66 (39)]
Sillimanite	-2427.10	-2438.99	-2442.06	-2439.26	[-2439.63 (44)]
Bayerite	*	*	*	*	[-1153.0 (**)]
Gibbsite	-1155.49	-1154.89	-1156.50	*	[-1154.9 (53)]
Nordstrandite	*	*	*	*	[-1154.1 (**)]
Boehmite	-908.97	-918.40	-916.07	*	[-918.4 (9)]
Halloysite	*	-3780.71	-3783.19	*	[-3783.2 (15)]
Dickite	*	-3796.31	-3798.77	*	[-3798.8 (15)]

<sup>1</sup> Values in square brackets were taken from other sources; see text.

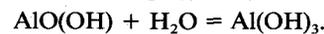
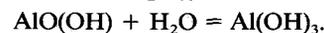
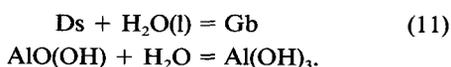
\* No data for this phase are given in this source.

\*\* No uncertainty given.

spore is small, so the P-T slope of the polymorphic transition is steep (Perkins *et al.*, 1979). Thus, if boehmite is stable at STP, the entropy and volume relations require that it remain stable with respect to diaspore at higher temperatures. Yet, diaspore is the ubiquitous aluminum hydroxide in metamorphosed bauxites (e.g., Zen, 1961). In other words, the occurrence of metamorphic diaspore, in combination with entropy and volume data, requires diaspore to be the stable AlO(OH) phase at STP. Furthermore, Neuhaus and Heide (1965) converted boehmite to diaspore at 400°C and 2 kbar (where diaspore itself is already metastable with respect to corundum + H<sub>2</sub>O), and Dacheille and Gigi (1983) transformed boehmite to diaspore at 315°C, 60 kbar. Because boehmite has a larger entropy and a larger volume than diaspore, it cannot be stable relative to diaspore at higher pressure or lower temperature and therefore must be metastable at STP.

At higher temperatures, boehmite will be less stable than corundum + H<sub>2</sub>O, and it is therefore metastable either with respect to diaspore or to corundum + H<sub>2</sub>O or to both assemblages. Thus, experimental and thermodynamic data and field observations all show that boehmite is less stable than diaspore under normal earth surface conditions. The common occurrence of boehmite in sedimentary rocks, like that of aragonite, magnesian calcite, and calcian dolomite, must be ascribed to nonequilibrium processes.

Available data strongly suggest that gibbsite (Gb), bayerite (By), and nordstrandite (Nrd) are metastable relative to diaspore and water at STP, and similar arguments apply to their stabilities at higher pressures and temperatures. Thus, these phases also appear to occur metastably. Their stabilities are constrained by the reactions:



The Gibbs energies of all three reactions (3.44, 4.24, and 5.34 kJ/mole, respectively) are consistent with the observation (Apps *et al.*, 1989) that both bayerite and nordstrandite are always more soluble than gibbsite, and with the suggestion that all three are metastable with respect to diaspore + water at STP. In a study which emphasized the importance of Ostwald ripening in the formation of aluminum hydroxides, Hemingway (1982) summarized a large amount of solution data on gibbsite, nordstrandite, and bayerite (e.g., Bye and Robinson, 1964; Barnhisel and Rich, 1965; Hem and Roberson, 1967; Turner and Ross, 1970; Schoen and Roberson, 1970; Ross and Turner, 1971; Parks, 1972; Smith and Hem, 1972; Lind and Hem, 1975; Kwong and Huang, 1979; Kitterick, 1980; May *et al.*, 1979; Violante and Violante, 1980). He concluded that gibbsite is more stable than nordstrandite, which is more stable than bayerite, but that microcrystalline gibbsite may be less stable than either bayerite or nordstrandite. He also concluded that both the high temperature work of Hemley *et al.* (1980) and the solubility studies of Russell *et al.* (1955) clearly indicate that diaspore should be the stable aluminum phase under surface weathering conditions.

Because steam is the stable H<sub>2</sub>O phase >373.15 K at 1 atm, evaluation of the stabilities of gibbsite, nordstrandite, and bayerite relative to diaspore at T > 100°C must be calculated relative to H<sub>2</sub>O(v) rather than H<sub>2</sub>O(l). Under either condition, however, the entropies of reactions (11), (12), and (13) are negative [-35.8, -35.8, and -24.9 J/mole·K, respectively, for H<sub>2</sub>O(l) and -155.6, -155.6, and -144.7 J/mole·K, respectively for H<sub>2</sub>O(v)]. These values are larger than uncertainties

in the entropy data. Thus, neither gibbsite, nordstrandite, nor bayerite are stable at low pressures and at temperatures  $>25^\circ\text{C}$ . The negative volume changes of these reactions ( $-3.97$ ,  $-3.97$ , and  $-4.69$   $\text{cm}^3/\text{mole}$ , respectively) suggest that stability fields may exist for gibbsite, nordstrandite, and bayerite at higher pressures, but even considering the uncertainties in the thermodynamic data, calculations show that the lowest pressures at which reactions (11), (12), and (13) could occur are 3.8, 3.8, and 11.9 kbar, respectively. Dache and Gigi (1983) reversed the transformation of diaspore +  $\text{H}_2\text{O}$  to  $\delta\text{-Al}(\text{OH})_3$  between  $275^\circ\text{C}$ , 45 kbar and  $400^\circ\text{C}$ , 30 kbar, with  $\delta\text{-Al}(\text{OH})_3$  being the high-pressure/low-temperature phase, confirming that other  $\text{Al}(\text{OH})_3$  polymorphs may be more stable than diaspore at high pressures. Although they succeeded in transforming gibbsite and bayerite to diaspore,  $\delta\text{-Al}(\text{OH})_3$ ,  $\beta\text{-Al}(\text{OH})_3$ , or boehmite at various pressures and temperatures, none of these reactions were reversed, and no high-pressure stability range for these phases can be confirmed. These data clearly show, however, that neither gibbsite, bayerite, nor nordstrandite is stable at or near the earth's surface and their occurrence in soil horizons must be ascribed to nonequilibrium processes.

Phase equilibria can also be considered for polymorphs in the system  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ : kaolinite, dickite, and halloysite. Wilson and Pittman (1977) document occurrences of dickite in rocks which have undergone clastic diagenesis, but the data of Haas *et al.* (1981) and of Robinson *et al.* (1982) show that kaolinite is the stable polymorph at 1 bar to temperatures well above those at which it breaks down to diaspore, pyrophyllite, and water. Their Gibbs energy data for kaolinite, dickite, and halloysite were based both on the experimental work cited above for kaolinite and the HF solution calorimetry of Barany and Kelley (1961). Robinson *et al.* (1982) calculated the Gibbs energies of kaolinite, dickite, and halloysite at STP as  $-3802.5$ ,  $-3798.8$ , and  $-3783.2$  kJ/mole respectively. The uncertainties in the Gibbs energies of kaolinite and dickite ( $\pm 1.5$  kJ/mole) suggests that it is unlikely that dickite, rather than kaolinite may become the stable polymorph. Recent HF solution calorimetry measurements (B. S. Hemingway, U.S. Geological Survey, Reston, Virginia, personal communication) also support this conclusion. The relative stabilities of kaolinite and halloysite is also consistent with the solubility experiments of Huang (1974), La Iglesia and Galan (1975), and Tsuzuki and Kawabe (1983). Analogous to the aluminum hydroxides, the volumes of halloysite and dickite are slightly smaller than that of kaolinite, and they may tend to be stabilized by increased pressure. Nonetheless, they are metastable at surface conditions and, like gibbsite and nordstrandite, they must form nonequilibrium process in soils and during diagenesis.

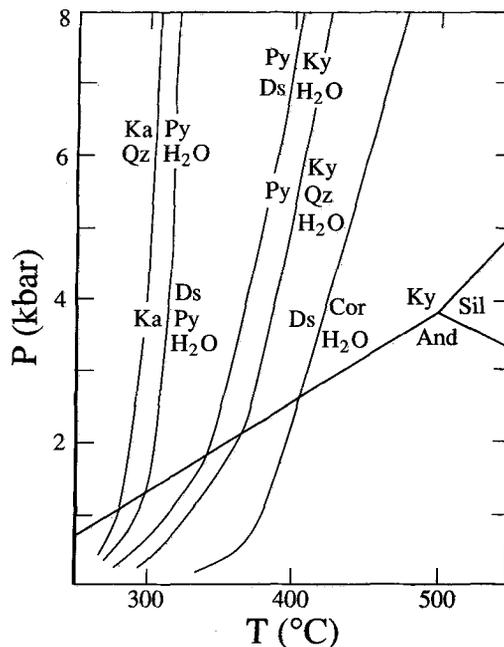


Figure 3. Phase diagram showing stable equilibria in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ . Abbreviations defined in Table 1.

## CONCLUSIONS

We conclude that the formation of given mineral assemblages at the earth's surface provides no certain guide to the stability of such phases or phase assemblages. In other words, equilibrium concepts may have little relevance to pedology (*contra* Chesworth, 1980a). Indeed, structurally complex and/or disordered minerals, such as certain clays and zeolites, may always be metastable with respect to denser, lower entropy minerals in the environments in which they form. Careful testing will be required to evaluate this hypothesis, both because of large uncertainties in equilibrium and kinetic aspects of ordering in many of these phases, and because of grave experimental difficulties in obtaining equilibrium at  $T < 200^\circ\text{C}$ .

Given the thermodynamic data base derived above (Tables 1 and 3) and the results of our analysis of the stabilities of the diaspore and kaolinite polymorphs, a phase diagram may be calculated for  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system (Figure 3), which includes all stable mineral reactions. This diagram is similar to that of Hemley *et al.* (1980) and model 4 of Perkins *et al.* (1979). It suggests that the natural assemblages And-Ka-Qz, Py-Ka-And-Qz, Ds-Qz-Py, and Py-Ka-Ky-Qz (Zen, 1961) cannot represent equilibria in crustal rocks. Most likely, kaolinite and diaspore found in these assemblages are alteration or retrograde products of other aluminosilicates (cf. Perkins *et al.*, 1979). This inference further reinforces our conclusion that one must be quite careful in determining which phases in a given rock or

sediment represent equilibrium assemblages, and which are the results of processes leading to the formation or the presence of metastable materials.

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