

SOLID-GAS INTERFACE IN WEATHERING REACTIONS*

by

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ABSTRACT

Most weathering reactions have been interpreted in terms of the solid-liquid interface. In dry climates or at low humidity, weathering might be initiated or controlled by a solid-gas reaction. The stability of gibbsite and some hydrous borates involves the activity of water vapor; and the stability of azurite depends on a ratio of the partial pressures of both water vapor and carbon dioxide. Much additional work is required on the rates of equilibrium dehydration to contribute to our knowledge of the solid-gas interface in weathering.

INTRODUCTION

Much of the experimental work done on chemical weathering at 25°C and one atmosphere total pressure has been reported in terms of weathering reactions taking place at a solid-liquid interface. In certain realms of weathering, especially those where rainfall is infrequent (low humidity), where vegetation is sparse, and in the upper 1 to 2 ft of the weathering zone, the formation of a weathered product on a mineral surface may be initiated or controlled by a solid-gas type of reaction. In this type of environment, there can occur many interesting reactions of significance to geologists and soil scientists, for example the reactions or hydrated phases listed in Table 1.

In order for atmospheric gases, such as water vapor and carbon dioxide, to react with solids in soils, it is necessary that a gaseous exchange take place between the gases associated with the soil and the atmosphere above the soil. This exchange can be accomplished by mass flow as a result of total pressure gradients or by diffusion as a result of partial pressure gradients. If diffusion is the controlling mechanism of gas availability, then the amount of gas available at any time would depend on the rate of gaseous diffusion through soil, the amount adsorbed by the soil, and the amount produced in the soil from biological activity. If the water content (moisture) of a soil and gaseous diffusivity (D_g) remain constant with respect to time, it can be shown (Klute, 1960, p. 4) that an equation based on both Fick's first law of diffusion and

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the equation of continuity can be used to express the partial pressure of the diffusing gas with respect to time:

$$\frac{\partial P}{\partial t} = \nabla \cdot (D_g \nabla P) + B(x, y, z, t) \quad (1)$$

where

P = partial pressure of the diffusing gas

t = time

D_g = diffusivity function, which depends on water content and porosity of soil

$B(x, y, z, t)$ = a function representing the rate of production of gas per unit time per unit volume of soil. The function is negative if gas is consumed during adsorption on soil

∇ = a vector operator

Van Bavel (1951) has shown that the partial pressure of CO_2 developed from the top to the bottom of a soil column depends on both the rate at which CO_2 is evolved and the porosity of the soil. At 1 per cent porosity and a flow-rate of 4.47×10^{-7} mg per cm^3 per sec, the partial pressure of CO_2 changes from a very low value at the top of the column 1 ft in length to 77 mm Hg at the bottom; at 10 per cent porosity, the P_{CO_2} at the bottom of an equal column is only 8 mm Hg. These data suggest that carbon dioxide can build up significant partial pressures without great difficulty. Gaseous diffusion of components in soil prior to build-up of a partial pressure of a diffusant depends on a complex set of soil parameters as indicated above.

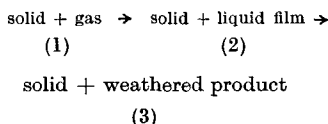
TABLE 1.—SOLID-GAS REACTIONS WHICH CAN OCCUR UNDER WEATHERING CONDITIONS

(1)	BAUXITE DEPOSITS $\text{Al}(\text{OH})_3 \rightleftharpoons \text{AlO}(\text{OH}) + \text{H}_2\text{O}_{(\text{v})}$ (Gibbsite) (Boehmite)
(2)	COPPER DEPOSITS $2 \text{Cu}_3(\text{CO}_3)_2(\text{OH})_2 + \text{H}_2\text{O}_{(\text{v})} \rightleftharpoons 3 \text{Cu}_2\text{CO}_3(\text{OH})_2 + \text{CO}_2_{(\text{v})}$
(3)	ARID-CLIMATE BORATES Inyoite ($\text{Ca}_2\text{B}_2\text{O}_{11} \cdot 13\text{H}_2\text{O}$) Meyerhofferite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7 \text{H}_2\text{O}$) Colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5 \text{H}_2\text{O}$)

SOLID-GAS REACTION MECHANISM

In solid-gas reactions in the geologic or soil environment, a possible reaction mechanism from the condition solid-gas to solid-weathered product might involve the adsorption of gas from soil air on the solid, the subsequent condensation of gas to a liquid film on the solid, and reaction of the liquid film

with the solid to bring about a weathered product on the surface of the solid, such as



The first part of this reaction (1) depends on the ability of the solid to adsorb gas on its surface. The simplest way to achieve adsorption is through physical adsorption. Physical adsorption can take place at the solid-gas interface without being specific and at relatively low heats of adsorption (usually less than 10 kcal/mole); i.e. adsorption depends only upon the condensability of the gas to a liquid. Chemisorption is much more complex; both the chemical properties of the gas and solid are involved, the adsorption being specific and usually occurring at heats of adsorption greater than 10 kcal/mole. If physical adsorption dominates in the weathering environment, liquid films of water can easily form on solids when warm gases of the soil air permeates through cooler parts of the soil. As an example, the saturated vapor pressure of water is 23.37 mm Hg at 20°C and 8.72 mm Hg at 5°C; air saturated at 20°C would yield liquid water at 5°C until the lower vapor pressure were established. For CO₂, the same type of reasoning is valid, at least to temperatures of 31°C, the critical temperature of CO₂. The reaction between the liquid film and the solid (2) to form a weathered product (3) is beyond the scope of this paper.

EXAMPLES OF SOLID-GAS REACTIONS IN NATURE

The Gibbsite Dehydration

In bauxite deposits, the dehydration reaction of gibbsite to form boehmite plus water vapor is of interest:

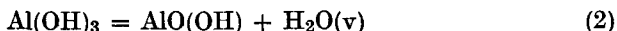


Table 2 lists the various alumina hydrates reported in bauxite deposits throughout the world. The data suggest that gibbsite is the dominant phase and probably the most stable. It is significant to determine the equilibrium vapor pressure of water to satisfy equation (2). As calculated from thermodynamic constants given by the Bureau of Standards (1952) and Kuznetsov (1950), the equilibrium vapor pressure of water for dehydration of gibbsite is high, even at low temperatures; however, as calculated from the data of Pourbaix (1956), it is reasonably low (Fig. 1). It is difficult to determine which of the calculated curves is correct. The dehydration curves (Fig. 1) determined experimentally by Wayman (1959) and by Funaki and Uchimira (1952) lead, in extrapolation, to the conclusion that the vapor pressure of water over gibbsite is extremely low at weathering temperatures; the experimental curves probably do not represent equilibrium values and indicate the difficulty of representing the dehydration of gibbsite or rehydration to boehmite under

TABLE 2.—VARIOUS ALUMINA HYDRATES REPORTED IN BAUXITE DEPOSITS

Phases Present	Location	Reference
	Europe	
B,G	Spain	Miralles (1952)
B,D,G	Spain	Tullet (1951)
G	Ireland	Eyles (1952)
D,B	Greece	Vachtl (1956)
G	Poland	Spangenberg (1949)
G,B	Croatia-Bosnia	Miholic (1956)
Bayerite	Hungary	Gedeon (1956)
G	Hungary	Nemerz (1954)
G,D	Hungary	Kiss (1952)
G,B,D	Hungary	de Weisse (1948)
G	Russia	Chirvinskii (1940)
	Africa	
G,D	Portugese Guiana	de Weisse (1954)
	Asia	
B,D	Turkey	Ekrem (1954)
G,B,D	India	Oda (1955)
	Pacific	
G	Australia	Ragatt (1945)
G	Hawaii	Sherman (1957)
	United States	
G,D	Arkansas	Wysor (1916)
G	Oregon	Allen (1948)
G	Georgia	Alexander, Hendricks and Faust (1941)
G	N. Carolina	Alexander, Hendricks and Faust (1941)
G	S. Carolina	Alexander, Hendricks and Faust (1941)
G,D	Missouri	Wysor (1923)
	Caribbean Area	
G,B	Jamaica, B.W.I.	Hill (1955)
G,B	Jamaica, B.W.I.	Hose (1950)
G	Grenada, B.W.I.	Hardy, Rodrigues (1939)
G,B	Dominican Republic	Goldich, Berquist (1947)
G	British Guiana	Bishopp (1955)
G,B	Surinam	van Kersen (1956)
G	Brazil	de Ravol (1953)

G = Gibbsite B = Boehmite D = Diaspore

The first letter of each series represents the predominant form.

equilibrium conditions in weathering profiles. The experimental values of Funaki and Uchimira have been extrapolated to weathering temperatures (Wayman, 1961, p.328) to represent the stability of gibbsite in terms of a relative humidity relation:

$$\text{R.H.} = \frac{\text{D.P.}}{\text{S.P.}} \quad (3)$$

where, at any specified temperature

R.H. = relative humidity in %

D.P. = dissociation pressure of the gibbsite-boehmite dehydration at that temperature

S.P. = saturated vapor pressure of water at that temperature

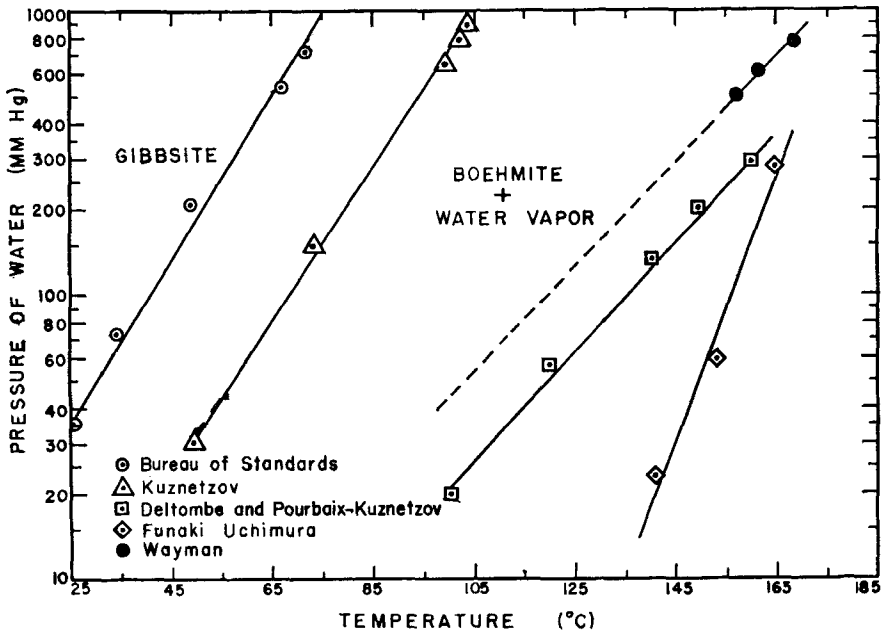


FIGURE 1.—Vapor pressure of water for dehydration of gibbsite to boehmite.

Figure 2 shows that gibbsite is stable with respect to boehmite for a range of weathering temperatures, unless the relative humidity is reduced to about 0.0001 per cent, which is probably never achieved on weathering surfaces. If the experimental values of water vapor from dehydration of gibbsite are even approximately correct, then boehmite should be metastable with respect to gibbsite on weathering profiles.

The mechanism of gibbsite dehydration.—The most important consideration in dehydration-rehydration reactions is the rate at which mineral surfaces are altered. At weathering temperatures (10°C to 65°C), the rates might be so slow that geologic time is necessary to form a weathered product of boehmite on gibbsite, unless intense heat is available locally. If gibbsite has been

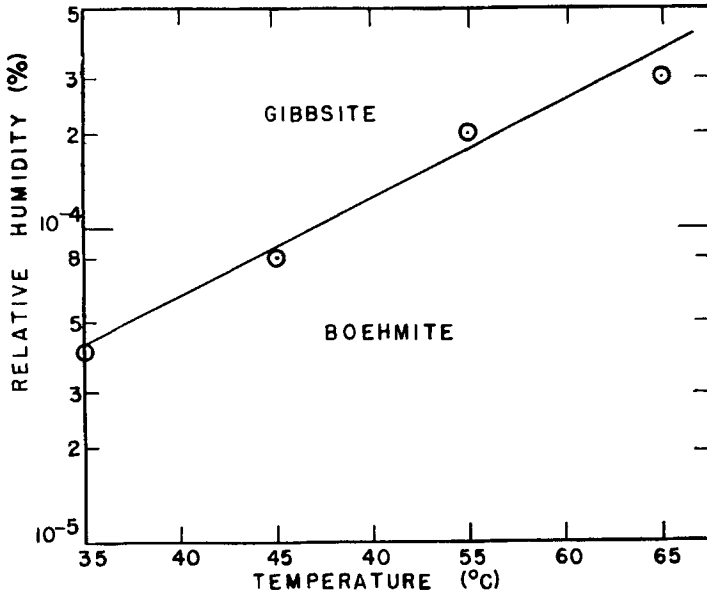


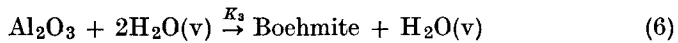
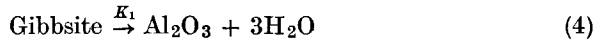
FIGURE 2.—Stability of gibbsite with respect to boehmite with varying temperature and humidity.

dehydrated to boehmite in weathering profiles as suggested from the data of Table 2, then dehydration must be somewhat continuous in nature even at low temperatures. One reasonable manner to account for the existence of both gibbsite and boehmite on weathering surfaces is that gibbsite has dehydrated locally to boehmite and that rehydration of boehmite to gibbsite is so slow that alteration has not yet occurred.

The thermodynamic or equilibrium dehydration of gibbsite depends only on the state of the system and is independent of the amounts of reacting constituents. When kinetics and mechanisms are brought into consideration, dehydration is quite complex and can be influenced by surface area of the material, external pressure, amounts and nature of the reacting constituents and other variables. The dehydration mechanism for dihydrates can be visualized as a set of consecutive first order reactions. For trihydrates the mechanism cannot be as simply visualized. One possible mechanism for the dehydration of a single crystal of gibbsite can be described based on the following set of assumptions:

- (1) gibbsite dehydrates to water vapor and alumina
- (2) alumina reacts with water vapor to form boehmite
- (3) the evaporation of water to water vapor is rapid and not the rate determining step
- (4) the amount of alumina existing at any time is constant (steady-state condition) because it readily reacts with water vapor to form boehmite.

On the basis of these assumptions, the equations are:



where

$K_1, K_2, K_3 =$ specific rate constants;

for the conditions

$$K_2 \gg K_1 \quad \text{or} \quad K_3$$

$$\frac{d \text{Al}_2\text{O}_3}{dt} = 0 \quad (\text{steady state condition});$$

thus

$$\frac{-d \text{ gibbsite}}{dt} = K_1 C \text{ gibbsite} \quad (7)$$

where

$C =$ concentration (arbitrary units)

$t =$ time;

$$\frac{d \text{Al}_2\text{O}_3}{dt} = K_1 C \text{ gibbsite} - K_3 C_{\text{Al}_2\text{O}_3} \cdot C^2_{\text{H}_2\text{O}(v)}, \quad (8)$$

hence

$$\frac{-d \text{ gibbsite}}{dt} = K_3 C_{\text{Al}_2\text{O}_3} \cdot C^2_{\text{H}_2\text{O}(v)} \quad (9)$$

Similarly,

$$\frac{d \text{ boehmite}}{dt} = K_3 C_{\text{Al}_2\text{O}_3} \cdot C^2_{\text{H}_2\text{O}(v)} \quad (10)$$

and

$$\begin{aligned} \frac{d \text{H}_2\text{O}(v)}{dt} &= K_3 C_{\text{boehmite}} \cdot C_{\text{H}_2\text{O}(v)} - K_3 C_{\text{Al}_2\text{O}_3} \cdot C^2_{\text{H}_2\text{O}(v)} \\ &\quad - K_2 C_{\text{H}_2\text{O}(v)} \end{aligned} \quad (11)$$

but the last term in (11) can be ignored because K_2 is not rate determining.

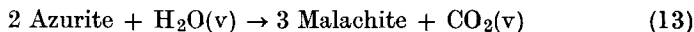
From equation (8)

$$C_{\text{Al}_2\text{O}_3} = \frac{K_1 C_{\text{gibbsite}}}{K_3 C_{\text{H}_2\text{O}(v)}^2} \quad (12)$$

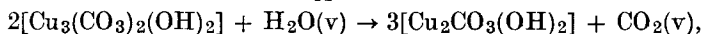
Thus equations (9) through (12) indicate that the mechanism of the dehydration of gibbsite is complex and is time-dependent upon the concentration of reactants and products.

The Azurite-Malachite Reaction

The gibbsite dehydration represents a solid-gas reaction with a single gas. In copper deposits, the stability of azurite or malachite depends upon the ratio of the partial pressures of both water vapor and carbon dioxide. From the reaction:



or



the equilibrium constant (K) can be reduced to

$$K = \frac{P_{\text{CO}_2}}{P_{\text{H}_2\text{O}}} \quad (14)$$

where P = partial pressure of the gas.

A thermodynamic basis has been used previously (Wayman, 1963) to calculate the equilibrium partial pressures of water vapor at fixed partial pressures of carbon dioxide for (13) at various weathering temperatures. With use of the relative humidity relation equation (3), it can be shown that azurite is stable with respect to malachite to a temperature of 65°C if the relative humidity is 50 per cent (Fig. 3). Changing the partial pressure of CO₂ by 100 times seems to exert little influence on this reaction. On the basis of this calculation, it seems most probable that layers of malachite would appear upon azurite surfaces at temperatures in excess of 65°C and humidities above 50 per cent, i.e. in the range of conditions indicated in Fig. 3.

Solid-Gas Reactions in Borate Deposits

Christ and Garrels (1959) have investigated in some detail three hydrous borates occurring in the Kramer borate deposit near Boron, California. The three borates of interest in this deposit are borax, tincalconite, and kernite having formulas of Na₂B₄O₅(OH)₄·8 H₂O, Na₂B₄O₄(OH)₄·3 H₂O, and Na₂B₄O₆(OH)₂·3 H₂O respectively. They observed that borax can be associated with either kernite or tincalconite; it was deduced that all three phases could not coexist under equilibrium conditions. These investigators concluded that borax dehydrates to tincalconite at low temperature and low relative humidity and that kernite is stable only at higher temperature and pressure. Tincalconite rehydrates rapidly to borax, indicating reversibility, but the rate of formation of kernite is infinitely slow at room temperature.

This study represents another instance of the importance of solid-gas reactions in weathering and also the significance of reaction rates in dehydration.

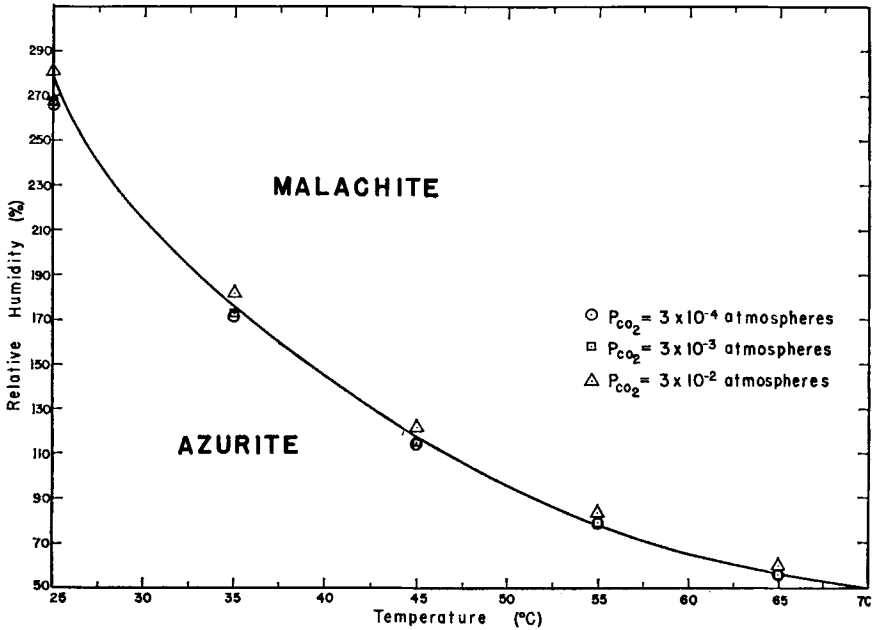


FIGURE 3.—Stability of azurite with respect to malachite with varying temperature and relative humidity.

SUMMARY

The importance of solid-gas reactions in weathering has been stressed. A few of the variables influencing these reactions have been developed. Actual examples of dehydration under equilibrium conditions, or rates of dehydration taking place in bauxite deposits, copper deposits, and borate deposits have been enumerated. Much additional work is required on dehydration studies in mineral systems to emphasize the importance of solid-gas reactions in weathering.

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