THE STABILITY OF GIBBSITE AND BOEHMITE AT THE SURFACE OF THE EARTH

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Abstract—Two mutually exclusive views exist concerning the relative stabilities of gibbsite and boehmite in soils. These are examined in terms of experimental and thermodynamic evidence and it is shown that all three possible divariant assemblages of two phases that can exist between gibbsite, beohmite and H_2O, may do so at 25°C and 1 atmosphere total pressure depending on the status of H_2O. It is further shown that the conditions of H_2O chemical potential needed to stabilize boehmite + H_2O relative to gibbsite + H_2O or gibbsite + boehmite, are unlikely to occur in natural waters in the zone of weathering.

INTRODUCTION

GIBBSITE is the commonest form of $Al(OH)_3$, and boehmite the commonest form of $Al(OOH)$, to occur in soils and bauxites. Each has a number of polymorphs, the rather confusing nomenclature of which is shown in Table 1.

Concerning the relative stabilities of gibbsite and boehmite two views exist. One holds that "the stable form at low temperatures is gibbsite" (Marshall, 1964, p. 147), whereas the other maintains that there is a stability sequence "amorphous aluminum hydroxide < gibbsite < boehmite < diaspore" (Kittrick, 1969, p. 160) such that boehmite is more stable than gibbsite under earth-surface conditions.

In the following pages these antithetical viewpoints are critically examined, primarily in terms of the evidence on which they are based. Following the critical analysis an experiment is described that helps to clarify relationships between the minerals.

EXPERIMENTAL EVIDENCE

Marshall bases his belief that gibbsite is the stable low temperature form on experimental studies of phase equilibrium. In particular he cites the work of Ervin and Osborne (1951) and could, in the same context, have referred to Kennedy's (1959) experiments. Both of these studies are brought together in Fig. 1, which shows that the experimental results are mutually consistent at 25°C and 1 atmosphere pressure. These conditions will be taken here as a model for the low temperatures and pressures that prevail at the surface of the earth and that therefore are of paramount importance to the soil scientist.
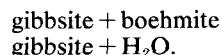
In order to apply the phase diagram to soils or

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bauxites, it is necessary to bear in mind the constraints imposed on the system by the experimentalists. It is particularly important to note that (a) the experiments were performed in a closed system, and (b) the equilibrium partial pressure of H_2O (Greenwood, 1961) was equal to the total pressure in that system. In practical terms this means that H_2O was present as a separate phase during the experiments and that its chemical potential was a function of total pressure, temperature and the bulk composition of the system. In fact the chemical potential of H_2O under the conditions of low temperature and pressure that are of interest here would be essentially that of pure H_2O under the same conditions.

Now, the univariant reaction curves of Fig. 1 mark the locus of points in PT space where the hydration/dehydration reaction

$$\text{gibbsite} = \text{boehmite} + H_2O \qquad (1)$$
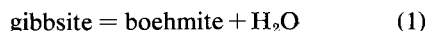
is at equilibrium in a closed system. The curves represent two experimental versions of the upper stability limit for two possible divariant assemblages:

$$\text{gibbsite} + \text{boehmite}$$
$$\text{gibbsite} + H_2O.$$

Under the experimental constraints discussed in the preceding paragraph (i.e. with H_2O present as a separate phase) gibbsite + H_2O would necessarily be the stable assemblage found at 25°C and 1 atmosphere total pressure. This fact is the real basis for Marshall's viewpoint.

However, had the closed system been undersaturated with respect to H_2O (i.e. had H_2O been absent as a separate phase) then the stable divariant assemblage at 25°C and 1 atmosphere total pressure would have been gibbsite and boehmite. In

Table 1. Nomenclature of Aluminum Hydroxide (from Pascal (1961) 6, 574, with additions)

Chemical name and formula	Nomenclature			
	Mineralogical	Haber	Alcoa	Other
Aluminum trihydroxide Al(OH)₃	Gibbsite or hydrargillite	γ trihydrate	α trihydrate	
	Bayerite Nordstrandite		β trihydrate	α trihydrate
Aluminum oxyhydroxide Al(OOH)	Boehmite Pseudoboehmite	γ monohydrate	α monohydrate	bauxite*
	Diaspore	α monohydrate		

*Commonly used now to denote any rock or surficial material largely composed of aluminum hydroxides irregardless of species.
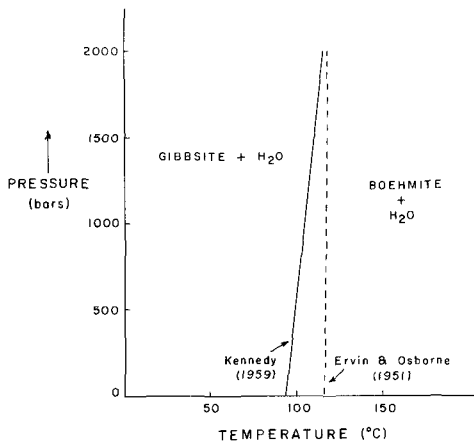

Fig. 1. Two versions of the reaction curve Gibbsite—Boehmite + H₂O in a closed system oversaturated with respect to H₂O.

other words, if soil may be treated as a closed system, then both gibbsite *and* boehmite can be considered stable phases under earth surface conditions, the controlling factor being status of H₂O. The univariant assemblage gibbsite + boehmite + H₂O is also a possibility but only in an academic sense. The chances of natural conditions producing the exact combination of pressures and temperatures to fall directly on the PT curve are very remote.

The system Al_2O_3–H_2O forms a more realistic model for soil and bauxite genesis when it is considered open to H_2O. In this case H_2O becomes a perfectly mobile component (Korzhinskii, 1959) with a chemical potential that is controlled by the surroundings of the arbitrary region of space under consideration. In this case the chemical potential of H_2O is no longer a dependent variable, but must be considered with total pressure and temperature as an independent intensive parameter of the equi-

libria that exist between phases. What effect this has on the equilibria in question, is best illustrated graphically.

In terms of the independent variables pressure, temperature and chemical potential of H_2O, the reaction curve of Fig. 1 becomes a reaction surface (Fig. 2A). The surface can be projected onto the PT plane and contoured with respect to the chemical potential of water, μH_2O (Fig. 2B). It can be shown that the slope of the individual contours is

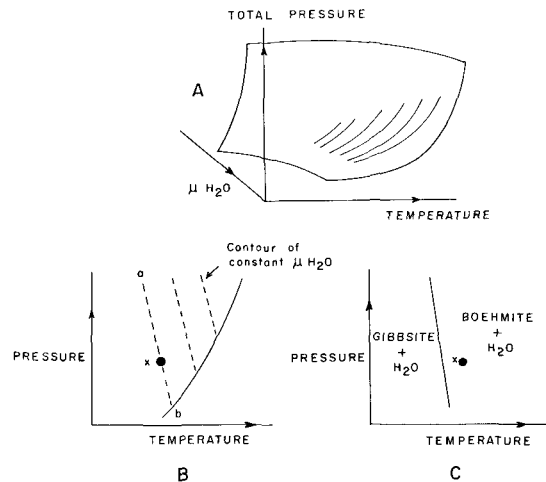$$\left(\frac{\partial P}{\partial T}\right)_{\mu H_2O} = \frac{\Delta S}{\Delta V_s}$$

Fig. 2. A diagramatic representation of the reaction Gibbsite = Boehmite + H₂O as a function of three independent variables. 2A is the complete reaction surface. 2B is the reaction surface projected onto the PT plane and contoured for μH₂O. 2C is the reaction curve at a particular, constant value of μH₂O. The point labelled x represents the generalized low PT of the earth's surface. The μH₂O contour a–b is the critical one that passes through x.

where ΔS is the entropy change of reaction and ΔV_s is the volume change of the solid phases (i.e. ignoring the H_2O phase).

Let x in Fig. 2B represent generalized conditions of P and T for the surface of the earth. The μH_2O contour $a-b$ that passes through x represents a critical value in that if μH_2O is higher than $a-b$ then the assemblages gibbsite $+ H_2O$ and gibbsite $+$ boehmite are stabilized as before. On the other hand if μH_2O is lower than $a-b$ boehmite $+ H_2O$ becomes the stable divariant assemblage (Fig. 2C).

the standard states chosen and the methods of calculation used are internally consistent.

The uncertainties quoted in Table 2 are two standard errors and obviously the error involved in the ΔG_f for boehmite is large enough to make any calculation of the energy change of reaction (1) useless as an indicator of the direction the reaction will take. Thus the calculated free energy change of reaction lies within the range $+ 2 \cdot 4$ to $- 4 \cdot 7$ Kcal, so that the reaction could go either to the right or the left as written.
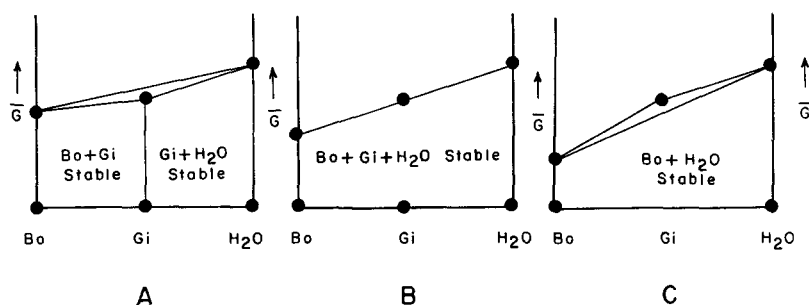

Fig. 3. Schematic molar free energy (chemical potential diagrams) for three conditions. 3A below the reaction curves of Figs. 1 and 2, 3B on the curves, and 3C above the curves. Gi – gibbsite, Bo – boehmite.

Under such low μ_{H_2O} conditions gibbsite would not be stable at the earth's surface.

Phase equilibrium relationships can be used then to "prove" the stability of three different divariant assemblages at the surface of the earth. Statements that gibbsite or boehmite is *the* stable phase are therefore meaningless unless qualified by some indication of the status of H_2O.

THERMODYNAMIC EVIDENCE

Kittrick's view quoted above, that boehmite is more stable than gibbsite under conditions of low temperature and pressure is based on thermodynamic arguments. This aspect of the problem can be conveniently examined by considering the free energy change that would accompany reaction 1 at 25°C and 1 atmosphere total pressure. Pertinent free energy data for all three phases involved are presented in Table 2. This data, of Robie and Waldbaum (1968), is preferred to any other because

Table 2. Free energies of formation for 25°C and 1 atmosphere pressure (from Robie and Waldbaum, 1968)

	ΔG_f (Kcal/gfw)	Uncertainty
Gibbsite	$- 273 \cdot 486$	$0 \cdot 310$
Boehmite	$- 217 \cdot 674$	$3 \cdot 510$
Water	$- 56 \cdot 688$	$0 \cdot 020$

The obvious conclusion is that the thermodynamic data used here is not sufficiently precise to support Kittrick's contention that boehmite is stable relative to gibbsite in soil. Nor for that matter is it precise enough to support the opposite conclusion, reached on thermodynamic grounds by Garrels and Christ (1965, p. 10) that "gibbsite is the stable phase relative to boehmite in dilute aqueous solution, at 25°C and 1 atmosphere total pressure".

It might be argued that the other workers used different data to arrive at their conclusions. However they did not attempt to estimate the error of the free energy values employed so that the significance of their conclusions is questionable.

DISCUSSION

The problem can be clarified by the introduction of free energy-composition diagrams of which Fig. 3A is an example. These diagrams are based on the fact that free energies are additive so that the free energy of a system composed of gibbsite and H_2O is equal to the linear sum of the free energies of the two individual phases. This sum is represented for all possible proportions of gibbsite and H_2O by the tie line that joins the two phases in Fig. 3A.

It is clear from Fig. 3A that the free energies of systems composed of boehmite and H_2O are in all cases greater than those of equivalent mixtures of boehmite + gibbsite or gibbsite + H_2O for the con-

ditions for which the diagram was drawn. The implication therefore is that combinations of boehmite + gibbsite or gibbsite + H_2O are stable relative to any combination of boehmite + H_2O. Thus the diagram represents the situation at 25°C and 1 atmosphere total pressure according to the experimental work of Ervin and Osborne (1951) and Kennedy (1959).

In a system that is open to H_2O, the chemical potential of H_2O becomes (as has already been noted) an independently variable intensive parameter of the system. Consequently, if μH_2O (which is equivalent to the molar free energy of H_2O) is lowered to the value represented by contour a–b in Fig. 2B, the resulting free energy-composition diagram would be that of Fig. 3B indicating an isobaric, isothermal, invariant equilibrium between the three phases gibbsite, boehmite and H_2O. To lower μH_2O still further would have the effect of stabilizing boehmite + H_2O relative to gibbsite + H_2O (Fig. 3C).

If now, the data of Table 2 is used to construct free-energy/composition diagrams, it is possible to estimate the maximum lowering of μ_{H_2O} necessary to stabilise boehmite relative to gibbsite at 25°C and 1 atmosphere pressure.
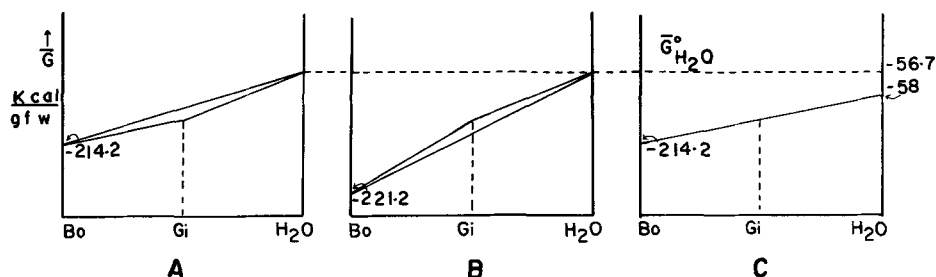
Figures 4A and 4B show diagrams constructed

face environments. One obvious mechanism by which such a lowering could be accomplished is by the introduction of impurities into the H_2O. Alternatively undersaturation with respect to H_2O can accomplish the same end. Both of these mechanisms can be demonstrated in a qualitative manner in the laboratory.

SYNTHESES OF Al(OH)₃ AND Al(OOH) UNDER EARTH SURFACE CONDITIONS

An aluminum amalgam was used in a technique described elsewhere (Chesworth, 1971). The purpose was to demonstrate the above mechanisms in the laboratory, and not to claim equilibrium.

The amalgam was immersed in pure water and in salt solutions of various strengths. This is an experimental equivalent of the mechanism by which μH_2O may be lowered in natural waters by the presence of impurities. The amalgam was also placed in an open vial and suspended over aqueous solutions in a closed flask. This is experimentally equivalent to a natural situation wherein the soil atmosphere contained water vapour under conditions where μH_2O was less than the saturation value. Results at 25°C and 1 atmosphere total pressure are shown in Table 3.

From the table it can be seen that the trihydroxide

Fig. 4. Molar free energy composition diagrams for the system AlOOH—H_2O at 25°C and 1 atmosphere total pressure, using the values of Table 2. 214·2 and 221·2 Kcal/gfw are extreme values of the free energy of formation of boehmite. The numerical values on the diagram are correct, but the scale has been exaggerated to demonstrate the relationships clearly.

extreme values of the free energy of boehmite. Figure 4c shows a critical tie line of three phase equilibrium drawn on the basis that μ_{H_2O} can be lowered from its value for pure water. It pertains to a μ_{H_2O} of about −58 Kcal, (cf. −56·7 Kcal for pure H_2O). In other words μ_{H_2O} would have to be lowered by 1·3 Kcal to enable it to be said with certainty that boehmite was more stable than gibbsite in a particular earth surface environment. It is perfectly conceivable that the amount of lowering necessary may be much less than this, especially considering the fact that boehmite is not an unusual mineral to find in earth sur-

phase synthesised is bayerite, while pseudoboehmite is the oxyhydroxide phase synthesised. It is significant that the oxyhydroxide does not appear until salinities are much higher (greater than 12%) than can be expected in the surface waters of the earth.

Experiments at higher temperatures where kinetic barriers are less formidable indicate that bayerite has a tendency to age to gibbsite, while pseudoboehmite ages to boehmite. If, then, the above experiments provide a reasonable model for the formation of gibbsite and boehmite at the surface of the earth it appears unlikely that μH_2O can

Table 3. Mineral syntheses using Al-amalgam at 25°C and 1 atmosphere total pressure. Phases determined by X-ray powder diffractometry

Reacting medium		Products
Liquid phase	H_2O	Bayerite
	1M NaCl Solution	Bayerite
	2M NaCl Solution	Bayerite
	2·5M NaCl Solution	Bayerite + Pseudoboehmite
	3M NaCl Solution	Bayerite + Pseudoboehmite
Vapour phase	H_2O	Bayerite
	1M NaCl Solution	Bayerite
	2M NaCl Solution	Bayerite
	2·5M NaCl Solution	Bayerite + Pseudoboehmite
	3M NaCl Solution	Bayerite + Pseudoboehmite

be lowered sufficiently in the zone of weathering to produce the assemblage boehmite + water. In this case the undoubted presence of boehmite at the earth's surface would need to be ascribed to a different mechanism, or a different assemblage, possibly gibbsite + boehmite. In fact all published reports checked show that boehmite is always found in the presence of gibbsite. Has it ever been found in a surficial deposit in the absence of gibbsite?

CONCLUSIONS

At the low temperatures and low pressures of the earth's surface, it can be shown experimentally that in the system Al_2O_2–H_2O the following divariant assemblages can be stabilized:

(1) boehmite + gibbsite
(2) boehmite + H_2O
(3) gibbsite + H_2O

Earth surface conditions appear unlikely to give the low μH_2O required for formation of assemblage (2) so that (1) and (3) remain as the most probable stable assemblages in the zone of weathering. It is therefore misleading to say (see Marshall, 1964, p. 147) that one or other of the phases gibbsite and boehmite is the stable phase at the earth's surface without first specifying whether the system is deficient in water or not i.e. whether or not H_2O is present as a separate phase.

In most environments at the earth's surface water will be present, consequently gibbsite will be stable relative to boehmite. In arid and semi-arid regions or in micro-environments in soils where clay skins or reaction rims effectively seal off units of the soil from contact with water, then boehmite and gibbsite can be stabilized together. Stated in another way this analysis shows that boehmite will not be stable at the earth's surface except in the presence of gibbsite and the absence of water as a separate phase.

None of the above rules out the possibility of metastable assemblages persisting at the earth's surface. However the stable assemblages represent the end point towards which metastable systems will tend to change. Their recognition is therefore an important objective of the earth scientist.

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Résumé – Deux conceptions s'excluant mutuellement existent à propos de la stabilité relative de la gibbsite et de la boehmite dans les sols. Elles sont examinées sur la base de données expérimentales et thermodynamiques et l'on montre que chacune des trois combinaisons divariantes possibles entre deux phases, susceptibles d'exister entre la gibbsite, la boehmite et l'eau, peuvent effectivement se rencontrer à 25°C et 1 atmosphère de pression totale, selon l'état de H_2O. On montre en outre que les conditions de potentiel chimique de H_2O nécessaires pour stabiliser boehmite + H_2O par rapport à gibbsite + H_2O ou gibbsite + boehmite ont peu de chance d'être satisfaites dans les eaux naturelles de la zone d'altération.

Kurzreferat – Es bestehen zwei sich gegenseitig ausschliessende Ansichten über die relativen Beständigkeiten von Gibbsit und Boehmit in Böden. Diese werden auf Grund von experimentellem und thermodynamischem Beweismaterial untersucht und es wird dargelegt, dass alle drei möglichen, divarianten Zusammenstellungen von zwei Phasen die zwischen Gibbsit, Boehmit und Wasser bestehen können, bei 25°C und 1 Atmosphäre Gesamtdruck vorhanden sein können und zwar je nach dem Status des H_2O. Es wird ferner gezeigt, dass die für die Stabilisierung von Boehmit + H_2O im Verhältnis zu Gibbsit + H_2O oder Gibbsit + Boehmit erforderlichen Bedingungen des chemischem Potentials von H_2O kaum in natürlichen Wässern in der Verwitterungszone vorhanden sein werden.

Резюме — Существуют два взаимоисключающих взгляда об относительной устойчивости гиббсита и бемита в почве. Этот вопрос рассматривался в свете экспериментальных и термодинамических показаний и стало видно, что все три возможные диварианты группы двух фаз, которые могут существовать между гиббситом, бемитом и H_2O могут быть устойчивыми при 25°C и общем атмосферном давлении 1 в зависимости от состояния H_2O. Добавочно заметили, что состояние химического потенциала H_2O требующегося для стабилизации бемита + H_2O относительно гиббсита + H_2O или гиббсита + бемита навряд ли встречается в естественных водах зон выветривания.