

MINERAL METASTABILITY IN THE SYSTEM $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$: A DISCUSSION

Key Words—Diaspore, Gibbsite, Low P/T.

In the following discussion, I dispute three major points made by Anovitz *et al.* (1991), concerning the stability of aluminum hydroxides at the surface of the earth and whether their work supercedes previously published discussions of the matter.

DOES EXPERIMENTAL DATA PROVE THAT DIASPORE IS THE STABLE PHASE?

Anovitz *et al.* (1991) believe that the answer to this question is yes. They state:

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.* (1991), show that diaspore is the only stable aluminum hydroxide phase at near-surface conditions on the earth (p. 225).

Elsewhere, the claim is made in a nonequivalent, less emphatic form. In the Abstract and on p. 230, for example, the authors state that their data only “suggests” that diaspore and water are the stable assemblage at STP. Even this version is unjustified, as an examination of their thermodynamic data shows.

The issue is simple. Does the free energy data of Anovitz *et al.* (1991, Table 3) when applied to the reaction

Diaspore + Water (liq) = Gibbsite (at 25°C, 100 kPa)

allow an unequivocal statement to be made concerning the stability of gibbsite under earth-surface conditions? Anovitz *et al.* (1991, p. 230) calculate the ΔG_r to be 3.44 kJ mol⁻¹ and conclude that gibbsite is metastable with respect to diaspore and water. The error in this value, calculated by the method of Sposito (1981), is ± 5.3 kJ mol⁻¹. Thus, their conclusion is invalid and their data cannot be used rigorously to decide whether or not gibbsite is stable or metastable under earth-surface conditions. Furthermore, for reasons enumerated by Helgeson *et al.* (1978) the error calculated above is likely to be an underestimate.

In a subsidiary claim, Anovitz *et al.* (1991, p. 231) state that their data show that the formation of gibbsite in soil horizons “must be ascribed to non-equilibrium processes.” Why “must” it? Are the authors saying that metastability and equilibrium are incompatible with

each other? Even if the authors’ data lived up to the claims made for it, gibbsite could still participate in metastable equilibria at STP (see Day, 1976; Chesworth, 1978, 1980b).

DO FIELD OCCURRENCES SHOW THAT DIASPORE FORMS UNDER EARTH SURFACE CONDITIONS?

Diaspore has been recorded worldwide, in many bauxitic materials (Valeton, 1972, and Bardossy, 1982, for details). Bardossy (1982; Appendix 3) provides a convenient mass of readily available data to check this claim. He gives details of 77 karst bauxites that contain diaspore. If it could be shown that the latter deposits were unaffected by diagenesis, or by tectonism, a case could be made for claiming that the diaspore formed under the low PT conditions of the weathering regime. In fact, each of Bardossy’s diaspore-bearing examples has undergone diagenesis. Also, most of the localities where diaspore makes up 100% of the Al hydroxides present have been subjected to strong or very strong deformation and even metamorphism. There is no way that this significant collection of field data can be used to suggest that diaspore forms in the weathering zone.

By contrast Anovitz *et al.* (1991) cite four references from this vast literature as proof that diaspore forms under earth-surface conditions. Of these all but one deal with materials that have undergone diagenesis and are, therefore, inappropriate citations. The one that does not deal with diagenetically altered material, Hsu (1977), makes *absolutely no claim whatsoever* that diaspore forms in earth-surface deposits.

If diaspore is indeed the stable Al hydroxide at STP, it would appear to be unique in not forming there. Any other system for which a significant body of data is available regarding earth-surface occurrences shows that metastable phases have not formed to the exclusion of the putative stable phase, in spite of the fact that such an eventuality is theoretically possible. As examples consider the system CaCO_3 and SiO_2 . At the surface of the earth, metastable aragonite and vaterite do not form to the exclusion of stable calcite. Nor do metastable cristobalite nor tridymite form to the exclusion of stable quartz. So why should the system $\text{Al}_2\text{O}_3\text{--H}_2\text{O}$ be different; and why, of all the Al-hydroxides formed at the earth’s surface, should the postulated stable phase diaspore be uniquely absent? It *is* possible, but it would appear to make diaspore unique amongst mineral species. Such a unique eventuality needs far more discus-

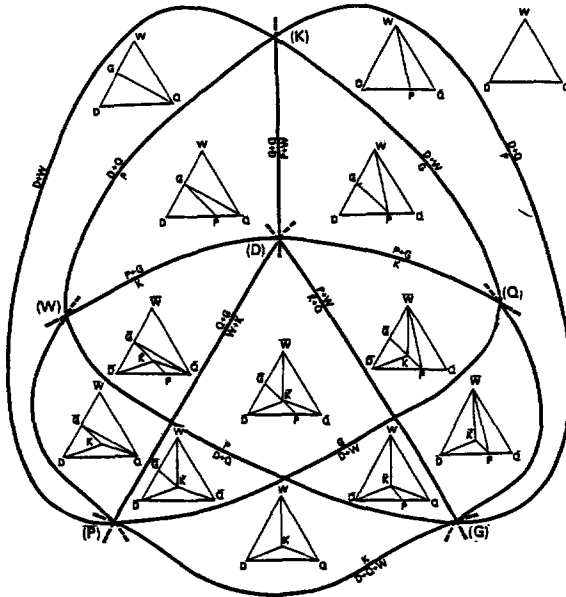


Figure 1. Multisystem net for six phases in a three-component system.

sion than Anovitz *et al.* (1991) give it. Certainly the literature they cite provides no evidence for their assertion.

ARE EARLIER INTERPRETATIONS WRONG?

Next I examine the interpretations that Anovitz *et al.* (1991) make of my own work. Again, I quote:

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 soil (p. 225).

The most significant quotation I would draw attention to is to be found in Chesworth, 1980b. This is the culminating paper in a series that deals with equilibrium phase diagrams for minerals that form in weathering systems, including soils. After developing low PT diagrams for the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-K}_2\text{O-MgO-H}_2\text{O}$, Chesworth (1980b) makes the following statement:

there is the possibility that some, at least, of the equilibria presented here are metastable rather than stable. *Those involving gibbsite are examples . . . the validity of the diagrams is by no means impaired by this (982-983).*

In other words, whether the equilibria in question are stable or metastable, the diagrams are still applicable to earth-surface deposits. Since Anovitz *et al.* (1991) are specifically concerned with the metastability of gibbsite and since they claim that this is a major difference between us, it is astonishing that they would ignore the phrase that I have italicized.

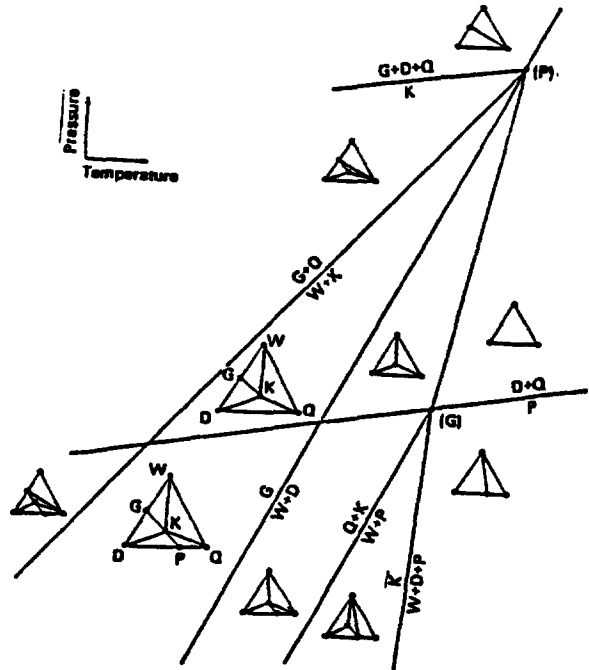


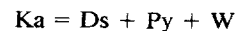
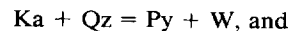
Figure 2. The gibbsite-absent (G) and pyrophyllite-absent (P) invariant points oriented with respect to temperature and pressure axes.

Anovitz *et al.* (1991) further state: "Chesworth (1972, 1975, 1980a, 1980b) presented several phase diagrams showing boehmite and gibbsite to be stable a STP without considering that diaspore is more stable" (p. 229). Chesworth (1972) examines "the relative stabilities of gibbsite and boehmite" (p. 369) since this was a question under dispute at that time. In determining the relative stabilities of two minerals, the stability of a third (in this case diaspore) is irrelevant.

AN INTERNALLY CONSISTENT PHASE DIAGRAM

In a desire to be constructive, I offer the following attempt at an internally consistent phase diagram.

The analysis of Anovitz *et al.* (1981) leads to the phase relations shown in their Figure 3, which includes at the lowest temperatures, two reactions:



To relate this to the problem in hand, gibbsite must be added, and a multisystem net for six phases in a three-component system needs to be constructed. Use of Zen and Roseboom's (1972) technique allows a shortcut to the desired diagram since the system in question has the chemography of their type Tb (Zen and Roseboom, 1972, p. 697), with two degenerate features. A multisystem net appropriate to current concerns is presented as Figure 1. The relevant invariant

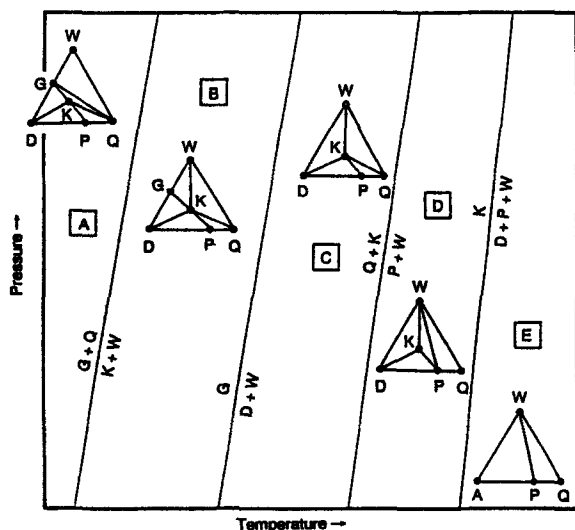


Figure 3. Qualitative PT diagram consistent with Anovitz *et al.* (1991) and earlier work of Chesworth.

points are (G) and (P). When these are oriented to agree with Day (1976), Figure 2 is obtained. The section of Figure 2 that refers to pressures lower than the univariant curve $P + D + Q$ is directly relatable to Figure 3 of Anovitz *et al.* (1991) as well as to earlier work of mine (Chesworth, 1975). Figure 3 shows a sequence of dehydration reactions with increasing temperature. Anovitz *et al.* (1991) consider only the two at higher temperatures. Their work has no bearing on the positions of the lower temperature pair of curves. The possibility that the compatibility triangle of PT field B represents STP is entirely consistent with Anovitz *et al.*'s (1991) analysis of the situation (their Figure 3). Neither their thermodynamic data nor their phase diagram precludes this possibility.

CONCLUSIONS

The experimental error associated with their thermodynamic parameters quoted by Anovitz *et al.* (1991) negates their contention that diaspore is the only Al hydroxide stable under earth-surface conditions. Nor is their phase diagram incompatible with the idea that gibbsite is stable at low PT. Furthermore, their use of primary, published sources does not support their statements.

The authors' parting suggestion that their work somehow leads to the conclusion that equilibrium concepts may not be relevant to pedology I suggest is superficial and unacceptable. To name only three, the influential works of Garrels and Christ (1965), Lindsay (1979) and Sposito (1981) are testament to the fact that the application of equilibrium concepts to low PT materials, including soils, has led to many fruitful insights.

The thermodynamicist constructs idealized models of natural systems (igneous and metamorphic rocks

included). The models either resemble or differ from the natural system studied. In both their resemblances and their differences, the models have heuristic value, leading to a greater understanding of the natural state. In turn, the latter provides feedback that leads to a refinement of the models. The cycle is repetitive, endless, and endlessly fascinating.

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