

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

Key Words—Boehmite, Diaspore, Equilibrium, Gibbsite, Kaolinite, Metastability.

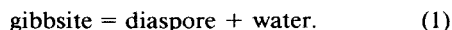
The authors are grateful for an opportunity to clarify issues related to the formation of metastable and unstable minerals at the surface of the earth. Chesworth (1994) misrepresents and misinterprets much of the paper by Anovitz *et al.* (1991), which contains straightforward conclusions that were made on the basis of experimental and thermodynamic data on the relative stabilities of hydrous aluminum oxides and silicates. The inferences of Anovitz *et al.* (1991) are not theirs alone. Kittrick (1969), Day (1976), Hemingway *et al.* (1978, 1991), Perkins *et al.* (1979), Hemingway (1982), Apps *et al.* (1989), and Verdes *et al.* (1992) concluded that bayerite, boehmite, dickite, gibbsite, halloysite, and/or nordstrandite are metastable in the system $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$. These inferences are also consistent with thermodynamic data in compilations by Helgeson *et al.* (1978), Robie *et al.* (1978), Haas *et al.* (1981), and Robinson *et al.* (1982). For instance, Anovitz *et al.* (1991) showed that boehmite, having a greater entropy than diaspore, cannot react at equilibrium to produce diaspore in response to increasing temperature. Yet, diaspore has been shown to crystallize from boehmite in nature and the laboratory. This phenomenon provides compelling evidence for relative stability of diaspore and instability of boehmite, and the ability of boehmite to form at the earth's surface despite its instability relative to diaspore. Rather than representing even metastable equilibrium, at or above STP, the boehmite–diaspore transition, therefore, involves a non-equilibrium process, which can be discussed cogently only in terms of kinetics or irreversible thermodynamics. Experimental and thermodynamic data also indicate that dickite and halloysite are less stable than kaolinite and that all polymorphs of $\text{Al}(\text{OH})_3$ are metastable relative to diaspore and water at STP.

In contrast, on the basis of natural occurrences and unreversed synthesis experiments, Chesworth (1972) concluded that gibbsite and boehmite must be stable phases at the earth's surface. Chesworth (1975, 1980) applied hypothetical phase equilibrium topologies to minerals without full consideration of the thermodynamic properties of the phases under consideration, emphasizing Schreinemaker's approach rather than directly calculating their loci. Chesworth reiterates many

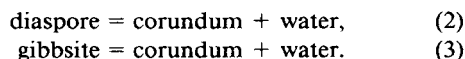
of these views in the accompanying criticism, although he finally seems to have abandoned the quest for stable boehmite. In the following sections, the authors respond to each of the topics raised by Chesworth (1994).

THE STABILITY OF DIASPORE

Chesworth (1994) maintains that gibbsite is stable in the presence of water at 1 bar and 298 K (STP). He combines errors for the Gibbs energy of each phase relative to the elements as the square root of the sum of the squares of error for each phase in the reaction:



This is an inappropriate procedure in the case of highly correlated errors (Anovitz *et al.*, 1991). Significant uncertainties remain in the reduction of many refractory oxides and silicates to metals, as are indicated by large errors in Gibbs energies relative to the elements. Instead, one should consider errors in the Gibbs energies of compounds from the equivalent oxides as an approximation to the uncertainties involved (Robie *et al.*, 1978). That is, one must evaluate errors in the Gibbs energies of the reactions:



At STP, a 2σ uncertainty of ± 0.5 kJ/mol was derived from direct experiments on Reaction 2 (Anovitz *et al.*, 1991), but Reaction 3 has not been located experimentally and must be calculated from thermodynamic data. Unfortunately, there is a discrepancy in the error cited for gibbsite by Anovitz *et al.* (1991). The value of ± 5.3 kJ/mol was taken from Apps *et al.* (1985), but the source of their data (Robie *et al.*, 1978) gave a 2σ error of only ± 1.2 kJ/mol for the Gibbs energy of gibbsite, an error that should have been cited by Apps *et al.* (1985) and by Anovitz *et al.* (1991). The uncertainty given for gibbsite by Apps *et al.* (1985) appears to be an error (Apps, personal communication, 1993). The uncertainty in the reduction of corundum to aluminum metal is ± 1.3 kJ/mol (Robie *et al.*, 1978). Using an error estimate of $2(1.2) - 1.3 = \pm 1.1$ kJ/mol for Reaction 3, one obtains an estimated uncertainty of $([0.5/2]^2 + [1.1/2]^2)^{1/2} = \pm 0.6$ kJ/mol for Reaction 1 (where division by factors of 2 relate to reaction stoichiometries). From these data, the Gibbs energy of Reaction 1 is -3.4 ± 0.6 kJ/mol. Based on solubility measurements, Verdes *et al.* (1992) obtained another

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estimate of the Gibbs energy of diaspora, which yields -6.8 ± 2.9 kJ/mol for Reaction 1 by a similar calculation as that above. The two results marginally overlap at the limits of error; both indicate that diaspora + water are more stable than gibbsite at STP even considering error brackets.

FORMATION OF DIASPORE AT EARTH SURFACE CONDITIONS

Chesworth (1994) questions the assertion that diaspora may form at the surface of the earth. He cites Bardossy (1982) regarding observations of 77 bauxite samples that contain diaspora and then states that all of these occurrences have undergone diagenesis. No evidence is given to support this proclamation. In a more recent treatise Bardossy and Aleva (1990) stated:

Diaspora has long been considered to be a rarity in lateritic bauxite; however, in the last two decades it has been found by X-ray diffraction methods in a large number of deposits in the amounts of 0.1–0.5%. Such is the case for almost all surface deposits. Up to 4% diaspora occurs locally in some deposits of the West Coast district in India, mainly in the top part of the bauxite (p. 154).

So much for the non-existence of surficial diaspora! Simply the occurrence of diagenetic diaspora has implications for its stability at low temperature, as diagenesis spans the range of P–T–X conditions ranging from those encountered during weathering through authigenesis to deep diagenesis. Many diaspora-bearing deposits given in Bardossy (1982) and Bardossy and Aleva (1990) were not subjected to deep burial, and any diagenesis that may have occurred still closely approximated earth surface conditions.

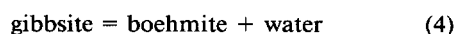
THE UNIQUENESS OF DIASPORE STABILITY AT STP

Chesworth (1994) challenges the concept that diaspora might be stable at STP yet never form there; he suggests that this would be unique and, therefore, highly unlikely. However, Anovitz *et al.* (1991) addressed this issue, citing stable phases or assemblages (rutile, magnesite–brucite–water, muscovite–pyrophyllite \pm water) that are apparently not known to form at or near STP. Graphite, dolomite, and perhaps even quartz–water should be included in this group. Graphite (\pm CH₄, CO₂ and/or H₂O) is always more stable than tars, complex hydrocarbons or humans, but it begins to form only above ca. 300°C. Dolomite does not form at earth surface conditions; a structure analogous to protodolomite that is metastably calcian and that contains disordered Ca/Mg and CO₃ groups is found instead (e.g., Wenk *et al.*, 1983). Although quartz grows diagenetically at low temperatures (e.g., Herkimer “diamonds,”

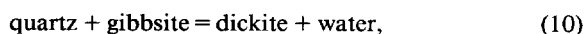
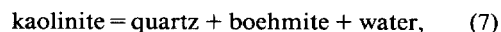
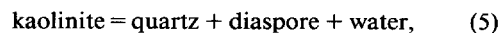
chalcedony), it may always be preceded by opaline or amorphous silica precursors. In any case, contrary to Chesworth’s assertions, diaspora forms in many surface deposits in minor amounts (Bardossy and Aleva, 1990).

METASTABLE EQUILIBRIA IN THE SYSTEM Al₂O₃–SiO₂–H₂O

Chesworth (1994) chastises the authors for failing to consider metastable equilibria in their 1991 paper. The authors maintain that consideration of metastable equilibria is not necessary when discussing stable minerals and assemblages. Calculations in the system Al₂O₃–H₂O reveal that the univariant boundary for the reaction



is located at $7 \pm 24^\circ\text{C}$ (Anovitz *et al.*, 1991) or at $25 \pm 28^\circ\text{C}$ (Verdes *et al.*, 1992) at 1 bar, has a steep positive slope and is metastable relative to Equilibrium 1 (Figure 1). Equilibrium boundaries for other reactions equivalent to Reaction 4 involving other Al(OH)₃ polymorphs are located at even lower temperatures as they are less stable than gibbsite. Reaction 4 could be operative in some soil horizons. Calculation of metastable equilibria in the system Al₂O₃–SiO₂–H₂O:



reveals that Equilibria 5–8 are found at relatively high temperatures (230–460°C at P > 0.1 kb) (Figure 1), whereas 9 and 10 occur below 0°C. In contrast, Chesworth (1994) emphasizes that Reactions 1 and 9 are stable equilibria above STP (his Figure 3). Metastable Reactions 5–10 are not located in a P–T range appropriate for consideration in diagenetic systems (compare the loci of the reactions with those of the diagenetic window in Figure 1). The loci of Reactions 5–8 in P–T space may coincide with that of some hot springs and hydrothermal systems at 200–400°C. However, their applicability would require destruction of kaolinite or dickite to form metastable quartz and boehmite at high temperatures, very near conditions of decomposition of kaolinite or dickite to pyrophyllite, which seems improbable to the authors. Reactions 9 and 10 are unlikely to occur in nature even as metastable equilibria. Consideration of the full Schreinemaker’s net in the system Al₂O₃–SiO₂–H₂O yields few insights for geological systems.

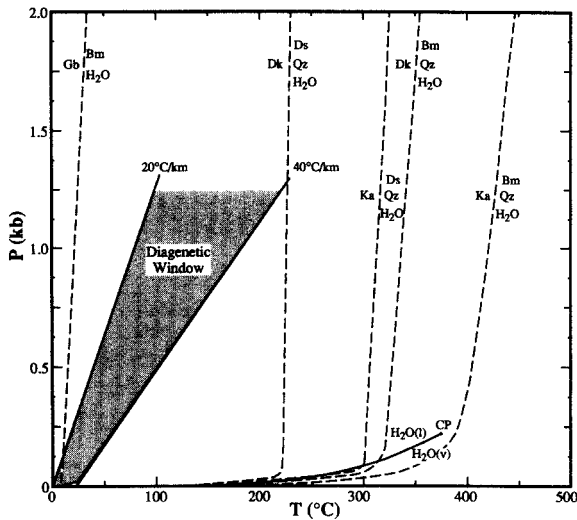


Figure 1. P-T diagram of metastable dehydration reactions in the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ compared with the window for diagenesis and the critical curve for H_2O . Note the lack of invariant points involving aluminous phases in this P-T range. Diagenetic window calculated assuming a range of geotherms from 20 to $40^\circ\text{C}/\text{km}$, T of 0° to 40°C at one bar, an average rock density of 2.5 g/cc and a maximum sedimentary basin thickness of 5 km. Diagenetic conditions in sedimentary basins are unlikely to intersect the metastable curves involving kaolinite and dickite. Abbreviations: Bm—boehmite, CP—critical point, Dk—dickite, Ds—diaspore, Gb—gibbsite, Ka—kaolinite, Qz—quartz.

DISCUSSION

Available physicochemical data, which restrict the relative Gibbs energies of diaspore + water vs. gibbsite and diaspore vs. boehmite, make it clear that gibbsite and boehmite cannot be stable at STP. They do not constrain the absolute Gibbs energies of formation for individual phases as well because the uncertainties are highly correlated. An important corollary is that any equilibria involving gibbsite or boehmite must be metastable relative to other equilibria involving diaspore or corundum at or above STP. This corollary applies to phase diagrams using activity, fugacity, or other intensive variables as well as to P-T diagrams. Many aqueous geochemistry diagrams portray gibbsite and/or boehmite without an indication of their metastability. Although metastable equilibria may be useful, differences between metastable and stable equilibria represent a potential driving force that could be registered in nature or in the laboratory, and their unlabeled use on phase diagrams is at best misleading. More generally, geological systems at or near the earth's surface usually do not approach either stable or metastable equilibrium, and therefore equilibrium models can have only limited applicability. In addressing rather different systems Chernov and Lewis (1967) stated:

The composition and structure of a crystal formed in a multicomponent system are determined by the equilibrium diagram only if the conditions of crystal growth are close to those of equilibrium. If the departure from equilibrium is considerable, both the composition and the actual structure of the crystal will depend on the crystallization kinetics. . . . There is, consequently, a broad class of actual crystallization conditions in which a purely thermodynamical approach may lead to inaccurate or simply incorrect results (p. 2185).

For instance, large supersaturation relative to dolomite and/or calcite is the rule in oceans, marl lakes, and salt lakes. Such disequilibrium processes predominate below 2 kb and 200°C , conditions that encompass the realms of diagenesis, hot springs, and hydrothermal ore deposits. These environments are the breeding grounds for the formation of metastable phases. Contemplation of such materials requires a deep understanding of the kinetics of dissolution, nucleation and growth, topics far beyond the scope of studies by Chesworth (1980) and Anovitz *et al.* (1991).

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