Clays and Clay Minerals, Vol. 31, No. 3, 239–240, 1983.

EFFECTS OF AlOOH-FeOOH SOLID SOLUTION ON GOETHITE-HEMATITE EQUILIBRIUM

Key Words—Aluminum, Diaspore, Goethite, Hematite, Solid solution, Thermodynamic stability.

The relative thermodynamic stabilities of the common sedimentary minerals goethite and hematite are represented by the reaction: goethite = hematite + water. The thermodynamic relationship of these minerals has been the subject of considerable study (Posnjak and Merwin, 1919; Smith and Kidd, 1949; Schmalz, 1959; Berner, 1969; Pollack *et al.*, 1970; Langmuir, 1971). The work of Langmuir (1971) represents a culmination of these studies, because it addresses the effect of particle size, as well as temperature and pressure on the equilibrium. Langmuir concluded that goethite cubes less than about 0.1 μm on an edge are thermodynamically less stable than hematite under geologic conditions. Thus, the finely-divided goethite in soils (Schwertmann and Taylor, 1977) is regarded by Langmuir (1971) as thermodynamically unstable. Provided that the thermodynamic data employed by Langmuir are valid, this conclusion is correct for *pure* goethite, because purity was an implicit assumption in all the thermodynamic stability studies cited above.

However, the assumption of purity in natural goethites is not generally appropriate (Posnjak and Merwin, 1919). Norrish and Taylor (1961), Nahon *et al.* (1977), and Fitzpatrick and Schwertmann (1982), among others, have found that aluminum substitutes for iron in goethites in a variety of soils. The aluminum can be interpreted to be present as the diaspore component in a solid solution between the isomorphs goethite and diaspore. Norrish and Taylor (1961) found that the substituted aluminum (as AlOOH) constitutes as much as 29 mole % of the finely divided soil goethite with the higher concentrations of aluminum apparently occurring in the smallest particles. Fitzpatrick and Schwertmann (1982) measured an AlOOH content as high as 32 mole %. Franz (1978) and Lewis and Schwertmann (1979) described laboratory procedures for preparing Al-substituted goethite at 25°C to 70°C and one atm and confirmed that the Al substituted for Fe in the goethite structure.

The existence of solid solutions of diaspore in goethite in fine-grained goethite in soils has important implications for the stability of such goethite. These implications are evident in the following thermodynamic treatment of this solid solution.

THERMODYNAMIC MODEL

The relative stability of a goethite-diaspore solid solution compared to an Fe_2O_3–Al_2O_3 solid solution can be represented as follows:

$$2X\ FeOOH + 2(1 - X)\ AlOOH = X\ Fe_2O_3 + (1 - X)\ Al_2O_3 + H_2O_{(L)}, \quad (1)$$

where X = mole fraction of FeOOH in the goethite-diaspore solid solution. Although Fitzpatrick and Schwertmann (1982) did not observe more than about 32 mole % AlOOH in natural goethites, it will be assumed for simplicity that the goethite-diaspore solid solution is ideal over the entire compositional range. The existence of Fe_2O_3–Al_2O_3 solid solutions in soil hematites has been widely reported (e.g., Nahon *et al.*, 1977). This solid solution will also be presumed to be ideal. With these conditions the following expression is obtained:

$$\ln a_W = X[\ln X] + (1 - X)[\ln(1 - X)] - AX - B, \quad (2)$$

where a_W = equilibrium activity of liquid water, X = mole fraction of FeOOH in the goethite-diaspore solid solution and the mole fraction of Fe_2O_3 in the hematite-corundum solid solution, $A = (\mu_H^\circ - \mu_C^\circ - 2\mu_G^\circ + 2\mu_D^\circ)/RT$, $B = (\mu_C^\circ + \mu_W^\circ - 2\mu_D^\circ)/RT$, and μ_i° = standard state molar Gibbs free energy of formation of pure substance "i" from its constituent elements at one atm and some specified temperature. H = hematite, C = corundum, W = water, G = goethite, D = diaspore, R = gas constant, T = absolute temperature. Because no data are available on the effects of particle size on the μ_i° of the aluminum oxides, all μ_i° data employed in this work are for "coarse" particles at 25°C and one atm. With the exception of goethite, the data were obtained from Robie *et al.* (1978). The value of μ_G° for coarse-grained goethite was calculated from the reaction ΔG° data of Langmuir (1972) using the μ_H° and μ_W° values in Robie *et al.* (1978). These free energy data are in Table 1.

RESULTS AND DISCUSSION

The calculated equilibrium activities of water at 25°C and one atm as a function of mole fraction FeOOH are listed in Table 2 and plotted in Figure 1. The salient feature of Figure 1 is the indication of the rapid drop in a_W that accompanies small degrees of substitution of aluminum into the goethite structure. In fact, at about 20 mole % AlOOH the equilibrium activity of liquid water is about an order of magnitude lower than for pure goethite (see Table 2). If water vapor is assumed to behave as an ideal gas, the values of a_W in Table 2 and Figure 1 are numerically equal to relative humidity expressed as a decimal fraction. Thus, in the absence of liquid water, a relative humidity as low as 0.044 at 25°C is apparently sufficient to stabilize "coarse-grained" goethite containing 20 mole % AlOOH in ideal solution. This degree of substitution of Al into goethites in soils appears to be common (Norrish and Taylor, 1961; Fitzpatrick and Schwertmann, 1982).

The assumption of ideal solution over the entire compositional range in Figure 1 is probably not valid. However, a significant departure from ideality in the observed natural substitution range (mole fraction of AlOOH less than 0.33) is necessary to invalidate the general result evident in Figure 1 over this same range.

The exact effect of particle size variation on the result in Figure 1 is not known, but it seems reasonable to expect that the *general* consequences of Al substitution would not be affected. Thus, Al substitution might significantly lower the equilibrium a_W even for very finely divided particles.

The assumption that the range of Fe_2O_3–Al_2O_3 solid solution is the same as that between goethite and diaspore is probably not generally valid (Nahon *et al.*, 1977). However, the extreme effect of *no* solid solution between Fe_2O_3 and Al_2O_3 can be calculated. Such calculations are included in Table 2. Note that a_W is somewhat lower at any given value of X for no Fe_2O_3–Al_2O_3 solid solution than for the corresponding case of complete hematite-corundum miscibility. Thus, the Al-substituted goethite is even more stable in the former system. The en-

Table 1. Standard state molar Gibbs free energies of formation (from the elements) of the indicated pure substances at 25°C and 1 atm.[1]

Substance	μ° (kcal/mole)
Hematite (Fe_2O_3)	−177.46
Goethite (FeOOH)	−117.3[2]
H_2O (Liq)	−56.67
Diaspore (AlOOH)	−220.31
Corundum (Al_2O_3)	−378.07

[1] All data from Robie *et al.* (1978) except as noted.
[2] Calculated from data in Langmuir (1972). See text.

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https://doi.org/10.1346/CCMN.1983.0310312 Published online by Cambridge University Press

Table 2. Calculated activities of liquid water as a function of the mole fraction of FeOOH in an ideal goethite-diaspore solid solution in equilibrium with hematite and corundum.

X_{FeOOH}	a_W for ideal solution between hematite and corundum	a_W for immiscible hematite-corundum products
1.00	0.45	0.45
0.98	0.34	0.31
0.96	0.27	0.22
0.94	0.21	0.17
0.92	0.16	0.12
0.90	0.13	0.095
0.85	0.075	0.049
0.80	0.044	0.027
0.70	0.016	0.0086
0.60	0.0060	0.0030
0.50	0.0023	0.0012
0.40	0.00096	0.00049
0.30	0.00041	0.00022
0.20	0.00018	0.00011
0.10	0.000088	0.000063
0.00	0.000049	0.000049

Mole fraction of hematite in hematite-corundum solid solution is presumed to be the same as the mole fraction of FeOOH in the goethite-diaspore solid solution.

hanced stability of goethite-diaspore solid solutions has been suggested by Nahon *et al.* (1977) and Fitzpatrick and Schwertmann (1982) based on studies of naturally occurring soil goethites. In particular, Nahon *et al.* (1977) observed that Al-substituted hematite had been converted to Al-substituted goethite. Nahon (1976) performed some calculations which illustrate the effect of goethite-diaspore solid solution on the free energy change of the reaction: goethite = hematite + water for *pure* liquid water. Nahon's results incorporated somewhat different thermodynamic data, but his trends are consistent with the equilibrium results presented herein for the varying activity (or relative humidity) of the environmental water (as liquid or vapor).

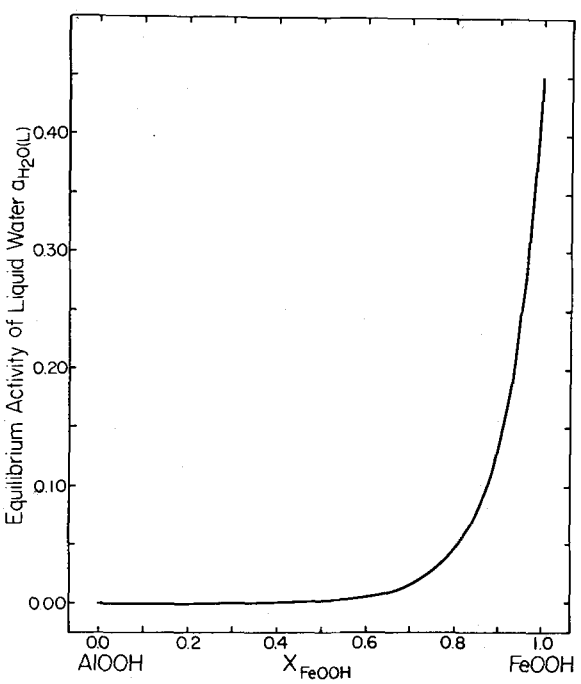


Figure 1. Plot of the calculated activity of liquid water in equilibrium with goethite-diaspore and Fe_2O_3–Al_2O_3 ideal solid solutions as a function of the mole fraction of FeOOH in the goethite. The actual range of X_{FeOOH} over which this curve is likely to be valid for natural samples is about 0.68 to 1.00 (see text).

In summary, the solid solution of AlOOH in goethite can increase the thermodynamic stability of goethite with respect to hematite. Consequently, even very fine-grained, Al-bearing goethite particles in soils may in fact be thermodynamically stable rather than unstable as suggested by Langmuir (1971).

ACKNOWLEDGMENTS

This work was supported, in part, by a grant from Sandia National Laboratories. I thank J. A. Grambling for helpful discussion. Critical comments of F. A. Mumpton and two anonymous reviewers improved this communication.

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(Received 13 September 1982; accepted 18 November 1982)

https://doi.org/10.1346/CCMN.1983.0310312 Published online by Cambridge University Press