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CONDITIONS FOR DIRECT FORMATION OF GIBBSITE
FROM K-FELDSPAR—FURTHER DISCUSSION

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ABSTRACT

Theoretical analysis indicates that direct alteration of K-feldspar to gibbsite in the zone of weathering probably occurs only under conditions of good soil drainage and only if the pH is above 4.3. The analysis also indicates that gibbsite should not form if the soil water has an initial dissolved silica concentration above $10^{-4.6}$ moles/liter. The calculations further show that, in the pH range 2 to 8, K-mica should not form as an initial precipitate in the hydrolysis of K-feldspar but must always be preceded by the precipitation of some kaolinite and/or gibbsite. This result may partly explain the rather infrequent occurrence of K-mica as a direct alteration product of K-feldspar.

INTRODUCTION

The occurrence of delicate gibbsite vermiforms and pseudomorphs after K-feldspar in the Pensauken Formation of New Jersey indicates that under suitable conditions it is possible for K-feldspar to alter directly to gibbsite in the zone of weathering (Lodding, 1961). Lodding (1961, p. 399) suggests that this occurs under conditions of poor drainage where the hydrolysis of K-feldspar leads to localized high pH around feldspar grains and therefore to high silica solubility. The problem with this model is that it provides no mechanism for the removal of alkalis and silica and thus one might expect the formation of montmorillonite or K-mica rather than gibbsite. An alternative model is suggested by the calculations of Helgeson, Garrels, and Mackenzie (1969) who, using thermodynamic data, have determined theoretically the sequence of minerals that should form through the hydrolysis of K-feldspar in distilled water with an initial pH of 7. These calculations indicate that the first mineral to form in the hydrolysis process should be gibbsite (see Figure 1 in Helgeson *et al.*, 1969, p. 459). However, as the aqueous solution proceeds towards final equilibrium with K-feldspar the initially precipitated gibbsite latter reacts with K-feldspar to form kaolinite and is eventually totally consumed. At final equilibrium the solution is in equilibrium with kaolinite, K-mica, and K-feldspar at pH 9.2. Thus under conditions of high permeability and good drainage it may be that soil water passes through the K-feldspar system so rapidly that the hydrolysis reaction never progresses beyond the initial gibbsite stage, thereby allowing the direct formation of gibbsite from K-feldspar.

The question then arises as to whether there are other conditions besides permeability and drainage which limit the direct formation of gibbsite. In an earlier report (Gardner, 1970) the author has shown from thermodynamic considerations that gibbsite should not form from the dissolution of kaolinite if the pH is less than 4 and/or if the initial concentration of dissolved silica is greater than $10^{-4.6}$ moles/liter. An attempt will now be made to show that the same conditions also apply to the direct formation of gibbsite from K-feldspar. The calculations that follow will employ the thermodynamic data and equilibrium constants shown in Tables 1 and 2 of Gardner (1970).

pH LIMITATIONS

As for the pH limitations let us consider the congruent dissolution of K-feldspar in solutions which have no initial dissolved potassium,

TABLE 1

Calculated Activities of Species and Apparent Solubility Products of Intersection of K-Feldspar Congruent Dissolution Line and Gibbsite Stability Boundary.

pH	pA^{+3}	pK^+	pH_4SiO_4	pK_{sp} Kaolinite	pK_{sp} K-mica	pK_{sp} K-feldspar
8.0	16.1	7.60	7.12	82.34	- 2.74	13.02
7.0	13.1	8.60	8.12	84.44	2.35	18.06
6.0	10.1	8.95	8.47	85.14	4.66	20.46
5.0	7.1	6.80	6.32	80.84	- 2.94	12.86
4.5	5.6	5.48	5.00	78.20	- 7.72	8.08
4.0	4.1	4.06	3.58	75.36	-12.90	2.90
3.0	1.1	1.10	0.62	69.42	-23.76	-7.94
3.0 ^a	1.1	1.10	2.60	73.40	-17.80	-2.00

^a. Recalculated assuming saturation with respect to amorphous silica, $pH_4SiO_4 = 2.60$.

aluminum, or silica. Thus for the congruent dissolution of K-feldspar ($KAlSi_3O_8$) under these conditions we can write:

$$\Sigma \text{ dissolved } SiO_2 = 3 \times \Sigma \text{ dissolved Al} = 3 \times \text{concentration of } K^+. \quad (1)$$

Let us next assume that at any pH the first stability boundary intersected by the congruent dissolution line is that of gibbsite. As indicated above, the calculations of Helgeson, *et al.* (1969) show that for distilled water with an initial pH of 7 this is actually the case. Assuming that activities of aqueous species equal their concentrations we can calculate the activities of aqueous species at the intersection of the congruent dissolution line and the gibbsite stability boundary at any

TABLE 2

Calculated Activities of Species and Apparent Solubility Products at Intersection of K-Feldspar Congruent Dissolution Line and Kaolinite Stability Boundary.

pH	pAl^{+3}	pK^+	pH_4SiO_4	pK_{sp} Gibbsite	pK_{sp} K-mica	pK_{sp} K-feldspar
8.0	14.80	6.30	5.82	32.80	-11.54	6.56
7.0	11.31	6.81	6.33	32.31	-10.27	15.11
6.0	8.14	6.99	6.51	32.14	-9.06	10.66
5.0	6.21	5.91	5.43	33.21	-9.17	8.41
4.5	5.37	5.25	4.77	33.87	-9.33	6.93
4.0	4.57	4.53	4.05	34.57	-9.61	5.25
3.0	3.06	3.06	2.58	36.06	-10.02	1.86
2.0	1.56	1.56	1.08	37.56	-10.52	-1.64
2.0 ^a	0.05	0.05	2.60	36.05	-12.00	-0.10

a. Recalculated assuming saturation with respect to amorphous silica, $pH_4SiO_4 = 2.60$.

pH, given the solubility product of gibbsite (K_{sp} gibbsite = $10^{-34.1}$). For example at pH 5

$$[Al^{+3}] = \frac{K_{sp} \text{ gibbsite}}{[OH^-]} = \frac{10^{-34.1}}{10^{-27}} = 10^{-7.1} \quad (2)$$

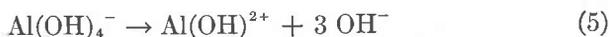
and by Equation 1,

$$\begin{aligned} [K^+] &= \sum Al = [Al^{+3}](1 + K_1[OH^-] + K_1K_2[OH^-]^4) \\ &= 10^{-7.1}(1 + 10^{9.0} \times 10^{-9.0} + 10^{9.0} \times 10^{23.5} \times 10^{-36}) \\ &= 10^{-6.8} \end{aligned} \quad (3)$$

where K_1 and K_2 are the equilibrium constants given in Table 2 in Gardner (1970) for the reactions



and



Thus by Equation 1,

$$[\text{H}_4\text{SiO}_4] = 3 \times \Sigma \text{Al} = 3 \times 10^{-6.8} = 10^{-6.32} \quad (6)$$

The solubility product given by Gardner (1970) for kaolinite is

$$K_{sp} \text{ kaolinite} = [\text{Al}^{3+}]^2 [\text{H}_4\text{SiO}_4]^2 [\text{OH}^-]^6 = 10^{-77.3} \quad (7)$$

At the intersection of the gibbsite stability boundary and the congruent dissolution line for K-feldspar at pH 5 the apparent solubility product for kaolinite is given by,

K_{sp} kaolinite apparent

$$= [\text{Al}^{3+}]^2 [\text{H}_4\text{SiO}_4]^2 [\text{OH}^-]^6 = 10^{-80.84} \quad 10^{-77.3} \quad (8)$$

Since at pH 5 the apparent solubility product for kaolinite is much smaller than the actual solubility product this indicates that at pH 5 the congruent dissolution line of K-feldspar intersects the gibbsite stability boundary, as assumed, before reaching the kaolinite stability field. Thus at pH 5 the hydrolysis of K-feldspar is behaving in a manner similar to its behavior at pH 7; that is, gibbsite appears as the initial precipitate and may later dissolve. The results for the above series of calculations at other pH values are summarized in Table 1. From the data of Table 1 it can be seen that below a pH of about 4.3 the apparent solubility product of kaolinite exceeds the actual solubility product. This means that below pH 4.3 the congruent dissolution line of K-feldspar must intersect the kaolinite stability boundary before reaching the stability boundary of gibbsite. Thus we should not expect direct formation of gibbsite below a pH of about 4.3.

Also shown in Table 1 are the calculated apparent solubility products for K-mica and K-feldspar. Based on free energies of formation of -892.817 kcal and -1330.1 kcal for K-feldspar and K-mica (Robie and Waldbaum, 1968) respectively, the actual solubility products are

$$K_{sp} \text{ K-mica} = \frac{[\text{K}^+][\text{Al}^{3+}]^3[\text{H}_4\text{SiO}_4]^3}{[\text{H}^+]^{10}} = 10^{15.2} \quad (9)$$

and

$$K_{sp} \text{ K-feldspar} = \frac{[\text{K}^+][\text{Al}^{3+}][\text{H}_4\text{SiO}_4]^3}{[\text{H}^+]^4} = 10^{0.88} \quad (10)$$

It should be noted in Table 1 that at pH 3 the apparent solubility products of both K-mica and K-feldspar also exceed their actual solubility products. In order to clarify the meaning of these results the apparent solubility products for gibbsite, K-mica, and K-feldspar have been calculated using the procedure employed in Table 1 but with the assumption that the congruent dissolution line for K-feldspar first intersects the kaolinite stability boundary rather than the gibbsite stability boundary. The results of the calculations, shown in Table 2, confirm the gibbsite-kaolinite transition of pH 4.3 arrived at in Table 1. Also, as can be seen from Table 2, the apparent solubility product for K-mica does not exceed its actual solubility product in the pH range 2 to 8. This suggests that K-mica forms as an alteration product only when the soil solution closely approaches final equilibrium with K-feldspar and after precipitation of some kaolinite. The fact that K-mica does not appear as an initial precipitate in this pH range may explain its relatively rare occurrence as a direct alteration product of K-feldspar.

EFFECT OF INITIAL DISSOLVED SILICA

Mineral stability relationships in the K-feldspar system depend upon four independent variables: pH, pK^+ , Σ dissolved silica, and Σ dissolved Al. Thus a four dimensional diagram would be required to show these relationships. Regardless of how one may choose to represent this system, the stability boundaries for quartz, kaolinite, and gibbsite will be independent of pK^+ . Therefore the intersection of the gibbsite and kaolinite stability fields, which occurs at $[\text{H}_4\text{SiO}_4] = 10^{-4.6}$ moles/liter (Figure 3 in Gardner, 1970), will also be independent of pK^+ . Therefore any solution approaching equilibrium with K-feldspar with an initial silica concentration greater than $10^{-4.6}$ moles/liter will not be able to intersect the gibbsite stability boundary without first encountering either the kaolinite, K-mica, or K-feldspar stability boundary. Thus direct gibbsite formation should not be expected at soil depths below which dissolved silica exceeds $10^{-4.6}$ moles/liter. Also the occurrence of authigenic gibbsite in soil that contains quartz or other primary silicates is probably an indication that the kinetics of dissolution of the primary silicates is very slow compared to the kinetics of feldspar dissolution and the rate of soil water drainage.

SUMMARY AND CONCLUSIONS

The results of this theoretical analysis indicate that direct gibbsite formation probably occurs under conditions of high soil permeability and good soil drainage. Also gibbsite formation probably does not occur where the soil pH is less than about 4.3 or where the initial concentration of dissolved silica exceeds $10^{-4.6}$ moles/liter. The analysis further indicates that alteration of K-feldspar to K-mica probably does not occur without antecedant production of kaolinite. In general, the analysis demonstrates that the formation of clay minerals in the zone of weathering involves the complex interplay of parent material, pH, rates of soil drainage, kinetics of dissolution of primary silicates and precipitation of clays, initial composition of the soil solution, and biologic factors. There is probably no simple universal sequence of alteration products in the zone of weathering, the exact sequence of formation and relative proportions of clays in a particular situation being determined by the above factors.

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STABILITY OF BIOTITE: A DISCUSSION

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ABSTRACT

Distribution data for magnesium and iron from a variety of ferro-magnesium silicates and coexisting biotites indicate that the mixing properties of these constituents in biotite and the other silicates do not deviate greatly from the ideal solution (activity coefficients within a factor or two of unity). This result is in conflict with some inferences which have been drawn from experimental data on the phlogopite-annite system. Examination of these experimental data