

An Approach to Estimating Mineral Stability in Salt Affected Soils

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The stability of minerals has generally been estimated on the basis of their nature. GOLDICH [8] proposed a stability sequence opposite the Bowen series, considering that the more the environmental parameters differ from the parameters of formation, the less stable is the mineral. PETTIJOHN [19] set up a stability sequence according to the persistence of minerals under the great variety of environments in the geological past. JACKSON and SHERMAN [12] gave a weathering sequence for clay-size minerals.

The theories mentioned above considered the stability of minerals in the light of their mineralogical nature. However, this stability depends upon environmental factors as well. The liquid phases in the surroundings are taken into account when evaluating the activity diagrams.

The calculations of these diagrams (KITTRICK [15]) are based on the standard free energy of formation (ΔG^0). The free energy value depends on the nature of the bonds in, and the chemical composition of the minerals. Therefore, it is an adequate tool for comparing the stability of minerals. Considering the liquid phase, on the one hand the solution is unsaturated in respect to certain minerals, which are expected to undergo decomposition; thus, a weathering sequence of primary minerals can be estimated for the given environment. On the other hand, the solution is supersaturated with respect to other minerals, which are stable and their neof ormation can be expected.

However, there are many limitations of this approach; when setting up the activity diagrams, equilibrium conditions must be considered. In spite of this, the soil is an open system, which never reaches complete, but only quasi-equilibrium. A quasi-equilibrium with respect to clay minerals can be expected more often, because of their smaller size and greater specific surface area. Kinetics and the rate of reaction should also be taken into consideration because due to their effect metastable phases can also be expected in the soils.

The calculations of the activity diagrams are based on the standard free energy of solid phase formation. There is some controversy about these figures, although recently a comprehensive compilation of the data of different authors (BRINKMAN [1], GARRELS and CHRIST [6], LINDSAY [16], ROBIE and WALDBAUM [22], TARDY and GARRELS [23]) has appeared.

The figures available are generally for ideal crystals, whereas in soils real crystals exist. Some attempts have been made to overcome this

problem by determining these values for the given mineral (KITTRICK [13, 14, 15]).

Concerning the liquid phase, activity values for the ions in soil solutions were not available for a long time. Nowadays, it is possible to calculate them from ionic concentrations or to measure them directly (DARAB, RÉDLY and CSILLAG [4], RÉDLY [21]). Cation activity values in soil extracts are available for some Hungarian soils (DARAB, CSILLAG and PINTÉR [2, 3]). In this respect there are still some limitations concerning the calculations or the direct determination of the activities of Si and Al.

It must also be taken into consideration that the stability of minerals in a given environment is not permanent. The stability of minerals depends — among other factors — upon the pH of the solution (LINDSAY [16]). The moisture content of soils has an influence on the concentration of ions as well as on the pH, which affect the stability (FERNANDEZ-MARCOS et al. [5]).

Table 1

Activities of H^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions and $(H_4SiO_4)^0$ expressed as negative logarithms in saturation extracts of meadow solonetz soils

Soil type, location of profile, symbols of horizons	pH	pNa	pK	pMg	pCa	$p(H_4SiO_4)$
Solonchak-like meadow solonetz soil, Apaj						
A_1	7.40	2.01	3.90	3.35	3.68	3.82
B_1	8.20	1.94	3.78	3.40	3.84	3.85
B_2	8.35	1.93	3.77	3.44	3.82	3.77
BC	8.70	1.89	3.87	3.51	3.82	3.78
C	8.75	1.77	3.79	3.62	3.92	3.97
Solodized meadow solonetz soil, Dévaványa						
A	7.05	2.14	3.91	3.56	3.51	3.30
A_2	7.32	1.60	3.75	3.20	3.44	3.44
B_1	7.32	1.27	3.87	2.73	3.39	3.71
B_2	7.70	1.19	3.74	2.52	3.19	3.71
BC	7.90	1.40	3.63	3.10	3.73	3.90
C	8.25	1.66	3.91	3.48	3.82	4.06
Solodized meadow solonetz soil, Hortobágy						
A	7.60	1.62	3.98	3.66	3.77	3.45
B_1	7.80	1.21	3.90	3.39	3.71	3.52
B_2	7.85	1.44	3.99	3.69	3.67	3.64
BC	8.05	0.89	3.48	3.02	3.49	3.61
C	7.85	1.62	3.08	4.29	3.91	3.58

In activity diagrams two or three variables are taken into account. The third variable is generally the activity of the H^+ ion. Aluminosilicates are common minerals frequently occurring in soils; thus, in some cases the activities of Si and Al are considered (BRINKMAN [1], LINDSAY [16], RAI and LINDSAY [20]). In soils having neutral or alkaline reactions aluminium compounds are fairly immobile components, so in activity diagrams aluminium is often considered as an indifferent common element.

Materials and methods

Meadow solonetz soils were selected for the investigations. Two of the three soil profiles are solodized meadow solonetz from the Trans-Tisza region and one is a solonchak-like meadow solonetz from the Danube valley.

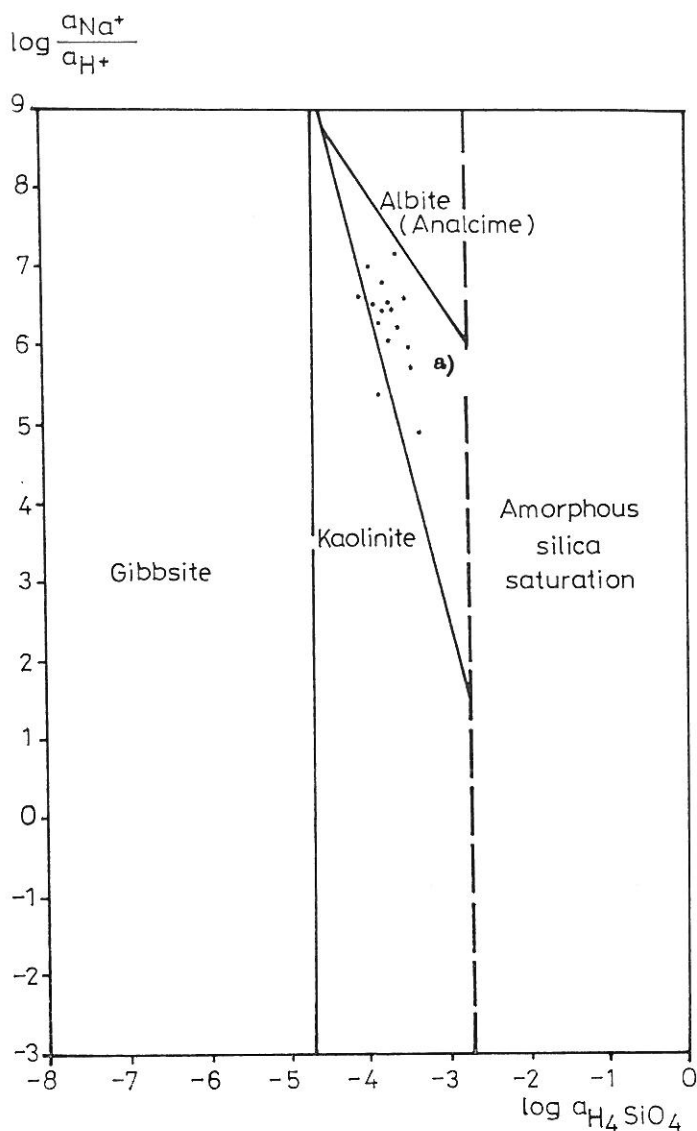


Fig. 1
 Activity diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system (after HELGESON, GARRELS and MACKENZIE [9]). Legend: points indicate the activities in saturation extracts of meadow solonetz soils. a) Na-montmorillonite

The activities of Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions were determined in a saturation extract by ion selective electrodes of the following types: Metronom EA109 for H, Beckman 39278 for Na, Orion 93-19 for K, Orion 93-32 for Ca and Mg and Orion 93-20 for Ca.

I am indebted to DR. M. RÉDLY and the staff members of the Department for Salt Affected Soils for the determination of the activity values.

The silica concentration was colorimetrically determined with ammonium molybdenate according to JACKSON [11]. The activity coefficient of silica was assumed to be unity. The figures are given in Table 1.

Discussion of experimental results

The stability of plagioclases (sodium feldspars) can be evaluated according to the activity diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system after

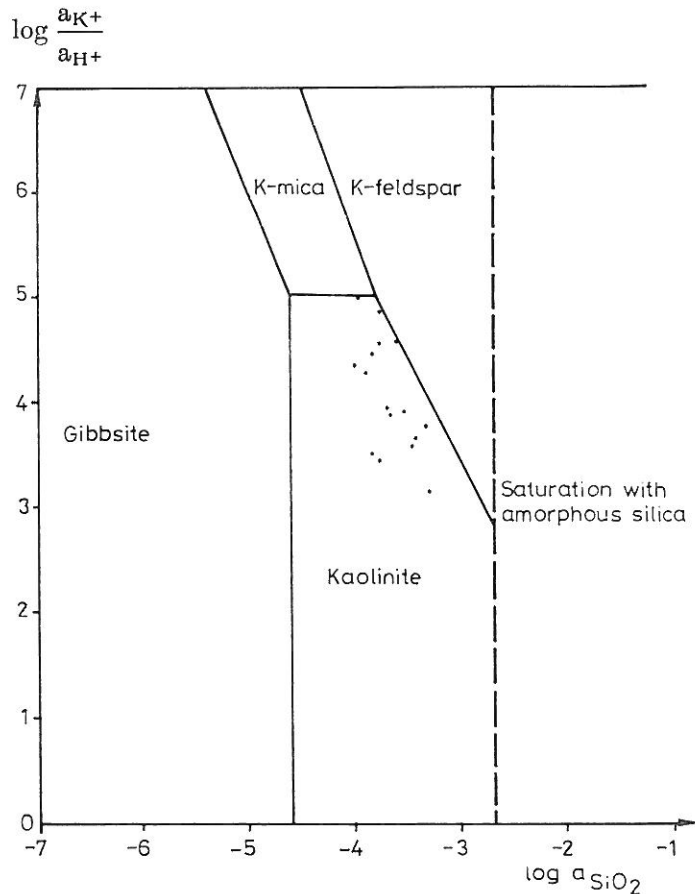


Fig. 2

Equilibrium diagram for some of the phases in the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system (after HELGESON, GARRELS and MACKENZIE [9]). Legend: points indicate the activities in saturation extracts of meadow solonetz soils

HELGESON, GARRELS and MACKENZIE [9]. (All the activity diagrams discussed are calculated for a temperature of 298.15°K (25°C) and a pressure of 1.013 bars (1 atm)). It can be seen in Fig. 1. that the solute activity values are beyond the stability field of albite. The same conclusion can be drawn from the activity diagram calculated by HESS [10] for the $K_2O-Na_2O-Al_2O_3-SiO_2-H_2O$ system.

According to the activity diagram for the $K_2O-Al_2O_3-SiO_2-H_2O$ system given by HELGESON, GARRELS and MACKENZIE [9] and LIPPMANN [17], the solute activities are beyond both K-feldspar and K-mica stability fields (Figs. 2 and 3). In the $K_2O-Na_2O-Al_2O_3-SiO_2-H_2O$ system calculated by HESS [10] the instability of K-mica and K-feldspars can again be concluded

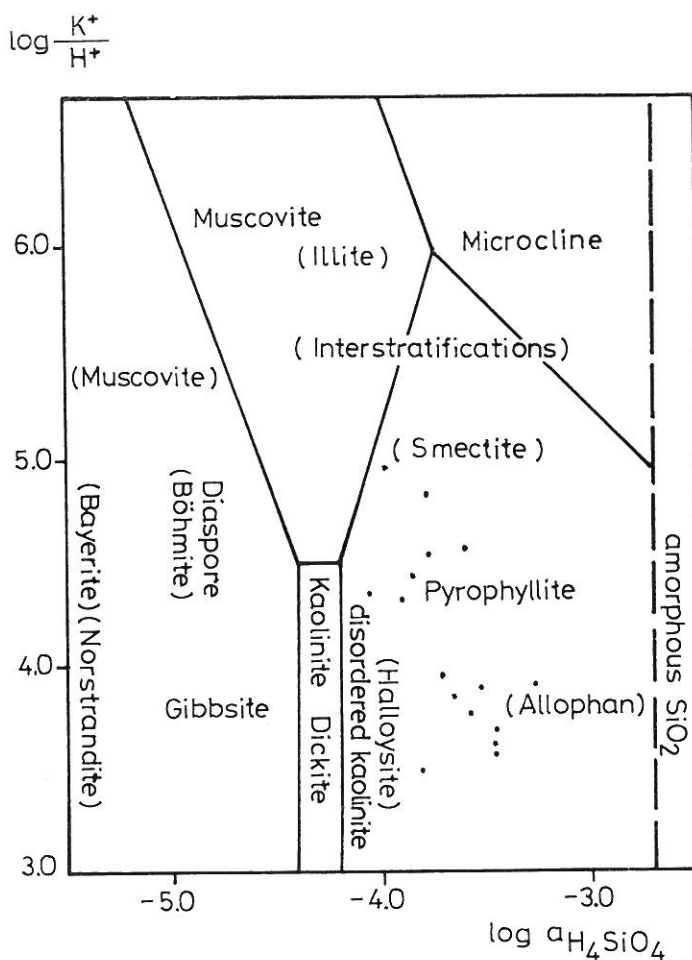


Fig. 3
Stability diagram in the $K_2O-Al_2O_3-SiO_2-H_2O$ system (after LIPPMANN [18]). Legend: parentheses denote metastable phase; points indicate the activities in saturation extracts of meadow solonetz soils

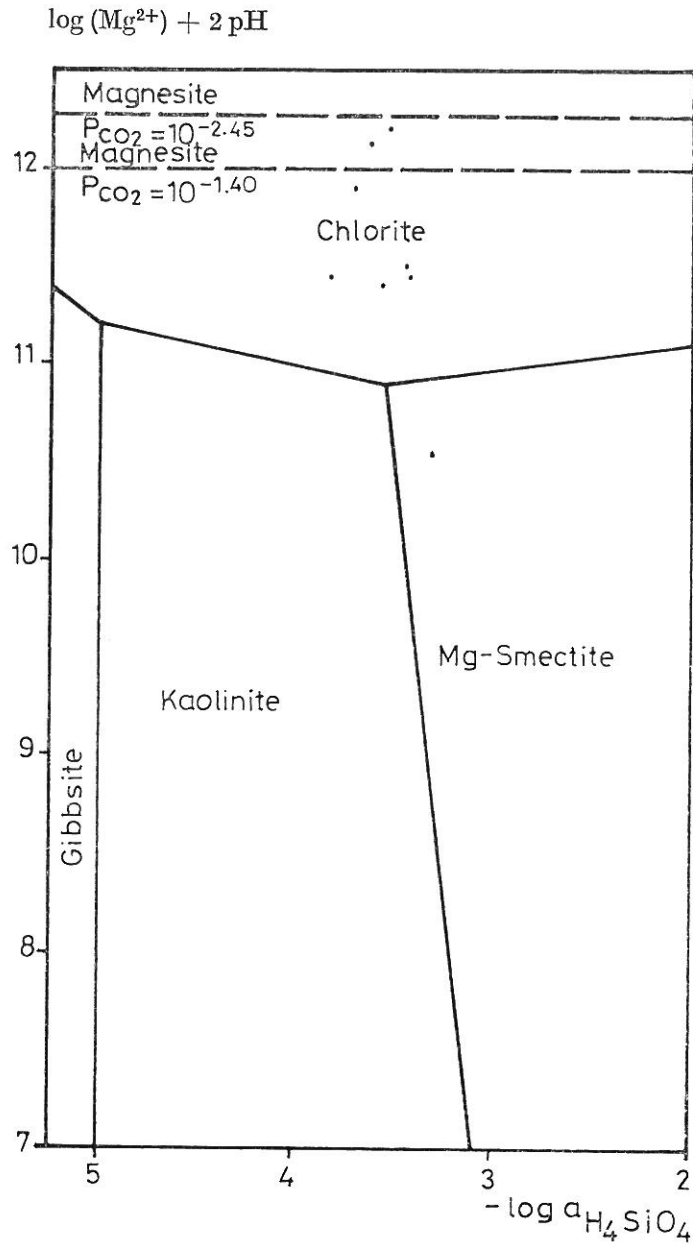


Fig. 4
 Stability diagram of minerals in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2/\text{g}$ system (after VERSTRATEN and SEVINK [24]). Legend: points indicate the activities in saturation extracts of meadow solonetz soils

Summarizing the stability of the common, so-called "primary" minerals, i. e. feldspars and mica, they are not stable in the investigated soils, so weathering is to be expected.

The following question is, which of the secondary minerals is stable in the investigated environment.

Considering the stability of zeolites (sodium-bearing zeolites), according to the activity diagram for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system given by HELGESON, GARRELS and MACKENZIE [9], analcime (zeolites) is unstable in this environment (Fig. 1). HESS [10] also took into consideration the activity of the K^+ ion. Evaluating these diagrams, zeolites (analcite and phillipsite) also appear to be unstable.

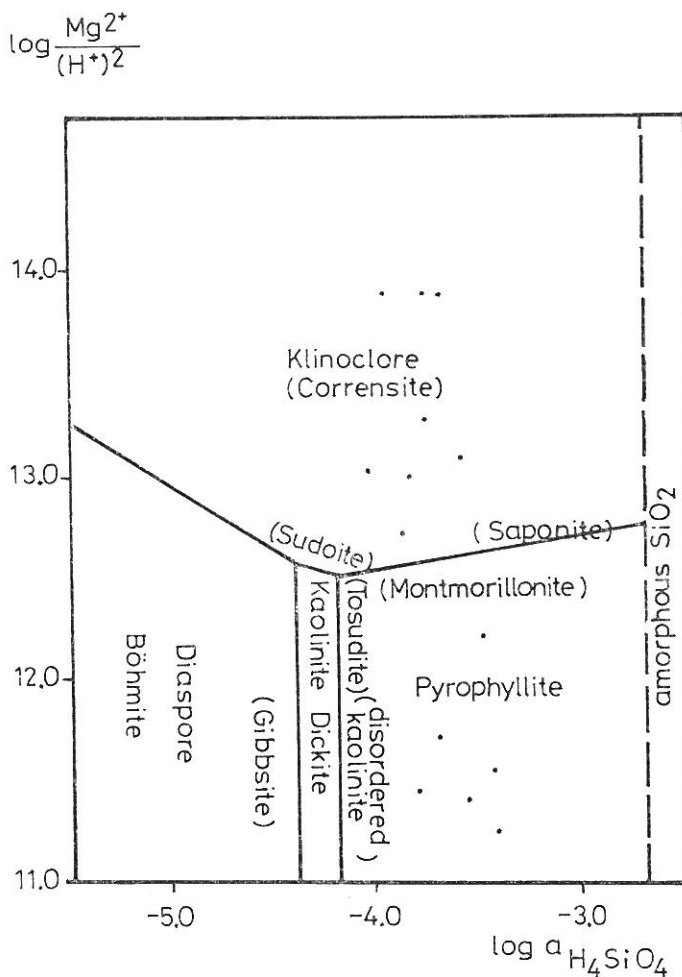


Fig. 5
Stability diagram in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system (after LIPPMANN [18]). Legend: see Fig. 3

The activity diagram given by HELGESON, GARRELS and MACKENZIE [9] for the $K_2O-Al_2O_3-SiO_2-H_2O$ system indicates that of the secondary minerals kaolinite is stable (Fig. 2). The occurrence of metastable phases is taken into consideration in the stability diagram given by LIPPMANN [18]. Evaluating the activity values according to this diagram, pyrophyllite, the alkali ion-free aluminosilicate end-member, is a thermodynamically stable mineral, but it is not common in soils (Fig. 3). The occurrence of these minerals should only be expected on reaching equilibrium. Concerning kaolinite, this mineral occurs in soils more often after long-lasting, intensive weathering. HESS [10] took into consideration the activity of sodium ions in this system as well. Evaluating these diagrams, in the majority of cases kaolinite is a stable mineral.

In the $MgO-Al_2O_3-SiO_2-H_2O$ system the solute activity functions fell into the stability field of Mg-montmorillonite in the activity diagram given by WEAVER, JACKSON and SYERS [25], indicating the stability of Mg-montmorillonite among the secondary minerals. In this diagram the common Mg-bearing minerals, chlorites are not taken into consideration. VERSTRATEN and SEVINK [24] took the chlorites into consideration, too, when calculating the activity diagram for the $MgO-Al_2O_3-SiO_2-H_2O-CO_2$ system. The majority of solute activity points fell into the stability field of chlorite. At lower magnesium activity (solodized meadow solonetz soil, Dévaványa, A horizon) chlorite also seems to be unstable (Fig. 4). Some of the solute activity points fell into the stability field of Mg-smectite, indicating the stability of these minerals at lower Mg^{2+} and H^+ ion activities.

LIPPMANN [18] also took into consideration the possibility of the occurrence of metastable phases. Evaluating the stability of secondary minerals in this system (Fig. 5), at higher Mg^{2+} and H^+ ion activities the chlorite minerals are stable, while at lower values pyrophyllite is the thermodynamically stable mineral. Montmorillonite can also be expected, as a metastable phase.

Summarizing the stabilities of secondary minerals, in the $Na_2O-Al_2O_3-SiO_2-H_2O$ system kaolinite and montmorillonite (but not analcime), in the $K_2O-Al_2O_3-SiO_2-H_2O$ system alkali-free aluminosilicate minerals (kaolinite and pyrophyllite) and in the $MgO-Al_2O_3-SiO_2-H_2O$ system chlorite and pyrophyllite are the stable minerals. In the latter system montmorillonite can occur as a metastable phase. Illite is considered in this approach as a metastable mineral in the stability field of K-mica. For the $Na_2O-K_2O-MgO-Al_2O_3-SiO_2-H_2O$ system, which is more complex and closer to the composition of the soil solution, activity diagrams are still not available.

The estimation of the stability of minerals on the basis of activity diagrams has many limitations, as was discussed in the introduction, but it may be considered as one of the possible approaches to estimating trends in the processes of mineral destruction, transformation and neof ormation in soils.

Summary

The processes of mineral destruction, transformation and formation contribute to the processes of soil formation.

There are different ways of studying the weathering and formation of minerals in soils, e.g. the evaluation of the mineral distribution in the sequence of horizons or in particle size fractions, the direct determination of intermediate products, etc.

The interpretation of mineral stability in soils is also an approach to estimating the trends of these processes.

There are different ways of estimating mineral stability, e.g. weathering sequences based on their frequency in different rocks and soils, on their persistence, their occurrence in rocks of various geological ages, etc.

One of these approaches is the interpretation of mineral stability diagrams in soils. Nevertheless, the application of stability diagrams has many limitations which must be taken into consideration.

The stability diagrams are applied to estimate mineral stability in some typical alkali soils of Hungary. Conclusions are drawn on the trends of mineral weathering and formation processes.

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Discussion

SINGH, N. T.

Pyrophyllite is not likely to be present in natural conditions. Why not omit its mention?

SZENDREI, G.

The mentioned stability diagrams of LIPPMANN are calculated for the end-members of the series. While evaluating the stability diagram it is taken into account that pyrophyllite does not occur in soils. Probably an alkali free phyllosilicate is the stable mineral in the given environment.

DARAB, K.

The kaolinite is the end-product of a weathering sequence. The presence of kaolinite depends on the age of the soil and on the intensity of weathering. The compound of the metastable phase may occur in soils for several hundred years.