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RELATIVE STABILITIES OF SOIL MINERALS

(with a summary in English)

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INTRODUCTION

The stability of soil minerals is frequently considered in the geochemical literature (WILDMAN et al., 1971; KITTRICK, 1971a, 1971b; RAI and LINDSAY, 1975; CURTIS, 1976; WEAVER et al., 1976; REESMAN, 1978). In most cases the possible composition of the aqueous solution coexisting with a certain mineral is discussed in detail, the composition being given in terms of activities of the relevant species in solution.

The Gibbs free-energy change of such a reversible dissolution equilibrium is zero if an infinitely small amount of the mineral dissolves ($(\Delta G)_R = 0$). Therefore, the mineral is only stable if for any other possible mineral made of components present in the system $(\Delta G)_R \leqslant 0$.

It is quite understandable that the second part of this statement is rather difficult to investigate.

The present paper will consider the importance of this aspect.

The Gibbs free-energy of formation of a mineral from its components in a well-defined system, e.g., an actual aqueous solution at 25 °C and 1 bar, is indicated by ΔG°_{rel} in this text.

ΔG°_{rel} can be used to quantitatively describe the relative stability of a mineral. In doing so, three aspects have to be considered:

1. The proper choice of molecular formula units enabling a comparison of ΔG°_{rel}-values of minerals.
2. A proper reference system must be defined.
3. The chemical potentials of the relevant components have to be defined.

For example, BROWN and SKINNER (1974) calculated stabilities per cation accounting for the first aspect.

HUANG and KELLER (1972) suggested that the ideal muscovite $KAl_2AlSi_3O_{10}(OH)_2$, $\Delta G^\circ_f = -1313.8$ kcal/mol[1] is less stable than a non-ideal muscovite $K_{.84}Ca_{.08}Mg_{.06}Na_{.01}Fe^{II}_{.23}Al_{2.32}Si_{3.14}Al_{.86}O_{10}(OH)_2$, $\Delta G^\circ_f = -1399.9$ kcal/mol.

The ΔG°_f-values, however, have been calculated from equilibrium with the same solution. This means per definition that $\Delta G^\circ_{rel} = 0$ for both minerals, i.e., both minerals are equally stable in relation to the reference system (cf. aspect 2). The differences in the values of the Gibbs free-energy of formation from the elements does not imply that both minerals have different stabilities in the soil system.

WILDMAN et al. (1971) accounted explicitly for the third aspect in concluding

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[1] 1 cal = 4.184 J

that Fe-rich montmorillonite is more stable than saponite in soils on serpentinites under certain conditions.

Reesman (1978) accounted for the second and third aspect by specifying five illite-equilibrated aqueous solutions, he did not observe the first aspect.

METHOD

The following notation, illustrated with wollastonite, is preferred because it clearly shows the relation between the mineral and the reference system

$$CaSiO_3 \rightarrow H_4SiO_4 + Ca^{2+} - 2H^+ - H_2O \qquad (1)$$

Furthermore, there is no reason to limit the choice of the reference system to (dilute) aqueous solutions. The actual soil system may well be rather dry or periodically wet.

Therefore, the use of chemical potentials of the oxide components is used instead of activities in solution (cf. Brown and Skinner, 1974).

This leads to

$$CaSiO_3 \rightarrow CaO + SiO_2 \qquad (2)$$

The relation at 25 °C and 1 bar between the oxide-potentials and the activities of the solved species follows from the hypothetical dissolution equilibria (c.f. Helgeson, 1968, eq. (7))

$$CaO + 2H^+ \Leftrightarrow Ca^{2+} + H_2O \qquad (3)$$

$$SiO_2 + 2H_2O \Leftrightarrow H_4SiO_4 \qquad (4)$$

as:

$$\Delta G_f(CaO) = \{\Delta G_f^\circ(Ca^{2+})_{aq} - 2\Delta G_f^\circ(H^+)_{aq} + \Delta G_f^\circ(H_2O)_L\} + (5.708\ kJ/mol) \cdot \{\log a_{Ca^{2+}} + 2pH + \log a_{H_2O}\} \qquad (5)$$

$$\Delta G_f(SiO_2) = \{\Delta G_f^\circ(H_4SiO_4)_{aq} - 2\Delta G_f^\circ(H_2O)_L\} + (5.708\ kJ/mol) \cdot \{\log a_{H_4SiO_4} - 2\log a_{H_2O}\} \qquad (6)$$

It follows from (5) and (6) that the chemical potentials of CaO and SiO_2 are a linear function of ($\log a_{Ca^{2+}} + 2pH$) and ($\log a_{H_4SiO_4}$) only if $a_{H_2O} \approx 1$.

A quantitative measure of mineral stability in a soil requires:

1. A proper choice of the formula unit
2. A definition of 'the chemical potentials of the oxides in a soil environment'.

A proper formula unit is easily chosen. The convention according to which the chemical composition of minerals is expressed in terms of one cation per formula unit meets all the requirements, cf. Niggli (1936), Van der Plas and Van Schuylenborgh (1970), Brown and Skinner (1974). H_2O and CO_2 are not included in the total number of cations because they are exchangeable with atmospheric H_2O and CO_2. The chemical potentials of these components are therefore externally determined and not by the soil system.

As to the second aspect, we must consider the question whether a Gibbs free-energy level can be found for a soil system as a function of chemical composition. More precisily, can chemical potentials be attributed to every oxide in such a way that for typical soil minerals $\Delta G^{\circ}_{rel} \approx 0$?
Mathematically this means that the Gibbs free-energy of formation of a typical soil mineral can be calculated by linear summation of the chemical potentials of the constituent oxides. Such a linear combination can be envisaged as a 'Gibbs-plane' (BROWN and SKINNER, 1974).

TARDY and GARRELS (1974) developed a comparable approach for the estimation of Gibbs free-energies of formation of certain clay minerals. This approach has been extended to other types of silicates (TARDY and GARRELS, 1977) and has been refined by NRIAGU (1975) and MATTIGOD and SPOSITO (1978).

Surveying the sets of minerals for which estimation methods have been developed by the authors just mentioned, it is clear that other important groups of minerals have also to be considered in the soil system. A description of the minerals present in the Goethite-facies (VAN DER PLAS and VAN SCHUYLENBORGH, 1970) lists the following groups:
oxides, hydroxides, phosphates, carbonates, hydrocarbonates, halides, sulfides, sulphates, the silicates belonging to the groups of smectites, hydrous micas, kandites, allophane, and the silica minerals quartz, low tridymite, low cristobalite.

If we take a set of minerals consisting of members of these groups it follows after some calculation that the minerals of the set show a spread of only a few kJ/mol per ion[2] from an average Gibbs free-energy level.

For the selection of the minerals of the set (see table 1) the following observations have been used:

1. A survey of the Gibbs free-energies of formation of the rock- and soil-forming minerals shows a large amount of normalized values near to a specific low Gibbs free-energy level.
2. Only a small amount of minerals have normalized values significantly lower than this level, for example dolomite.
3. A number of minerals not belonging to the soil environment have normalized values of a significantly higher level.
4. For the determination of a reference system minerals of group 1 were used for which the data are inserted in the recent data collection of ROBIE et al. (1978) as much as possible.
5. The selected minerals were used in a least-squares fitting procedure to develop mathematically a reference Gibbs-plane.

Table 2 contains the fitted oxide-potentials.

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[2] Cations and Cl^- are included in the number of ions N_{ions}.

TABLE 1. Gibbs free-energies of formation of selected minerals and their deviations per ion from least-squares fitted values, at 298.15 K and 1 bar.

Mineral	N^{1}_{ions}	Formula	$\frac{\Delta G^{o}_{f}}{\text{kJ/mol}}$	Ref[2]	$\frac{\Delta G^{o}_{\text{min}}}{\text{kJ/mol}}$
Alunite	6	$KAl_3(OH)_6(SO_4)_2$	− 4656.58	1	+1.8
Analbite	5	$NaAlSi_3O_8$	− 3706.507	2	+1.0
Analcime	4	$NaAlSi_2O_6 \cdot H_2O$	− 3091.730	2	−1.1
Anhydrite	2	$CaSO_4$	− 1321.696	2	+2.0
Arcanite	3	K_2SO_4	− 1319.7	3	−0.8
Bischofite	3	$MgCl_2 \cdot 6H_2O$	− 2114.8	3	+3.6
Bloedite	5	$Na_2Mg(SO_4)_2 \cdot 4H_2O$	− 3430.1	3	−0.8
Boehmite	1	$AlO(OH)$	− 918.400	2	−0.8
Calcite	1	$CaCO_3$	− 1128.842	2	−0.4
Chrysotile	5	$Mg_3Si_2O_5(OH)_4$	− 4034.024	2	+1.7
Epsomite	2	$MgSO_4 \cdot 7H_2O$	− 2871.240	2	−1.2
Fayalite	3	Fe_2SiO_4	− 1379.375	2	+0.8
Gaylussite	3	$Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$	− 3372.7	3	+0.6
Gibbsite	1	$Al(OH)_3$	− 1154.889	2	−1.5
Glauberite	5	$Na_2Ca(SO_4)_2$	− 2596.590	4	−1.3
Goethite	1	$FeO(OH)$	− 488.550	2	+1.2
Gypsum	2	$CaSO_4 \cdot 2H_2O$	− 1797.197	2	0.0
Halite	2	$NaCl$	− 384.212	2	−2.9
Hematite	2	Fe_2O_3	− 742.683	2	+0.6
Hercynite	3	$FeAl_2O_4$	− 1850.795	2	+3.2
Huntite	4	$CaMg_3(CO_3)_4$	− 4203.425	2	−2.8
Hydromagnesite	5	$5MgO \cdot 4CO_2 \cdot 5H_2O$	− 5864.166	2	+3.3
Hydromagnesite	4	$Mg_4(CO_3)_3(OH)_2 \cdot 3H_2O$	− 4633.7	3	−2.5
Hydroxyapatite	8	$Ca_5(PO_4)_3(OH)$	− 6338.434	2	−1.0
Kaliophillite	3	$KAlSiO_4$	− 2005.975	2	+3.9
Kaolinite	4	$Al_2Si_2O_5(OH)_4$	− 3799.364	2	−2.0
Leonhardite	14	$Ca_2Al_4Si_8O_{24} \cdot 7H_2O$	−13197.115	2	−1.3
Leucite	4	$KAlSi_2O_6$	− 2875.890	2	+0.5
Low-albite	5	$NaAlSi_3O_8$	− 3711.722	2	0.0
Magnetite	3	Fe_3O_4	− 1012.566	2	−2.7
Melanterite	2	$FeSO_4 \cdot 7H_2O$	− 2509.641	2	+1.5
Microcline	5	$KAlSi_3O_8$	− 3742.330	2	−0.9
Nahcolite	1	$NaHCO_3$	− 851.86	5	+1.9
Natron	2	$Na_2CO_3 \cdot 10H_2O$	− 3428.98	5	−2.0
Pirssonite	3	$Na_2CO_3 \cdot CaCO_3 \cdot 2H_2O$	− 2661.8	3	+1.8
Pyrophyllite	6	$Al_2Si_4O_{10}(OH)_2$	− 5269.384	2	+1.1
Rutile	1	TiO_2	− 889.446	2	—
Sanidine	5	$KAlSi_3O_8$	− 3739.776	2	−0.4
Siderite	1	$FeCO_3$	− 666.698	2	−1.5
Sylvite	2	KCl	− 408.554	2	−1.9
Talc	7	$Mg_3Si_4O_{10}(OH)_2$	− 5536.048	2	−1.3
Thenardite	3	Na_2SO_4	− 1269.985	2	−1.8
Tremolite	15	$Ca_2Mg_5(Si_8O_{22})(OH)_2$	−11627.910	2	+1.4
Trona	3	$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	− 2386.55	5	+2.0
Whitlockite	5	$Ca_3(PO_4)_2$	− 3895.654	2	+0.9

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[1] See page 3.

[2] 1: VAN BREEMEN (1972); 2: ROBIE et al. (1978); 3: DROUBI (1976); 4: KARPOV et al. (1968); 5: GARRELS and CHRIST (1965).

TABLE 2. Fitted chemical potentials of the oxides and other components at 25°C and 1 bar, using the set of minerals of table 1 (ΔG_f^{fit} per ion).

Component		ΔG_f^{fit}
ion	formula-unit	kJ/mol
Si^{4+}	SiO_2	−860.161
Al^{3+}	$AlO_{1.5}$	−799.731
Fe^{3+}	$FeO_{1.5}$	−371.897
Fe^{2+}	FeO	−260.777
Mg^{2+}	MgO	−616.804
Ca^{2+}	CaO	−724.016
Na^{+}	$NaO_{0.5}$	−331.429
K^{+}	$KO_{0.5}$	−357.788
Ti^{4+}	TiO_2	−889.446
P^{5+}	$PO_{2.5}$	−864.154
S^{6+}	SO_3	−601.617
Cl^{-}	HCl	−164.922
–	CO_2	−404.461
–	H_2O	−235.762

TABLE 3. ΔG^o_{min}-values per ion of some minerals at 25°C and 1 bar.

Mineral	N_{ions}	Formula	ΔG_f^o kJ/mol	Ref.[1]	ΔG^o_{min} kJ/mol
Andalusite	3	Al_2SiO_5	−2439.892	1	+6.6
Bayerite	1	$Al(OH)_3$	−1153.00	2	+0.4
Burkeite	8	$Na_6CO_3(SO_4)_2$	−3594.2	3	+0.3
Diaspore	1	$AlO(OH)$	− 921.986	1	−4.4
Diopside	4	$CaMg(SiO_3)_2$	−3036.554	1	+6.2
Dolomite	2	$CaMg(CO_3)_2$	−2161.672	1	−6.0
Ferrohydroxide	1	$Fe(OH)_2$	− 493.043	4	+3.5
Ferrosilite	2	$FeSiO_3$	−1123.195	5	−1.1
Illite, Fithian	6.77	see reference	−5521.6	6	−4.4
Illite, Grundite	6.74		−5534.2	6	−3.5
Illite, Rock Island	6.68		−5469.7	6	−2.3
Illite, Marblehead	6.77		−5484.4	6	−2.1
Kyanite	3	Al_2SiO_5	−4241.276	1	+6.1
Muscovite	7	$KAl_3Si_3O_{10}(OH)_2$	−5600.671	1	−3.9
Nepheline	3	$NaAlSiO_4$	−1977.498	1	+4.6
Palygorskite	5.97	$Si_{4.00}Al_{0.96}Mg_{0.91}Fe_{0.10}O_{10.5}$	−4785.2	7	+3.6
Paragonite	7	$NaAl_2Si_3AlO_{10}(OH)_2$	−5558.86	8	−1.7
Quartz	1	SiO_2	− 856.288	1	+3.9
Sepiolite	5	$2MgO \cdot 3SiO_2 \cdot 3.5H_2O$	−4625.8	9	+2.7
Serpentine	5	$Mg_3Si_2O_5(OH)_4$	−4044.88	5	−0.5
Sphene	3	$CaTiSiO_5$	−2459.855	1	+4.6
(Ca)-vermiculite	6.35	$Ca_{0.35}Si_{3.30}Al_{2.70}O_{10}(OH)_2$	−5454.68	10	+5.1
Water	–	H_2O	− 237.141	1	−1.4

[1] 1: Robie et al. (1978); 2: Hemingway et al. (1978); 3: Vergouwen (1979); 4: Naumov et al. (1971); 5: Karpov and Kashik (1968); 6: Reesman (1974); 7: Singer (1977); 8: Mattigod and Sposito (1978); 9: Christ et al. (1973); 10: Henderson et al. (1976).

Analogous to ΔG°_f and ΔG°_{ox}, where the reference system consists of the elements and the oxides respectively, ΔG°_{min} is specified as the particular ΔG°_{rel} for which the reference system is the set of minerals given in table 1.

The relative position of a number of interesting minerals in relation to the reference Gibbs-plane, is shown in table 3.

From tables 1 and 3 it follows that minerals belonging to the soil environment typically show a distance from the reference Gibbs-plane less than 4 kJ/mol per ion. This means that the ΔG°_{min}-values are situated in a Gibbs-slice with a width smaller than 8 kJ/mol per ion.

A discussion about the relative stabilities of minerals within this range is hardly significant because the typical absolute inaccuracy of experimental values of, for instance, clay minerals, is in the order of 1 kJ/mol per ion. In comparison with the width of the Gibbs-slice this value is too large for a reliable prediction of reactions between the minerals in the complex soil system. It is felt that the small Gibbs free-energy differences that govern the actual processes are too small to measure accurately enough. A comparable observation was made by Fyfe et al. (1958). In addition, the chemical composition and the structure of the clay minerals of a soil sample cover a wide range.

Differences of ΔG°_{min} *exceeding* 4 kJ/mol per ion may be used for quanti-

Table 4. ΔG°_{min}-values per ion of some smectites at 25°C and 1 bar, using data from Mattigod and Sposit

	Mineral	Formula
1.	Aberdeen	$Mg_{0.2075}(Al_{0.18}Si_{3.82})\,(Al_{1.29}Fe^{3+}_{0.335}Mg_{0.445})O_{10}(OH)_2$
2.	Aberdeen	$Al_{0.1383}(Al_{0.18}Si_{3.82})\,(Al_{1.29}Fe^{3+}_{0.335}Mg_{0.445})O_{10}(OH)_2$
3.	Belle Fourche	$Mg_{0.1325}(Al_{0.065}Si_{3.935})\,(Al_{1.515}Fe^{3+}_{0.225}Mg_{0.29})O_{10}(OH)_2$
4.	Belle Fourche	$Al_{0.0883}(Al_{0.065}Si_{3.935})\,(Al_{1.515}Fe^{3+}_{0.225}Mg_{0.29})O_{10}(OH)_2$
5.	Smectite from Houston Black Clay	$Mg_{0.225}(Al_{0.30}Si_{3.70})\,(Al_{1.345}Fe^{3+}_{0.405}Mg_{0.27})O_{10}(OH)_2$
6.	Beidellite (Mg-sat)	$Mg_{0.135}Ca_{0.01}Na_{0.07}K_{0.095}(Al_{0.45}Si_{3.55})$ $(Al_{1.41}Fe^{3+}_{0.415}Fe^{2+}_{0.055}Mg_{0.205})O_{10}(OH)_2$
7.	Beidellite (K-sat)	$K_{0.37}Ca_{0.01}Na_{0.07}(Al_{0.45}Si_{3.55})$ $(Al_{1.41}Fe^{3+}_{0.415}Fe^{2+}_{0.055}Mg_{0.205})O_{10}(OH)_2$
8.	Colony	$Mg_{0.195}(Al_{0.19}Si_{3.81})\,(Al_{1.52}Fe^{3+}_{0.22}Mg_{0.29})O_{10}(OH)_2$
9.	Colony I	$Mg_{0.185}(Al_{0.19}Si_{3.80})\,(Al_{1.58}Fe^{3+}_{0.19}Mg_{0.26})O_{10}(OH)_2$
10.	Colony II	$Mg_{0.21}(Al_{0.19}Si_{3.81})\,(Al_{1.52}Fe^{3+}_{0.21}Mg_{0.29})O_{10}(OH)_2$
11.	Castle Rock	$Mg_{0.21}(Al_{0.32}Si_{3.68})\,(Al_{1.52}Fe^{3+}_{0.14}Mg_{0.46})O_{10}(OH)_2$
12.	Upton	$Mg_{0.17}(Al_{0.07}Si_{3.93})\,(Al_{1.55}Fe^{3+}_{0.20}Mg_{0.24})O_{10}(OH)_2$
13.	Clay Spur (Na-sat)	$Na_{0.27}Ca_{0.1}K_{0.02}(Al_{0.06}Si_{3.94})\,(Al_{1.52}Fe^{3+}_{0.19}Mg_{0.22})O_{10}(OH)_2$
14.	Cheto (Ca-sat)	$Ca_{0.185}Na_{0.02}K_{0.02}(Al_{0.07}Si_{3.93})\,(Al_{1.52}Fe^{3+}_{0.14}Mg_{0.33})O_{10}(OH)_2$

[1] See table 7 of Mattigod and Sposito (1978).

[2] Estimated value has been corrected for charge deficiency in the molecular formula given (see text).

tatively estimating the stability of minerals with respect to the soil environment. Thus a mineral in the soil environment is assumed to be stable if $\Delta G^\circ_{min} \leqslant +4$ kJ/mol per cation.

APPLICATIONS

a. *Estimation of ΔG°_f of soil minerals*

It is possible to estimate the ΔG°_f-values of soil minerals not mentioned in table 1 on the basis of their chemical composition by a summation of the oxide contributions of table 2, assuming that these minerals are also situated in the Gibbs-slice discussed before. Examples are given in table 4.

In a survey of estimation methods for phyllosilicates MATTIGOD and SPOSITO (1978) mention the 'calibration' of the contributions of the components (hydroxides). They state that such a calibration 'contains a critical, ad hoc assumption that is difficult to justify on geochemical grounds'.

Their objection may hold for a descriptive structural model, it does not apply to phenomenological Gibbs-energy relations. The mathematical approach of this paper is not based on any structural consideration. It just fits oxide contributions to the Gibbs-energies of forty-five soil minerals belonging to various mineral groups.

Estimated value of $\frac{\Delta G^\circ_f}{kJ/mol}$ following					Experimental value[1]	
RDY and ARRELS 974)[1]	NRIAGU (1975)[1]	MATTIGOD and SPOSITO (1978, eq (9))[1]	MATTIGOD and SPOSITO (1978, eq (8))[1]	Present method	$\frac{\Delta G^\circ_f}{kJ/mol}$	$\frac{\Delta G^\circ_{min}}{kJ/mol}$
5220.6	−5173.0	−5254.1	−5211.6	−5224.5	−5218.7	+0.9
5193.3	−5159.7	−5224.2	−5182.8	−5206.6	−5200.0	+1.1
5223.6	−5184.6	−5248.6	−5209.4	−5228.7	−5222.8	+1.0
5206.2	−5175.3	−5229.7	−5188.5	−5217.0	−5213.4	+0.6
5209.4	−5158.8	−5261.5	−5208.5	−5210.9[2]	−5214.7	−0.6
5220.2	−5180.5	−5212.6	−5185.0	−5219.7	−5200.1	+3.1
5238.4	−5211.8	−5222.1	−5205.7	−5234.8	−5215.4	+3.0
5258.3	−5217.2	−5293.0	−5253.3	−5261.5	−5262.4	−0.2
5261.4	−5219.0	−5295.1	−5253.1	−5275.5[2]	−5267.6	+1.3
5264.6	−5222.7	−5349.9	−5261.9	−5267.0	−5262.1	+0.8
5329.8	−5293.8	−5364.7	−5333.0	−5338.0	−5336.8	+0.2
5236.9	−5195.6	−5267.6	−5226.8	−5239.0	−5218.0	+3.4
5268.4	−5227.4	−5266.3	−5242.1	−5263.8	−5226.4	+5.9
5287.5	−5227.2	−5307.7	−5262.7	−5298.1[2]	−5245.3	+8.5

Results of the present estimation method are given in table 4. This table, a combination of table 7 from Mattigod and Sposito (1978) and our calculations, shows that the values obtained are comparable with those obtained by all other methods. Only the calculated values of numbers 13 and 14 deviate considerably from the reported experimental values.

The 5th, 9th and 14th smectite in table 4 have a charge deficiency of 0.06, 0.03 and 0.02 respectively. This deficiency has been corrected before applying the calculation method under discussion. The correction is -350 kJ/mol per charge. This value is the mean of the oxide contributions corresponding with Ca^{2+}, Na^+ and K^+. The calculations show that a charge deficiency of more than 0.002 influences the ΔG^o_{min}-value by more than 0.1 kJ/mol per cation.

The absolute ΔG^o_{min}-values of the last column of table 4 are generally lower than 4 kJ/mol per ion, indicating that the smectites of table 4 belong to the group of soil minerals present in the Gibbs-slice.

Another example of the usefulness of this calculation method is given in table 5. Chen (1975) explored the ΔG^o_{rel}-limits of certain silicate minerals from different reference systems. A number of the reactions selected by Chen occur inside the Gibbs-slice of this paper. His procedure could imply a refinement of the positions of the minerals from the reference Gibbs-plane. The inaccuracy of

Table 5. Comparison of ΔG^o_{min}-values of some minerals at 25 °C and 1 bar with deviations per ion from Chen's[1] estimated values.

Mineral	N_{ions}	Formula	Deviation per ion of literature value from estimation	
			Chen's est.[1,2] (kJ/mol)	ΔG^o_{min} kJ/mol
Jadeite	4	$NaAl(SiO_3)_2$	+0.19	+ 0.2
Low Albite	5	$NaAlSi_3O_8$	−0.97	0.0
Analcime	4	$NaAlSi_2O_6 \cdot H_2O$	+0.64	− 1.1
Leucite	4	$KAlSi_2O_6$	+6.85	+ 0.5
Microcline	5	$KAlSi_3O_8$	+0.86	− 0.9
Muscovite	7	$KAl_3Si_3O_{10}(OH)_2$	+0.24	− 3.9
Ca-Al Pyroxene	4	$CaAl_2SiO_6$	+4.84	+18.8[3]
Anorthite	5	$CaAl_2Si_2O_8$	−1.03	+ 5.3
Grossular	8	$Ca_3Al_2Si_3O_{12}$	−0.20	+ 7.1
Akermanite	5	$Ca_2MgSi_2O_7$	+0.47	+21.2[3]
Merwinite	6	$Ca_3Mg(SiO_4)_2$	−1.38	+28.3[3]
Tremolite	15	$Ca_2Mg_5Si_8O_{22}(OH)_2$	−4.36	+ 1.4
Chrysotile	5	$Mg_3Si_2O_5(OH)_4$	+0.26	+ 1.7
Kaolinite	4	$Al_2Si_2O_5(OH)_4$	−3.13	− 2.0
Halloysite	4	$Al_2Si_2O_5(OH)_4$	+1.53	+ 2.7
Pyrophyllite	12	$Al_4Si_8O_{20}(OH)_4$	–	+ 1.1

[1] Chen (1975); [2] for ΔG^o_f-value of Robie and Waldbaum (1968) in most cases; [3] These are members of groups of minerals that evidently lie above the Gibbs-plane (see text).

the experimental values and the reported inaccuracy of CHEN's method cause results that are as good as the simple linear approach in this paper (see table 5). CHEN's method, however, has the merit of being applicable also to minerals that do not belong to the soil system, such as åkermanite, merwinite and Ca-Al pyroxene.

b. *Relative stabilities* ΔG^{o}_{min} *of soil minerals*

An example of using ΔG^{o}_{min}-values as a measure of the stabilities of minerals in soils is given in table 6. We calculated the ΔG^{o}_{min}-values of both the specific and the ideal minerals from the data of HUANG and KELLER (1972). Comparison of the differences between ΔG^{o}_{min}- and ΔG^{o}_{f}-values of the ideal and the specific minerals respectively, shows the same trend in both columns of table 6. This conclusion is not entirely trivial, because one may also choose a reference system for which the ΔG^{o}_{rel}-values are zero for all minerals concerned, namely the authors' experimental solutions.

The case of the muscovite in table 6 needs some discussion.

The ΔG^{o}_{min}-value of the specific muscovite calculated with the reported chemical formula gave an impossibly low result. Checking the charge deficiency and the stoichiometry of the dissolution reaction showed an oxygen imbalance. After correction in the same way as reported in section a, both results are much higher than literature values and not in accordance with the fact that muscovite belongs to the minerals of the soil environment.

TABLE 6. Comparison of ΔG^{o}_{min}-differences with ΔG^{o}_{f}-differences per ion for specific and ideal minerals, using the experimental data of HUANG and KELLER[1].

Minerals[1]		$\Delta G^{o}_{f\,exp}$ kJ/mol	N_{ions}	normalized per ion	
				ΔG^{o}_{f} kJ/mol	ΔG^{o}_{min} kJ/mol
Olivine	specific	−1931.3	2.89	−668.3	+ 9.9
	ideal	−1915.4	3	−638.5	+12.0
Augite	specific	−2842.6	3.85	−738.3	+13.3
	ideal	–	–	–	–
Labradorite	specific	−3901.2	5	−780.2	− 1.7
	ideal	−3895.7	5	−779.1	+ 3.0
Microcline	specific	−3712.5	4.91[2]	−756.1	+ 1.3
	ideal	−3734.6	5	−746.9	+ 0.7
Muscovite	specific	(−5857.2)[3]	–[3]	–[3]	+10.8
	ideal	−5517.9	7	−788.3	+ 7.9

[1] For complete data, see HUANG and KELLER (1972).

[2] Number of 2.86 Si-atoms misprinted as 2.68 in the reported formula.

[3] See text.

TABLE 7. Relative stabilities of the minerals for which CURTIS (1976) calculated the standard Gibbs free-energy changes of weathering.

Mineral	normalized per atom	N_{ions}	Formula	ΔG°_f [2]	normalized per ion	
	$(G^\circ)_R$ [1] kcal/mol			kJ/mol	ΔG°_{rel} kJ/mol	ΔG°_{min} kJ/mol
Forsterite	− 4.00	3	Mg_2SiO_4	− 2051.325	+ 63.0	+14.2
Clinoenstatite	− 2.98	2	$MgSiO_3$	− 1460.883	+ 43.7	+ 8.0
Diopside	− 2.72	4	$CaMg(SiO_3)_2$	− 3036.554	+ 39.7	+ 6.2
Anthophyllite	− 2.49	15	$Mg_7Si_8O_{22}(OH)_2$	−11365.000	+ 37.7	+ 4.7
Tremolite	− 2.24	15	$Ca_2Mg_5Si_8O_{22}(OH)_2$	−11627.910	+ 33.4	+ 1.4
Anorthite	− 1.32	5	$CaAl_2Si_2O_8$	− 4017.266	+ 19.7	+ 5.3
Low Albite	− 0.75	5	$NaAlSi_3O_8$	− 3711.722	+ 8.8	− 0.0
Microcline	− 0.51	5	$KAlSi_3O_8$	− 3742.330	+ 6.8	− 0.9
Muscovite	− 0.32	7	$KAl_2[AlSi_3O_{10}](OH)_2$	− 5600.671	+ 3.6	− 3.9
Fayalite	− 6.58	3	Fe_2SiO_4	− 1379.375	+ 73.2	+ 0.8
Ferrous Silicate	− 6.64	2	$FeSiO_3$	− 1123.195	+ 52.2	− 1.1
Laumontite	− 0.53	7	$CaAl_2Si_4O_{12} \cdot 4H_2O$	− 6686.030	+ 13.0	+ 3.0
Prehnite	− 1.60	7	$Ca_2Al_2Si_3O_{10}(OH)_2$	− 5814.920	+ 26.4	+ 7.0
Wairakite	− 0.92	7	$CaAl_2Si_4O_{12} \cdot 2H_2O$	− 6181.020	+ 17.4	+ 7.8
Zoisite	− 1.43	8	$Ca_2Al_3Si_3O_{12}(OH)$	− 6496.500	+ 23.9	+ 6.1
Wollastonite	− 3.32	2	$CaSiO_3$	− 1549.903	+ 48.5	+17.1
Grossular	− 2.34	8	$Ca_3Al_2Si_3O_{12}$	− 6294.919	+ 32.3	+ 7.1
Spinel	− 1.52	3	$MgAl_2O_4$	− 2174.860	+ 43.2	+13.8
Jadeite	− 1.09	4	$NaAl(SiO_3)_2$	− 2850.834	+ 12.1	+ 0.2
Lawsonite	− 0.76	5	$CaAl_2Si_2O_7(OH)_2 \cdot H_2O$	− 4525.617	+ 12.9	− 2.1
Kyanite	− 0.54	3	Al_2SiO_5	− 2441.276	+ 9.2	+ 6.1
Clinochlore	− 1.65	10	$Mg_5Al_2Si_3O_{10}(OH)_8$	− 8259.216	+ 33.0	− 5.2
Pyrite	−17.68	3	FeS_2	− 160.229	+408.7	−
Methane	−20.54	0	CH_4	− 50.708	−	−

[1] Calculated by CURTIS (1976) using ΔG°_f-data are from ROBIE and WLADBAUM (1968) in most cases.
[2] ΔG°_f-data taken from ROBIE et al. (1978) in most cases.

A second example compares the susceptibility to weathering of a set of minerals with differences in standard Gibbs free-energy changes of the weathering reactions. The values $(G^\circ)_R$ in table 7 are from CURTIS (1976, table IV). His values were recalculated on the basis of

1. one cation of the mineral instead of one atom of the reaction-products
2. a consequent reference system, i.e., reactions number 18 and 21 (CURTIS, 1976, table III)

$$\underset{\text{spinel}}{MgAl_2O_4} + 2H^+ + 2H_2O = \underset{\text{gibbsite}}{Al_2O_3 \cdot 3H_2O} + Mg^{2+} \tag{7}$$

$$2\,\underset{\text{kyanite}}{Al_2SiO_5} + 5\,H_2O = \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + \underset{\text{gibbsite}}{Al_2O_3 \cdot 3H_2O} \tag{8}$$

have been replaced by

$$\underset{\text{spinel}}{MgAl_2O_4} \rightarrow \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} - 2\,\underset{\text{quartz}}{SiO_2} + (Mg^{2+} - 2\,H^+) - H_2O \qquad (9)$$

$$\underset{\text{kyanite}}{Al_2SiO_5} \rightarrow \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} - \underset{\text{quartz}}{SiO_2} - 2\,H_2O \qquad (10)$$

Comparison of columns 6 and 7 in table 7 shows the ΔG°_{rel}-level of CURTIS' weathering reactions to be higher than the ΔG°_{min}-level. The Gibbs free-energy differences between the minerals are larger and ranking the minerals according to their ΔG°_{rel}- cq. ΔG°_{min}-values gives a different sequence. On the other hand, if typical soil minerals from CURTIS' list, e.g., muscovite and albite, are selected and their ΔG°_{rel}-values compared with those of the smectites of tables 4, calculated with his reference plane, they all occupy a narrow range (from +4 to +9 kJ/mol per cation) again.

CURTIS' conclusion that a 'general relationship between the rate of different weathering reactions and their free-energy changes' exists, is not at variance with the results found in this paper.

c. *Linear relationship between the oxide-potentials in soils and in aqueous solution*

TARDY and GARRELS (1977) give evidence for a linear correlation between the standard Gibbs free-energy of ortho- and metasilicates and the corresponding cations in a standard solution.

A similar relation is found if oxide-potentials in soils (table 2) are plotted against the oxide potentials in standard aqueous solution.

It is rather easy to arrive at the second plot from the plots of TARDY and GARRELS. Namely, their plotted quantities, viz.,

$$\Delta O^{2-}_{M} = 2/n\,\{\Delta G^\circ_f(MO_{n/2})_c - \Delta G^\circ_f(M^{n+})_{aq}\} \qquad (11)$$

$$\Delta\ \text{orthosilicate} = \Delta G^\circ_f(M_{4/n}SiO_4)_c - 4/n\,\Delta G^\circ_f(MO_{n/2})_c - \Delta G^\circ_f(SiO_2)_c \qquad (12)$$

both contain the term $\Delta G^\circ_f(MO_{n/2})_c$ as a common reference., cf. TARDY and GARRELS (1976, fig. 1) and TARDY and GARRELS (1977, fig. 2).

That means that Δ orthosilicate, Δ hydroxide etc. can be transformed to oxide-potentials, if the system is open to quartz in the same way as was assumed for CO_2 and H_2O in section Method.

For the X-axis (11) is transformed into:

$$\Delta G^\circ_f(\text{oxide})_{aq} = 2/n\,\{\Delta G^\circ_f(M^{n+})_{aq} - n\,\Delta G^\circ_f(H^+)_{aq}\} + \Delta G^\circ_f(H_2O)_L \qquad (13)$$

For the Y-axis (12) and others are transformed into:

$$\Delta G_f(\text{oxide})_{\text{metasilicate}} = \Delta G^\circ_f(M_{2/n}SiO_3)_c - \Delta G^\circ_f(SiO_2)_c \qquad (14)$$

$$\Delta G_f(\text{oxide})_{\text{orthosilicate}} = \tfrac{1}{2}\,\{\Delta G^\circ_f(M_{4/n}SiO_4)_c - \Delta G^\circ_f(SiO_2)_c\} \qquad (15)$$

$$\Delta G_f(\text{oxide})_{\text{hydroxide}} = \Delta G^\circ_f[M_{2/n}(OH)_2]_c - \Delta G^\circ_f(H_2O)_L \qquad (16)$$ [3]

---

[3] ΔG°_f(ice) used in the equations of TARDY and GARRELS (1976) is wrong. The correct value of ice is nearer to the tabulated value of water; therefore, the tabulated value of water is used in this equation.

while

$$\Delta G_f(\text{oxide})_{soil} = 2/n\ \Delta G_f^{fit}(MO_{n/2}) \qquad (17)$$

The differences between the oxide-potentials (14) to (17) and the ΔG_f^o-values of the crystalline oxides are plotted in figure 1 against $[\Delta G_f^o(\text{oxide})_{aq} - \Delta G_f^o(\text{oxide})_c]$.

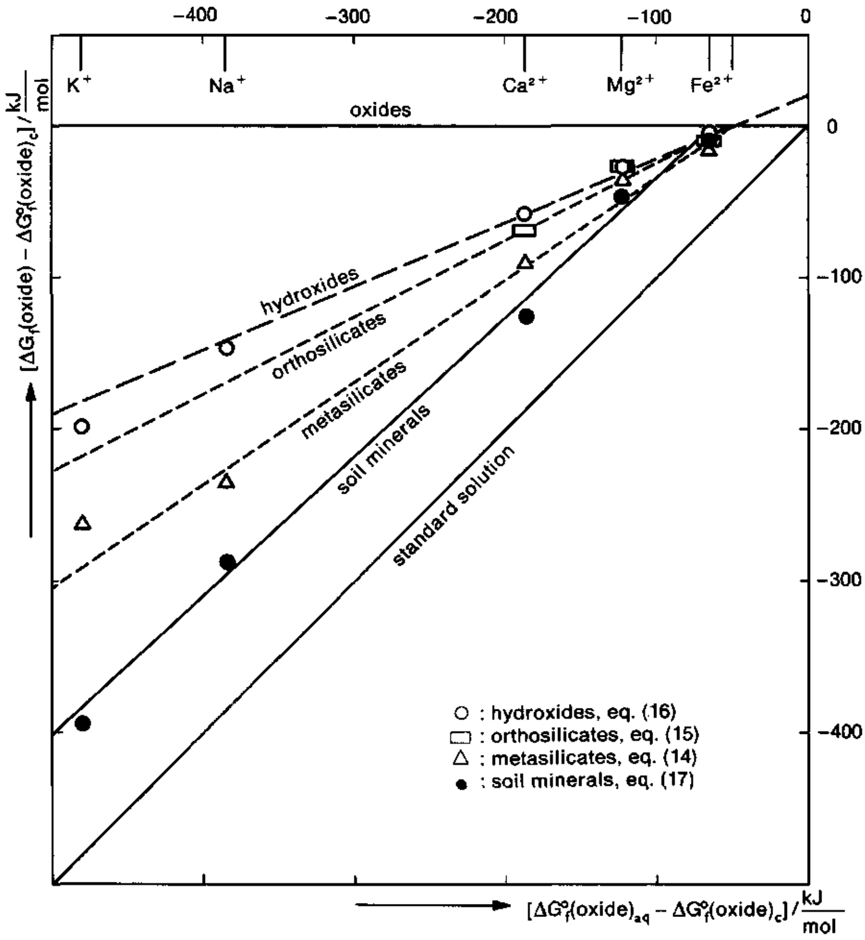

FIG. 1. Relationships between the Gibbs free-energy contributions[1] of oxides in hydroxides, metasilicates, orthosilicates, soil minerals, and those in standard aqueous solution at 25 °C, 1 bar, and fixed H_2O-SiO_2-potentials.

--- after TARDY and GARRELS (1976); ----- after TARDY and GARRELS (1977).

[1] calculated using the data of ROBIE et al. (1978) in most cases.

Data come mainly from ROBIE et al. (1978) and are given per mol O-atoms.

The integral Gibbs free-energies of formation of oxides in saturated salt solutions can be plotted in the same graph provided the thermodynamic data are available.

In other words, the linear relations in figure 1 can all be used as a reference system for an estimation of Gibbs free-energies of certain minerals. The assumption that the set of soil minerals occupies the lowest energy level is illustrated in this figure.

The point in figure 1 where the lines intersect the X-axis is a matter of discussion.

The tabulated data of $\Delta G_f^\circ(H_4SiO_4)_c$ give a Y-value close to zero. This may lead to the conclusion that $(H_4SiO_4)_c$, being a hydroxide of Si^{4+}, and quartz, being a meta- or orthosilicate of Si^{4+}, lie on the point where the lines intersect. This, however, requires a certain X-value with $\Delta G_f^\circ(Si^{4+})_{aq} = -480$ kJ/mol. Substitution of such a low value in the equilibrium

$$(SiO_2)_c + 4H^+ \Leftrightarrow Si^{4+} + 2H_2O \quad (18)$$

leads to a behaviour of silica in solution that has never been observed.

The discussion of TARDY and GARRELS (1976, 1977) on this subject therefore needs some revision, the more so since the tabulated value of ice ($\Delta G_f^\circ(H_2O)_c = -53.455$ kcal/mol) which they used, is wrong.

This value as reported in ROBIE and WALDBAUM (1968, p. 17) follows from the equation:

$$[\Delta G_f^\circ(\text{ice}) - \Delta G_f^\circ(\text{water})]_{25^\circ C} = [\Delta H_f^\circ(\text{ice}) - \Delta H_f^\circ(\text{water})]_{25^\circ C} - T[S^\circ(\text{ice}) - S^\circ(\text{water})]_{25^\circ C} \quad (19)$$

where $[\Delta H_f^\circ(\text{ice}) - \Delta H_f^\circ(\text{water})]_{25^\circ C}$ obviously has been approximated by $[\Delta H_f^\circ(\text{ice}) - \Delta H_f^\circ(\text{water})]_{0^\circ C} = +1.436$ kcal/mol.

The value, however, must be -1.436 kcal/mol which leads to $\Delta G_f^\circ(\text{ice}) = -56.327$ kcal/mol.

The assumed similarity between the equation (11) of an unknown cation Z^{n+} on the intersection point in the hydroxide plot of TARDY and GARRELS (1976)

$$\Delta G_f^\circ(Z_{2/n}O)_c - 2/n\, \Delta G_f^\circ(Z^{n+})_{aq} = -53 \text{ kcal/mol} \quad (20)$$

and

$$\Delta G_f^\circ(H_2O)_c - 2\, \Delta G_f^\circ(H^+)_{aq} = -53.455 \text{ kcal/mol} \quad (21)$$

is now lost since the corresponding values are -46.16 kcal/mol and -56.327 kcal/mol. Instead of H^+ and Si^{4+} a number of other cations must be considered to represent Z^{n+}.

Moreover, there is no reason to assume $(H_4SiO_4)_c$ to represent both a hydroxide of Si^{4+} and an orthosilicate of H^+ because $(H_4SiO_4)_c$ is not a point of the line of orthosilicates at the corresponding X-value.

Considering the reported error of ± 10 kJ/mol, i.e., a range of a few kJ/mol per cation, it follows that the position of the pertinent hydroxides in the Gibbs-slice is difficult to estimate. The same error causes the shape of the general function for silicates of TARDY and GARRELS (1977, p. 90):

$$\Delta\,\text{compound} = -1.01\,\frac{n_1\,\text{cation}\cdot n_2\,\text{silicon}}{n_1+n_2}\,(\Delta O^{2-}\text{cation} - \Delta O^{2-}\text{Si}) \qquad (22)$$

to deviate insignificantly from that for the ideal solid solution of oxides, on the basis of one O-atom. Both functions, with proper scale factors applied to minerals in the system CaO-SiO_2, are shown in figure 2.

d. *Comparison of different data-sets*

At present various self-consistent sets of thermodynamical data of minerals are available (ROBIE et al., 1978; HELGESON et al., 1978; LINDSAY, 1979). In our case mainly values from ROBIE et al. (1978) have been used in the calculations.

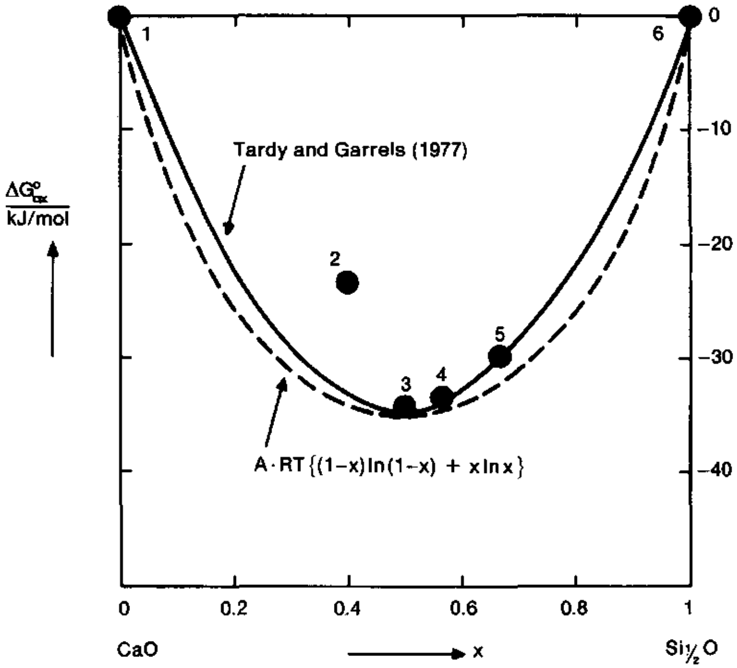

FIG. 2. Gibbs free-energies of formation from the oxides of the minerals in the system CaO-SiO_2 at 25°C and 1 bar.
—— after TARDY and GARRELS (1977); --- Gibbs free-energy function of ideal solid solution, multiplied by scale factor A = 20; 1: $(CaO)_c$; 2: 1/5$(Ca_3SiO_5)_c$; 3: 1/4$(Ca_2SiO_4)_c$; 4: 1/7$(Ca_3Si_2O_7)_c$; 5: 1/3$(CaSiO_3)_c$; 6: 1/2$(SiO_2)_c$.

Generally, other data-sets provide relative stabilities of soil minerals different from those in the tables of this paper.

The fitting procedure described may be applied to any self-consistent data-set. The ΔG^{o}_{min}-values thus obtained give a clear insight in the principal differences between data-sets with respect to relative stabilities of minerals in the soil milieu.

For instance, comparing the consequences of ROBIE et al. (1978) and LINDSAY (1979) shows that approximately forty percent of the minerals of table 1 that are common to both sets, shift 1 to 2 kJ/mol per ion.

DISCUSSION

Without a further detailed study of certain chemical equilibria in a specific soil it may be assumed that the products of weathering processes in a system, open for O_2, H_2O and CO_2 to a certain extent, are situated within the Gibbs-slice discussed before.

The nature of the products is a function of the chemical composition of the soil, of kinetics and of the exact position of the minerals in the Gibbs-slice. A thermodynamical analysis of the possible reactions in the soil system requires precise values of the Gibbs free-energies of minerals.

In geochemical literature the thermodynamical approach is mostly used for the interpretation of (partial) equilibria with an aqueous phase, because of the requirement of a dynamic equilibrium: the mobility of species.

Although this approach led to a successful interpretation for many soil processes, the complex process of the formation of natural clay minerals cannot be adequately treated by ranking solubility products.

Various arguments for this statement are:

1. Because of the large number of possible variations in the stacking of layers in clay minerals and of possible substitutions clay minerals cannot be presented as single positions in the Gibbs-slice. They have to be pictured as continuous Gibbs-surfaces. Exact data on the Gibbs free-energy functions of such solid solutions are still lacking.
2. The large specific surface of clay minerals constitutes an appreciable contribution to the Gibbs free-energy differences of clay minerals in the Gibbs-slice. Moreover, this contribution varies with the chemical composition of the soil environment. Therefore, the Gibbs-surfaces intrinsically are ill-defined.
3. Even without the presence of a soil solution, swelling clay minerals have their own mobile phase, the interlayer water.

   One should treat the wetting of such clay minerals as a continuous increase of the mobile phase from air dry to clay minerals in suspension.

   The accompanying changes of thermodynamic values are either ascribed to the dry clay mineral by arbitrarily defining the activity of water as unity (e.g., apparent Gibbs free-energies from dissolution experiments), or to H_2O (e.g., the integral heat of dehydration from DSC analyses), or to both (e.g., the partial H_2O-pressure from vapour pressure measurements).

One thing is certain, the interlayer water does not contain the same species with the same activities as the external solution. In this respect the edges of the clay minerals function as a kind of membrane setting a membrane equilibrium in the clay mineral-water system. On the external surface an adsorption equilibrium is reached.

Neoformation of clay minerals through precipitation from homogeneous solutions cannot be expected to occur in such systems as a rule.

It is argued in this paper that the size of the Gibbs free-energy differences that govern the overall weathering and soil-forming processes are in the order of the errors in specific experimental Gibbs free-energy data.

SUMMARY

In recent geochemical literature the stability of soil minerals is frequently considered. The question whether a certain mineral is unstable with respect to others in a soil environment is often answered by comparing Gibbs free-energies of formation. The results, however, of these investigations do not enable us to predict the mineralogical composition of a given soil system. In the present paper the theoretical limitations for such a prediction are worked out.

Starting from a newly defined reference system that is nearer to the soil situation than traditional reference states, and using normalized molecular formula units, it is shown that differences of Gibbs free-energies of soil minerals are small and that the values occupy a narrow range of ± 4 kJ per mol cations.

Because of the small differences the problem of comparing stabilities asks for a more rigorous treatment of thermodynamic data than is often encountered in the literature. It turns out that even with this approach the experimental Gibbs free-energy levels of a number of natural clay minerals do not vary significantly.

It is argued that the complexity of these minerals seriously hampers the refinement of free-energy data that could be used in thermodynamic modeling of soil formation.

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