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The Equilibrium of Clay Minerals with Aqueous Solutions in Soils

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Abstract—The paper presents a study into the total chemical and mineralogical compositions of fine colloids (fraction <0.08 μm) in the upper horizons of soils of contrasting compositions and properties. Based on the analytical data, the crystallochemical formulas of clay minerals with a 2:1 structure have been calculated, and the chemical potentials of independent components and the activity coefficients of the main end-members have been determined. Using the Selector software, the equilibrium phase-multicomponent composition of soils has been obtained, and the similarity and difference in the crystal chemistry of 2:1 clay minerals produced by two different methods are shown. The calculated Gibbs energy values of these minerals are close to the calorimetric data for smectites. It is demonstrated that the contents of typical elements in 2:1 clay minerals reflect the genetic properties of soils. In soils of alkaline series (Solonetz), such minerals are relatively enriched in sodium and magnesium; in soils of acidic series (Podzoluvisols and Cambisols), in hydrogen and iron; and in soils of the neutral series (Chernozems, Arenosols, and Umbric Gleysols), in calcium.

Keywords: physicochemical modeling, soils, fine colloids, clay minerals, humic acids, end-members, chemical potentials, activity coefficients

INTRODUCTION

Clay minerals are finely dispersed and rather variable components of the upper sedimentary lithospheric shell and form about 70% of the continental sedimentary cover and about 15 of oceanic deposits (Solotchina, 2009). In terms of their composition and structure, they belong to the group of layered hydrous aluminosilicates (phyllosilicates), in which the meshes of silicon-oxygen and partially aluminum-oxygen tetrahedra are combined with the ones of aluminum- or magnesium-oxygen-hydroxil octahedra thereby forming clusters with relationships between the numbers of tetrahedral and octahedral layers defined as 1:1, 2:1 and 2:1:1. Hence, two-layer (kaolinite group), three-layer (smectite and illite group), four-layer (chlorite group) and mixed-layer clay minerals are identified, the latter characterized with alteration of various cluster types (Deer et al., 1962–1963; Kotelnikov and Konyukhov, 1986; Drits and Kossovskaya, 1990; Chukhrov, 1992; Bulakh et al., 2014).

Genesis of clay minerals in soils, sedimentary rocks, lacustrine and marine sediments still remains a topical problem, despite numerous studies performed (Millot, 1964; Gorbunov, 1978; Gradusov, 1980; Sokolova, 1985; Velde, 1995; Środoń et al., 2000; Środoń and Kloprogge, 2004). Clay minerals are the most active component of soils and define their critical physical and physicochemical properties. Due to their large active surface, they play a major part in humic substance adsorption and form the basis of the clay-humic plasma of soils (Dobrovol'skii and Shoba, 1978). Distribution of these minerals in soils may be the result of various processes, the most important being transformation of layered silicates, primarily mica and chlorites, inherited from the rocks, nondestructive mineral transport, mineral destruction with generation of amorphous compounds, and *in situ* neosynthesis of clay material (Sokolova, 1985).

Interaction of these minerals with water and polyvalent cations dissolved in it plays a significant role in natural processes. Variable chemical composition due to isomorphic cationic replacement in the crystalline structure is a specific feature of clay minerals. Therefore, these nonstoichiometric minerals may theoretically be considered as mixtures of several components, i.e., minals that are present in mineral compositions in variable quantities. *Minals* are actual or theoretical end-members of isomorphic series of minerals represented by chemical compounds with constant compositions, which may be used to describe chemical compositions of minerals. It should be kept in mind that nonstoichiometric minerals do not include any individual end-members that would produce mixtures or mutual solutions. Minerals are integral compounds with groups of isomorphic chemical elements occupying equivalent positions in the crystalline structures (Bulakh et al., 2014).

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At present, thermodynamics interprets the ability of compounds to form solid solutions from the general perspective of free energy minimum (Khisina and Urusov, 1987). Formalized techniques for calculating activity coefficients for solid solutions of mineral systems are available (Ganguly, 2001; Avchenko et al., 2009). Despite the significant number of studies dedicated to the research of composition, structure, and properties of clay minerals in various natural formations, the problem of quantitative analysis of interaction of clay minerals with solutions and calculation of the respective equilibrium states, which is important from both theoretical and applied perspectives, remains poorly researched. It is explained by the complexity of the problem and lack of methods for determining activity coefficients of end-members in complex mineral systems. Thus, the goal of the present paper is to demonstrate the potential of calculating end-member activity coefficients and equilibrium states of clay minerals using the physicochemical modeling (PCM) method for the multiphase and multicomponent systems developed by a research team headed by I.K. Karpov. The use of soils as a research matter in these studies is explained by the possibility of joint analysis of clay minerals, solutions, and humic acids in them.

THEORETICAL FUNDAMENTALS

The concept of a component's chemical potential defining the direction of a chemical reaction and the chemical equilibrium state is a key for thermodynamic equilibrium analysis. In the broadest terms, the Gibbs function (G) of a system of known composition under the specified P and T values is as follows:

$$G = \sum_{i=1}^{k} \mu_i X_i \ ,$$

where μ_i denotes the chemical potential of the ith component; $X_i = m_i / \Sigma m_k$, the component's molar fraction; m, the number of moles of the ith component; Σm_k, the total number of moles; k, the number of chemical components in the system (Münster, 1969).

The component's potential in a perfect solution is proportional to its molar fraction:

$$\mu_i = \mu_0 + RT \ln X_i,$$

where μ_0 is the component's standard potential; R, the universal gas constant.

In actual (imperfect) solutions one obtains:

$$\mu_i = \mu_0 + RT \ln a_i = \mu_0 + RT \ln X_i + RT \ln \gamma_i,$$

where $a_i = X_i \gamma_i$ denotes the activity; γ_i, the activity coefficient of the ith component. In perfect solutions the activity coefficient equals to 1 and $a_i = X_i$.

If $RT \ln X_i$ is moved to the left part of the equation, then one obtains:

$$\mu_i - RT \ln X_i = \mu_0 + RT \ln \gamma_i.$$

In experimental or analytical studies of equilibrium states, the values in the left part of the equation ($\mu_i - RT \ln X_i$) are usually known, making it possible to calculate the values in the right part ($\mu_0 + RT \ln \gamma_i$). Eventually, determining activity coefficients of the components makes it possible to study imperfect systems using the equations designed for the perfect ones.

Thermodynamic modeling and calculation of equilibrium states in multicomponent and heterophase systems are usually based on minimization of Gibbs energy of the systems (Karpov, 1981; Chudnenko, 2010). According to the duality principle of optimization, for the minimum of the objective function of the primal problem there is a corresponding maximum of the dual problem, i.e., the following equation holds:

$$\min \sum_{i=1}^{k} \mu_i X_i = \max \sum_{j=1}^{N} u_j n_j .$$

The concepts of dependent and independent components are used to state a thermodynamic modeling problem. Dependent components (X_i) are the components with specific chemical compositions and stoichiometry (CO_2, H_2O, $KAl_3Si_3O_{10}(OH)_2$, etc.), for which standard values of Gibbs energies of formation are available (ΔG_f^o). Independent components (n_j, N is the number of independent components) are chemical elements, such as Al, Fe, K, Na, C, Ca, Mg, Si, H, O, etc., for which chemical potentials (u_j) are calculated using the duality principle. The equilibrium state is where the integral function of products of molar numbers and chemical potentials of the dependent components reaches its minimum, and the similar function for independent components reaches its maximum. Chemical potentials of independent components are calculated automatically as a result of the objective function minimization of the primal problem using the dual solution. In the physical sense, the concept of chemical potential of an independent component of the system characterizes the energy contribution of 1 mole of the jth stoichiometric unit into the total free energy of the system.

The possibility of determining thermodynamic parameters of substances in one equilibrium phase based on those in another is an important applied consequence of the theoretical condition of chemical potentials of independent components being equal in all equilibrium phases. Consider the basic aqueous solution subsystem of the known chemical composition, which is in the equilibrium with clay minerals, under standard T and P values. Assume that the mineral composition is known as well. The basic solution (air) subsystem includes all independent components of the solution–air–minerals system. By identifying the composition of this basic subsystem and calculating its equilibrium state, it becomes possible to calculate standard Gibbs energies for minerals in the equilibrium with the solution based on the calculated chemical potentials of independent components. On the other hand, including solid solution phase, which describes clay minerals and is composed of M end-members, into the system, makes it possible to estimate the Gibbs energy of the clay material as $\sum_{i=1}^{M} y_i \sum_{j=1}^{N} u_j n_j$, where y_i is the molar fraction of the *i*th end-member in the solid solution.

RESEARCH OBJECTS AND METHODS

When investigating finely-dispersed clay minerals, we mainly focused on fine colloids (fraction < 0.08 μm) in soils due to the fact that fine colloid fractions in the boreal belt loams were more monomineral and composed primarily of illite-montmorillonite mixed-layer structures (Gradusov, 1976). Fine colloid fractions in the Western Siberian soils developing on loamy blanket deposits are mostly composed of mixed-layer minerals with irregular alteration of illite and montmorillonite (or vermiculite) clusters and include small amounts of kaolinite. Larger soil clay fractions, such as precolloid (1–0.2 μm) and large colloid (0.2–0.08 μm) fractions, along with 2:1 clay minerals and kaolinite, also include fine-dispersed quartz, chlorites, mica, and other minerals (Kinsht, 1978; Simonov, 1983; Kurachev, 1991). In this context, determining the crystallochemical composition of the 2:1 minerals in the precolloid fraction and large colloids becomes problematic.

Fine colloids are isolated from the soils with contrasting acidity, compositions, and genesis. Mildly alkaline soils are represented by above-solonetz (N, A1) and solonetz (N, B1) horizons of the high-columnar meadow solonetz, i.e., *Gleyic Solonetz* (FAO classification), of the Barabinsk lowland. Neutral soils are represented by humic horizons of leached chernozem (CHl, A1), i.e., *Luvic Phaeozems*, ordinary chernozem (CHo, A1), i.e., *Haplic Chernozems,* and meadow-chernozem soil (MCH, A1), i.e., *Haplic Arenosols*, of the Ob' plateau, as well as southern chernozem (CHs, A1), i.e., *Calcic Chernozems*, of northern Kulunda and typical chernozem (CHt, A1), i.e., *Haplic Chernozems*, of Altai foothills. Weakly acidic soils are represented by humic horizons of soddy podzol (PZdy, A1), i.e., *Dystric Podzoluvisols*, soddy-gleyic (GLum, A1), i.e., *Umbric Gleysols*, and brown forest (CMeu, A1), i.e., *Eutric Cambisols*, soils of Salair low-hill terrains. Acidic soils are represented by the humic horizon of the brown taiga soil (CMdy, A1), i.e., *Dystric Cambisols*, of Sikhote-Alin foothills. Structure and chemical properties of these soils are presented in earlier papers (Kovalev et al., 1981; Shoba and Karpov, 2004).

Fine colloids were isolated from the clay fraction by triple mashing without adding chemical dispersing agents (Gorbunov, 1971). The clay fraction was also obtained by triple mashing of the soil without adding chemical agents. Elutriation and fractionation of clay and fine colloids was performed using a centrifuge (Shaimukhametov and Voronina, 1972). The centrate was evaporated in the water bath and divided into three parts. Total bulk chemical composition was identified in the first part, and humic carbon content was identified in the second part. The third part was consecutively treated with hydrogen peroxide and processed using the Mehra and Jackson technique to remove humus, nonsilicate forms of elements, and to determine the contents of the latter. This part was also the one used for mineralogical studies.

Crystallochemical formula (1/2 of the elementary cell) for the 2:1 layered minerals was calculated after the part of oxides accounting for humus, kaolinite, as well amorphous and crystalline forms of Fe, Al, and Mn, was subtracted from the total composition of fine colloids. The calculation was performed using the method proposed by B.B. Zvyagin (1957). Titanium from fine colloids was excluded from the calculations due to its low content and its behavior in soils being poorly researched. Bivalent iron was not identified in fine colloids and all its content was represented in the trivalent cation form. Exchange hydrogen content in layered silicates was estimated based on the difference between the cation content in soils and the part of its content accounting for humic acids.

Chemical potentials of independent components of clay minerals were determined by solving inverse FCM problems (Shoba and Karpov, 2004). The basic subsystem was composed of soil solution, gas phase, and combinations of relatively simple mineral phases. The latter were used to calculate chemical potentials of the elements not identified in the solution. These mineral phases for Si, Fe, Al, and Mn were introduced via the respective oxides and hydroxides, and calculated or standard Gibbs energies of formation for these compounds were used (Reesman, 1968; May and Nordstrom, 1986; Litaor, 1987; Woods and Garrels, 1987; Fox, 1988).

Equilibrium states were calculated using the 'Selector' software in the system exposed to the environmental effects with respect to independent components Si–Al–Fe–Ca–Mg–Mn–K–Na–Gb–Gc–Fa–Cl–S–C–N–H–O. Here, Gb ($1/2C_{20}H_9O_9N$) and Gc ($1/2C_{20}H_9O_9N$) represent two parts of the humic solid phase, which are isolated due to the peculiarities of calculating the humic composition as a two-phase system, Fa are fulvic acids of the aqueous solution $C_{29}H_{23}O_{19}$ or $C_{21}H_{12}(COOH)_6(OH)_5(CO)_2$ with molecular weight of 675 g/mol (Schnitzer and Hansen, 1970; Shoba and Chudnenko, 2012). In practice, when Gibbs energy minimization problem is solved in open systems with ordinary contents of aqueous solution (1 L) and solid phases (1 kg), the air volume is set rather high, for example 100 kg, to ensure that partial pressures and chemical potentials of gas components are nearly constant (Karpov et al., 1976). Standard Gibbs energies of formation for dependent components of aqueous solution, gases, and mineral phases used in the calculations are taken from earlier papers and reference books (Reid et al., 1977; Helgeson et al., 1978; Dorogokupets and Karpov, 1984; Yokokawa, 1988; Robie et al., 1995; Shock et al., 1997; Sverjensky et al., 1997).

Table 1. Clay fraction and fine colloid output from soil horizons (wt.%)

Fraction, µm	Soil, horizon										
	N, B1	N, A1	CHs, A1	CHo, A1	CHt, A1	CHl, A1	MCH, A1	PZdy, A1	CLum, A1	CMeu, A1	CMdy, A1
<1.00	27.3	17.2	21.2	23.2	22.0	19.7	26.0	12.3	8.1	8.9	16.3
<0.08	12.0	7.0	13.5	8.6	11.5	10.2	10.6	4.1	2.4	3.0	6.2

Table 2. Total chemical and phase compositions of fine colloids from soils (% on a dry matter basis)

Component	Soil, horizon										
	N, B1	N, A1	CHs, A1	CHo, A1	CHt, A1	CHl, A1	MCH, A1	PZdy, A1	CLum, A1	CMeu, A1	CMdy, A1
	Alkaline soil series		Neutral soil series						Acidic soil series		
SiO_2	46.21	39.42	44.80	45.48	44.46	40.49	44.90	43.53	32.05	30.21	36.22
Al_2O_3	17.16	15.99	20.29	20.10	19.81	18.60	20.14	19.60	15.49	15.08	25.95
Fe_2O_3	12.03	8.65	10.53	10.74	10.04	9.77	10.32	9.02	8.73	9.56	13.31
MnO	0.19	0.20	0.15	0.16	0.17	0.19	0.15	0.09	0.34	2.00	0.40
MgO	4.54	3.49	2.65	2.79	2.77	2.52	2.74	3.12	2.28	2.52	1.20
CaO	0.77	1.64	1.46	2.01	2.02	2.21	1.59	4.92	1.72	2.74	0.52
Na_2O	0.63	0.84	0.20	0.14	0.16	0.15	0.16	0.32	0.15	0.15	0.05
K_2O	2.17	2.50	2.90	2.82	2.67	2.44	3.06	2.67	1.97	1.57	0.55
Humus	4.22	10.97	4.49	5.19	4.83	8.65	4.15	16.16	25.17	21.23	9.68
Kaolinite	13.0	14.0	13.0	9.0	9.0	10.0	8.0	18.0	23.0	7.0	50.0
Fe_2O_3 nonsilicate	1.63	1.14	1.98	2.07	1.81	2.14	1.50	1.19	2.18	3.68	7.99
Al_2O_3 nonsilicate	0.95	0.80	0.72	1.06	0.64	0.66	0.65	1.17	2.15	1.78	1.31
MnO nonsilicate	0.11	0.11	0.10	0.09	0.10	0.12	0.08	0.05	0.21	1.28	0.26
Minerals (2:1)	80.1	73.0	79.7	82.6	83.6	78.4	85.6	63.4	47.3	65.0	30.8

RESEARCH RESULTS

The total output of fractions determined as a result of triple mashing and elutriation indicates that clay content in soils varies between 8.1 and 27.3, the fine colloids responsible for 30–60. The highest content of clay fractions and fine colloids was observed in solonetz and chernozems, and the lowest in podzol and brown forest soils (Table 1).

The results of the X-ray structural analysis[1] indicate that dioctahedral illite and mixed-layer illite-montnorillonite structures prevail in fine colloids from chernozems, podzol, and solonetz soils formed on quaternary loess-like loams, while kaolinite contents are low. In addition, chlorite-like structures are present in Podzoluvisols. Dioctahedral illite also prevails in fine colloids from the brown forest soils developed on the eluvium of chlorite schists, however mixed-layer kaolinite-smectite and chlorite-like structures are present as well. Mixed-layer kaolinite-smectite and smectite prevail in fine colloids from the brown taiga soil formed on the eluvium of basalts. Since illites, smectites, and mixed-layer illite-montmorillites present in fine colloids of soils have similar structures, they are considered within the same group or the 2:1 mineral phase below.

Studies of the total chemical and phase compositions of fine colloids from soils have shown that chernozem soils only have slight differences in contents of basic phases and oxides. Humus content in fine colloids from chernozems is either equal or slightly exceeds its accumulation rate for the horizon on the whole. Kaolinite content does not exceed 8–13%, whereas the prevailing 2:1 minerals account for 78–86 of the total mass (Table 2). Fine colloids from solonetz are characterized by higher total sodium and magnesium contents, which is typical for these soils. Fine colloids from podzol, soddy-gleyic, brown forest, and brown taiga soils have increased kaolinite and humus contents, which is why the amount of layered 2:1 minerals is lower only accounting for 31–63.

To calculate the chemical potentials of independent components in the basic subsystem solution–gas mixture–oxides and hydroxides of elements, the data on compositions of aqueous extracts of soils were used with soil-to-water ratio 1:2.5 (Shoba and Karpov, 2004). Calculation of chemical potentials using alternative methods of obtaining soil solutions, such as pressing, produced the results similar to those for the aqueous extract (Shoba and Sen'kov, 2011). The studies performed show significant differences in chemical potentials for potassium, sodium, calcium, and magnesium depending on soil types. The highest chemical potentials of elements are observed in mildly alkaline solonetz horizons, and the lowest in acidic brown taiga soils. Chemical potentials for iron, aluminum, silicon, oxygen, and hydrogen are constant (Table 3).

According to the calculation results, standard Gibbs energy values for the 2:1 minerals in the studied soils vary from –5091 to –5263 kJ/mol, which is close to calorimetric data for smectites, specifically –5293 kJ/mol (Gailhanou, 2012).

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[1] The authors thank T.A. Sokolova for the studies of mineral compositions of fine colloids from soils.

Table 3. Chemical potentials of independent components (J/mol)

Independent component	Soil, horizon										
	N, B1	N, A1	CHs, A1	CHo, A1	CHt, A1	CHl, A1	MCH, A1	PZdy, A1	CLum, A1	CMeu, A1	CMdy, A1
	Alkaline soil series		Neutral soil series						Acidic soil series		
Na	–348912	–352389	–361581	–361669	–362129	–363067	–358263	–357983	–368523	–366970	–372104
K	–379455	–379681	–382388	–382468	–383903	–384213	–378568	–382292	–386932	–384455	–391476
Ca	–719698	–723246	–727966	–723476	–726577	–727723	–720305	–723435	–737238	–731581	–749497
Mg	–620278	–623357	–631604	–628725	–631767	–633366	–624855	–627659	–642093	–635407	–652700
Al	–783178	–783178	–783178	–783178	–783178	–783178	–783178	–783178	–783178	–783178	–783178
Fe	–337281	–337281	–337281	–337281	–337281	–337281	–337281	–337281	–337281	–337281	–337281
Mn	–424090	–424090	–424090	–424090	–424090	–424090	–424090	–424090	–424090	–424090	–424090
Si	–852406	–852406	–852406	–852406	–852406	–852406	–852406	–852406	–852406	–852406	–852406
H	–117625	–117625	–117625	–117625	–117625	–117625	–117625	–117625	–117625	–117625	–117625
O	–1891	–1891	–1891	–1891	–1891	–1891	–1891	–1891	–1891	–1891	–1891

Table 4. Crystal chemical composition of 2:1 clay minerals calculated based on analytical data

Soil, horizon	Crystal chemical composition of minerals
N, B1	$(K_{0.252}Na_{0.076}Ca_{0.067}Mg_{0.167})(Mg_{0.435}Mn_{0.005}Al_{0.844}Fe_{0.711})[Si_{3.658}Al_{0.342}O_{10}](OH)_2$
N, A1	$(K_{0.349}Na_{0.151}Ca_{0.145}Mg_{0.046})(Mg_{0.494}Mn_{0.008}Al_{0.874}Fe_{0.622})[Si_{3.621}Al_{0.379}O_{10}](OH)_2$
CHs, A1	$(K_{0.337}Na_{0.033}Ca_{0.106}Mg_{0.073})(Mg_{0.286}Mn_{0.004}Al_{1.120}Fe_{0.591})[Si_{3.558}Al_{0.442}O_{10}](OH)_2$
CHo, A1	$(K_{0.309}Na_{0.025}Ca_{0.137}Mg_{0.063})(Mg_{0.291}Mn_{0.005}Al_{1.139}Fe_{0.563})[Si_{3.564}Al_{0.436}O_{10}](OH)_2$
CHt, A1	$(K_{0.298}Na_{0.024}Ca_{0.148}Mg_{0.063})(Mg_{0.293}Mn_{0.005}Al_{1.159}Fe_{0.541})[Si_{3.541}Al_{0.459}O_{10}](OH)_2$
CHl, A1	$(K_{0.303}Na_{0.026}Ca_{0.142}Mg_{0.077})(Mg_{0.285}Mn_{0.006}Al_{1.143}Fe_{0.565})[Si_{3.523}Al_{0.477}O_{10}](OH)_2$
MCH, A1	$(K_{0.331}Na_{0.023}Ca_{0.111}Mg_{0.086})(Mg_{0.260}Mn_{0.005}Al_{1.165}Fe_{0.568})[Si_{3.520}Al_{0.480}O_{10}](OH)_2$
PZdy, A1	$(K_{0.426}Na_{0.036}Ca_{0.091}Mg_{0.068})(Mg_{0,496}Mn_{0.020}Al_{0.617}Fe_{0.864})[Si_{3.738}Al_{0.262}O_{10}](OH)_2$
CLum, A1	$(K_{0.337}Na_{0.054}Ca_{0.411})(Mg_{0.454}\,Mn_{0.004}Al_{0.858}Fe_{0.590})[Si_{3.521}Al_{0.479}O_{10}](OH)_2$
CMeu, A1	$(K_{0.239}Na_{0.021}Ca_{0.230}Mg_{0.131})(Mg_{0.335}Mn_{0.077}Al_{1.016}Fe_{0.564})[Si_{3.434}Al_{0.566}O_{10}](OH)_2$
CMdy, A1	$(K_{0.176}Na_{0.017}Ca_{0.040}Mg_{0.302})(Mg_{0.149}Mn_{0.031}Al_{0.790}Fe_{1.025})[Si_{3.308}Al_{0.692}O_{10}](OH)_2$

Table 5. Standard Gibbs energies of formation and activity coefficients of end-members

End-member	End-member index	ΔG_f^o, J/mol	Activity coefficient, γ_i
$KAl_3Si_3O_{10}(OH)_2$	Ks	–5537189	$X_{Ks}^{8(XKs+XHs)}$ *
$NaAl_3Si_3O_{10}(OH)_2$	Nas	–5514261	$X_{Nas}^{5(XNas+XHs)}$
$Ca_{0,5}Al_3Si_3O_{10}(OH)_2$	Caf	–5512922	$X_{Caf}^{7(XCaf+XHs)}$
$Mg_{0,5}Fe_2AlSi_3O_{10}(OH)_2$	Mgf	–4568677	$X_{Mgf}^{14(XMgf+XHs)}$
$Mn_{0,5}Al_3Si_3O_{10}(OH)_2$	Mns	–5363888	$X_{Mns}^{XMns+XHs}$
$(H_3O)Al_3Si_3O_{10}(OH)_2$	Hs	–5509491	X_{Hs}^{8XHs}
$Ca_3Si_4O_{10}(OH)_2$	Cas	–5808626	$X_{Cas}^{34(XCas+XHs)}$
$Mg_3Si_4O_{10}(OH)_2$	Mgs	–5492504	$X_{Mgs}^{67(XMgs+XHs)}$
$Fe_2Si_4O_{10}(OH)_2$	Fes	–4338808	1
$Al_2Si_4O_{10}(OH)_2$	Als	–5229414	1

*X_{Ks}, … X_{Mgs} are molar fractions of end members in solid solution.

Crystallochemical formulas for the elementary cell of the layered 2:1 silicates are calculated taking into account compositions of fine colloids and the part of oxides accounting for kaolinite, humus, amorphous and crystalline iron, aluminum, and manganese (Shoba and Karpov, 2004). The calculation data for the 2:1 mineral compositions are presented in Table 4. In general, it is worth noting that their crystal chemistry in terms of typomorphic element content reflects genetic peculiarities of soils and their geochemical formation conditions. For instance, the 2:1 minerals in alkaline soils (solonetz) are characterized by higher sodium and magnesium contents. On the other hand, the 2:1 minerals in weakly acidic and acidic soils (Podzoluvisols and Cambisols) have increased hydrogen and iron contents. The same minerals in neutral soils (Chernozems, Arenosols, and Umbric Gleysols) show higher calcium contents.

Table 6. Calculation of phase–multicomponent composition of A1 horizon in typical chernozem based on chemical composition of fine colloids

Initial composition and equilibrium parameters of independent components of the system

Independent component	Total chemical composition, mol	Molar concentration, mol/l	Content, ppm, H_2O	Chemical potential, J/mol
Al	3.9420000	4.543×10^{-7}	0.012	–783203
C	1.0497700	9.128×10^{-5}	1.096	–410714
Ca	0.3590000	3189×10^{-4}	12.78	–726050
Fa	0.0000100	1.066×10^{-5}	7.177	–72977
Gb	01280000	–	–	–
Gc	0.1280000	–	–	–
Cl	0.0001650	1.759×10^{-4}	6.238	–76442
Fe	1.3420000	1.114×10^{-7}	0.006	–337306
K	0.6000000	4.296×10^{-5}	1.680	–383882
Mg	0.6980000	4.498×10^{-5}	1.093	–632014
Mn	0.0230000	3.343×10^{-8}	0.002	–424107
N	5465.0000	1.019×10^{-3}	14.27	–305
Na	0.0460000	5.209×10^{-5}	1.198	–362820
S	0.0002550	2.719×10^{-4}	8.719	–604956
Si	75800000	1.001×10^{-4}	2.811	–852461
H	11102069	8.320×10^{-5}	0.084	–117625
O	1600.0000	2.103×10^{-3}	33.65	–1891

Equilibrium phase composition of the system

Phase	Composition	Number of moles	Content, g	Content, %
Aqueous solution		52.0570	937.869	0.912
Gas mixture	N_2, O_2, CO_2	3492.6	100882.4	98.158
Gb	$1/2C_{20}H_9O_9N$	0.1280	29.815	0.029
Gc	$1/2C_{20}H_9O_9N$	0.1280	27.953	0.027
Kaolinite	$Al_2Si_2O_5(OH)_4$	0.3975	102.626	0.099
Quartz	SiO_2	0.0097	0.584	0.001
Al hydroxide	$Al(OH)_3$	0.0001	0.009	0.000
Fe hydroxide	$Fe(OH)_3$	0.3216	34.370	0.033
Mn hydroxide	$Mn(OH)_2$	0.0138	1.225	0.001
Minerals (2:1)		1.9189	757.770	0.737

Water solution

Dependent component	ΔG_f^o, J/mol	Content		Activity coefficient
		mol/l	mg/l	
Al^{+3}	–482737	4.677×10^{-13}	1.262×10^{-8}	0.685
$Al(OH)^{+2}$	–691314	6.301×10^{-11}	2.772×10^{-6}	0.846
$Al(OH)_2^+$	–900401	1.135×10^{-8}	6.922×10^{-4}	0.959
$Al(OH)_3^0$	–1104095	2.521×10^{-7}	1.967×10^{-2}	1.001
$Al(OH)_4^-$	–1298429	1.397×10^{-7}	1.328×10^{-2}	0.959
$AlOHFa^0$	–934078	5.096×10^{-8}	3.654×10^{-2}	1.002
$FeOH^{+2}$	–241923	1.541×10^{-11}	1.122×10^{-6}	0.846
$Fe(OH)_2^+$	–452813	6.041×10^{-9}	5.429×10^{-4}	0.959
$Fe(OH)_3^0$	–654244	5125×10^{-8}	5.477×10^{-3}	0.999
$Fe(OH)_4^-$	–844473	5.422×10^{-9}	6.717×10^{-4}	0.958
$FeOHFa^0$	–488064	4.865×10^{-8}	3.629×10^{-2}	1.002
K^+	–282462	4289×10^{-5}	1.677	0.959
Na^+	–261881	5.209×10^{-5}	1.178	0.959
Ca^{+2}	–552790	3.043×10^{-4}	12.195	0.845
$CaFa^0$	–769563	6.895×10^{-6}	4.917	1.000
Mg^{+2}	–453985	4.434×10^{-5}	1.078	0.846

(*continued on next page*)

Table 6 (*continued*)

Water solution

Dependent component	ΔG_f^o, J/mol	Content		Activity coefficient
		mol/l	mg/l	
$MgFa^0$	–669440	5.908×10^{-7}	4.119×10^{-1}	1.000
Mn^{+2}	–228028	3.054×10^{-8}	1.678×10^{-3}	0.846
$MnFa^0$	–446851	1.583×10^{-9}	1.152×10^{-3}	1.000
HCO_3^-	–586940	8.086×10^{-5}	4.934	0.959
Cl^-	–131290	1.759×10^{-4}	6.237	0.959
SO_4^{-2}	–744459	2.644×10^{-4}	25.400	0.845
SiO_2^0	–833411	9.987×10^{-5}	6.001	1.001
$HSiO_3^-$	–1013783	1.982×10^{-7}	1.528×10^{-2}	0.959
HFa^-	–220108	6.383×10^{-9}	4.302×10^{-3}	0.959
Fa^{-2}	–193861	3.069×10^{-6}	2.066	0.845
O_2^0	165446	2.745×10^{-4}	8.785	0.999
N_2^0	18188	5.093×10^{-4}	14.269	0.999
OH^-	–157297	1.797×10^{-7}	3.057×10^{-3}	0.959
H^+	0	6.213×10^{-8}	6.263×10^{-5}	0.958
H_2O	–237191	55.510	–	1.000

Gas mixture

Gas	ΔG_f^o, J/mol	Parameter		Activity coefficient
		Number of moles	Partial pressure, bar	
O_2	0	759.0460	0.21733	0.999
N_2	0	2732.499	0.78237	0.999
CO_2	–394384	1.049680	0.00030	0.999

Black humic acids

Monoionic form	ΔG_f^o, J/mol	Content		Activity coefficient
		Number of moles	Solid phase weight %	
$H_{1,5}Gb$	–176435	5.569×10^{-7}	0.00	1.000
$K_{1,5}Gb$	–571116	8.353×10^{-8}	0.00	0.999
$Na_{1,5}Gb$	–543920	4.927×10^{-7}	0.00	0.999
$Ca_{0,75}Gb$	–574882	1.213×10^{-1}	2.97	0.952
$Mg_{0,75}Gb$	–493712	1.774×10^{-3}	0.04	0.888
$Mn_{0,75}Gb$	–330118	7.189×10^{-5}	0.00	0.996
$Fe_{0,5}Gb$	–176607	1.349×10^{-3}	0.03	0,010
$Al_{0,5}Gb$	–404216	3.449×10^{-3}	0.08	0.026
$H_{1,5}Gc$	–176435	5.897×10^{-2}	1.27	1.000
$K_{1,5}Gc$	–523000	1.419×10^{-4}	0.00	0.000
$Na_{1,5}Gc$	–493712	2.065×10^{-4}	0.01	0.000
$Ca_{0,75}Gc$	–537226	4.185×10^{-2}	1.02	0.074
$Mg_{0,75}Gc$	–451872	4.923×10^{-3}	0.11	0.002
$Mn_{0,75}Gc$	–297064	2.906×10^{-3}	0.07	0.004
$Fe_{0,5}Gc$	–154808	5.344×10^{-3}	0.13	0.041
$Al_{0,5}Gc$	–382418	1.366×10^{-2}	0.31	0.106

$(H_{0.691}K_{0.002}Na_{0.002}Ca_{0.956}Mg_{0.039}Mn_{0.017}Fe_{0.026}Al_{0.067})GbGc$ ($GbGc=C_{20}H_9O_9N$)

Minerals (2:1)

End-member	ΔG_f^o, J/mol	Content		Activity coefficient
		Number of moles	Solid phase weight %	
$KAl_3Si_3O_{10}(OH)_2$ $NaAl_3Si_3O_{10}(OH)_2$	–5537189	5.997×10^{-1}	25.03	0.029
$Ca_{0,5}Al_3Si_3O_{10}(OH)_2$	–5514261	4.564×10^{-2}	1.83	0.181
$Mg_{0,5}Fe_2AlSi_3O_{10}(OH)_2$	–5512922	4.848×10^{-2}	1.93	0.091
$Mn_{0,5}Al_3Si_3O_{10}(OH)_2$	–4568677	5.968×10^{-2}	2.68	0.008
$(H_3O)Al_3Si_3O_{10}(OH)_2$	–5363888	1.398×10^{-2}	0.57	0.691
$Ca_3Si_4O_{10}(OH)_2$	–5509491	1.333×10^{-1}	5.28	0.232
$Mg_3Si_4O_{10}(OH)_2$	–5808626	7.069×10^{-2}	3.16	0.000
$Fe_2Si_4O_{10}(OH)_2$	–5492504	2.210×10^{-1}	8.78	0.000
$Al_2Si_4O_{10}(OH)_2$	–4338808	4.488×10^{-1}	19.66	1.000
	–5229414	2.776×10^{-1}	10.48	1.000

$(K_{0.312}Na_{0.024}(H_3O)_{0.069}Ca_{0.123}Mg_{0.064})(Mg_{0.297}Mn_{0.007}Fe_{0.530}Al_{1.166})[Si_{3.531}Al_{0.469}O_{10}](OH)_2$

Table 7. Crystal chemical composition and ΔG_f^o of layered 2:1 minerals calculated using PCM

Soil, horizon	Crystal chemical composition of minerals	ΔG_f^o, J/mol
N, B1	$(K_{0.257}Na_{0.114}(H_3O)_{0.013}Ca_{0.013}Mg_{0.210})(Mg_{0.422}Mn_{0.006}Fe_{0.478}Al_{1.097})[Si_{3.595}Al_{0.405}O_{10}](OH)_2$	–5212000
N, A1	$(K_{0.287}Na_{0.146}(H_3O)_{0.029}Ca_{0.012}Mg_{0.155})(Mg_{0.310}Mn_{0.005}Fe_{0.484}Al_{1.203})[Si_{3.516}Al_{0.484}O_{10}](OH)_2$	–5215184
CHs, A1	$(K_{0.322}Na_{0.033}(H_3O)_{0.070}Ca_{0.083}Mg_{0.082})(Mg_{0.262}Mn_{0.007}Fe_{0.532}Al_{1.202})[Si_{3.511}Al_{0.489}O_{10}](OH)_2$	–5194528
CHo, A1	$(K_{0.312}Na_{0.024}(H_3O)_{0.069}Ca_{0.123}Mg_{0.064})(Mg_{0.297}Mn_{0.007}Fe_{0.530}Al_{1.166})[Si_{3.531}Al_{0.469}O_{10}](OH)_2$	–5199666
CHt, A1	$(K_{0.307}Na_{0.028}(H_3O)_{0.069}Ca_{0.133}Mg_{0.057})(Mg_{0.315}Mn_{0.007}Fe_{0.522}Al_{1.159})[Si_{3.535}Al_{0.465}O_{10}](OH)_2$	–5205319
CHl, A1	$(K_{0.313}Na_{0.029}(H_3O)_{0.070}Ca_{0.115}Mg_{0.071})(Mg_{0.304}Mn_{0.007}Fe_{0.518}Al_{1.174})[Si_{3.525}Al_{0.475}O_{10}](OH)_2$	–5206348
MCH, A1	$(K_{0.327}Na_{0.026}(H_3O)_{0.069}Ca_{0.094}Mg_{0.074})(Mg_{0.267}Mn_{0.007}Fe_{0.532}Al_{1.197})[Si_{3.514}Al_{0.486}O_{10}](OH)_2$	–5195603
PZdy, A1	$(K_{0.267}Na_{0.027}(H_3O)_{0.144}Ca_{0.047}Mg_{0.131})(Mg_{0.227}Mn_{0.009}Fe_{0.589}Al_{1.179})[Si_{3.437}Al_{0.562}O_{10}](OH)_2$	–5181570
GLum, A1	$(K_{0.278}Na_{0.049}(H_3O)_{0.060}Ca_{0.322})(Mg_{0.377}Mn_{0.006}Fe_{0.464}Al_{1.084})[Si_{3.562}Al_{0.438}O_{10}](OH)_2$	–5262999
CMeu, A1	$(K_{0.230}Na_{0.030}(H_3O)_{0.122}Ca_{0.162}Mg_{0.079})(Mg_{0.352}Mn_{0.008}Fe_{0.556}Al_{1.087})[Si_{3.493}Al_{0.507}O_{10}](OH)_2$	–5210620
CMdy, A1	$(K_{0.118}Na_{0.015}(H_3O)_{0.230}Ca_{0.041}Mg_{0.132})(Mg_{0.169}Mn_{0.013}Fe_{0.740}Al_{1.084})[Si_{3.467}Al_{0.533}O_{10}](OH)$	–5090907

To calculate end-member activity coefficients and equilibrium states for clay materials in soils, the data on chemical potentials of independent components and crystal chemistry of minerals were used. The approach used for calculating activity coefficients of monoionic humic acids turned out to be effective in solving the stated problem. It was shown as a result of experimental study of equilibrium states and analysis of ion exchange properties of humic acids that the logarithm of the activity coefficient for the specific monoionic form equals the product of the sum of molar fractions for this monoionic form and H-form of humic acids and the logarithm of the molar fraction of the monoionic form taken with respective coefficients (Shoba and Chudnenko, 2012, 2014).

To calculate activity coefficients of clay end-members using this approach, H-form needs to be introduced into the end-member composition. Hydrogen in natural aqueous solutions is considered one of the most active ions, which makes its presence in clay minerals from soils more of a rule than an exception. For example, exchange hydrogen may significantly prevail over other exchange cations in acidic soils, whose exchange capacity is defined by clay minerals. Hence, the exchange hydrogen is taken into consideration in a number of papers studying crystallochemical features of clay minerals (Nikolaeva, 1977; Wolery and Jove-Colon, 2007).

The results of calculations of standard Gibbs energies and activity coefficients for clay end-members are summarized in Table 5. Activity coefficients for most end-members depend on their molar fraction raised to a power equal to the sum of molar fractions of the respective end-member and the H-form and multiplied by the specific coefficient. The calculation results and the initial analytical data show a good convergence for the studied soil series. However, it should be noted that activity coefficients of clay end-members are only valid for the specified mineral series. Exclusion of any present end-member or introduction of a new one would require revision of all coefficient values in the index.

Let us consider the calculation of phase-multicomponent composition for typical chernozem taking into account activity coefficients of layered silicate end-members as an example. The total bulk chemical composition of fine colloids and the composition of the aqueous extract of the soil are used as the initial data for the calculation. The sought parameters include quantities and compositions of the basic phases and chemical potentials of independent components of the system (Table 6). Equilibrium phases include aqueous solution, gas mixture, humic acids, layered 2:1 minerals, kaolinite, quartz, as well as iron, aluminum, and manganese hydroxides. The water phase shows contents of the dependent and independent components and ion activity coefficients. The black humic acid phase combines two acid groups, in which exchange cation contents and activity coefficients for monoionic forms are calculated. The 2:1 clay mineral phase represents contents and activity coefficients for all end-members, as well as the general crystallochemical formula of minerals.

To verify the model, fine colloid compositions were similarly calculated in all studied soils, and the data on compositions of 2:1 clay minerals were obtained (Table 7). In general, analytical and calculated values show satisfactory convergence. Stronger differences in mineral composition for the Podzoluvisol may be caused by the presence of chlorites in the fine colloid composition. The composition of 2:1 clay minerals in the brown taiga soil may be affected by high (up to 50) kaolonite content in fine colloids, which, when determined (or calculated) incorrectly, may lead to changes in the crystal chemical formula.

CONCLUSIONS

Clay minerals are nonstoichiometric compounds, whose crystal chemical formulae and equilibrium states in soils and other natural formations cannot be calculated without determining activity coefficients of basic end-members. Activity coefficients of clay end-members are calculated using the approach, which was used earlier to study ion exchange in humic acids in soils. Similarly to the latter case, H-forms of end-members play key role in clay minerals and should be taken into consideration in calculations of thermodynamic parameters of other end-members.

As a result, it is possible to calculate equilibrium states of the systems and obtain the data on phase compositions of aqueous solution, clay minerals, humic acids, and oxides and hydroxides of chemical elements based on total chemical composition of fine colloids, which is difficult or even impossible to do using alternative analytical methods and instruments. Determining standard Gibbs energies for the 2:1 minerals using the described calculation method provides additional information and allows for further physicochemical analysis of the studied minerals.

The contents of typical elements in the 2:1 clay minerals based on the calculated crystallochemical formulae reflect the genetic properties of soils. In soils of alkaline series (Solonetz), such minerals are relatively enriched in sodium and magnesium; in soils of acidic series (Podzoluvisols and Cambisols)—in hydrogen and iron; and in soils of the neutral series (Chernozems, Arenosols, and Umbric Greysols) the 2:1 minerals are enriched in calcium if compared to other soils.

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