

Possibility of Estimating Acid–Base Properties of Minerals and Rocks by Means of Physicochemical Simulations (with the Selector-C Program Package)

V. O. Khudolozhkin^a and A. S. Kuchma^b

^a Far East Geological Institute, Far East Branch, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159-V, Vladivostok, 690022 Russia

e-mail: pachihesa@mail.ru

^b Far East Federal University, ul. Sukhanova 8, Vladivostok, 690034 Russia

e-mail: Kuchma@ifit.phys.dvgu.mail.ru

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Abstract—The basicity–acidity of minerals and rocks is estimated by the Gibbs free energy minimization technique with the use of modern thermodynamic data (Selector-C program package). A provisional scale of acid–base properties of minerals and rocks is constructed based on the properties of pure water in equilibrium with them. The composition of solution under standard conditions and base–acid parameters (pH25) are calculated for reactions of pure water with various rock-forming minerals that dissolve congruently or incongruently. A method is suggested for evaluating the base–acid parameters of rocks on the basis of solving the inverse problems of convex programming of the composition and properties of solution (supercritical fluid) in equilibrium with a real mineral association.

Keywords: method of Gibbs free energy minimization, Selector-C program package, acid–base parameters of minerals and rocks

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INTRODUCTION

Evaluating acid–base (A–B) properties of minerals is an important problem of endogenic geology (Korzhin-skii, 1955). A consensus is currently reached that the acidity–basicity of solutions, minerals, and rocks is a very important parameter of mineral- and ore-forming processes. Attempts were made to evaluate the A–B properties of melt components and minerals in magmatic systems using energetic and steric parameters of oxides and cations (Zharikov, 1967, 1979). A thermodynamic approach to this process, with regard for the involvement of volatile components, was suggested by Kogarko and Ryabchikov (1979), who have arranged oxides contained in melts as an empirical sequence of their increasing acidity: K, Na, Ba, Sr, Li, Ca, Pb, Mg, Mn, and Fe. By analogy with hydrogen acids, it was suggested (Shwartsman and Tomilin, 1957) that acids in oxide system are components able to accept oxygen, and bases are component able to yield oxygen. This concept was then utilized to empirically estimate the A–B properties of silicate melts in the so-called poly-electrolytic model of melt structure and in attempts to make consistent the scales of hydrogen and oxygen acids (Anfilogov et al., 1982). The aforementioned researchers have arrived at the conclusion that various acidity–basicity can be made consistent by examining

hydrolysis processes, i.e., by studying distributions of components between fluid and melt phases.

The chemical affinity of a mineral to a proton determined as the free energy increment at interaction of the mineral with water as a universal and neutral medium was suggested in (Marakushev, 1973, 1976; Korzhinskii, 1974, 1982) as a measure of A–B properties of minerals. In the first publications on this problem, the A–B properties of elements and minerals were quantitatively evaluated from their ionization capability. Zharikov (1982) suggested a technique of petrochemical calculations (and presented calculation results) of the A–B strength of elements, acids, bases, and minerals from the conditional ionization potential c in kcal/mol (see below). The potentials were evaluated from the ionization parameters of components and were calculated as totals of the proton-normalized ionization potentials of the cations and anions of a compound. The potential c is the energy spent on the ionization of neutral elements to the valences shown by the respective ions in a compound. According to the author, the calculations have a self-evident physical meaning and require only reasonably accurate evaluations of the potentials (affinity with an electron). Marakushev et al. (Zharikov, 1973, 1976) have calculated the values of the A–B parameters of minerals as the chemical potentials of a proton in mineral–water reactions (these values are presented below as $\Delta Z'$, kcal/mol). The relative basicity of minerals on

Marakushev's scale is closer to our data obtained by the minimizing techniques using pH25 values (see below) and are remarkably different from the c values calculated by V.A. Zharikov.

Korzhinskii (1974) believed that A–B properties can be inferred not from a mineral assemblage but from parameters of its dissolution and suggested to quantify A–B properties based on those of pure water in equilibrium with minerals. In this context, the problem is formulated as the calculation of the pH of solution in hydrolysis reactions of minerals or rocks under standard conditions (25°C, 1 atm). The calculations are carried out in the form of minimizing the Gibbs free energy using modern thermodynamic constants (Chudnenko, 2010). The possibilities of calculating the composition and properties of reaction solutions in water (electrolyte)–mineral–rock systems were lately significantly widened thanks to the application of computer simulations and modern algorithms and thermodynamic databases on the structure and properties of minerals and components of aqueous solutions. Computer simulations of a diversity of problems in water–mineral–rock systems were conducted by Ryzhenko (Ryzhenko et al., 1979) at the Vernadsky Institute, Borisov (2000) at the Department of Geochemistry of the Moscow State University, Avchenko (Avchenko et al., 2009) at the Far East Geological Institute, and other researchers (see references in the aforementioned papers).

Methods of thermodynamic calculations. To solve the problems specified above, we made use of the Selector-C multipurpose program package. Descriptions of the program package, its operation algorithm, databases on minerals, aqueous species, and gases (Holland-1998, SPONS98, and g-Reid, respectively), and experience in their use are described in much detail elsewhere (Avchenko, 2009; Chudnenko, 2010; Avchenko et al., 2011; Khudolozhkin, 2007). The solid phases were assumed to involve the maximum number of minerals (more than 70) that can, in principle, be formed by water–rock reactions at any given composition of the mineral system. For the sake of accuracy of the calculations, much attention was paid to forming reaction solution with a ionic strength no lower than 0.1 to 0.01. The output model data included molar, weight, and volume contents of the solid phases, the composition and concentrations of solute components (mol/kg H₂O), their activities ($\ln \gamma_j$), molal free energy values $g(t, P)$, and the chemical potentials of solution components. The calculations were conducted for a great number of aqueous species, first and foremost, H⁺, OH⁻, K⁺, KCl⁰, KHCO₃⁰, KCO₃⁻, Na⁺, NaCl⁰, NaHCO₃⁰, MgCO₃⁰, HCl⁰, Cl⁻, CO₃²⁻, HCO₃⁻, H₂CO₃⁰, Al³⁺, Al(OH)²⁺, Al(OH)₂⁺, AlO₂²⁻, AlCl₂⁺, H₃SiO₄⁻, SiO₂⁰, etc (Chudnenko, 2010). The molality of the solute components and pH values were determined using the routine for calculating physicochemical parameters of aqueous solutions based on the dual solutions of con-

vex programming problems according to formulas 3.40–3.44 in (Chudnenko, 2010). The calculations of the redox state Eh of solutions in equilibria with minerals are not presented herein because they were a matter of another research.

Note that calculations of low H⁺ and OH⁻ concentrations and the activity coefficients should be particularly accurate and consistent, and require comprehensive thermodynamic information on all components of the water–mineral–rock system. To derive information on the composition and A–B properties of a reaction solution (its pH) in standard state, hydrolysis reactions were calculated for the minimum water/mineral ratio as a necessary condition for A–B buffering of the solution by components of the dissolved mineral (rock). The minimization technique is principally different from and advantageous over calculations by simplified stoichiometric (petrochemical) equations that have been previously utilized to calculate the A–B properties of minerals. Obviously, the method is maximally optimized for solving the formulated problem, and the yielded information involves parameters that make it possible to completely or partly verify the solution.

One of the reasons for discrepancies between the data obtained by other researchers was the different accuracy of their simulations and the comprehensiveness and consistency of the used thermodynamic parameters for minerals and solute components. It is particularly important that petrochemical calculations cannot take into account the mechanisms of interaction between minerals and water, when hydrolysis reactions involve a multitude of neutral and charged aqueous species (simple and complex) and secondary minerals, which are formed by the distribution or because of metastability of the original minerals. The A–B properties of minerals and rocks cannot be evaluated by simple petrochemical equations (Marakushev, 1973, 1976), by summing up the free energy values of acidic and basic components in hydration reactions of minerals, and particularly, without taking into account all pertinent aqueous species and their interactions, i.e., without applying the minimization method. The calculations were verified using the solubility values of minerals and pH25 of the reaction solution, if such information was available (Rafal'skii, 1987); we have also previously obtained such data (Avchenko, 2011; Khudolozhkin, 2007). The results are based on the stability sequences of rock-forming and accessory minerals in supergenic environments (Logvinenko, 1967): 1—highly stable (quartz, limonite, muscovite, orthoclase, microcline, K–Na feldspars, and grossular–andradite garnet), 2—less stable (plagioclase of intermediate composition, pyroxenes, amphiboles, calcite, dolomite, glaucophane, disthene, ugrandite garnet), and 3—highly instable (calcic plagioclase, biotite, siderite, olivine, pyralspite garnet, and feldspathoids). The stability sequence of minerals may, of course, be modified in various physicochemical environments but is nevertheless consistent with our simulations and those in

(Logvinenko, 1967). The calculated pH values are not very accurate (even for the standard state) because of the imperfect quality of modern thermodynamic databases. However, at the modern level of consistency, comprehensiveness, and accuracy of thermodynamic data on minerals and aqueous species used by several researchers (Avchenko, 2009; Avchenko et al., 2011; Borisov, 2000; Khudolozhkin and Sharova, 2011), the A-B parameters that have been calculated for most of the minerals and rocks in question by the minimization technique can be regarded as a reasonably accurate approximation.

Calculated A-B properties of minerals and rocks. The composition of the solution and the evaluation of the A-B properties of minerals from the pH of the reaction solution are listed in Table 1. As seen in the table, minerals can be grouped according to their A-B properties as follows:

- (1) Minerals whose pH25 values correspond to the A-B parameters of compounds that dissolve congruently, i.e., the proportions of components in the solutions corresponds to the stoichiometric proportions of the dissolving mineral (these minerals are labeled *cong* in Table 1).
- 2 (2) Minerals (kaolinite, sillimanite, corundum, quartz, and others) that provide no strong alkalis and bases to solution when dissolved and thus insignificant modify (buffer) the A-B properties of real multicomponent solutions.
- (3) Aluminosilicates of the very strong bases Ca and Mg and of the alkalis K and Na (feldspars, feldspathoids, and others) that dissolve incongruently (the stoichiometry of the solution differs from that of the mineral) and that maximally modify the A-B properties of the solution. This type of hydrolysis is denoted in Table 1 as "...+(secondary minerals)". Under standard conditions, for example, the reaction of albite hydrolysis at the minimum solution/mineral ratio (<0.1 by weight) produces the equilibrium association $Ab + (Mu + Q)$. At a Na concentration of approximately 2.2×10^{-3} , Si concentration of 1.7×10^{-3} , and Al concentration of 1.2×10^{-6} mol/kg H₂O, the solution acquires pH25 = 10.75. At an insignificant increase in the water/albite ratio, the association $Ab + Kln + Qz$ is produced, and the solution contains $Na < 1.9 \times 10^{-3}$ mol/kg H₂O, $Si < 1.4 \times 10^{-3}$ mol/kg H₂O, and $Al < 1.4 \times 10^{-6}$ mol/kg H₂O. The value pH25 = 10.75 for Ab is assumed as the A-B parameter. The calculated value of pH25 = 9.22 for solution in equilibrium with microcline ($Mc + Mu + Qz$) is explained by the lower K concentration (10^{-5}). This implies that Na-feldspar under standard conditions is a more basic mineral, which is consistent with the estimates in (Marakushev, 1973, 1976).
- (4) Most minerals (spinel, diopside, phlogopite, pyrophyllite, and others) occur in a metastable state. In reactions with small amounts of water at 25°C, they

should inevitably *completely* decompose into secondary minerals (denoted by *arrows* in front of the sums of mineral symbols in parentheses. *In this situation, their own A-B properties cannot be evaluated.* However, given that the metastability of many minerals is quite real and the hydration of a primary mineral is associated with the synthesis of stable secondary phases, it can be provisionally assumed that this metastable equilibrium characterizes their A-B parameter. For example, in the reaction of anorthite hydrolysis $An + H_2O \rightarrow CaAl_2Si_2O_7(OH) \cdot 2H_2O$ (lawsonite *Lws*), the solution acquires pH25 = 9.01. With regard for the thermodynamic and real instability of anorthite (Logvinenko, 1967; Krainov and Shvets, 1992), it is reasonable to believe that the value of pH25 corresponds to its A-B parameter. At the decomposition of several metastable minerals (spinel, olivine, nepheline, and others), the A-B parameter of the solution forms the maximally alkaline (basic) decomposition products (Table 1). Some minerals that contain strong bases (antigorite, cordierite, talc, pyrope, almandine, enstatite, and others) can react with water to decompose into low soluble minerals (<-7 to 10^{-9} mol/kg H₂O) (Table 1). These minerals merely weakly affect the A-B state of the water.

To understand the mechanism forming the A-B properties of reaction solutions during the dissolution of incongruent and metastable minerals, we have conducted additional calculations of the partial contributions of secondary minerals (Table 1). Our results are consistent with the conclusions in (Krainov and Shvets, 1982) that surface waters on Earth cannot be in equilibrium with primary minerals but approach equilibria with associations of metastable minerals.

The data presented above led us to the following provisional conclusions:

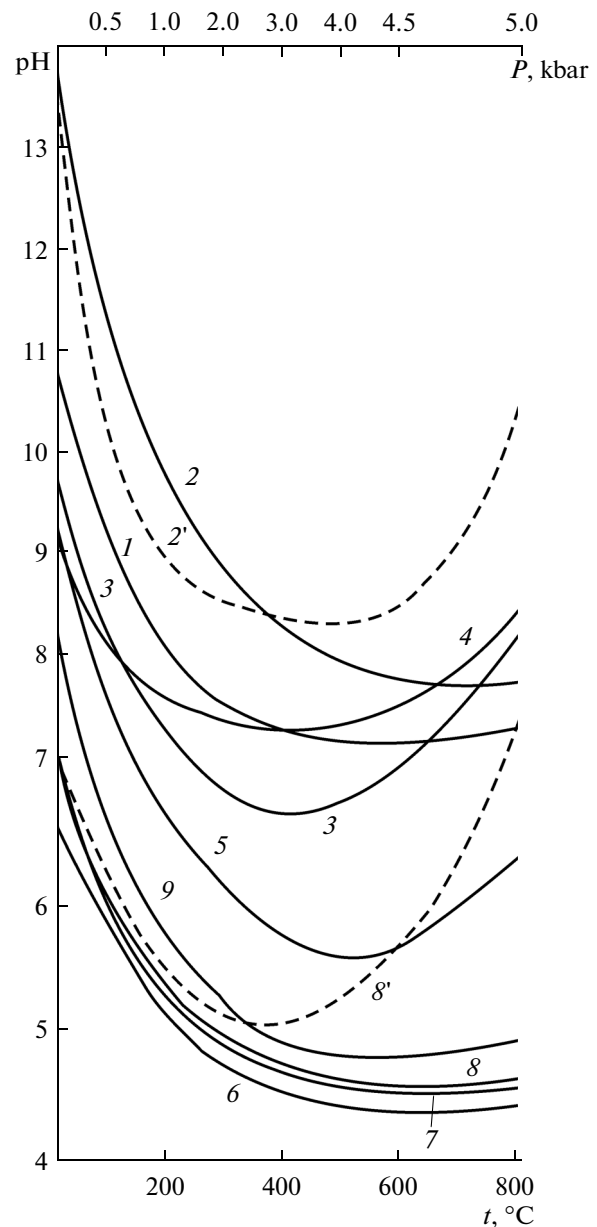
- (a) Most rock-forming minerals that dissolve congruently or incongruently are variably alkaline or basic, and the A-B parameters of these minerals are predetermined by their composition and solubility and are generally controlled by the thermodynamic properties of the mineral (or minerals) and by the individual properties of components of the solutions (Helgeson, 1967, 1969).
 - (b) The pH25 values of minerals that dissolve congruently correspond to their acid–base state.
 - (c) The complete decomposition of metastable minerals may likely be regarded as a type of *extreme incongruent* solubility in the sequence from congruent (without secondary minerals) to incongruent solubility with the preservation of the primary mineral, and finally to incongruent solubility without its preservation. The pH25 values of such minerals can be estimated only formally.
- With regard for the aforesaid, the pH25 values of reaction solutions can likely be formally assumed, within the framework of Korzhinskii's condition of equilibrium with the stable products of partial and even

complete decomposition of metastable minerals, as a parameter characterizing their A-B properties.

The calculations of pH as a function of temperature and pressure were carried out to qualitatively estimate the behavior of the A-B parameters of minerals when they are formed or in the course of retrograde processes. The $pH = f(t, P)$ curves of all minerals, regardless of their composition and type of their dissolution, have similar configurations (figure) [along the geothermal trends $t^\circ\text{C}/\text{kbar}$ assumed by several researchers, for example, Ryzhenko (1999): 25/0.001, 100/0.5, 200/1, 300/2, 400/3, 500/4, 600/4.5, 700/5, and 800/5.5], which are also similar to the configuration of the $pH = f(t, P)$ curve of pure water or electrolytes in the H_2O – NaOH and H_2O – HCl systems (Rafal'skii, 1987).

It was proved that the proton activity along the assumed t/P trend in a homogeneous aqueous (fluid) phase varies (as an intensive parameter) as a smooth function that is almost independent of the variations in the concentrations and compositions of the secondary minerals. Thereby the A-B properties of most rock-forming minerals remain basic, if basicity is calculated relative to reference $pH = f(P, t)$ values of almost neutral pure water as the difference $pH(t, P)_{\text{REAC}} - pH(t, P)_{\text{H}_2\text{O}}$. As can be seen in the figure, minerals containing no strong cations (quartz, kaolinite, and others) remain near-neutral or weakly acidic. The bend of the pH curve and further increase at $\sim 500^\circ\text{C}$ are explained by a superposition of the total contributions of the activities of acidic and basic components of the solution and, of course, also H^+ and OH^- as functions of $P(t = \text{const})$ and $t(P = \text{const})$. The effect of temperature at a constant $P = 1.6$ kbar is illustrated in the figure by lines 2' for nepheline and 8' for water.

The above results of our calculations of the A-B properties of minerals from water–mineral reactions characterize the intrinsic thermodynamic properties of the minerals and were proved to provide merely limited information in terms of the real properties of multicomponent naturally occurring fluid–rock systems. Ryzhenko et al. (1999) have estimated the A-B parameters of rocks using the minimization techniques (the GIBBS program package, which had been developed by Yu.V. Shvarov at the Department of Geochemistry of the Moscow State University) and the whole-rock compositions of granite and dunite (no models of minerals as solid solutions were utilized) in their reaction with pure water at $t = 25$ – 800°C , $P = 1$ – 5 kbar, and a water/rock ratio of approximately 0.01. These authors have determined that the A-B parameters of ultramafic rocks are principally different from those of any other rock in showing strong predominance of the basic cations Mg and Ca (at a minimum concentrations of alkalis) and yielding pH_{25} as high as 15–17. The values of pH_{25} of any other rock (granite, gabbro, diorite, or syenite) are closely similar to one another: 8.5 ± 0.2 . At 600 – 800°C and 4 – 5 kbar, the pH values of all rocks (including ultramafic ones) were proved to approach



Temperature and pressure dependences of acid–base parameters (pH) of minerals) along the t/P trend, see text) (1) Albite; (2) nepheline; (2') nepheline at 1.6 kbar and temperature on the trend; (3) calcite; (4) orthoclase; (5) dolomite; (6) kaolinite; (7) quartz; (8) water; (8') water at 1.6 kbar; (9) magnetite.

the value of 6.5 ± 0.5 , which characterizes the basicity of these rocks, whereas the neutral state of pure water at $700^\circ \pm 100^\circ/4.5 \pm 1$ kbar corresponds to $pH = 4.8 \pm 0.1$.

The calculated A-B parameters of rocks assumed as an integral intensive property of the reaction solution within broad t – P ranges, i.e., regardless the real crystallization parameters of the mineral assemblages are controlled by the model associations of minerals that are not in equilibrium with one another. Under standard conditions, minerals of a rock association are, of course,

Table 1. Acid–base properties of minerals calculated by the minimization technique under standard conditions

Mineral, its formula, and name	pH25, calc.	$\Delta Z'$, kcal/mol	"c", C kcal/mol	Products and dissolution type of mineral	Concentration (mol/kg H ₂ O) in the sequence Na/K/Mg/Ca/Fe/Al/Si
H ₂ O	6.999	200	—	—	—
SiO ₂ , <i>Qz</i>	6.73	227.3	—	cong	10 ⁻⁵
CaCO ₃ , <i>Cal</i>	9.92	187.0	5.66	cong	1.4 × 10 ⁻⁴
MgCO ₃ , <i>Mgs</i>	10.04	203	5.79	cong	2 × 10 ⁻⁴
FeCO ₃ , <i>Sd</i>	7.65	221	4.95	+ <i>gth</i>	1.5 × 10 ⁻⁵
CaFe(CO ₃) ₂ , <i>Ank</i>	9.05	199.5		→ (<i>cal</i> , <i>gth</i>)	7 × 10 ⁻⁴ , 7 × 10 ⁻⁸
CaMg(CO ₃) ₂ , <i>Dol</i>	9.94	195	4.99	cong	7 × 10 ⁻⁵ , 7 × 10 ⁻⁵
Ca(OH) ₂	12.35			cong	10 ⁻²
Mg(OH) ₂ , <i>Brc</i>	10.26	160		cong	10 ⁻⁴
AlO(OH), <i>Dsp</i>	7.00	197.2		cong	2 × 10 ⁻⁹
MgAl ₂ O ₄ , <i>Spl</i>	10.19	176.3	9.03	→ (<i>dsp</i> , <i>brc</i>)	10 ⁻⁴ , 10 ⁻⁶
MgFe ₂ O ₄ , <i>Spl</i>	10.26	185.4	13.15	→ (<i>dsp</i> , <i>gth</i>)	10 ⁻⁴ , 10 ⁻¹²
Fe ₃ O ₄ , <i>Spl</i>	8.33	190.9	5.66	cong	10 ⁻⁶
Al ₂ O ₃ , <i>Cor</i>	6.98	190		→ <i>dsp</i>	10 ⁻⁹
Al ₂ SiO ₅ , <i>Ky</i>	7.0	204	3.35	→ (<i>kln</i> , <i>dsp</i>)	10 ⁻⁹
Al ₂ SiO ₄ (OH) ₂ , <i>Tpz</i>	6.93	220*		→ (<i>kln</i> , <i>dsp</i>)	10 ⁻⁸ , 10 ⁻⁵
Al ₄ Si ₄ O ₁₀ (OH) ₈ , <i>Kln</i>	6.93	214.9		cong	10 ⁻⁹ , 10 ⁻⁵
CaSiO ₃ , <i>Wo</i>	10.56	186.8	10.53	cong	10 ⁻⁴ , 10 ⁻⁴
Fe ₂ Si ₂ O ₆ , <i>Opx</i>	8.87			→ (<i>amp</i> , <i>mag</i>)	5 × 10 ⁻⁶ , 5 × 10 ⁻⁶
MgSiO ₃ , <i>En</i>	6.73		9.35	→ (<i>atg</i> , <i>qz</i>)	10 ⁻¹⁸ , 10 ⁻⁴
NaAlSiO ₄ , <i>Nph</i>	13.76	185.3	14.45	+(<i>anl</i> , <i>dsp</i>)	0.6 × 10 ⁻¹ , 10 ⁻² , 10 ⁻²
NaAlSi ₂ O ₆ H ₂ O, <i>Anl</i>	11.28	198.1		→ (<i>anl</i> , <i>mu</i> , <i>ab</i>)	5 × 10 ⁻³ , 10 ⁻⁶ , 10 ⁻³
KAlSiO ₄ , <i>Nph</i>	13.74	182.7	12.77	+ <i>mu</i>	0.5 × 10 ⁻¹ , 10 ⁻³ , 10 ⁻³
CaAl ₂ Si ₄ O ₁₂ (H ₂ O) ₄ , <i>Lmt</i>	7.00			→ <i>wrc</i>	10 ⁻⁸ , 10 ⁻⁹ , 10 ⁻⁷
CaAl ₂ Si ₄ O ₁₂ H ₂ O, <i>Wrk</i>	8.85			→ (<i>lmt</i> , <i>kln</i> , <i>qz</i>)	10 ⁻⁵ , 10 ⁻⁸ , 10 ⁻⁴
Mg ₂ SiO ₄ , <i>Fo</i>	10.26	188.9	9.89	→ (<i>atg</i> , <i>brc</i>)	10 ⁻⁴ , 0
Fe ₂ SiO ₄ , <i>Fa</i>	8.88	178.6	7.09	→ (<i>amp</i> , <i>mag</i>)	0.5 × 10 ⁻⁶ , 0.5 × 10 ⁻⁶
Fe ₇ Si ₈ O ₂₂ (OH) ₂ , <i>Amp</i>	8.57			cong	10 ⁻⁶ , 10 ⁻⁵
CaAl ₂ Si ₂ O ₈ , <i>An</i>	9.01	197.4	9.68	→ <i>lws</i>	7 × 10 ⁻⁶ , 10 ⁻⁷ , 10 ⁻⁵
CaAl ₂ Si ₂ O ₇ (OH) ₂ H ₂ O, <i>Lws</i>	9.01			cong	10 ⁻⁶ , 10 ⁻⁷ , 10 ⁻⁵
NaAlSi ₃ O ₈ , <i>Ab</i>	10.75	204.7	9.42	+(<i>mu</i> , <i>qz</i>)	10 ⁻³ , 10 ⁻⁶ , 10 ⁻³
KAlSi ₃ O ₈ , <i>Mc</i>	9.22	203.3	5.47	+(<i>mu</i> , <i>qz</i>)	0.5 × 10 ⁻⁵ , 10 ⁻⁸ , 10 ⁻⁴
KAl ₃ Si ₃ O ₁₀ (OH) ₂ , <i>Ms</i>	9.17	201.6		cong	10 ⁻⁵ , 10 ⁻⁷ , 10 ⁻⁵
KMg ₃ AlSi ₃ O ₁₀ (OH) ₂ , <i>Phl</i>	13.2	185.8		→ (<i>atg</i> , <i>kls</i> , <i>dsp</i>)	3 × 10 ⁻¹ , 0, 6 × 10 ⁻³ , 10 ⁻⁴
KFe ₃ AlSi ₃ O ₁₀ (OH) ₂ , <i>Ann</i>	11.79	188.7		+(<i>chl</i> , <i>ms</i> , <i>mag</i>)	10 ⁻² , 10 ⁻⁶ , 10 ⁻¹² , 10 ⁻⁶
NaAlSi ₂ O ₆ , @жадеит	11.27	197.9	11.54	+(<i>anl</i> , <i>ms</i> , <i>ab</i>)	5 × 10 ⁻³ , 10 ⁻⁶ , 10 ⁻³
NaFeSi ₂ O ₆ , <i>Agt</i>	10.8	201.1		+ <i>qz</i>	10 ⁻³ , 10 ⁻¹¹ , 10 ⁻³
CaAl ₂ SiO ₆ , <i>Cpx</i>	11.35			→ (<i>dsp</i> , <i>lrs</i> , <i>lws</i>)	10 ⁻³ , 10 ⁻⁵ , 10 ⁻⁷

Table 1. (Contd.)

Mineral, its formula, and name	pH25, calc.	$\Delta Z'$, kcal/mol	"c", C kcal/mol	Products and dissolution type of mineral	Concentration (mol/kg H ₂ O) in the sequence Na/K/Mg/Ca/Fe/Al/Si
CaMgSi ₂ O ₆ , <i>Di</i>	10.32		8.70	→ (<i>atg, wo, gz</i>)	0, 10 ⁻⁴ , 10 ⁻⁴
CaFeSi ₂ O ₆ , <i>Hd</i>	10.29	193.6		cong	10 ⁻⁴ , 10 ⁻⁸ , 10 ⁻⁴
CaAl ₂ Si ₂ O ₇ (OH) ₂ H ₂ O, <i>Lws</i>	15.1			→ (<i>lrn, wrk, dsp</i>)	4.0, 10 ⁻¹ , 10 ⁻¹³
Ca ₂ SiO ₄ , <i>Lrn</i>	13.76			+ <i>rnk</i>	7 × 10 ⁻¹ , 10 ⁻¹⁰
Mg ₄₈ Si ₃₄ O ₈₅ (OH) ₆₂ , <i>Atg</i>	7.7	193		cong	10 ⁻⁶ , 0
Mg ₆ Si ₄ O ₁₀ (OH) ₈ , <i>Srp</i>	10.26	190.7		→ (<i>atg, brc</i>)	10 ⁻⁴ , 0
Al ₂ Si ₄ O ₁₀ (OH) ₂ , <i>Prl</i>	6.73	218.5		→ (<i>kln, qz</i>)	10 ⁻¹⁰ , 10 ⁻⁴
Mg ₃ Si ₄ O ₁₀ , <i>Tlk</i>	6.73	200.9		→ (<i>atg, qz</i>)	10 ⁻¹⁸ , 10 ⁻⁴
Mg ₃ Al ₂ Si ₃ O ₁₂ , <i>Prp</i>	6.93	192		→ (<i>atg, kln, dsp</i>)	10 ⁻¹⁸ , 10 ⁻⁹ , 10 ⁻⁵
Fe ₃ Al ₂ Si ₃ O ₁₂ , <i>Alm</i>	7.4	197.8		→ (<i>chl, kln, qz</i>)	10 ⁻⁷ , 10 ⁻¹⁰ , 10 ⁻⁵
Ca ₃ Al ₂ Si ₃ O ₁₂ , <i>Grs</i>	12.35	187.6	8.75	cong	10 ⁻⁴ , 10 ⁻⁸ , 10 ⁻⁴
Ca ₃ Fe ₂ Si ₃ O ₁₂ , <i>Adr</i>	9.97	190.8		cong	10 ⁻⁴ , 10 ⁻¹² , 10 ⁻⁴
Mn ₃ Al ₂ Si ₃ O ₁₂ , <i>Sps</i>	9.42			→ (<i>chd, rdn</i>)	10 ⁻⁵ , 10 ⁻⁷ , 10 ⁻⁵
Mg ₃ Fe ₂ Al ₂ Si ₃ O ₁₀ (OH) ₈ , <i>Chl</i>	8.89	193		+ (<i>atg, mag, dsp</i>)	0, 10 ⁻⁶ , 10 ⁻⁷ , 10 ⁻¹¹
Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈ , <i>Chl</i>	8.60			cong	10 ⁻⁶ , 10 ⁻⁷ , 10 ⁻¹⁰
Mg ₂ Al ₄ Si ₅ O ₁₈ , <i>Crd</i>	6.93	202.7		→ (<i>atg, èâî, dsp</i>)	10 ⁻¹⁸ , 10 ⁻⁹ , 10 ⁻⁵
KCa ₂ Mg ₄ Al ₃ Si ₆ O ₂₂ (OH) ₂ , <i>Amp</i>	13.93			→ (<i>atg, lws, dsp, kls, grs</i>)	10 ⁻¹ , 0, 10 ⁻⁷ , 10 ⁻² , 10 ⁻⁴
Na ₂ Fe ₃ Al ₂ Si ₈ O ₂₂ (OH), <i>Amp</i>	11.73			+ (<i>chl, ab, qz</i>)	10 ⁻² , 10 ⁻⁹ , 10 ⁻⁷ , 10 ⁻²
Ca ₂ Fe ₃ Si ₈ O ₂₂ (OH) ₂ , <i>Act</i>	9.68			cong	10 ⁻¹⁰ , 10 ⁻⁵ , 10 ⁻⁷
Ca ₂ FeAl ₂ Si ₃ O ₁₂ (OH), <i>Ep</i>	9.64			→ (<i>grt, gz, gth</i>)	10 ⁻⁴ , 10 ⁻¹² , 10 ⁻⁷ , 10 ⁻⁴
Ca ₂ Al ₃ Si ₃ O ₁₂ (OH), <i>Ep</i>	11.35			→ (<i>grt, law, dsp</i>)	10 ⁻³ , 10 ⁻⁵ , 10 ⁻⁷
Ca ₂ Fe ₂ AlSi ₃ O ₁₂ (OH), <i>Ep</i>	9.64			→ (<i>grt, law, gz, gth</i>)	10 ⁻⁴ , 10 ⁻¹¹ , 10 ⁻⁸ , 10 ⁻⁴ ,
Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂ , <i>Tr</i>	10.32	195.2		→ (<i>atg, qz, wo</i>)	10 ⁻¹⁰ , 10 ⁻⁴
Ca ₂ Mg ₃ Fe ₂ Si ₈ O ₂₂ (OH) ₂ , <i>Act</i>	10.07	197.1		→ (<i>atg, qz, cpx</i>)	10 ⁻¹⁰ , 10 ⁻⁵ , 10 ⁻⁷ , 10 ⁻⁵
Mg ₄ Fe ₃ Si ₈ O ₂₂ (OH) ₂ , <i>Cum</i>	8.10	199.7		→ (<i>atg, qz</i>)	0, 10 ⁻⁶ , 10 ⁻⁵
Mg ₅ Al ₄ Si ₆ O ₂₂ (OH) ₂ , <i>Ged</i>	4.75			→ (<i>chl, prl, qz</i>)	10 ⁻⁶ , 10 ⁻⁵ , 10 ⁻²
Mg ₇ Si ₈ O ₂₂ (OH) ₂ , <i>Ath</i>	5.33			→ (<i>chl, tlc</i>)	10 ⁻⁵ , 10 ⁻³
Na ₂ Mg ₃ Al ₂ Si ₈ O ₂₂ (OH) ₂ , <i>Gln</i>	7.74			→ (<i>chl, tlc, ab</i>)	10 ⁻² , 10 ⁻⁹ , 10 ⁻⁴

"Cong" means congruent dissolution of mineral; +(...) mineral symbols in parentheses correspond to minerals that are formed by hydrolysis, additionally to the primary mineral; → (...) mineral symbols in parentheses correspond to minerals that produced by metastable decomposition and replacement of the original mineral; $\Delta Z'$, kcal/mol is the free energy as a measure of the acid–base properties of minerals (Marakhushev, 1976); c, kcal/mol is the conditional ionization potential (Zharikov, 1973, 1976). Mineral symbols are according to (Rup, 1983; Whitney and Evans, 2010).

in equilibrium with one another. It is logical to suggest that, when water reacts with minerals of an unequibrated association, the pH25 of the solution should be controlled first of all by minerals that release the maximum amounts of bases and alkalis into the solution. In other words, data in Table 1 can be used to formally evaluate the A–B properties of a rock from the composition of the association of this rock. In modeling the system water–mineral assemblage of granite (or phase composition according to Zavaritskii, 1960), we have

determined (as expected) that the pH25 of the solution is controlled by the solubility of feldspar: pH25 ~ 10.3.

To evaluate the effect of mineral solid solutions on pH(*t, P*) and to compare (verify) with data in (Ryzhenko et al., 1999), we have recalculated water reactions with the rock under *conditions assumed herein (solid solutions of minerals were ignored)*. The newly calculated pH(25–300°C) values for ultramafic rocks are high, pH25 is no higher than 12, and the pH(300–

Table 2. Composition (wt %) of metamorphic rocks chosen for modeling

Component	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
	1	2	3	4	5	6	7	8	9	10	
10v	45.60	0.25	9.81	3.45	24.84	0.80	8.66	2.16	0.81	0.67	97.33
39e	47.62	0.57	9.28	15.20	15.84	0.56	3.37	2.54	0.74	1.07	98.77
127g	65.78	0.55	18.13	3.16	2.46	0.22	2.95	1.46	1.88	1.55	99.81
136e	47.96	1.26	14.84	5.54	9.65	0.27	5.61	10.25	2.58	0.46	99.81

600°C) are close (deviate for no more than ± 0.4) to those in (Ryzhenko et al., 1999). In simulating water–rock systems, we have determined that an increase in t and P [along the geothermal trend in (Ryzhenko et al., 1999)] is associated with an increase in the concentrations not only of alkaline but also of acidic components: Na, K ($\approx 10^{-1}$ to 10^{-3}), Ca ($\approx 10^{-7}$), Fe ($\approx 10^{-4}$), Al ($\approx 10^{-2}$), and Si ($\approx 10^{-1}$) mol/kg H₂O. The data illustrate the mechanism controlling pH and the fact that our values and behavior of pH(t , P) are closely similar to those in (Ryzhenko et al., 1996, Ryzhenko et al., 1999). Since much information has been summarized in (Ryzhenko et al., 1999), we do not quote here data of our calculations. The similarities in the configurations of pH(t , P) and the fact that the pH values of rocks of various composition become more similar at high t and P are explained by the fact that the *intensive* parameter pH of fluid supercritical phase is formed at an increase in the solubility of minerals, first of all, due to silica and alkalis (Avchenko et al., 2001), and, what is important, at a decrease in the dissociation constants of components of strong bases (Helgeson, 1969). Note that the compositions of the simulated assemblages at t and P values close to real ones are principally different from the compositions of the natural assemblages, even if the former were simulated with regard for the thermodynamics of mineral solid solutions. Moreover, both our simulations and those in (Ryzhenko et al., 1999) of interaction between pure water and rocks that were specified as *real mineral associations* not only under standard conditions but also at elevated t and P demonstrate that no real associations can be formed and preserved in this variant.

The simulations presented above show that the minimization techniques under standard conditions or at elevated t and P cannot be applied to estimate the real A–B properties of rocks from the properties of reaction *pure water*. Note that it is impossible to calculate the pH25 of rocks with regard for the composition of natural mineral solid solutions because the latter cannot be stable under standard conditions. The calculations of reactions between pure water and rocks in (Ryzhenko et al., 1999) and our own calculations over broad t and P ranges characterize the composition and properties of the solutions at maximally unequilibrated, strongly disturbed, and unreal composition of the mineral associations. These values have very little in common with the

parameters of real solutions because the real parameters (composition of the solutions, their pH, etc.) can be derived from water–rock models only if a mineral assemblage is simulated that is adequate to the natural one (Avchenko et al., 2009). Thereby the necessary conditions of their adequateness are the fluid/rock ratio, oxygen potential, and t , P parameters. It is particularly important that no adequateness can be reached without substituting pure water for fluid of corresponding composition, redox, and A–B properties and without using models for mineral solid solutions.

Because of this, the conditions of solving the problem formulated by D.S. Korzhinskii (evaluation of the A–B parameters of minerals and rocks based on their composition and properties of reaction water under standard conditions) are reformulated as estimation of the A–B properties of a rock based on the composition and properties of fluid in equilibrium with the mineral assemblage relative to always neutral water (see below).

Modern simulations of water–rock reactions (Avchenko et al., 2009, 2011; Khudolozhkin and Sharova, 2011) unambiguously demonstrate that no model of a mineral association adequate to a natural one can *in principle* be development if the water (fluid)/rock ratio and the t , P , and composition of the fluid (including oxygen fugacity) are unknown. These parameters can be evaluating by solving the inverse problem of convex programming (Chudnenko, 2010; Avchenko et al., 2009), which makes it possible to simulate an assemblage that is close (or better, even identical) to the real one. We made use of this approach in studying the regime of oxygen inertness–mobility when simulating the redox conditions (fO_2) of metamorphic rocks (Khudolozhkin and Sharova, 2011). In other words, a successful solution of the inverse problem is a necessary condition of reaching consistency between the compositions of simulated and real mineral associations and, hence, evaluation of the A–B properties of the rock. In this instance, the A–B parameter of the rock manifest itself in the form of pH(t , P) relative to the pH(t , P) of neutral pure water when the inverse problem is solved.

An illustrative example of evaluating A–B properties is provided by data from (Avchenko et al., 2007) on four metamorphic rocks from the Ohotsk and Chogar complexes (Table 2). The rocks are Ca-poor garnet–orthopyroxene, garnet–cordierite, and garnet–biotite–silli-

Table 3. Acid–base parameter pH(*t*, *P*) and the composition (wt %) of simulated fluid in equilibrium with the mineral assemblage of the rock

Sample	H ₂ O	CO ₂	CO	CH ₄	H ₂	R/W	pH(<i>T/P</i>)
	1	2	3	4	5	6	
10v	74.2	19.7	0.34	5.6	0.09	9	7.1
127g	91.9	7.3	0.05	0.65	0.05	9	6.4
39e	9.94	90.0	0.01	–	–	20	7.2
136e	17	83	0.01	–	–	20	7.2

Table 4. Comparison of the composition of minerals in (1) the real mineral assemblage and (2) simulated mineral assemblage

Sample	X_{Fe}^{Gr}		X_{Fe}^{Opx}		X_{Fe}^{Bi}		X_{An}^{Pl}		X_{Ca}^{Gr}		X_{Fe}^{Cpx}		X_{Fe}^{Hb}	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
10v	0.82	0.81	0.63	0.61	0.58	0.53	0.40	0.40	0.11	0.12	–	–	–	–
39e	0.81	0.82	0.65	0.60	–	–	0.35	0.35	0.16	0.19	–	–	–	–
127g	0.73	0.70	–	–	0.35	0.37	0.30	0.28	0.06	0.04	–	–	–	–
136e	0.80	0.80	0.51	0.57	–	–	0.49	0.48	0.20	0.27	0.42	0.41	0.59	0.53

@Примечания. Fe/(Fe + Mg) – железистость граната (X_{Fe}^{Gr}), X_{Fe}^{Opx} – ортопироксена, X_{Fe}^{Bi} – биотита, X_{Fe}^{Cpx} – клинопироксена, X_{Fe}^{Hb} – роговой обманки; X_{An}^{Pl} – содержание анортита в плагиоклазе, X_{Ca}^{Gr} – кальциевость Ca/(Ca + Mg + Fe + Mn) граната. “–” – нет анализа.

manite gneisses, gneiss-quartzites, and granulites (metapelites) and Ca-rich amphibole–orthopyroxene–clinopyroxene mafic granulites (metabasites). In the models, a rock, which was specified in the form of its chemical composition, interacted with H₂O–CO₂ fluid in the system H₂O–C–CH₄–CO–H₂–O₂ (the equilibrium composition of the fluid is shown in Table 3).

The thermodynamic system simulated with Selector-C in these models consisted of 69 components that formed the major observed and possible minerals of granulite-facies metamorphic rocks. To constrain the solutions of the inverse problem, we also used minerals

of the amphibolite facies. Our results are completely consistent with the real mineral assemblage (Table 4).

We have determined that the pH values of the solutions are 7 ± 0.1 at $t = 700–740^\circ\text{C}$ and $P = 6–6.8$ kbar. Considering that the pH of pure water at these t , P parameters is 4.7, it is reasonable to believe that the basicity of the rocks is $7(\pm 0.1)–4.7(\pm 0.1) = 2.4 \pm 0.1$ pH units. The equilibrium fluid contained practically no Ca, Mg, Fe, and its dominant components were Na, K, Al, and Si (Table 5).

For comparison, within the framework of the original model for interaction between *pure water* and the rock of sample 10v at 720° C and 6.3 kbar, we obtained

Table 5. Concentration (μmol/kg H₂O) of solution components in the model aqueous electrolyte–rock at given *P* and *t*

Sample	<i>P</i> , @кбар	<i>t</i> °C	R/W	KOH ⁰	NaOH ⁰	CH ₄ ⁰	CO ₂ ⁰	H ₂ ⁰	NaAlO ₂ ⁰	AlO ₂ [–]	HCO ₃ [–]	HSiO ₃ [–]	K ⁺	Na ⁺	SiO ₂ ⁰
	1	2	5	6	7	8	9	10	11	12	13	14	15	16	17
10v	6.2	740	7.5	–	–	4382	6767	2653	–	–	1.25	0.37	0.93	4.1	538
39e	6.5	710	20	0.64	0.12	–	77148	4.1	1.4	3.0	6.5	–	1.4	8.9	338
127g	6.8	700	8	0.94	0.19	256	2040	1066	2.3	8.8	0.34	0.28	1.3	10	572
136e	6.0	720	15	–	0.12	–	78257	5.4	1.5	2.7	4.4	–	–	7.7	295

$\text{pH}^{\text{reac}} = 6.85$, and the basicity was 2.2 ($\text{pH}_{25} = 12.87$). In another model of interaction between rock 136e with a specified contents of minerals (vol %: *Grt* = 22, orthopyroxene = 52, plagioclase = 16, biotite = 7.8, quartz = 1.1, and ilmenite = 0.3) with *pure water*, we obtained $\text{pH}^{\text{reac}} = 8.4$ and basicity of 3.7 ($\text{pH}_{25} = 13.26$). The mineral associations in both models (in reactions with pure water, even if solid solutions are taken into account) were principally different from the real ones in terms of both phase composition and mineral chemistries.

It follows that the pH values and mechanisms forming $\text{pH}(t, P)$ simulated using the minimization technique led us to conclude that A-B parameters of rocks can be estimated using only fluid parameters that are acquired in equilibrium with real mineral associations, which is a robust verification factor of such simulations. The A-B properties of rocks estimated by solving the inverse problem illustrate a new efficient approach to (and a method for) estimating their A-B state. However, it is principally impossible to evaluate the A-B parameters of real rocks, within the frame of the problem formulated above, from the properties of *pure water* in equilibrium with the rocks.

CONCLUSIONS

1. Acid–base properties of stable rock-forming minerals under standard conditions are evaluated by minimizing the Gibbs free energy.
2. Alkalis and other basic cations of rock-forming minerals and rocks are the main components controlling their *basic* properties.
3. The acid–base parameters of most rock-forming minerals at their incongruent dissolution under standard conditions are formed with the participation of secondary minerals.
4. The intrinsic acid–base parameters of several metastable rock-forming minerals under standard conditions cannot be calculated by the minimization technique. Their acid–base properties seem to be formed with the involvement of the decomposition products.
5. Real acid–base properties of rocks in their reactions with *pure water* under standard conditions or at elevated temperatures and pressures cannot be evaluated by the minimization technique.
6. The acid–base properties of rocks can be evaluated by the minimization method only with the application of a new approach: solving the inverse problem, i.e., by simulating equilibrium of fluid with a real mineral association.

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SPELL: 1. adequateness, 2. sillimanite