

Metasomatic Interaction between Rock and Solution under Varying Pressure–Temperature Conditions

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Abstract—Variations in the activity of major components in a rock and solution initially equilibrated with the activity were evaluated under thermal and pressure gradient conditions by the example of the system granite–chloride solution. These variations are controlled by the shifts of mineral hydrolysis reactions in the rock and dissociation equilibria of salts, acids, and bases in the solution. The resulting relationships between $a_{\text{Me}^+} / a_{\text{H}^+}^{\text{sol}}$ and $a_{\text{Me}^+} / a_{\text{H}^+}^{\text{rock}}$ control the direction of infiltration metasomatism. There is a high-temperature region, where the behavior of Mg and Fe is very different from that of Na and K and the behavior of Ca is transitional, and a low-temperature region, where these components are similar to each other. The processes of acidic and alkalic metasomatism may be accompanied in various combinations by the processes of basification and debasification, as well as rock silicification and desilication. The type of these combinations is controlled by the character of the gradient field, involving either a decrease or an increase in temperature and pressure, and can be correlated with a particular metasomatic association.

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INTRODUCTION

A necessary condition for the occurrence of metasomatic processes is disequilibrium between a solution and rock, which is expressed by the inequality of the chemical potentials of major components in these systems. The reasons for the development of such an inequality are among the most important problems of metasomatic petrology. A special case with $\mu_i^{\text{sol}} < \mu_i^{\text{rock}}$, where i is K_2O or Na_2O , corresponding to acid leaching has been studied in the most detail. This process results in the replacement of minerals with a high potential of alkalis by minerals with a lower potential. It was attributed to the mechanisms of the filtration effect, condensation of acid gases, and acid dissociation [1–3]. The latter two effects are associated with a temperature decrease, which causes the development of acid leaching by cooling postmagmatic solutions. The inversion of solution properties results in alkalic metasomatism ($\mu_i^{\text{sol}} > \mu_i^{\text{rock}}$) [1, 2]. The most obvious occurrence of inversion is related to the filtration effect after the passage of the advancing wave of acidic components. However, the neutralization of the acid solution owing to its reaction with the rock cannot by itself result in inversion, because it includes gradual saturation of the solution by rock components, after which the interaction ceases.

The diversity of natural metasomatic rocks and their spatial and temporal relationships are not always fully

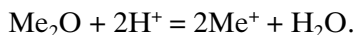
consistent with the above simplified model. Both acidic and alkalic metasomatic assemblages may develop pervasively over the whole temperature range [4]. In some particular objects, products of alkalic metasomatism are earlier and more diverse, whereas acidic processes are suppressed [5]. Moreover, there are many metasomatic rock varieties showing the accumulation of bases (Ca, Mg, and Fe) coupled with the removal of alkalis [4], in particular, biotite glimmerites, skarnoids, chloritoidites, etc. Therefore, the processes of basification and debasification need to be distinguished and independently analyzed. Finally, the above types of processes may be accompanied by both the gain and loss of SiO_2 . The former case is widespread and leads to the formation of quartz veins and rock silicification. The latter case is associated with the formation, for instance, of quartz-free carbonaceous sericitoidites described in a number of gold ore deposits [5].

The above considerations demonstrate the need for an analysis of the behavior of components in the disequilibrium solution–rock system, which in turn is controlled by the mechanisms of the generation of disequilibrium in this system.

Generally speaking, there are two possible reasons for the generation of disequilibrium states: the presence of two rocks of contrasting compositions and the existence of temperature and/or pressure gradients along the pathways of solution migration. Contact-type metasomatic complexes are formed in the former case, including skarns, rodingites, corundum plagioclases, etc.

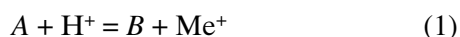
They are beyond the scope of this paper. Metasomatic complexes related to the latter mechanism can be referred to as a temperature–pressure gradient or simply as gradient ones. Such a metasomatic process occurs if at least one of the two parameters, T or P , changed compared with the parameters of the solution source (intrusive body or an area of prograde metamorphism).

During the analysis of processes occurring in systems with excess water, it is convenient to use the ratios $a_{\text{Me}^+}/a_{\text{H}^+}$ instead of the chemical potentials of components:



The fraction of Me^+ species in the total concentration of the component in the solution is of no importance.

Before the beginning of the interaction, the activities of the components in the pore solution are controlled by the equilibria of mineral hydrolysis of the type



and, consequently, are fully defined by the bulk composition of the rock. Such systems are referred to as rock-dominated [6–8]. They can exist if the solution/rock (W/R) ratio is low, usually no higher than 1.

The activities of the components in the solution before the onset of its interaction with rock are controlled by the dissociation reactions of salts, acids, and bases; such systems are referred to as fluid-dominated. In essence, this concept is equivalent to the concept of open systems, in which all components are perfectly mobile (PMC) [9]. The interaction of a solution with rock produces a metasomatic column with a sequence of zones differing in the set of PMC. It is evident that in each zone, the solution–rock system is fluid-dominated with respect to the PMC of the zone and rock-dominated with respect to all the other components (inert). This implies that the data obtained for free solutions can be used to characterize those components of metasomatic rocks which are perfectly mobile in the given zone.

Under temperature and pressure gradient conditions, the activities of components in rock- and fluid-dominated systems vary differently. The dependence of the equilibrium constants of mineral hydrolysis reactions on T and P is described by the equations

$$(\partial \ln K / \partial T)_P = \Delta H / RT^2 \text{ and}$$

$$(\partial \ln K / \partial P)_T = -\Delta V / RT,$$

where ΔH and ΔV are the enthalpy and volume effects of the reaction. The reactions of silicate hydrolysis usually have $\Delta H < 0$, which results in the displacement of equilibria (1) to the left in response to a temperature increase (left-hand rule of Garrels) [10].

The same relationships are characteristic of reactions between solution species; however, the activities of the components in fluid-dominated systems are

defined by the combination of simultaneously occurring dissociation reactions under the conditions of mass and charge conservation. This provides an opportunity to calculate the effects. Such estimates of the influence of changes in T and P on the pH values of the NaCl solution with CO_2 , NaOH, and HCl [11] showed that a temperature decrease leads to an increase in acidity, and a pressure decrease causes an increase in the alkalinity of solution. However, these authors ignored the aforementioned changes occurring under the same conditions in the rock. In contrast, the latter effects were used for the estimation of the direction of metasomatic processes in [8, 10]. These authors concluded that acidic metasomatism occurs as a result of a decrease in temperature (muscovite replaces feldspar in granites), and alkalic metasomatism occurs during decreasing pressure, but they probably ignored the effects of changes in the activity of components in the solution.

The disequilibrium character of the solution–rock system is obviously an integral result of the simultaneous occurrence of the aforementioned effects in the solution and rock. This means that the direction of the metasomatic transformations caused by solution flows in rocks under temperature and pressure gradient conditions is controlled by the relationships between the $a_{\text{Me}^+}/a_{\text{H}^+}$ values in the solution and in the rock, i.e., the sign and the magnitude of the difference $\Delta_{\text{Me}} = a_{\text{Me}^+}/a_{\text{H}^+}^{\text{sol}} - a_{\text{Me}^+}/a_{\text{H}^+}^{\text{rock}}$. The following cases can be considered:

for $\text{Me} = \text{Na}, \text{K}$

$\Delta_{\text{Me}} < 0$, acid leaching and

$\Delta_{\text{Me}} > 0$, alkalic metasomatism subdivided into the Na and K types;

for $\text{Me} = \text{Ca}, \text{Mg}, \text{Fe}$,

$\Delta_{\text{Me}} < 0$, debasification and

$\Delta_{\text{Me}} > 0$, basification subdivided into Ca-, Mg-, and Fe-metasomatism.

Therefore, the problem is to explore the conditions under which the particular variants of processes occur.

Theoretically, both temperature and pressure may increase or decrease along the flow path of a solution. The most common is the case of a solution cooling during its movement upward and away from the magmatic source [10]. The numerical simulation of heat and mass transfer in convection cells showed that temperature increases in the downwelling and, especially, focused limbs of such cells [12]. Decompression phenomena were established in those fault zones where the data of microstructural analysis suggested the occurrence of syndeformation crystallization under extensional regimes [13]. On a regional scale, decompression is manifested during the final stage of orogenic belt development, when it is accompanied by a transition from the kyanite–sillimanite to andalusite–sillimanite type of metamorphism, granitization, and metasomatism

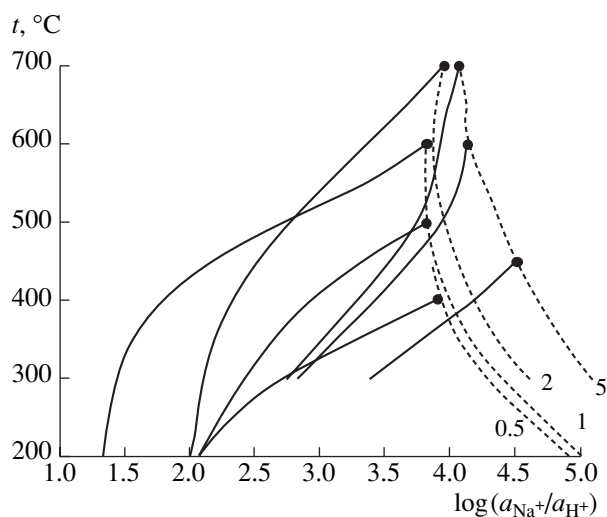


Fig. 1. Dependence of the $a_{\text{Na}^+}/a_{\text{H}^+}$ ratio on temperature in a model chloride solution (solid lines) and in a solution equilibrated with granite (dashed lines). Circles show the parameters of the initial state of model solution in equilibrium with granite. Numerals near the lines indicate pressure in kilobars.

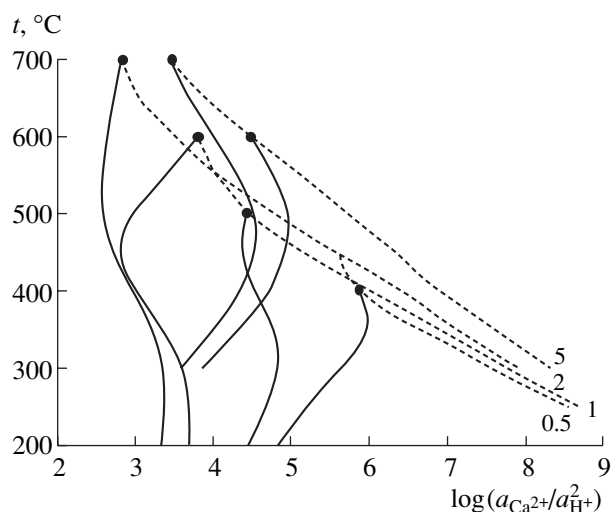


Fig. 2. Dependence of the $a_{\text{Ca}^{2+}}/a_{\text{H}^+}^2$ ratio on temperature in a model chloride solution and a solution equilibrated with granite. Symbols are the same as in Fig. 1.

[3]. The possibility of compression in the solution–rock system was demonstrated by McCaig [14] for the model known as the seismic pump. This mechanism may operate in compression and shear zones distinguished by the development of brecciation, cataclasis, and mylonitization [5].

METHODS AND RESULTS OF CALCULATION

Let us consider the most important geochemical consequences of changes in temperature and pressure in the solution–rock system. The model substances correspond to the average composition of granite after Daly (cited by [15]) and chloride solution with initial bulk concentrations of 1 M Cl and 1 M CO₂. The progress in solution composition was quantified by calculating its equilibrium with granite under given T and P conditions and a low W/R ratio (usually, 0.1).

A comparison of the solutions with and without CO₂ suggests a significant influence of CO₂ concentration [11]. However, natural hydrothermal systems are almost never completely devoid of CO₂. The investigation of mineral assemblages and fluid inclusions suggests that the CO₂ content of solutions is usually no less than 0.1 M and may be as high as 5 M or even higher [5]. According to calculations, the differences in $a_{\text{Me}^+}/a_{\text{H}^+}$ between the solutions containing such amounts of CO₂ are negligible. Because of this, variations in this parameter are not further considered.

The compositions of solutions in rock- and fluid-dominated systems were calculated using the thermodynamic constants of solid phases after [16] with mod-

ifications for Na- and K-bearing minerals described in [17]. The constants of HCl⁰, KOH⁰, KCl⁰ were taken from [17]; CaCl⁺, CaCl₂⁰, MgCl⁺, and MgCl₂⁰, from the UNITHERM database [18]; Al(OH)₃⁰, Al(OH)₄⁻, and NaAl(OH)₄⁰, from [19]; and other species, from the SUPCRT92 database [20].

Figures 1–4 show the temperature dependence of $a_{\text{Me}^+}/a_{\text{H}^+}$ ratios for Na, Ca, Mg, and Fe ions in the fluid-dominated system “initial solution” and the rock-dominated system “granite–solution.” The behavior of $a_{\text{K}^+}/a_{\text{H}^+}$ in response to a change in temperature is identical to that of $a_{\text{Na}^+}/a_{\text{H}^+}$, and the respective diagram is therefore not shown. During cooling, the points of solution and rock move along corresponding curves. Since the phases in which the solution is oversaturated (quartz, magnetite, etc.) may precipitate changing the activity of components, the composition of solution was calculated by the method of flow-through reactors using its variant designed for the simulation of hydrothermal veins [21], i.e., ignoring the interaction with wallrocks.

As can be seen from Fig. 1, the acidity of a solution under a temperature decrease, expressed by the parameter $a_{\text{Na}^+}/a_{\text{H}^+}$ increases steadily relative to the rock within the whole T and P interval. The effects of shifts in dissociation reactions in the solution (solid curves deviate to the left) and mineral hydrolysis (dashed curves deviate to the right) augment each other for Na and K, which implies $\Delta_{\text{Na}, \text{K}} < 0$. This is responsible for

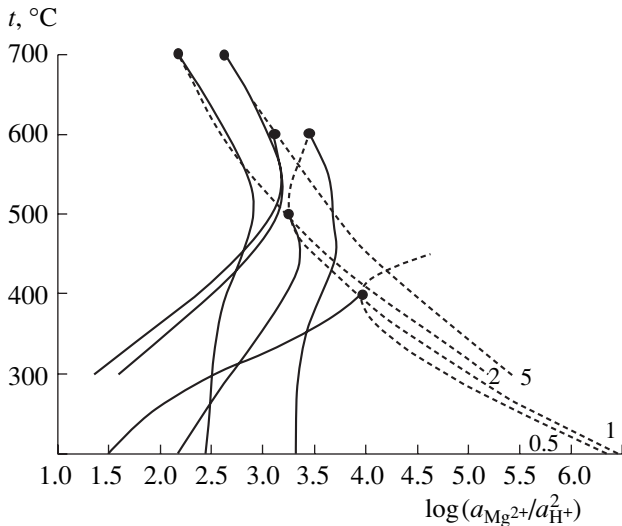


Fig. 3. Dependence of the $a_{Mg^{++}}/a_{H^+}^2$ ratio on temperature in a model chloride solution and a solution equilibrated with granite. Symbols are the same as in Fig. 1.

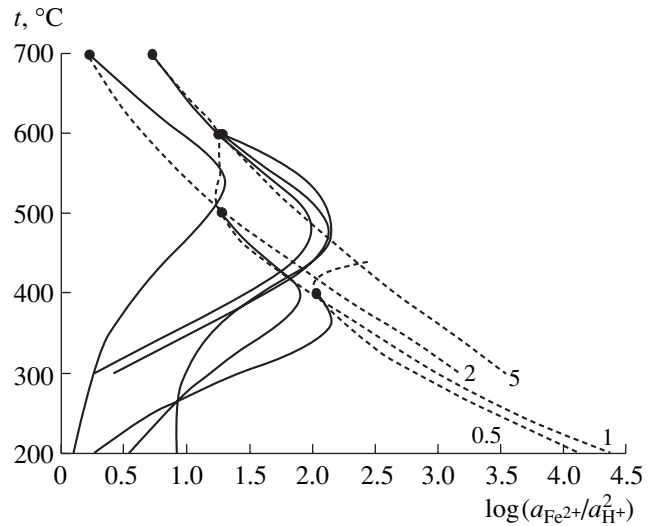


Fig. 4. Dependence of the $a_{Fe^{++}}/a_{H^+}^2$ ratio on temperature in a model chloride solution and a solution equilibrated with granite. Symbols are the same as in Fig. 1.

the development of acid leaching of granite and is in agreement with the wide occurrence of acid metasomatic rocks above cooling magmatic bodies. This phenomenon is most pronounced at a low P and high T . In the region of elevated T and P , the acidity of the solution increases less extensively.

It is obvious that these phenomena show opposite trends at increasing temperature ($\Delta_{Na,K} > 0$). In the zones of a positive temperature gradient, the relative alkalinity of solutions increases, which must result in the development of alkalic metasomatism.

The behavior of the bases in thermal gradient fields is more complicated. All bases show a considerable displacement of hydrolysis equilibria in accordance with the left-hand rule of Garrels (Figs. 2–4). On the other hand, variations in $a_{Me^{++}}/a_{H^+}^2$ in the solution have opposite directions owing to the competitive influences of the processes of HCl and $MeCl_2$ dissociation. The dominance of the former leads to a decrease in $a_{Me^{++}}/a_{H^+}^2$; the behavior of the bases approaches that of alkalis, which enhances the integral effect of the leaching of bases from the rock. This is largely characteristic of the low-temperature region, where $\Delta_{Ca,Mg,Fe} < 0$. The prevalence of the second tendency results in an absolute increase in $a_{Me^{++}}/a_{H^+}^2$, which may become even higher than that of the rock. This effect was observed in the high-temperature region for Mg and, especially, Fe. In the Ca–Mg–Fe sequence, the behavior of Ca is closer to the behavior of the alkali metals Na and K. Despite the complex character of $a_{Ca^{++}}/a_{H^+}^2$ variations, $\Delta_{Ca} < 0$ within the whole P – T range (Fig. 2), which must result

in Ca leaching from the rock at decreasing T . The same is true for Mg in the medium- and low-temperature part of the field, whereas $\Delta_{Mg} \equiv 0$ (Fig. 3) and $\Delta_{Fe} > 0$ (Fig. 4) at $T = 600$ – 700°C . This must be reflected in the persistence of mafic minerals and their relative enrichment in the rocks at the expense of feldspar dissolution, which can be characterized as high-temperature basification. It is changed by debasification with decreasing temperature. The opposite trends are observed at an increase in

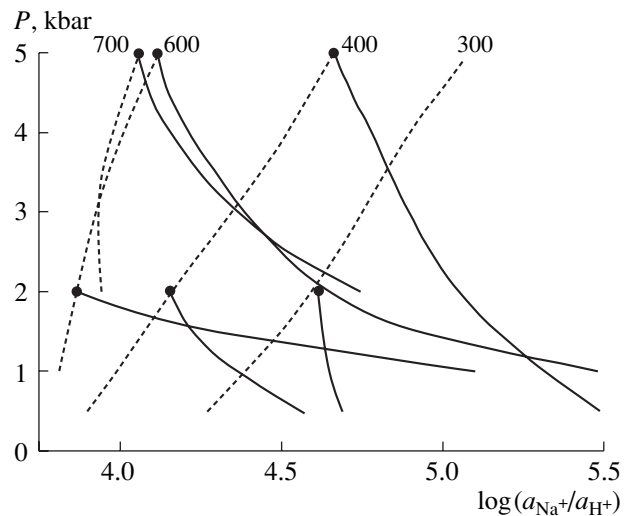


Fig. 5. Dependence of the a_{Na^+}/a_{H^+} ratio on pressure in a model chloride solution (solid lines) and in a solution equilibrated with granite (dashed lines). Numerals near the lines indicate temperature in degrees centigrade.

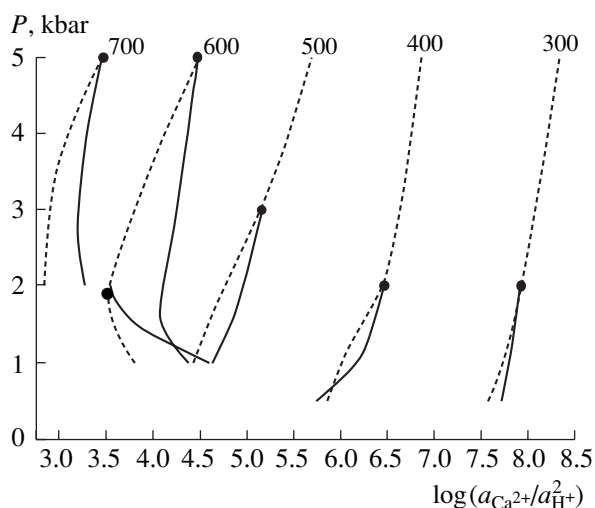


Fig. 6. Dependence of the $a_{Ca^{2+}}/a_{H^+}^2$ ratio on pressure in a model chloride solution and a solution equilibrated with granite. Symbols are the same as in Fig. 5.

temperature. Basification occurs under low-temperature conditions, and debasification, at high temperatures.

At any temperature, decompression results in a shift in the hydrolysis equilibria toward lower a_{Na^+}/a_{H^+} values owing to the negative volume effect of the respective reactions (Fig. 5). Simultaneously, the degree of dissociation of salts, acids, and bases decreases, and the net effect is that a_{Na^+}/a_{H^+} increases in the solution. Thus, the two processes operate in the same direction increasing $\Delta_{Na,K} > 0$ and promoting alkaline (sodic or

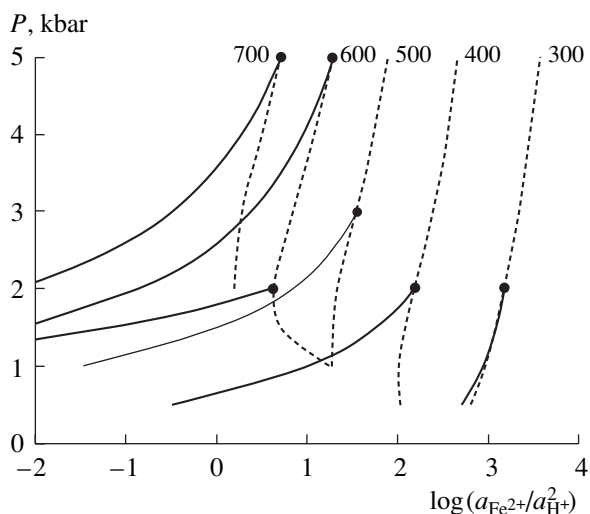


Fig. 8. Dependence of the $a_{Fe^{2+}}/a_{H^+}^2$ ratio on pressure in a model chloride solution and a solution equilibrated with granite. Symbols are the same as in Fig. 5.

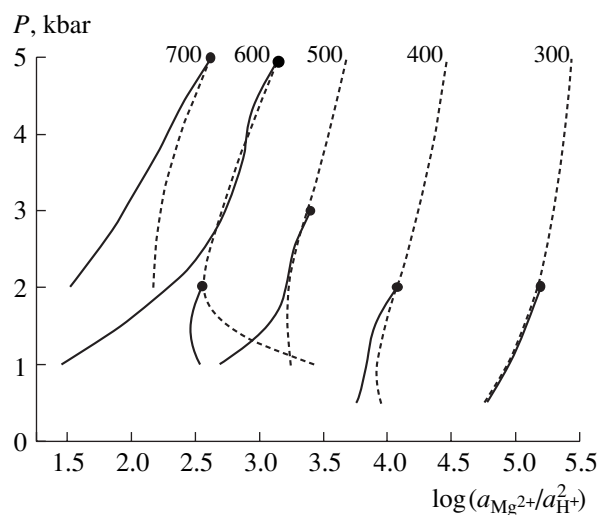
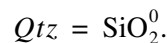


Fig. 7. Dependence of the $a_{Mg^{2+}}/a_{H^+}^2$ ratio on pressure in a model chloride solution and a solution equilibrated with granite. Symbols are the same as in Fig. 5.

potassic) metasomatism at a pressure decrease. In contrast, acid leaching must occur under compression conditions.

The behavior of Mg and Fe differs from that of Ca under pressure-gradient conditions. Similar to thermal gradient conditions, the departure from the behavior of alkalis increases in the sequence Ca–Mg–Fe. At high temperatures Ca shows a tendency to $\Delta_{Ca} > 0$ during decompression; it weakens at decreasing temperature and $\Delta_{Ca} \leq 0$ at $t = 300\text{--}400^\circ\text{C}$ (Fig. 6). Decompression at high temperatures ($t = 600\text{--}700^\circ\text{C}$), especially at low pressures, is characterized by $\Delta_{Mg, Fe} < 0$ owing to an extensive association of ions at the transition to, relatively, low-density solutions (Figs. 7, 8). This tendency fades out with decreasing temperature and vanishes at $T = 300^\circ\text{C}$, which is related to the enhancement of dissociation under such conditions. Thus, under decompression conditions, the high-temperature debasification with the participation of Mg and Fe is changed by the quasi-inert behavior of these elements at low temperatures. These processes are accompanied by a weak tendency to Ca metasomatism; otherwise, the behavior of Ca can remain almost inert. Correspondingly, high-temperature basification occurs under compression conditions.

The behavior of silica is important for the characterization of metasomatic processes. In contrast to other components, in quartz-bearing rocks it depends on the direction of shift of the quartz dissolution reaction



In terms of the model considered, the effects of quartz deposition–dissolution are controlled solely by

the pressure–temperature dependency of SiO_2^0 activity (concentration) in equilibrium with this mineral. As can be seen from Fig. 9, this parameter decreases almost universally with decreasing temperature and pressure. This must result in quartz precipitation during cooling and decompression and dissolution (rock desilication) during heating and compression. Only within a narrow field of low-density solutions, the opposite behavior of quartz dissolution is observed, an increase in its solubility with decreasing temperature.

NUMERICAL SIMULATION OF GRANITE–SOLUTION INTERACTION

The data presented above were obtained by a separate analysis of the evolution of the solution and rock before the beginning of their interaction. The results of the latter process can be assessed using model columns obtained by the method of flow-through step reactors [21, 22]. It should be pointed out that such a simulation is not restricted to the summation of data for particular components. For instance, if a solution is simultaneously oversaturated in several components, the phase relative to which the degree of oversaturation is the highest remains stable [23]. During modeling, the composition of a solution was first calculated in equilibrium with granite under initial P and T (see above), and then the interaction between the now disequilibrium solution and the granite was simulated under different, but constant P and T values. The metasomatic column was represented by a sequence of reactor cells; in each cell the solution formed in the previous cell reacted with the rock under given W/R values. Rock was absent in the first cell, where a vein mineral association was formed at the expense of solution oversaturation only; the associations of the metasomatic zones, from the rear to the frontal ones, were formed in the following cells with W/R from 10^5 to 1.

In the high-temperature region, the cooling of a solution resulted in the acid leaching of Na, K, and Ca, which was reflected in feldspar replacement by muscovite (table, column 1). This was accompanied by basification leading to the development of biotite and cordierite in the rear zones and silicification. The axial vein is made up of quartz with minor amounts of magnetite and cordierite.

Under low-temperature conditions, the same processes of silicification and acid leaching leading to rock muscovitization were accompanied by debasification, which resulted in the disappearance of chlorite and then calcite and magnetite (table, column 2).

Under the same temperature conditions, the heating of a solution produced the opposite effect characterized by the relation $\Delta > 0$ for alkalis and bases. Competitive relationships between these components resulted in the albitization and basification of rocks accompanied by quartz dissolution (table, column 3). In the inner zone, albite is replaced by chlorite and a carbonate vein is

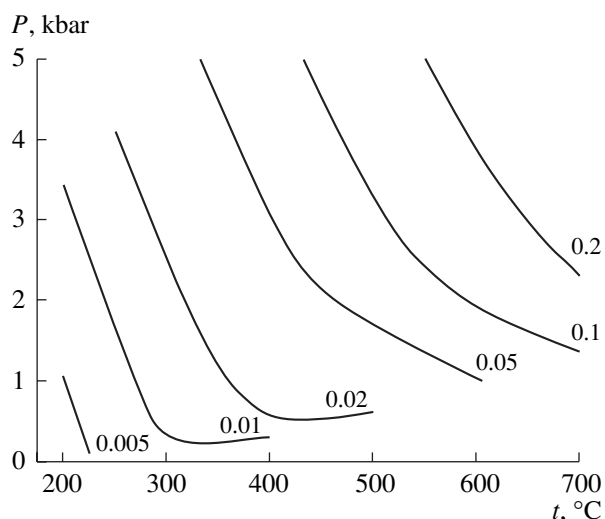


Fig. 9. Dependence of SiO_2^0 activity (mol/kg H_2O) in a solution equilibrated with granite on temperature and pressure.

formed. Variations in the CO_2 content in the solution resulted in various modifications of the column with the participation of epidote and calcite.

High-temperature decompression is characterized by the relations $\Delta_{\text{Na, K, Ca}} > 0$ and $\Delta_{\text{Mg, Fe}} \leq 0$, which resulted in the development of alkalic metasomatism accompanied by (Mg, Fe) debasification and silicification (table, column 4). As can be seen in Figs. 5 and 6, $\Delta_{\text{Na, K}}$ increased faster than Δ_{Ca} during decompression, which lowered the anorthite mole fraction of plagioclase. The alkalic character of the process was also reflected in a biotite change to a less aluminous composition (Al decreased from 1.4 to 1.1 atoms per unit cell). Then, both minerals were replaced by potassium feldspar. The axial vein was composed of quartz with minor potassium feldspar.

Low-temperature decompression also resulted in alkalic metasomatism, but debasification did not occur, because $\Delta_{\text{Mg, Fe}} \cong 0$ (table, column 5). The potassium feldspar and muscovite of the initial granite were replaced by albite, whereas biotite was preserved up to the proximal zone. The axial quartz vein contained biotite and calcite.

Opposite trends were observed for compression-related processes (table, column 6). Acid leaching and desilication resulted in the formation of a monomineral muscovite rear zone without a quartz vein.

DISCUSSION

All the modeled metasomatic rocks can be divided into quartz-bearing and quartz-free classes, which can be formed at a decrease and an increase in T and P , respectively. Each class can be further subdivided into four groups of metasomatic rocks: acidic and alkalic in

Model metasomatic columns formed under temperature and pressure gradient conditions in the granite--solution system

Column no.	Process type and conditions	Axial vein	Zone					
1	Cooling from 650 to 600°C, P = 2 kbar	<i>Qtz</i> <i>Mgt</i> (<i>Cd</i>)	<i>Qtz</i> <i>Cd</i>	<i>Qtz</i> <i>Cd</i> <i>Bt</i>	<i>Qtz</i> <i>Ms</i> <i>Bt</i>	<i>Qtz</i> <i>Pl₂₀</i> <i>Bt</i> <i>Ms</i>	<i>Pl₂₅</i> <i>Qtz</i> <i>Kfs</i> <i>Bt</i>	
2	Cooling from 350 to 300°C, P = 1 kbar	<i>Qtz</i> (<i>Ms</i>)	<i>Qtz</i> <i>Ms</i>	<i>Qtz</i> <i>Ms</i> <i>Mgt</i>	<i>Qtz</i> <i>Ms</i> <i>Cal</i> <i>Mgt</i>	<i>Qtz</i> <i>Ms</i> <i>Cal</i> <i>Chl</i> <i>Mgt</i>	<i>Qtz</i> <i>Ab</i> <i>Ms</i> <i>Chl</i> <i>Cal</i> <i>Mgt</i>	<i>Qtz</i> <i>Ab</i> <i>Kfs</i> <i>Ms</i> <i>Chl</i> <i>Cal</i> <i>Hem</i>
3	Heating from 250 to 300°C, P = 1 kbar	<i>Dol</i> (<i>Hem</i>)	<i>Chl</i>	<i>Ab</i> <i>Chl</i> (<i>Hem</i>)	<i>Ab</i> <i>Chl</i> <i>Cal</i> <i>Mgt</i>	<i>Ab</i> <i>Chl</i> <i>Qtz</i> <i>Cal</i> <i>Mgt</i>	<i>Ab</i> <i>Qtz</i> <i>Chl</i> <i>Kfs</i> <i>Cal</i> <i>Mgt</i>	<i>Ab</i> <i>Qtz</i> <i>Kfs</i> <i>Chl</i> <i>Ms</i> <i>Cal</i> <i>Mgt</i>
4	Decompression from 3 to 2 kbar at T = 600°C	<i>Qtz</i> (<i>Kfs</i>)	<i>Kfs</i> <i>Qtz</i>	<i>Kfs</i> <i>Qtz</i> <i>Bt</i>	<i>Kfs</i> <i>Qtz</i> <i>Bt</i> <i>Mgt</i>	<i>Kfs</i> <i>Qtz</i> <i>Pl₁₀</i> <i>Bt</i> <i>Mgt</i>	<i>Pl₂₅</i> <i>Qtz</i> <i>Kfs</i> <i>Bt</i> <i>Mgt</i>	
5	Decompression from 2 to 1 kbar at T = 350°C	<i>Qtz</i> <i>Cal</i> (<i>Bt</i>)	<i>Kfs</i> <i>Bt</i> <i>Qtz</i>	<i>Kfs</i> <i>Qtz</i> <i>Ab</i> <i>Bt</i>	<i>Pl₁₀</i> <i>Kfs</i> <i>Qtz</i> <i>Chl</i> <i>Mgt</i>	<i>Pl₁₀</i> <i>Qtz</i> <i>Kfs</i> <i>Chl</i> <i>Mgt</i> (<i>Cal</i>)	<i>Pl₁₀</i> <i>Qtz</i> <i>Kfs</i> <i>Chl</i> <i>Ms</i> <i>Cal</i> <i>Mgt</i>	
6	Compression from 1 to 2 kbar at T = 300°C	Missing	<i>Ms</i>	<i>Ms</i> <i>Chl</i>	<i>Qtz</i> <i>Ms</i> <i>Chl</i> <i>Mg</i>	<i>Qtz</i> <i>Ms</i> <i>Cal</i> <i>Chl</i> <i>Mgt</i>	<i>Qtz</i> <i>Ms</i> <i>Ab</i> <i>Chl</i> <i>Cal</i> <i>Mgt</i>	<i>Qtz</i> <i>Ab</i> <i>Ms</i> <i>Kfs</i> <i>Chl</i> <i>Cal</i> <i>Mgt</i>

Note: Minerals are listed in the sequence of decreasing abundance in the rocks. The minerals whose contents are lower than 1% are shown in parentheses.

combination with either basification or debasification products. The independence of these features follows from the different behavior of alkalis and bases, which is especially clear in the high-temperature region. If this behavior is of the same direction, acid leaching is accompanied by debasification, and alkalic metasomatism is accompanied by basification.

Classic acid associations of greisens, secondary quartzites, and beresites are formed in the former case, which is exemplified by column 2 (table). These rocks are usually located in the contact zone and at the roofs of granitoid intrusions at relatively shallow depths, which defines a considerable thermal gradient at temperatures of up to 400–450°C [24]. Acid leaching occurs most extensively under such conditions (Fig. 1).

An anomalous temperature dependency of quartz solubility is observed in this region (Fig. 9). This leads to a combination of acid leaching and rock desilication at decreasing temperatures. These processes are probably responsible for the formation of quartz-free varieties of secondary quartzites and greisens described in [24]. A decrease in $\Delta_{Na,K}$ at high T and P (Fig. 1) must cause the attenuation of acid leaching with depth under the conditions of formation of granite–gneiss complexes, which was noted by Korzhinskii [25].

The second group is represented by various quartz–biotite–potassium feldspar, quartz–biotite–albite, quartz–chlorite–potassium feldspar, and other wallrock metasomatic assemblages (table, column 5). Some of them are confined to fault zones and were formed in

extensional settings, which provided the leading role of pressure gradient [5].

The two remaining groups are characterized by the opposite behaviors of alkalis and bases. Under high temperatures, cooling-related acid leaching is accompanied by rock basification (table, column 1). This group probably includes quartz–cordierite, quartz–garnet, and other metasomatic rocks formed in metamorphic complexes during their retrograde development [26]. Their common feature is the absence of feldspars in the inner zones and retention of Mg–Fe aluminosilicates.

The fourth group includes the quartz–feldspar metasomatic rocks of regional fault zones, which are characterized by the alkalic trend of processes and removal of bases from inner zones [4]. They correspond to column 4 (table), which is formed under high-temperature decompression conditions.

Metasomatic rocks belonging to the quartz-free apogranite class are rarer because of the limited occurrence of heating and compression processes. Carbonaceous sericitolites from fold zones can be assigned to this class with a high degree of certainty [5]. In these rocks, sericite replaces all other minerals of metapelites in inner zones, including quartz, plagioclase, and chlorite. This suggests that desilication is combined with acid leaching and debasification, which requires low-temperature compression conditions (table, column 6). The latter is supported by structural observations (brecciation, cataclasis, mylonitization, and formation of slickensided surfaces).

Another group of desilication products includes various chloritoides, epidotes, carbonate, and other similar metasomatic rocks. They show development of basification with the formation of Ca, Mg, and Fe silicates replacing micas, feldspars, and quartz [4, 27]. These processes are illustrated by column 3 (table), which is formed under low-temperature heating conditions. The origin of this group of metasomatic rocks, as well as high-temperature basified rocks, is most controversial. They are usually assigned to the acid leaching of bases and their subsequent precipitation owing to the gradual neutralization of solution [4, 26, 27]. However, as was shown above, cooling solutions are continuously maintained in a state of undersaturation in alkalis and bases (Figs. 1–4). On the other hand, in an infiltration column, a solution is sequentially saturated in rock components up to the attainment of equilibrium, but oversaturation cannot be reached in such a case [23]. As was repeatedly noted, a transition from leaching to the precipitation of components requires an inversion in the state of the system [2]. In the gradient model considered here, the inversion is caused by a change in T and P gradients, which may occur in convective flows [10, 12] or during changes in the tectonic regime [5]. In the former case, the transition from leaching to basification can be promoted by a change in the direction of solution flow in a thermal gradient field, which provides

both the conjugation of corresponding metasomatic products and their repeatedly noted spatial isolation [4, 27].

Up to now, no reliable examples were reported for the two other groups of desilicated metasomatic rocks related to acid basification and alkalic debasification. Although the rocks of appropriate compositions are known (quartz-free anthophyllite–cordierite and feldspar metasomatic rocks, respectively, described in [4]), geologic and petrologic evidence is required for their formation under the influence of thermal and pressure gradients.

There are many other types of natural metasomatic rocks, even without considering rocks related to contact processes. This is related to the compositional diversity of the initial rocks affected by replacement and the sources (rocks or melts) of solutions. Moreover, both T and P usually vary under natural conditions, which may result in the appearance of transitional types of metasomatic columns not restricted to the types described above. Nonetheless, the tendencies established for the granite–solution system are applicable for other systems, because they are based on the general physicochemical relations in the behavior of minerals and solution species. The stringent relationships between the behavior of major components and T and P gradients provide a means of reconstructing these gradients from the observed natural trends in metasomatic transformations and, consequently, estimating the conditions of migration and precipitation of ore elements.

CONCLUSIONS

(1) The $a_{\text{Me}^+}/a_{\text{H}^+}$ values change in various directions in rock- and fluid-dominated systems under temperature and pressure varying conditions. The character of metasomatic processes accompanying the solution–rock interaction is controlled by the sign and magnitude of the integral effect of these changes.

(2) The behavior of Na and K in the granite–solution system is qualitatively uniform at various P and T . These components are leached at a decrease in T and an increase in P , whereas alkaline metasomatism occurs at an increase in T and a decrease in P . The behavior of Mg and Fe in the high-temperature region is very different from that of alkalis, and is similar to it at low temperatures. The behavior of Ca is transitional. Basification occurs during cooling at high temperatures and heating at low temperatures. High-temperature decompression results in the debasification of rocks. The precipitation of SiO_2 occurs at a decrease in T and P , and the desilication of rocks accompanies an increase in these parameters.

(3) The processes of acidic and alkalic metasomatism may be combined in different ways with the processes of basification and debasification, as well as with rock silicification and desilication. Each of these combinations is controlled by the type of the gradient field, with a decrease or an increase in temperature and pres-

sure, and can be correlated with a particular metasomatic association.

REFERENCES

1. D. S. Korzhinskii, "Acidity of Postmagmatic Solutions," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 12, 3–12 (1957).
2. V. A. Zharikov, "Problems of the Acidity of Ore-Bearing Fluids," in *Main Parameters of Natural Processes in Endogenous Ore Formation* (Nauka, Novosibirsk, 1979), Vol. 1, pp. 9–29 [in Russian].
3. V. A. Glebovitskii, "Geological and Physicochemical Relations of Metasomatism with Regional Metamorphism," in *Precambrian Metasomatism and Its Ore Potential* (Nauka, Moscow, 1989), pp. 197–207 [in Russian].
4. *Regional Metamorphic–Metasomatic Associations*, Ed. by D. V. Rundquist (Nedra, Leningrad, 1983) [in Russian].
5. A. B. Kol'tsov, *Metasomatic Processes at Gold Deposits in Metaterrigenous Sequences* (St. Petersburg Gos. Univ., St. Petersburg, 2002) [in Russian].
6. W. Fyfe, N. Price, and A. Thompson, *Fluids in the Earth's Crust* (Elsevier, Amsterdam, 1978; Mir, Moscow, 1981).
7. C. A. Heinrich, "The Chemistry of Hydrothermal Tin (-Tungsten) Ore Deposition," *Econ. Geol.* **85**, 457–481 (1990).
8. M. Yu. Korotaev, A. A. Pek, and M. N. Kim, "Infiltration Metasomatism in Gradient Fields: Modeling of the Formation of Metasomatic Veins," *Geokhimiya*, No. 1, 20–35 (1992).
9. D. S. Korzhinskii, "Open Systems with Perfectly Mobile Components and the Phase Rule," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 2, 3–14 (1949).
10. H. C. Helgeson, "Effects of Complex Formation in Flowing Fluids on the Hydrothermal Solubilities of Minerals as a Function of Fluid Pressure and Temperature in the Critical and Supercritical Regions of the System H_2O ," *Geochim. Cosmochim. Acta* **56**, 3191–3208 (1992).
11. S. A. Bushmin and A. L. Skvirskii, "Physicochemical Relationship of Metasomatism with the Retrograde Stage of Regional Metamorphism," in *Geology of Metamorphic Complexes* (Nauka, Sverdlovsk, 1990), pp. 13–20 [in Russian].
12. J. P. Raffensperger and G. Garven, "The Formation of Unconformity-Type Uranium Ore Deposits: I. Coupled Groundwater Flow and Heat Transport Modeling," *Am. J. Sci.* **295**, 581–636 (1995).
13. A. B. Kol'tsov and K. V. Zakharevich, "Syndeformation Metasomatic Processes in Fault Zones," *Vestn. St. Peterb. Univ. Ser. 7*, No. 21, 55–63 (1997).
14. A. M. McCaig, "Deep Fluid Circulation in Fault Zones," *Geology* **16**, 867–870 (1988).
15. V. F. Barabanov, *Geokhimiya* (Nedra, Leningrad, 1985) [in Russian].
16. R. G. Berman, "Internally Consistent Thermodynamic Data for Minerals in the System $Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$," *J. Petrol.* **29**, 445–522 (1988).
17. D. A. Sverjensky, J. J. Hemley, and W. M. D'Angelo, "Thermodynamic Assessment of Hydrothermal Alkali Feldspar–Mica–Aluminosilicate Equilibria," *Geochim. Cosmochim. Acta* **55**, 989–1004 (1991).
18. Yu. V. Shvarov, "Algorithmization of the Numeric Equilibrium Modeling of Dynamic Geochemical Processes," *Geokhimiya*, No. 6, 646–652 (1999) [*Geochem. Int.* **37**, 571–576 (1999)].
19. I. Diakonov, G. Pokrovski, J. Schott, et al., "An Experimental and Computational Study of Sodium–Aluminum Complexing in Crustal Fluids," *Geochim. Cosmochim. Acta* **60**, 197–211 (1996).
20. J. W. Johnson, E. H. Oelkers, and H. C. Helgeson, "SUPCRT 92: Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species and Reactions from 1 to 5000 bars and 0 to 1000°C," *Comp. Geosci.* **18**, 899–947 (1992).
21. M. V. Borisov, *Geochemical and Thermodynamic Models of Hydrothermal Vein Mineralization* (Nauchnyi Mir, Moscow, 2000) [in Russian].
22. D. V. Grichuk, *Thermodynamic Models of Submarine Hydrothermal Systems* (Nauchnyi Mir, Moscow, 2000) [in Russian].
23. D. S. Korzhinskii, *Theory of Metasomatic Zoning* (Nauka, Moscow, 1982) [in Russian].
24. *Metasomatism and Metasomatic Rocks*, Ed. by V. A. Zharikov and V. L. Rusinov (Nauchnyi Mir, Moscow, 1998) [in Russian].
25. D. S. Korzhinskii, "Sketches of Metasomatic Processes," in *Main Problems in the Theory of Magmatogenic Ore Deposits* (AN SSSR, Moscow, 1955), pp. 334–456 [in Russian].
26. V. A. Glebovitskii and S. A. Bushmin, *Postmigmatite Metasomatism* (Nauka, Leningrad, 1983) [in Russian].
27. V. B. Chekvaidze, *Wallrock Metasomatites of Sulfide–Base-Metal Deposits and Their Prospecting Significance* (Nedra, Moscow, 1981) [in Russian].