

Acid–Base Properties of Cooling Magmatic Fluid and D.S. Korzhinskii’s “Acidic Wave” Mechanism: Physicochemical Simulation Results

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*

Received June 16, 2014; in final form, November 18, 2014

Abstract—Data on the component composition and acid–base properties of cooling fluid in the systems H₂O–CO₂, H₂O–NaCl, and H₂O–rock-forming minerals, which were derived by minimizing the Gibbs free energy, and the evaluated contributions of major fluid components to its acid–base properties suggest that the main reason for the inversion of acid–base properties of magmatic fluids in the fluid–granite system is the opposite tendencies in the changes of the dissociation constants of acidic and basic fluid components in the course of fluid cooling.

DOI: 10.1134/S0869591115030029

INTRODUCTION

D.S. Korzhinskii’s hypothesis of the acidic effect accompanying fluid filtration through rocks provides the basis for the mechanism forming the so-called acidic wave as one of the main means of metasomatism in rocks in the absence of thermodynamic acid–base equilibrium between magmatic (supercritical) fluid and the material from which it has been derived (Korzhinskii, 1994). In his extensive review of natural metasomatic processes, D.S. Korzhinskii placed emphasis on the acid–base properties of endogenic solutions (which are hereafter referred to as A-B properties, components, and parameters). Based on the analysis of natural processes, he has concluded that “...each metasomatic process ... must pass through a stage of an acidic state of the solution” (Korzhinskii, 1955). Korzhinskii’s hypothesis of acidic filtration effect is able to qualitatively realistically describe the general acid–base evolutionary trends of natural magmatic fluids. The most significant progress in understanding the general evolutionary trends of natural solutions has been made in numerous models of systems fluid–rock as a mineral buffer (Karpov et al., 2001; Borisov, 2000; Grichuk, 2000; Ryzhenko et al., 1996, 1999; Avchenko et al., 2011). The determining factors of equilibrium and evolution of reaction solutions in these models are pressure, temperature, the fluid/rock (W/R) ratio, the mineral composition of the transport medium, and the chemical composition (which is usually unknown) of the deep or “external” fluid. Most of the models a priori assume that the deep

(magmatic) fluid is acidic, and neither the reasons for these properties of the fluid nor the mechanisms controlling them are discussed, in spite of at the clearly pronounced basic properties of the material of the source (chamber) from which the fluid is derived and the transport medium through which it percolates (Avchenko, 2009; Ivanov and Borisov, 1980; Karpov et al., 2001; Borisov, 2000).

In a few experimental studies, the different mobility of acidic and basic fluid components was explained by such mechanisms associated with solution filtration through porous materials as two-phase filtration, screening effect, and the differentiating of cations and anions in the course of diffusion under pressure and/or under the effect of electro-kinetic processes (Zharikov, 1963; Zharikov et al., 1961, 1999). These experimental studies have demonstrated that cations and anions can be differentiated in the process of two-phase filtration, thermodiffusion, and thermogravitation. It should be mentioned that some researchers have cast doubts on the plausibility of the hypothesis of the filtration effect itself as the major reason for and the driving force of the acidic wave (Kigai, 2009). The mechanism of acidic wave as the “outrunning” movement of volatile acidic components in fluid, as explained by D.S. Korzhinskii’s filtration effect, generally seems to be fairly realistic but can hardly play a determining role (Kigai and Tagirov, 2010). Doubts in the efficiency of this mechanism are provoked by the fact that high concentrations of alkalis and their conventionally accepted perfectly mobile behavior in metasomatic

processes should result in at least the neutralization of the acidic components of magmatic fluid.

Most researchers are prone to believe that the A-B properties of magmatic fluids (solutions) are controlled by the distribution reactions of minerals, and the dominant contribution to the composition and the A-B properties of magmatic fluid is thereby made by the most soluble rock-forming minerals containing alkalis (K and Na) and basic cations (Ca and Mg). Physicochemical simulations (for example, Ryzhenko et al., 1996, 1999) have demonstrated that practically all rock types (ranging from dunite to granite) should be in equilibrium with alkaline fluid at any geologically realistic P - T parameters, and the major components of this fluid should be K, Na, Si, Ca, Mg, Fe, and Al. In other words, the magmatic rocks from which the fluid is derived and rocks through which this fluid later percolates when ascending from the chamber should inevitably buffer the A-B properties of the fluid by means of water–rock (W/R) reactions. The A-B properties of deep fluids can also be affected by the composition and volume of meteoric fluids or those of unknown composition and by the A-B properties of magmatic fluids (Korzhinskii, 1973; Zotov and Pertsev, 1982).

As is known from recent thermodynamic simulations, the structure and, hence, the A-B properties of fluid (in P - T - X space) evolve in accordance with the temperature evolution of the complexation constants of acidic and basic components (Helgeson, 1964, 1969). Since any temperature and/or pressure decrease always increase the acidity of natural metasomatic fluid (Korzhinskii, 1955), it is reasonable to hypothesize that this factor should play an important (if not determining) role in the inversion in the A-B properties of the original deep (magmatic) fluid. Preservation of the acidic properties of the fluid filtering to the surface is hampered by its buffering by the host rocks, a process inevitable under any P - T conditions. At the same time, analysis of naturally occurring metasomatic and hydrothermal systems indicates that situations may often occur in which fluid ascent, its cooling, and the precipitation of ore mineralization from it take place at a significant weakening (if any at all) of interaction between the fluid and rocks. For instance, cooling fluid moving along significant fractures in rocks in a metasomatic process can merely insignificantly interact with the rocks, or not interact with them at all, i.e., the regime of the process is fluid-dominated ($W \gg R$). Weakening fluid buffering with rocks may occur in the course of metasomatism when vast volumes of deep fluid cease to interact with the rock that is sealed from the fluid by secondary minerals (usually quartz and micas) as an inevitable consequence of long-lasting reactions and equilibration with the first fluid portions according to the “flow through a pipe” scenario (Karpov et al., 2001). In such situations, it is reasonable to expect that fluid cooling should be associated with changes in its A-B properties

predominantly according to changes in the dissociation constants of the hydrolysis products (Helgeson, 1964). In other words, the A-B properties of fluid are modified as a result of a structural (internal according to Helgeson) transformation of the fluid without changes in its chemical composition. Another condition necessary for the A-B properties of a cooling fluid to vary is that the fluid should contain certain amounts of acidic components (along with basic ones), which can be borrowed from cooling melt, rock, or deep fluid (Korzhinskii, 1973). It is therewith important that the rates of the processes of component (structural) transformation of the fluid during its cooling are several orders of magnitude higher than the dissolution rates of minerals (Helgeson, 1964).

Within the framework of Korzhinskii’s theory, thermodynamic simulations have been carried out in attempt to explain the effects of the evolution in the composition and A-B properties of natural solutions by tendencies in the temperature variations in the properties of alkali metals as fluid components. It has been proved (Naumov and Dorofeeva, 1975; Naumov and Naumov, 1977; Kigai and Tagirov, 2010) that “the cooling of chloride solutions is associated with a systematic evolution of the A-B equilibrium according to D.S. Korzhinskii’s concept”. The evolution in the acid–base properties of solutions was thereby estimated using the $\text{pH}(P-T)$ relative to the $\text{pH}(P-T)$ of neutral water. These calculation data can be assumed as provisional in the absence of estimates of the effects of the host rocks. It has been experimentally established that the acidity of chloride solutions may vary depending on the chemical composition of solutions and the presence of various solid phases in equilibrium with these solutions (Rafal’skii, 1987). In hydrothermal experiments in solution–mineral–rock systems (for example, Zharikov et al., 1961; Zharikov, 1963; Zharikov and Rafal’skii, 1987; Zarskii et al., 1981), inevitable kinetic effects make it hard to derive reliable enough equilibrium data on the acid–base properties of the reaction solutions within broad P - T ranges.

In view of the aforesaid, our research was focused on thermodynamic simulation of variations in the acid–base properties of magmatic fluid in the course of its cooling. We planned to conduct the simulations in the following sequence: (1) to estimate the contributions of dominant components of natural fluids to their composition and A-B properties in the systems H_2O – CO_2 , H_2O – NaCl , and H_2O –chlorides of basic cations; (2) to evaluate the effects of major components of natural fluids (CO_2 , NaCl , etc.) on the composition and A-B properties of the reaction solutions in systems water–rock-forming minerals; and (3) to calculate the composition and evaluate the A-B properties of cooling fluid in equilibrium with granite during fluid ascent without interaction with wall rocks.

THERMODYNAMIC SIMULATION

Our thermodynamic simulations were conducted with the Selector-C program package (Karpov, 1981). The theory, algorithms, and software are described in (Chudnenko and Karpov, 2003; Chudnenko, 2010). Application of the multipurpose Selector-C software in studying petrogenetic processes and principal results is described in (Avchenko et al., 2009). Temperature and pressure were specified in the vicinity of the most thoroughly studied critical trends in the ternary and binary fluid systems $\text{CO}_2\text{--H}_2\text{O--NaCl}$ (Shmulovich, 1988; Helgeson, 1979; Takenouchi and Kennedy, 1964; Popp and Frantz, 1989; Duan and Sun, 2003). For the sake of interpretation simplicity of the results, the pressure and temperature were assumed according to values on a straight line from $650^\circ\text{C}/1300$ bar to $25^\circ\text{C}/50$ bar (low-pressure trend). To verify the results and compare them with those in (Ryzhenko et al., 1996), a trend from $650^\circ\text{C}/5500$ bar to $25^\circ\text{C}/50$ bar was applied. The models of the thermodynamic fluid–rock system involved independent (according to J. Gibbs) acidic and basic components (Al–Si–Ca–Fe–Mg–K–Na–C–Cl–S–H–O–e) and numerous primary and (possibly) newly formed mineral phases. The models involved 140 components of aqueous solution and a gas phase consisting of CO , CO_2 , CH_4 , HCl , H_2S , SO_2 , H_2 , and O_2 . We made use of the multireservoir flow-through model (Karpov et al., 1997) in which the reaction fluid cooled according to an assumed P - T trend as a result of single fluid–mineral–rock interaction acts in the course of fluid flow from the first reservoir (which contained fluid and a solid phase) through the other nine reservoirs and the associated precipitation of secondary minerals from this fluid.

It is known that the major components of mineral-forming solutions are (along with water) alkali chlorides and carbon dioxide (Roedder, 1972). The concentrations of alkali chlorides can be as high as 10 mol/kg H_2O , within 34–82 wt % (Naumov and Dorofeeva, 1975; Li et al., 2011), and the carbon dioxide contents can be higher than that of water, although the former is commonly the second most abundant component. Because of the scarcity of data on the $\text{H}_2\text{O--CO}_2\text{--NaCl}$ system (Shmulovich, 1988; Helgeson, 1979), we have conducted our simulations with diluted solutions (to decrease the ionic strength and preclude the onset of immiscibility; Franz et al., 1992). The information is presented in the form of plots showing pH, $\log m_{\text{OH}^-}$, $\log m_{\text{H}^+}$, and $\log m_i$ of aqueous species within the range of 10^1 to 10^{-9} and thus well enough illustrates how the A–B state of the fluid is formed. To unify the results and make it possible to compare them, the simulations were carried out with solutions in 1 kg of H_2O . The systematic variations in the pH(P - T) values were viewed as indications of the evolution of the solution acidity, whereas the

proportions of H^+ and OH^- provided visual and quantitative information. In other words, information on any inversion in the A–B properties of the fluid was provided by the $\pm(\log m_{\text{OH}^-} - \log m_{\text{H}^+})$ expression, whose sign and value are indicators of the A–B state of the solution, the onset of solution neutrality ($\log m_{\text{OH}^-} = \log m_{\text{H}^+}$), and the degree of any deviations in solution properties from neutrality.

THERMODYNAMIC SIMULATION RESULTS

It has been established that 1 m carbon dioxide solution is neutral at $650\text{--}500^\circ\text{C}$ and becomes progressively more and more acidic as the temperature decreases (Fig. 1a). A decrease in the CO_2 concentration suppresses the acidity inversion temperature (T_{inv}): for example, the neutrality field of 0.1 m, 0.001 m, and 0.0001 m solutions expands from 650 to 500, 350, and 300°C , respectively. Solutions of Na and K chlorides (0.001 m and 0.1–1.0 m) at high temperatures are alkaline but become neutral when cooled below 250 and 350°C , respectively (Fig. 1b). The reason for the neutralization of chloride solution is HCl^0 complexation and its greater dissociation at cooling (Figs. 1b, 1c for the $\text{H}_2\text{O--}0.1\text{mNaCl--}0.1\text{mCO}_2$). In view of these results, we cannot agree that, according to (Naumov and Dorofeev, 1975; Naumov and Naumov, 1977), “chloride and carbon dioxide solutions show analogous temperature tendencies in the variations of the hydrogen indicator”. As follows from our simulations, alkali chlorides in cooling fluid at a high temperature weaken the acidic properties of carbon dioxide solutions and shift their inversion temperature toward lower values (Fig. 1c). In the region of high concentrations of components in the $\text{H}_2\text{O--}0.1\text{mNaCl--}0.1\text{mCO}_2$ system, the T_{inv} of the cooling fluid varies, depending on the NaCl/CO_2 mole ratio (from 0.9 to 0.1), merely insignificantly, within $\pm 50^\circ\text{C}$. At low NaCl concentrations (from 0.0001 to 0.1 m) in 0.1 m aqueous carbon dioxide solution, T_{inv} decreases from 500 to 400°C .

A tendency toward an acidic inversion at cooling is proved to be also typical of chloride solutions of basic cations. For example, 1 m MgCl_2 and CaCl_2 solutions become acidic when cooled from 650 to 540°C . At high temperatures, originally acidic aqueous FeCl_2 , SO_2 , and H_2S solutions (0.001 m) become even more acidic when cooled. HCl and NaOH solutions preserve their A–B properties throughout the whole P - T range. Our simulations thus indicate that fluids in carbonate- and chloride-rich systems become acidic mostly under the effect of increasing proton activity as a consequence of more significant dissociation of carbonic, sulfuric, and hydrochloric acid solutions when the fluids are cooled.

During the next phase of our research, we examined the effects of CO_2 and NaCl on the A–B state of

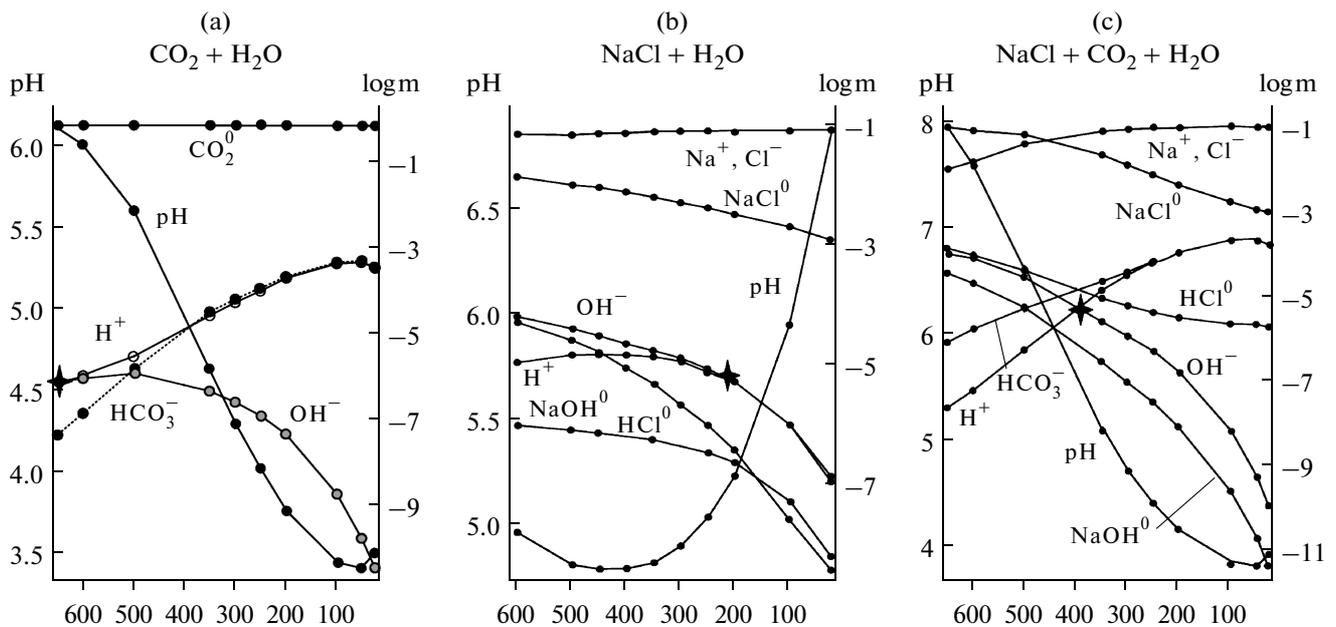


Fig. 1. Evolution of the component composition of fluid and its pH in the course of cooling in the systems (a) H₂O–CO₂, (b) H₂O–NaCl, and (c) H₂O–NaCl–CO₂. The asterisk marks the temperature of acidic inversion.

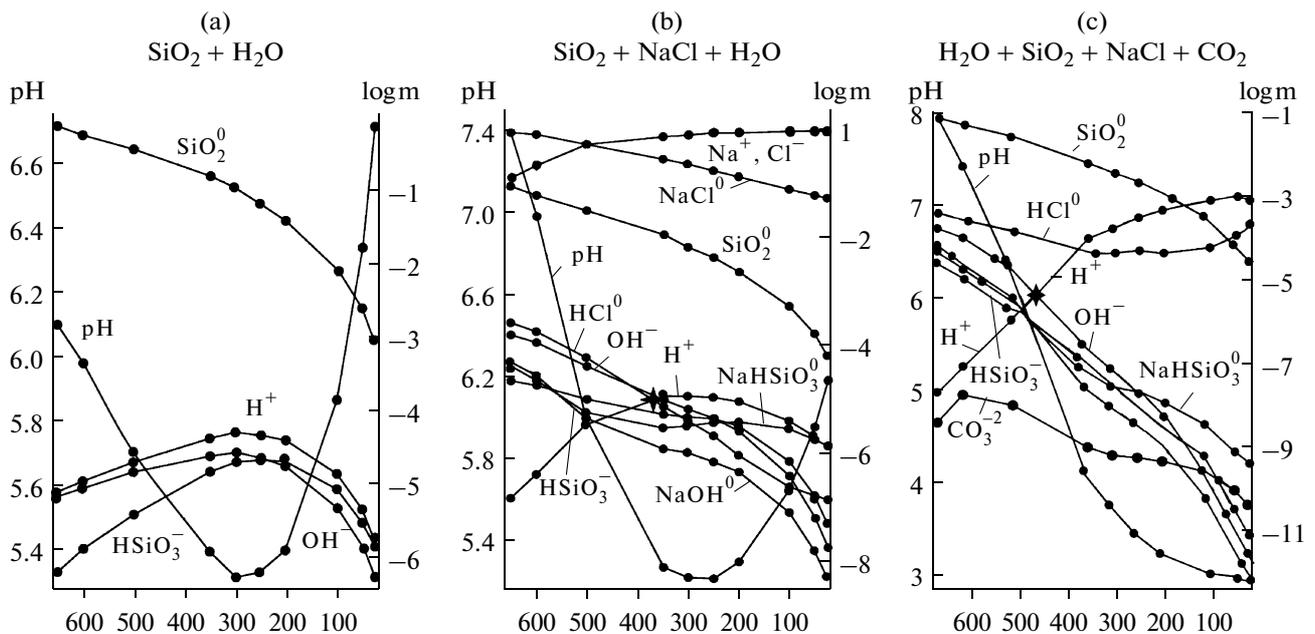


Fig. 2. Component composition and pH of solution in the systems (a) H₂O–SiO₂ (a), H₂O–SiO₂–NaCl, and (c) H₂O–SiO₂–NaCl–CO₂. The asterisk marks the temperature of acidic inversion.

cooling fluids in fluid–mineral systems. The simulations were conducted with regard for data on the parameters under which the mineral assemblages have crystallized: *P*–*T* data derived from studying gas–liquid inclusions (Roedder, 1972; Naumov and Tugarinov, 1969). Minerals free of alkalis and bases (quartz, kaolinite, corundum, and magnetite) generate acidic solu-

tions when occurring in equilibrium with pure H₂O or solutions with CO₂ and NaCl at any *P*–*T* parameters. As an illustrative example, Figs. 2a–2c show how does the acidity of the cooling solution in the H₂O–SiO₂–NaCl system change. At high *P*–*T* conditions, solutions originally in equilibrium with quartz (Fig. 2a) to which 1 m NaCl is added are alkaline (Fig. 2b), but

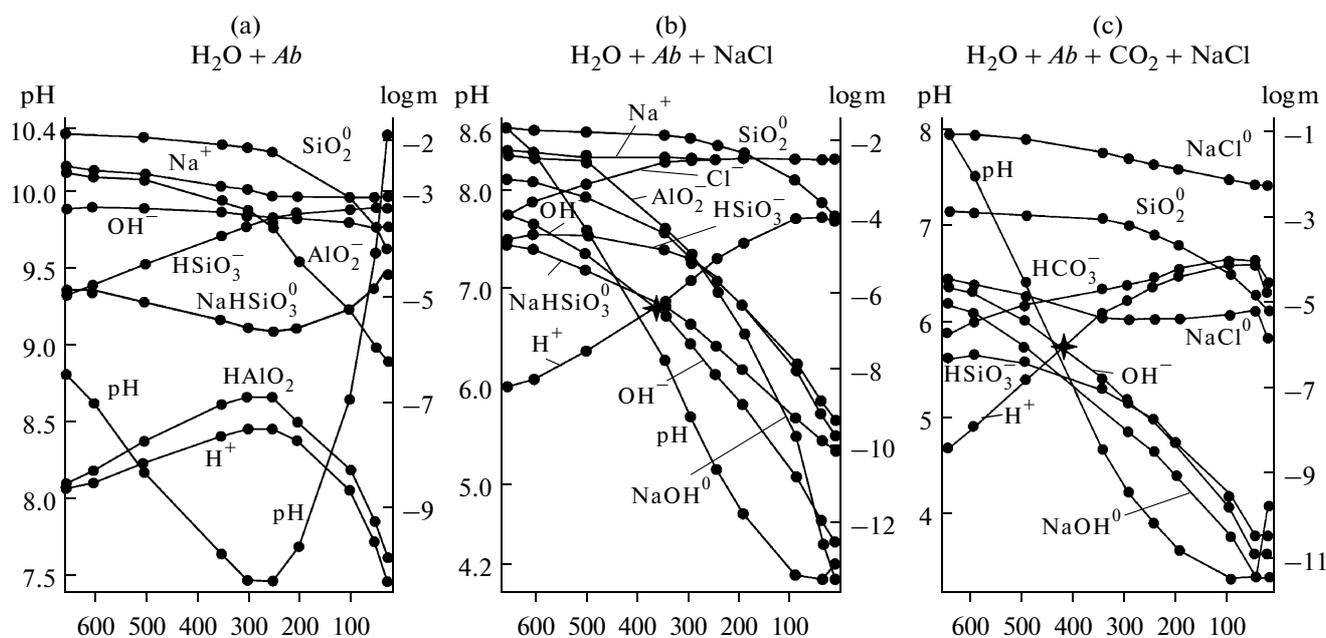


Fig. 3. Component composition and the temperature of pH inversion of cooling fluid in the systems (a) H₂O–Ab, (b) H₂O–Ab–CO₂, and (c) H₂O–Ab–CO₂–NaCl. The asterisk marks the temperature of acidic inversion.

undergo an acidic inversion when cooled to 350°C because of dissociation of the aqueous components SiO₂⁰, NaHSiO₃⁰, and HCl⁰. Addition of 1 m CO₂ results in a significant increase in the acidity of the solution cooled below approximately 460°C because of strong CO₂ buffering (i.e., at the dissociation of carbonic acid) (Fig. 2c).

Solutions in the systems water–(K, Na) feldspars–biotite and other minerals are always alkaline, i.e., log OH⁻ >> log H⁺ throughout the whole *P*–*T* range. When 1 m CO₂ is added to originally alkaline solution in the water–albite system (Fig. 3a), and an acidic inversion occurs when the solution is cooled to 270°C (Fig. 3b). The alkaline properties of cooled solution in the H₂O–Ab–NaCl–CO₂ system are preserved to a temperature of 350°C, and the solution becomes acidic when cooled. The inversion temperature of this solution increases to 430°C if the NaCl concentration is increased to 1 m (Fig. 3c).

Our analysis of a great number of model simulations for aqueous solutions of other aluminosilicates (biotite, dioctahedral micas, and pyroxenes) in the presence of 0.5–1 moles of CO₂ and NaCl has shown that inversion in the acidity of the originally alkaline fluid is also reached when the fluids are cooled, mostly because of the HSiO₃⁻ and HCO₃⁻ species and the dissociation of HCl⁰. Origin of HCl⁰ as a result of reactions of NaCl as a major fluid component with minerals of the rocks and dissociation of the former in H₂O–silicate–NaCl models are consistent with data in (Shinohara, 1989; Kazahaya and Shinohara, 1991), in

which a model was suggested for the origin of HCl and was proved that this component plays a significant role in controlling the acidity of volcanic gases when they ascend to the surface. The simulations thus imply that carbon dioxide and chlorides of alkalis (as major fluid components) in solutions in systems of water with rock-forming minerals induce an inversion of the A–B properties of the solutions when they are cooled. An increase in the concentrations of these components in the solutions oppositely affect the inversion temperatures: an increase in the carbon dioxide concentrations increase these temperatures, whereas increasing concentrations of chlorides conversely decrease these temperatures. The main reasons for the inversion of cooling fluids are differences in the behavior of the dissociation constants of the hydrolysis products: an increase in the constants of acidic components and a decrease in the constants of less soluble basic components of the solutions (Johnson et al., 1992).

The aforementioned data derived from the calculation of reactions (CO₂, NaCl)–fluid–minerals demonstrate that it is principally possible for a multicomponent natural fluid to become acidic when cooled. This conclusion is fully applicable to cooling fluids in fluid–rock systems. As a model rock, we made use of granite of the following composition (wt %): 71.75 SiO₂, 14.41 Al₂O₃, 1.7 FeO, 1.22 Fe₂O₃, 0.71 MgO, 1.63 CaO, 3.70 Na₂O, and 4.09 K₂O. The granite was assumed to contain the following clark concentrations: 240 ppm Cl, 300 ppm C, and 400 ppm S (Vinogradov, 1962). To simplify the composition of the simulated assemblage, we assumed that the rock was sulfur-free. The composition of the *original* mag-

matic fluid was simulated by solving the inverse problem (Avchenko, 2009), i.e., was derived from the condition of its equilibrium with the model mineral assemblage adequate to the naturally occurring one. At $W/R = 0.01$ (10 g of H_2O per 1 kg of rock), $650^\circ C$, and 1200 bar, we have simulated the following equilibrium mineral assemblage of granite (in wt %): 31.8 feldspar $(K_{0.73}Na_{0.27})(AlSi_3)_4O_8$ + 31.11 plagioclase $(Ca_{0.25}Na_{0.75})(Al_{1.25}Si_{2.75})_4O_8$ + 1.33 biotite $Na_{0.13}Al_{1.18}Fe_{0.25}K_{0.87}Mg_{2.6}Si_{2.9}H_2O_{12}$ + $3.06Fe_3O_4$ + 2.7 cordierite $Al_4Mg_2Si_5H_{0.72}O_{18.4}$ + $30.0SiO_2$. Note that the simulations were carried out with solid solutions of rock-forming minerals that were necessary to form the mineral assemblage (Avchenko, 2009; Chudnenko, 2010). In this situation, similarities between the modal and chemical compositions of the simulated and natural associations are a criterion of the plausibility of the simulated A-B properties of the reaction solutions. The redox state of granite at $650^\circ C$ and 1200 bar is close to the QFM buffer, $\log f_{O_2}$ 10–16, and fluid in equilibrium with the granite has pH 6.53, which is consistent with data in (Ryzhenko et al., 1999).

Figure 4 shows the simulated original composition and properties of fluid in equilibrium with granite and its evolution at cooling. This figure also illustrates the variations in pH of the fluid and its logm along the low-pressure P - T path. It is not possible to show the $\log m = f(P-T)$ dependences for all of more than 50 aqueous species in this figure, and the figure displays only such dependences for dominant species whose concentrations are higher than 10^{-4} to 10^{-9} m. These dependences illustrate the extent of the quantitative transfer, transformation, and redistribution of acidic and basic aqueous species and generally reflect the mechanism of the inversion of the A-B properties of cooling fluids. The factor undoubtedly controlling the acidity of the fluids is the origin and dissociation of silicic, carbonic, and hydrochloric acids, the weak solubility of major rock components ($Ca, Mg \approx 10^{-7}$), and extremely high SiO_2^0 concentrations of approximately 10^{-1} to 10^{-4} m (Avchenko, 2009; Khudolozhkin and Sharova, 2011; Borisov, 2000).

As can be seen in Fig. 4, the model reaction solution in equilibrium with granite becomes acidic when cooled to $600^\circ C$ if the rock contains even such low (0.001 m) carbon and chlorine concentrations. Simulations indicate that a decrease in the chlorine and carbon concentrations by one order of magnitude decreases T_{inv} to approximately $200^\circ C$. An increase in the concentrations of these acidic components relative to their clark concentrations assumed in these simulations, or introduction of sulfur and, particularly, fluorine, are favorable for an increase in the inversion temperature up to values close to melt temperatures. It is pertinent to mention that fluid cooling in all models with silicates is associated with the precipitation of

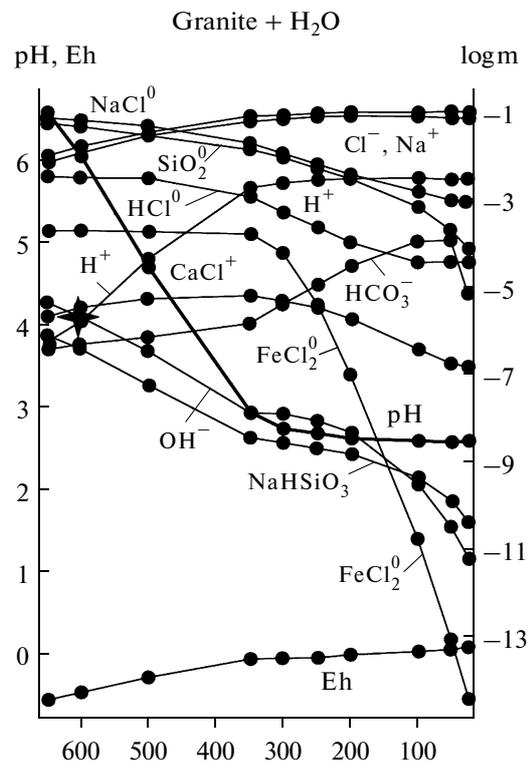


Fig. 4. Component composition of cooling solution, T_{inv} , pH, and Eh in the system granite–water. The asterisk marks the temperature of acidic inversion.

quartz throughout the whole P - T range. Its mass in the reservoirs is controlled by temperature and the amount of fluid. The acidic properties of quartz (Fig. 2a) maintain the acidity of fluid in later portions. The thermodynamic model of cooling fluid turned out to be highly instrumental in studying the behavior of ore-forming components (Au and Ag) as functions of parameters of ore-transporting fluid according to the “flow through a pipe” model (Karpov et al., 2001).

In light of our results, it is pertinent to emphasize the following important comments and conclusions expressed by D.S. Korzhinskii: (1) “the early stage of the postmagmatic process should be referred to as a high-temperature stage ... and only provisionally as alkaline, because the actual state of solutions during this stage was neutral rather than alkaline”; (2) “however, the onset of an acidic stage under various conditions is not marked by any temperature value, and this stage can begin at the lowest temperatures of the high-temperature range or those of the medium-temperature one”; and (3) “the main role is played by processes of internal regrouping in the cooling fluid” (Korzhinskii, 1955, 1994). These conclusions and observations are completely corroborated by our simulation results. However, it should be stressed that the nearness or farness of the onset of the acidic stage of fluid relative to its source can hardly be somehow related to the filtration effect.

The model of cooling magmatic fluid in the absence of any buffer control of its A-B properties by the host rocks corresponds to an idealized situation and should be appended by real models, in which the original fluid interacts with host rocks when cooling. The flow of magmatic fluid along fractures and permeable zones to which fluid fluxes are focused, its filtration through rocks of various permeability, the cooling rate of the magmatic chamber, the variations in the concentrations and solubility of acidic gases in the melts, the variations in the composition of the A-B components of the host rocks (Omel'yanenko, 1968, 1978), the possible effects of usually acidic meteoric waters (Karpov et al., 2001) and/or intratelluric fluids as agents of granite-forming processes (Yarmolyuk, 1982; Korzhinskii, 1973; Volokhov, 1982), and particularly, pressure and temperature gradients in "contact leaching" regions (Korzhinskii, 1955) predetermine the real spatiotemporal variations in mineralogical and geochemical characteristics of fluid-rock systems, including the acid-base and redox properties of their fluids. This gives rise to a multitude of diverse models, ranging from the above model in which the effects of the host rocks are ignored to those realistically enough reproducing naturally occurring (in accordance with Korzhinskii's concept) situations of neutralization and basic buffering of acidic magmatic fluid by host rocks. In view of this our further efforts shall be focused on the application of the suggested model to real fluid-rock systems and verification of the model using mineralogical and geochemical information on the fluid sources and rocks on the *P-T* cooling trend.

CONCLUSIONS

Our simulations indicate that fluid can become acidic, i.e., an "acidic wave" can be generated, if (a) the fluid is cooled and the solubility (and hence, the acid-base effect) of basic components of the rocks decreases, whereas the effects of acidic components increase because of their stronger dissociation; (b) the rocks contain necessary concentrations of acidic components, which ensure the dominance of the chemical (isothermal-isobaric) potential of proton over the potential of hydroxyl. The increase in the proton potential in the cooling solution is caused by a systematic change in the ratios of the isobaric-isothermal potentials of dependent and independent components of the fluid-rock system, see formula 3.44 in (Chudnenko, 2010). This condition is fulfilled when the A-B properties of solutions are formed in chemical titration reactions (Pauling and Pauling, 1975) and the redox parameters of gases (f_{O_2}) are established in fluid-rock redox reactions (Khudolozhkin and Sharova, 2011). The only difference between them is that an A-B state of a cooling "acidic wave" is a function not only of the proportions of reacting masses but also of the thermodynamic effect of the transformation of the component composition of the fluid. In

such situations, the total activity (capacity) of acidic components of the fluid during its thermodynamic transformation increases and becomes high enough to neutralize and overpass the total capacity of basic components of the rock.

REFERENCES

- Avchenko, O.V., Chudnenko, K.V., and Aleksandrov, I.A., *Osnovy fiziko-khimicheskogo modelirovaniya mineral'nykh sistem* (Principles of Physicochemical Modeling of Mineral Systems), Moscow: Nauka, 2009.
- Avchenko, O.V., Chudnenko, K.V., Aleksandrov, I.A., and Khudolozhkin, V.O., Adaptation of the SELECTOR-C program package for solving petrogenetic problems of metamorphic rocks, "Geochem. Int.," 2011, vol. 49, no. 2, 139–153.
- Borisov, M.V., *Geokhimicheskie i termodinamicheskie modeli zhil'nogo gidrotermal'nogo rudoobrazovaniya* (Geochemical and Thermodynamic Models of Vein Hydrothermal Ore Formation), Moscow: Nauchnyi mir, 2000.
- Borisov, M.V. and Shvarov, Yu.V., Effect of wall rocks on the efficiency of hydrothermal ore-forming processes, *Geochem. Int.* 2010, vol. 48, no. 9, pp. 940–945.
- Chudnenko, K.V., *Termodinamicheskoe modelirovanie v geokhimii* (Thermodynamic Simulations in Geochemistry), Novosibirsk: GEO, 2010.
- Chudnenko, K.V. and Karpov, I.K., *Selektor-Windows, programnoe sredstvo rascheta khimicheskikh ravnovesii minimizatsiei termodinamicheskikh potentsialov. Kratkaya instruksiya* (Selector-Windows, a Program Tool for Calculation of Chemical Equilibria by Minimization of Thermodynamic Potentials: A Concise Manual), Irkutsk, 2003.
- Duan, Z.H. and Sun, R., An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar, *Chem. Geol.*, 2003, vol. 193, pp. 253–271.
- Frantz, J.D., Popp, R.K., and Hoering, T.C., The compositional limits of fluid immiscibility in the system H₂O–NaCl–CO₂ as determined with the use of synthetic fluid inclusions in conjunction with mass spectrometry, *Chem. Geol.*, 1992, vol. 98, nos. 3–4, pp. 237–255.
- Grichuk, M.V., *Termodinamicheskie modeli submarinnykh gidrotermal'nykh sistem* (Thermodynamic Models of Submarine Hydrothermal Systems), Moscow: Nauchnyi mir, 2000.
- Helgeson, H., Thermodynamics of hydrothermal systems at elevated temperatures and pressures, *Am. J. Sci.*, 1969, vol. 267, pp. 729–804.
- Ivanov, I.P. and Borisov, M.V., Assessment of composition of primary melt during metasomatic replacement of the rocks, *Geokhimiya*, 1980, no. 12, pp. 1797–1806.
- Johnson, J.W., Oelkers, E.H., et al. Supcrt-92: software package for calculating the standard molal thermodynamic properties of mineral, gases, aqueous species, and reactions from 1 to 5000 bars and 0 to 1000°C, *Comp. Geosci.*, 1992, vol. 18, pp. 899–947.
- Karpov, I.K., *Fiziko-khimicheskoe modelirovanie na EVM v geokhimii* (Physicochemical Numerical Simulations in Geochemistry), Novosibirsk: Nauka, 1981.
- Karpov, I.K., Chudnenko, K.V., and Kulik, D.A., Modeling chemical mass-transfer in geochemical processes: thermodynamic relations, conditions of equilibria and numerical algorithms, *Am. J. Sci.*, 1997, vol. 297, pp. 767–806.

- Karpov, I.K., Chudnenko, K.V., Kravtsova, R.G., and Bychinskii, V.A., Simulation of physicochemical processes of dissolution, transport, and deposition of gold in epithermal Au–Ag deposits in northeastern Russia, *Russ. Geol. Geophys.*, 2001, vol. 42, no. 3, pp. 393–408.
- Helgeson, H., *Complexing and Hydrothermal Ore Deposition*, New York: Moscow, 1964.
- Helgeson, H., Mass transfer among minerals and hydrothermal solutions, in *Geochemistry of Hydrothermal Ore Deposits*, New York: Wiley, pp. 567–610, 1979.
- Khudolozhkin, V.O. and Sharova, O.I., Oxygen regime of granulite metamorphism: modeling by the method of Gibbs free energy minimization, *Petrology*, 2011, vol. 19, no. 1, pp. 102–107.
- Kigai, I.N., On controversial resolutions of some problems of metasomatism and ore formation, in *Tez. dokl. "Fiziko-khimicheskie faktory petro- i rudogeneza: novye rubezhi". Materialy konferentsii, posvyashchennoi 110-letiyu so dnya rozhdeniya akademika D.S. Korzhinskogo* (Abstracts "Physicochemical Factors of Rock- and Ore-Forming Processes: New Frontiers," Proceedings of Conference Dedicated to the 110th Anniversary of D.S. Korzhinskii), Moscow: IGEM RAN, 2009, pp. 167–170.
- Kigai, I.N. and Tagirov, B.R., Evolution of acidity of hydrothermal fluids related to hydrolysis of chlorides, *Petrology*, 2010, vol. 18, no. 3, pp. 252–261.
- Korzhinskii, D.S., On problem of the derivation of equations of infiltration and diffusion metasomatic zoning, *Dokl. Akad. Nauk SSSR*, 1953, vol. 88, no. 3, pp. 1102–1114.
- Korzhinskii, D.S., Essay on metasomatic processes, in *Osnovnye problemy v uchenii o magmatogennykh rudnykh mestorozhdeniyakh* (Main Problems in the Theory of Magmatogenic Ore Deposits), Moscow: Izd. AN SSSR, 1955, pp. 376–377.
- Korzhinskii, D.S., Metamagmatic Processes, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1973, no. 12, pp. 3–7.
- Korzhinskii, D.S., *Izbrannye trudy. Kislotno-osnovnoe vzaimodeistvie v mineraloobrazuyushchikh sistemakh* (Selected Works. Acid–Base Interaction in the Mineral-Forming Systems), Moscow: Nauka, 1994.
- Li, J.X., Li, G.M., Qin, K.Z., and Xiao, B., High temperature magmatic fluid exsolved from magma at the Duobuza porphyry copper–gold deposit, northern Tibet, *Geofluids*, 2011, vol. 11, pp. 134–143.
- Naumov, V.B. and Tugarinov, A.I., *PT* conditions of formation of hydrothermal uranium deposits, *Geokhimiya*, 1969, no. 2, pp. 131–146.
- Naumov, G.B. and Dorofeeva, V.A., Chemical evolution of acidity of endogenic solutions, *Geokhimiya*, 1975, no. 2, pp. 248–258.
- Naumov, G.B. and Naumov, V.B., Effect of temperature and pressure on the acidity of endogenic solutions and staged formation, *Geol. Rudn. Mestorozhd.*, 1977, no. 1, pp. 13–23.
- Omel'yanenko, B.I., Physicochemical conditions of beresitization-type wall-rock alteration, in *Metasomatizm i drugie voprosy fiziko-khimicheskoi petrologii* (Metasomatism and Other Problems of Physicochemical Petrology), Moscow: Nauka, 1968, pp. 364–381.
- Omel'yanenko, B.I., *Okolorudnye gidrotermal'nye izmeneniya porod* (Wall-Rock Hydrothermal Alterations Associated with Ore Mineralization), Moscow: Nedra, 1978.
- Pauling, L. and Pauling, P., *Chemistry*, San Francisco: W.H. Freeman, 1975.
- Popp, R.K. and Frantz, J.D., Fluid immiscibility in the system H₂O–NaCl–CO₂ as determined from synthetic fluid inclusions, *Annu. Rept. Dir. Geophys. Lab.*, 1989, p. 135.
- Rafal'skii, R.P., On the problem of acidity of hydrothermal solutions, *Geokhimiya*, 1987, no. 3, pp. 402–415.
- Roedder, E., Composition of fluid inclusions, in *Data of Geochemistry*, Fleischer, M., Ed., *U.S. Geol. Surv. Prof. Pap.*, 1971, no. 440-JJ.
- Ryzhenko, B.N., Barsukov, Vikt.L., and Knyazeva, S.N., Chemical characteristics (composition, pH, and Eh) of a rock–water system: 1. The granitoids–water system, *Geochem. Int.*, 1996, no. 5, pp. 390–407.
- Shinohara, H., Does acid volcanic gas represent magmatic discharge at depth?, *Rept. Geol. Surv. Japan*, 1989, no. 279, pp. 152–155.
- Shinohara, H., Generation of HCl by high temperature hydrolysis of NaCl, *Rept. Geol. Surv. Japan*, 1991, no. 277, pp. 101–103.
- Shmulovich, K.I., *Dvuokis' ugleroda v vysokotemperaturnykh protsessakh mineraloobrazovaniya* (Carbon Dioxide in High-Temperature Mineral-Forming Processes), Moscow: Nauka, 1988.
- Takenouchi, S. and Kennedy, G., The binary system H₂O–CO₂ at high temperatures and pressures, *Am. J. Sci.* 1964, vol. 262, no. 9, pp. 1055–1074.
- Vinogradov, A.P., Average content of chemical elements in the major types of igneous rocks of the Earth's crust, *Geokhimiya*, 1962, no. 7, p. 555–571.
- Volokhov, I.M., Magmatic formations and intratelluric fluids, in *Flyuidy v magmaticheskikh protsessakh* (Fluids in Magmatic Processes), Moscow: Nauka, 1982, pp. 63–75.
- Yarmolyuk, V.V., Volatiles in volcanic process, in *Flyuidy v magmaticheskikh protsessakh* (Fluids in Magmatic Processes), Moscow: Nauka, 1982.
- Zaraiskii, G.P., Shapovalov, Yu.B., and Belyavskaya, O.N., *Ekspperimental'noe issledovanie kislotnogo metasomatoza* (Experimental Studies of Acid Metasomatism), Moscow: Nauka, M, 1981.
- Zharikov, V.A., Dyuzhikova, T.N., and Maksakova, E.M., On the different filtration rates of anions and cations during percolation through finely dispersed filters, *Dokl. Akad. Nauk SSSR*, 1961, vol. 141, no. 1, pp. 135–138.
- Zharikov, V.A., Experimental study of the acid–base effect, in *Tez. Dokl. konferentsii "Problemy postmagmaticheskogo rudoobrazovaniya"* (Proceedings of Conference on Problems of Postmagmatic Ore Formation) Praga: 1963, vol. 1, pp. 466–471.
- Zharikov, V.A., Alekhin, Yu.V., and Lakshtanov, L.Z., Main mechanisms of directed compositional evolution of pore solutions: current state of the filtration effect problem, in *Tez. dokl. "Fiziko-khimicheskie problemy endogennykh geologicheskikh protsessov". Materialy konferentsii, posvyashchennoi 100-letiyu akademika D.S. Korzhinskogo* (Proceedings of Conference on Physicochemical Problems of Endogenic Geological Processes Dedicated to the 100th Birth of Academician D.S. Korzhinskii), Moscow, 1999, pp. 7–8.
- Zotov, I.A. and Pertsev, N.N., Evidence of the operation of transmagnetic fluids in intrusions, in *Flyuidy v magmaticheskikh protsessakh* (Fluids in Magmatic Processes), Moscow: Nauka, 1982, pp. 7–27.

Translated by E. Kurdyukov