INTERACTION OF GRANITE WITH WATER AT DIFFERENT TEMPERATURES. RESULTS OF KINETIC-THERMODYNAMIC MODELING

Novoselov A.A., Mironenko M.V. (GEOKHI RAS)
elevfaniy@rambler.ru; fax: (495) 938-20-54; phone: (495) 939-70-27

Key words: *minerals, gases, aqueous solution, chemical equilibria, kinetics of mineral dissolution, kinetic-thermodynamic modeling*

As the first approximation, a thermodynamic modeling is used to simulate water-rock interactions. An assumption of chemical equilibrium means very fast chemical reactions. Otherwise it is known that in real, especially low-temperature systems, it takes a significant time to reach a chemical equilibrium. This study combines thermodynamic and kinetic approaches to geochemical modeling. We have studied numerically a time, needed for approaching chemical equilibria in water-rock systems at various temperatures as well as reaction paths in systems.

Methods of modeling

To calculate irreversible chemical interactions of rock-forming minerals with water, we used a model which combines description of kinetics of a mineral dissolution with calculation of partial chemical equilibria at each time step.

Chemical interactions were modeled as a number of equilibria. A chemical balance of the systems was calculated from a current composition of aqueous solution and masses of dissolved minerals to be dissolved during a time step (Δt). A mole mass x_i of the dissolved mineral at each time step was calculated as $x_i = Fs_i \cdot S_i \, r_i \, \Delta t$, where S_i is a surface area of ith mineral, r_i is a current rate of a mineral dissolution, $mol \cdot m^{-2} \cdot sec^{-1}$, Δt – duration of a time step. Minerals, which were dissolved at previous time steps, are considered as primary minerals and can be subjected to dissolution if they are not in equilibrium with water solution. Surface areas of primary minerals are calculated from specified initial mineral composition and grain sizes, and further are recalculated taking into account dissolution or deposition of minerals. A parameter Fs_i ($0<Fs_i<1$) controls degree of exposure of mineral surface areas to aqueous solution. Surface areas of secondary minerals were calculated from masses of newly formed minerals with specified grain sizes (0.001 mm).

Rates of mineral dissolution were calculated for current pH and degree of undersaturation of a mineral with respect to solution:

$$r_i = \left[k_{0H+}(a_{H^+})^n + k_{0H2O} + k_{0OH-}(K_W a_{OH^-})^m \right] \times \exp\left[\frac{Ea}{R}\left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \times \left\{ 1 - \exp\left[p(\frac{\Delta G}{RT})^q \right] \right\}$$

The equation is a combination of Ladler equation, Arrhenius equation, and the transition state theory equation [2, 3, 4]. More detailed description of the applied approach is in [5]. Kinetic constants of mineral dissolution are listed in the table. The modeling is based on GEOCHEQ_M program [6].

Table

Kinetic parameters of congruent mineral dissolution

	Eact	lgKH	lgKH$_2$O	lgKOH	nH	mOH	Reference
Albite	1.50E+04	-9.60E+00	-1.20E+01	-9.90E+00	5.00E-01	3.00E-01	7
Clinochlore	1.70E+04	-9.79E+00	-1.30E+01	-1.08E+01	4.90E-01	4.30E-01	98
Daphnite	1.70E+04	-9.79E+00	-1.30E+01	-1.08E+01	4.90E-01	4.30E-01	98
Illite	8.15E+03	-1.18E+01	-1.51E+01	-1.20E+01	5.86E-01	7.60E-01	98
Kaolinite	1.37E+04	-1.24E+01	0.00E+00	-1.18E+01	3.50E-01	5.50E-01	9
Magnetite	7.00E+03	-8.77E+00	0.00E+00	0.00E+00	2.50E-01	0.00E+00	10
Microcline	1.40E+04	-9.65E+00	0.00E+00	-9.80E+00	4.50E-01	5.00E-01	7,9
Quartz	1.70E+04	0.00E+00	-1.20E+01	-1.00E+01	0.00E+00	3.00E-01	11,12
Oligoclase	1.50E+04	-9.60E+00	-1.20E+01	-9.90E+00	5.00E-01	3.00E-01	7,9
Biotite	1.37E+04	-9.06E+00	-1.16E+01	-7.69E+00	6.90E-01	5.50E-01	9
Goethite	1.00E+03	0.00E+00	-1.15E+01	0.00E+00	0.00E+00	0.00E+00	10
Hematite	1.00E+03	0.00E+00	-1.15E+01	0.00E+00	0.00E+00	0.00E+00	10
Stellerite	1.90E+04	-9.65E+00	0.00E+00	0.00E+00	4.50E-01	0.00E+00	8

The system under investigation

We modeled chemical interactions in granite-water system (12-component system O-H-K-Mg-Ca-Al-C-Si-Na-F-Cl-Fe) at temperatures of 25°C, 100°C, 200°C, and 300°C and at water saturation pressures.

We took a disintegrated granite consisted of 2-mm spherical mineral grains. Initial mineral composition (weight %) is microcline (65), quartz (20), oligoclase (10), and biotite $K(Fe_{0.75}Mg_{0.25})_3[AlSi_3O_{10}](OH)_{1.5}F_{0.45}Cl_{0.05}$ (5). Water/rock ratio was 1. Initial water solution was 1×10^{-4} M HCl solution. The system was opened with respect to CO_2 ($P_{CO2}=10^{-6}$ bar).

Results

As a result of kinetic-thermodynamic computations chemical equilibria were achieved for any temperatures. Final results are practically the same as the results of point calculations of complete equilibria in the systems of the specified chemical composition. Time of approaching chemical equilibrium significantly decreases with temperature increase. At 25° C the system was equilibrated in 324790 years, at 100°C - 94.6 years, at 200°C - 0.89 years, at 300°C - 0.25 years (fig. 1).
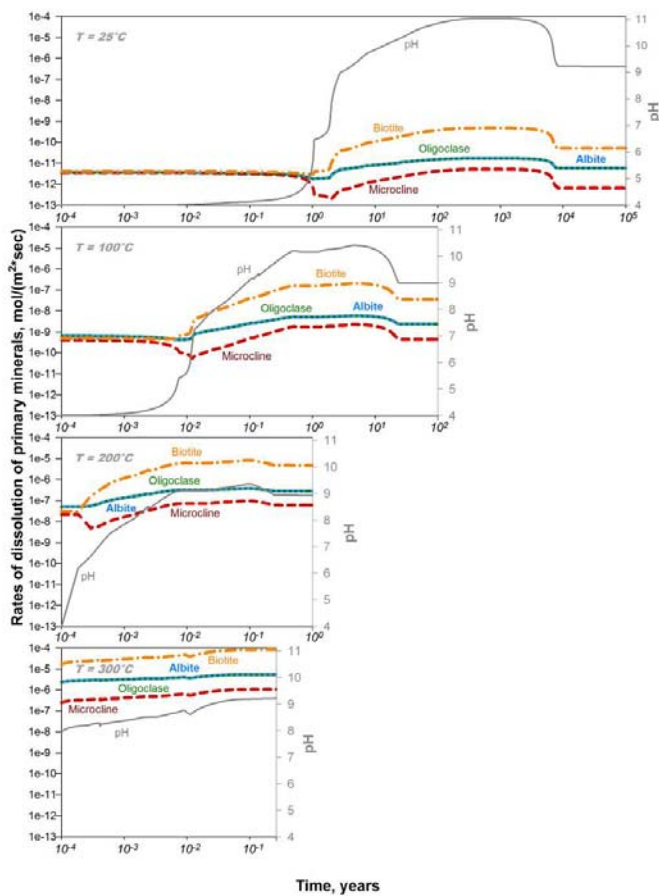

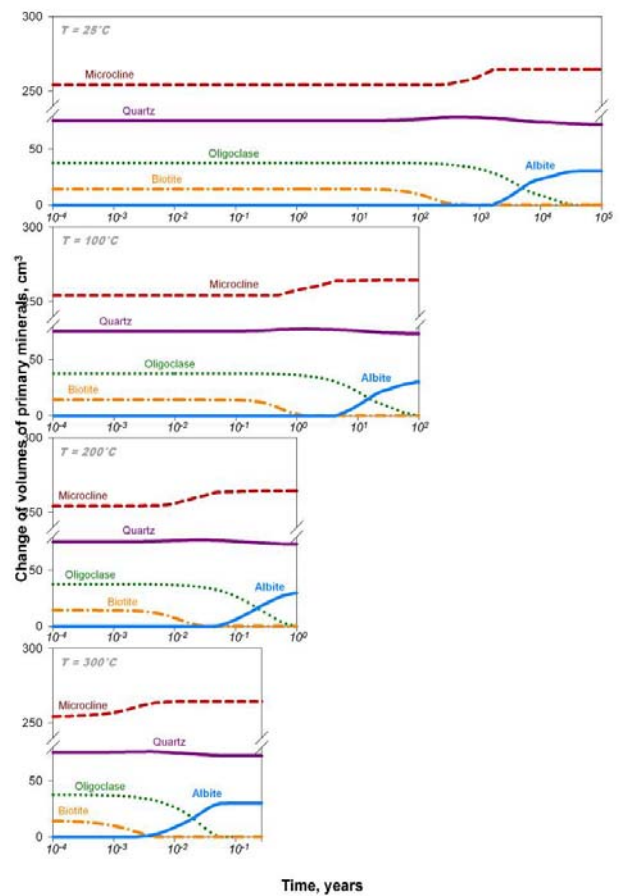**Fig.1.** Rates of dissolution of some minerals at various temperatures

Fig.2. Change of volumes of primary minerals in time at various temperatures

Primary minerals. At various temperatures the alteration of primary minerals is suitable (fig.2). The content of microcline finally increases. Albite, zeolites, and calcite replace oligoclase. Biotite was completely dissolved.

Secondary minerals. Secondary minerals (fig. 3) are albite, chlorite (clinochlore and daphnite), zeolites (stellerite at 25°C and lomontite), carbonites (calcite and dolomite), fluorite, magnetite (at 300°C).
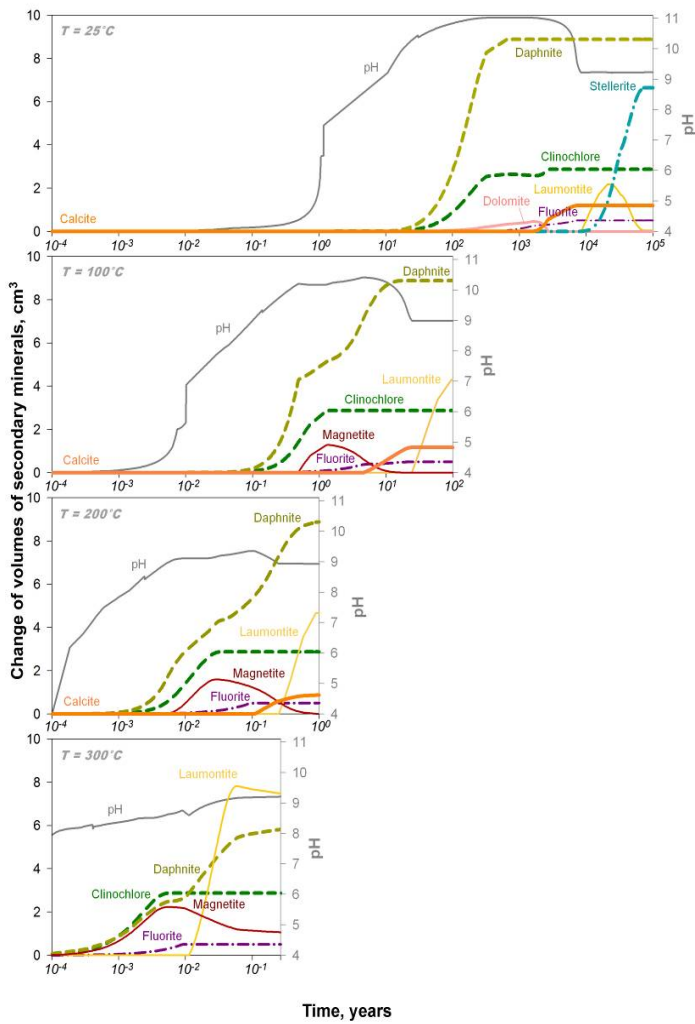
Fig.3. Change of volumes of secondary minerals in time at various temperatures
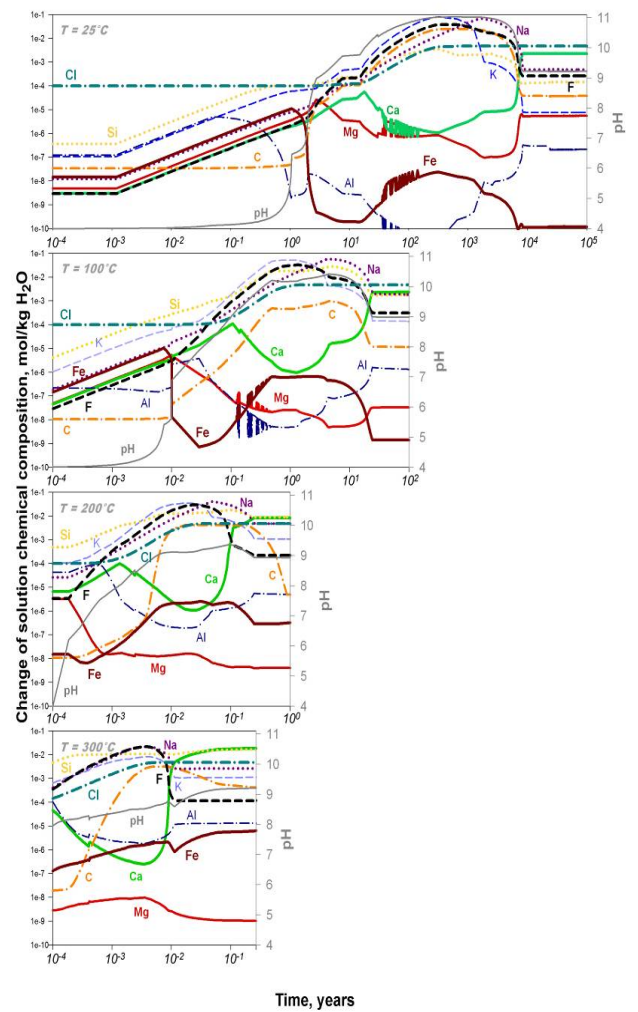
Fig.4. Change of solution chemical composition in time at various temperatures

Change of solution composition. Just after start of interaction cations and anions come into solution in equivalent amounts (fig. 4). After finalization of the stage of congruent mineral dissolution, potassium becomes the dominant cation, and fluorine is the main anion. Later, after significant alkalinity increase, solution becomes sodium, and then calcium-chloride.

Conclusions
1. Kinetic-thermodynamic modeling of water-rock interaction approaches a chemical equilibrium.
2. Time of approaching of chemical equilibrium decreases with temperature increase.
3. Formation of equilibrium mineral assemblage passes through intermediate mineral assemblages and intermediate stages of evolution of solution chemistry.

References

1. Laidler K.J. Chemical Kinetics // Harper and Row. 1987.
2. Brantley S.L. Reaction kinetics of primary rock-forming minerals under ambient conditions // Treatise on Geochemistry. Elsevier. 2004. V. 5. P. 73-118.

3. Lasaga A.C. Transition state theory. In: Kinetics of Geochemical Processes (eds. A.C. Lasaga and R.J. Kirkpatrick) // Mineralogical Society of America. 1981. V. 8. P. 135-169.

4. Aagaard P., Helgeson H.C. Thermodynamic and kinetic constaints on reaction rates among minerals and aqueous solutions. I. Theoretical considerations. // Amer. J. Sci. 1982. V. 282. No 3. P. 237-285.

5. Zolotov M.Y., Mironenko M.V. Timing of acid weathering on Mars: A kinetic-thermodynamic assessment // J. Geophys. Res. 2007. V. 112. E07006, doi:10.1029/2006JE002882.

6. Mironenko M.V., Melikhova T.Yu., Zolotov M.Yu., Akinfiev N.N. GEOCHEQ_M: Program complex for thermodynamic and kinetic modeling of geochemical processes in rock-water-gas systems. Version 2008.
URL: *http://www.scgis.ru/russian/cp1251/h_dgggms/1-2008/informbul-1_2008/mineral-22e.pdf.*

7. Brady P.V., Walther J.V. Controls on silicate dissolution rates in neutral and basic pH solutions at 25^oC // Geochim. Cosmochim. 1989. Acta. 53. P. 2823-2830.

8. Alekseev V.A. Equations for the dissolution reaction rates of montmorillonite, illite, and chlorite // Geochemistry Intl. 2007. 45. No 8. P. 770-780.

9. Alekseev V.A. Kinetics of reactions of rock-forming minerals with aqueous solutions. In: Shvartsev, S. L. (Ed.), Geological Evolution and Self-Organization of the Water-Rock System. V. 1. // Publishing House of the Siberian Branch of Russian Academy of Sciences. Novosibirsk. 2005. P. 71-107 (in Russian).

10. Sidhu P.S., Gilkes R.J., Coenell R.M., Posner A.M., Qurik J.P. Dissolution of iron oxides and oxyhydroxides in hydrolic and perhydrolic acids // Clays and Clay Minerals. 1981. 29. P. 269-276.

11. Rimstidt J.D., Barnes H.L. The kinetics of silica-water reactions // Geochim. Cosmochim. Acta. 1980. 44. P. 1683-1699.

12. Icenhower J.P., Dove P.M. The dissolution kinetics of amorphous silica into sodium chloride solutions: effects of temperature and ionic strength // Geochim. Cosmochim. Acta. 64. P. 4193-4203.

13. Brady P.V., Walther J.V. Kinetics of quartz dissolution at low temperatures // Chem. Geol. 1990. 82. P. 253-264.