EXPERIMENTAL METASOMATIC COLUMN AS A TOOL FOR SECURING OF KINETIC CONSTANTS OF METASOMATIC REACTIONS

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Experimental modeling of rock metasomatic replacement ***due*** to interaction with hydrothermal solutions above 400°C [1] leads to formation of zonal metasomatic columns over initially homogeneous rock. These columns are characterized by sharp zone boundaries, by equilibrium mineral paragenesis in zones, and by thermodynamic sequence of mineral zones, which is in a correspondence with local equilibrium model of metasomatic zoning of D.S. Korzhinskii [2]. Nevertheless for temperatures less than 400°C the zone boundaries smear, the non-equilibrium relict minerals conserve, and the column structure deviates from local equilibrium, the role of kinetic factors increases. It was shown that a structure of such columns could find a good description in the frame of macrokinetic model with reversible chemical reactions [3, 4]. In macrokinetic model the component transport and dissolution of initial minerals with precipitation of new minerals are considered in time and space accordingly to self-consistent system of transport and kinetic equations. Model results in a full quantitative description of metasomatic column as a definite concentration distribution of minerals, porosity and components of aqueous solution along the column length for a given time. The goal of this communication is a demonstration of a possibility to determine quantitative information on kinetic constants and rates of heterogeneous chemical reactions aqueous solution – rock on the basis of experimental modeling data with help of numerical macrokinetic model.

The column of diffusion metasomatism was taken as an object of experimental modeling. This column is formed as result of interaction of acid aqueous solution of potassium chloride with haplogranite mixture of natural minerals at temperature 350 C and pressure 100 MPa due 118 hours. The powder of haplogranite mineral mixture Qtz (38 wt %) + Ab (38 wt %) + Kfs (24 wt %) was densely pressed into an open platinum tube with diameter 10 mm and length 30 mm which was placed inside of large platinum capsule with diameter 10 mm and length 100 mm. The platinum capsule was filled by the solution with addition of 0.1 g quartz powder for the solution saturation by silica. The capsule was sold and put in exoclave reactor of Tuttle type. During the experiment the solution interacted with haplogranite because the diffusion of components through opening of small tube. The distribution of minerals in altered granite was studied in thin sections with help of microprobe by local analysis of minerals and by scanning of cross profiles to define the change of total chemical rock composition in sequent cross sections of column from the opening to the bottom of tube. The distance between the scanned profiles was varied from 0.5 to 1 mm. The results of microprobe analysis for each profile were recalculated on quantitative mineral composition.

Theoretically the local equilibrium process of metasomatic haplogranite alteration at given experimental parameters is the replacement of feldspars by muscovite and quartz in central column zones and the replacement of feldspars by pyrophillite and quartz in rear zones with formation of a equilibrium zone sequence:

$$\rightarrow \mid \text{Qtz} \mid \text{Qtz} + \text{Prl} \mid \text{Qtz} + \text{Ms} \mid \text{Qtz} + \text{Ms} + \text{Kfs} \mid \text{Qtz} + \text{Ab} + \text{Kfs} \mid .$$

The experimental column is remarkably differed from local-equilibrium column. Only the rear quartz-pyrophillite zone and the frontal zone of non-altered rock (Qtz + Ab + Kfs) correspond to theoretical equilibrium zone sequence. The central part of column lacks muscovite equilibrium zones. The zone boundaries are characterized by smooth decrease of initial mineral concentrations and by smooth increase of new-formed pyrophillite concentration. The pyrophillite is observed not only in rear zone but can be

traced along all columns. It may conclude that the structure of experimental column in large degree is defined rather by kinetic rates of chemical reactions than by local equilibrium.

In calculations on macrokinetic model 8 minerals were taken into account: quartz, albite, K-feldspar, pyrophillite, muscovite, andalusite, kaolinite and corundum. Three last minerals were thermodynamically unstable and not realized in model. The kinetic constants of mineral dissolution were found from the literature experimental data treatment. The component diffusion coefficients in aqueous solution were considered equal to average value for KCl and NaCl at 350 C and 100 Mpa (2.22 10^{-8} m^2/s). Effective diffusion coefficient in model was equal to production of aqueous solution diffusion coefficient on variable porosity, which had been determining in model calculations. The reactive transport system of equations was solved by implicit finite differences method.

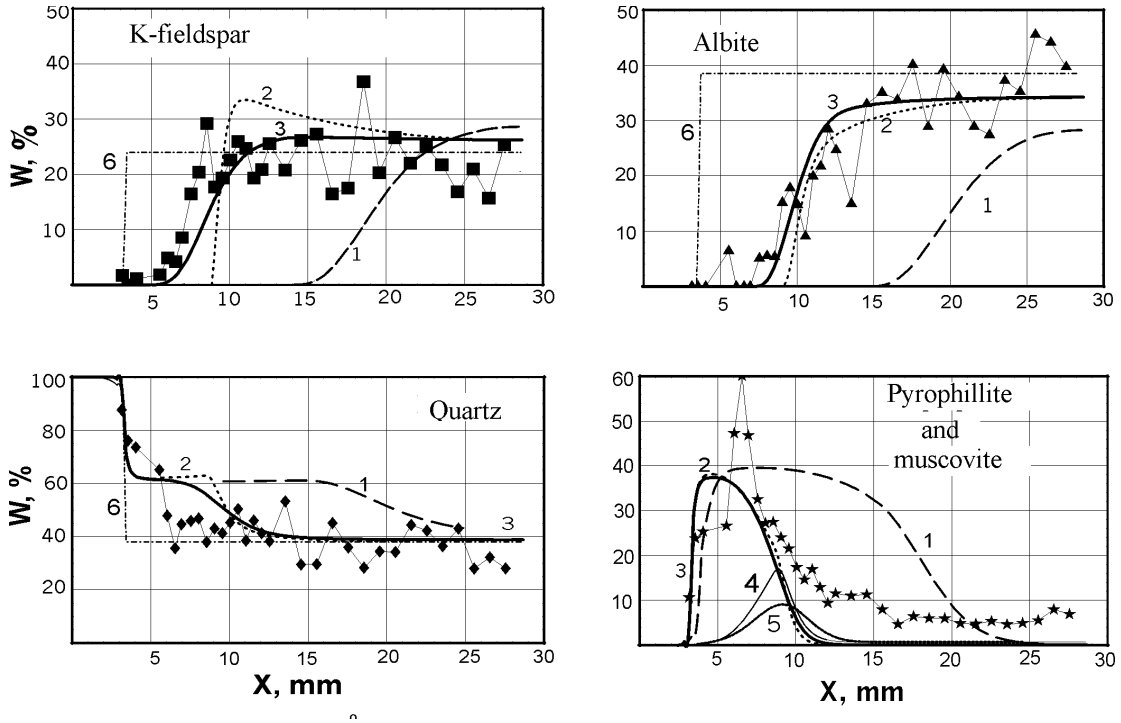

Fig. 1. Run MU-8: T=350°C, P=100MPa, 0.25m HCl + 0.25m KCl, t=118 hours.
The mineral distribution (K-feldspar, albite, quartz, pyrophillite, muscovite) along the length of experimental (signed with geometrical marks) and theoretical (curves 1, 2, 3) metasomatic columns. The theoretical curves were calculated by means of macrokinetic model with the different values of kinetic constants:
1 – diffusion coefficient and kinetic constants taken from literature data (Balashov, 1995).
2 - diffusion coefficient, 5 times less than it was taken initially, and kinetic constants from literature data
3 - diffusion coefficient, 5 times less than it was taken initially, and the best "fitted" kinetic constants values:
k^+Ab = 0.2 of literature value; k^+Kfs = 0.1 of literature value;
k^-Kfs = 0.5 of literature value; the other constants values correspond to literature data.
Curves 4 and 5 show the distribution of muscovite calculated with literature constants values (4) and with the best "fitted" kinetic constants values (5); Curve 6 – the initial distribution of each mineral.

The calculated distributions of minerals along column length due 118 hours show more intensive haplogranite alteration relatively to experiment (fig. 1). The theoretical model can fit the data much better at lower aqueous diffusion coefficient. The required diffusion coefficient is 5 times less than it was taken

initially. The next approximation of model data to experiment requires the decreasing of kinetic constants: the theoretical mineral distributions at dissolution are steeper than experimentally observed. The best correspondence between theory and experiment is found for kinetic constants: $k^{+}Ab = 0.2$ literature value, $k^{+}Kfs = 0.1$ literature value, $k^{-}Kfs = 0.5$ lit-value; all other constants are equal to their literature values. Model calculations show the formation of small amount of muscovite. The muscovite maximum is shifted to right (further along column) relatively of pyrophillite maximum. It may be assumed that some amount of muscovite is hidden in experimental columns as intergrowths with pyrophillite. It confirms by presence of 2-3% of K_2O in local microprobe analysis of pyrophillite. Thus we demonstrate the principal possibility to determine the kinetic and diffusion parameters from data treatment of reactive transport experiment, which is maximally close to natural metasomatic mineral formation.

References

1. *Zaraisky G.P.* (1989). Zoning and Formation Conditions of Metasomatic Rocks // Moscow. Nauka. 342 p. (in Russian).
2. *Korzhinsky D.S.* (1969) Theory of Metasomatic Zonning // Moscow. Nauka. 342 p. (in Russian).
3. *Balashov V.N., Lebedeva M.I.* (1989) On going to local equilibrium at development of diffusion metasomatic zone // Doklady Academii Nauk. V.307. P.703-707 (in Russian).
4. *Zaraisky G.P., Balashov V.N., Lebedeva M.I.* (1989) Macrokinetic model of metasomatic zoning // Geokhimiya. N.10 P.1386-1395 (in Russian).