Geochemical modeling of magmatic–hydrothermal systems: Petrological evaluations and metallogenic application

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Abstract: Proposed modeling approach (Shnyukov & Lazareva 2017; Shnyukov et al 2018; Lazareva et al. 2018 etc.) is based on a set of equations for trace element behavior during the melt crystallization/partial melting (Rayleigh–Neumann–Ryabchikov–Shaw et al.) and widespread accessory minerals (WSAM — Ap, Zrn, Mnz etc.) solubility equations (Watson–Harrison–Montel), which are mainly used to derive the model evaluation of the temperature (T_{model}) and fluid regime in the magmatic system from the whole-rock geochemical data. Furthermore, such models include principally new components: (1) calibrated $\ln K_Y^{Ap/Zrn}$ vs. 1/T(K) dependence with the equation for the inverse problem solution ($K_Y^{Ap/Zrn} = C_Y^{Ap}/C_Y^{Zrn}$; C^F, C^L=Y content in coexistent apatite and zircon respectively) which allows to verify obtained T_{model} values (key input parameter for most of calculations), (2) equations for calculation of the fluid/melt distribution coefficient ($K^{F/L} = C^F/C^L$; C^F, C^L=element content in the fluid and melt respectively) and the model element composition of the hydrothermally altered rocks, (3) procedures for evaluation of ore-generating potential of the system.

Introduction

Geochemical modeling is crucial for the investigation of magmatic–hydrothermal systems, including evaluation of their ore potential. The main objectives (see Shnyukov 2001, 2002, etc.) are following:

1. Determination of the leading magmatic formation mechanism (fractional crystallization, partial melting, etc.).
2. Determination of major and trace element behavior in the magmatic evolution.
3. Evaluation of physico–chemical conditions of formation.
4. Evaluation of its ore-bearing fluids generation ability corresponding to hydrothermal–metasomatic ore formation.

Theoretical basis and methodology for solving of tasks (1) and (2) proposed by Neumann et al. (1954); Ryabchikov (1965, 1975); Allegre & Minster (1978) etc., are widely used in the study of magmatic complexes. The methodology for the tasks (3) and (4) proposed by Shnyukov et al. (1989, 1993); Shnyukov & Lazareva (2002) etc. It is complex modeling of major and trace elemental distribution in the series of igneous rocks, experimental data on water (Ryabchikov 1975; Holtz et al. 2001, etc.) and widespread accessory minerals solubility in silicate melts (WSAM — Ap, Zrn, Mnz, etc.) (Watson & Harrison 1983; Harrison & Watson 1984; Montel 1993), as well as the data on the distribution of trace elements in WSAM's associations (Shnyukov & Lazareva 2017, etc.). But the solution of the problem (4) should be considered as incomplete without a quantitative evaluation of the elemental supply from the melt in magmatic–hydrothermal system. The solution was suggested by Shnyukov et al. (2016, etc.).

Modeling procedures are given below on an example of the magmatic system of precambrian Korosten Pluton (KP) in the Ukrainian Shield and hydrothermal–metasomatic ore occurrences and deposits connected with KP and Suschano–Perzhanskaya area (SPA).

Modeling of the magmatic system

Geochemical model of KP granitoids magmatic evolution was prepared using representative geochemical data set which covers their main varieties (rapakivi, granite–porphyry, veined granites etc.) and Rayleigh fractional crystallization model to approximate the trace element data. Following crucial results have been obtained:

1. Typical incompatible behavior with approximately constant bulk distribution coefficient was determined for Rb (D_{Rb}=0.5). Model *f* values (weight fraction of liquid phase in magma chamber) were calculated for each granitoid type (residual melt portion) from Rayleigh equation and Rb content in rocks (C_{Rb})

assuming minimum concentration in granitoids (169 ppm) as Rb content in parent magma (C_0^{Rb}).

2. C vs. f curves for trace and major elements were approximated by means of $C=C_0 \cdot f^{D-1}$ equations or polynomial ones respectively (Fig. 1, Table 1). This set of equations is an idealized model of elements behavior. Corresponding bulk distribution coefficient (D) and C_0 values for trace elements are shown in Table 1.
3. Monotonous decrease of both Zr and P contents indicate melt saturation for zircon and apatite. Therefore, the model temperature (T_{model}) of the melt was estimated using equations for their solubility (Watson & Harrison 1983; Harrison & Watson 1984). The temperature evolution in magma chamber is presented as T_{model} vs. f equation (T_{model} range: 900–720 °C).
4. Inversion in LREE content (f=0.185) indicates the apatite/monazite replacement in the crystallizing material. Water content in melt for this f value for corresponding T_{model} was calculated from monazite solubility equation (Montel 1993), which yielded C_0^{H2O}=2.36 wt. % (assuming D_{H2O}=0.1) for the liquidus of initial granite melt. P_{total} ~6.3 kbar corresponds to this value (Ryabchikov 1975; Holtz et al. 2001, etc.) (Fig. 1).
5. Water saturation was reached at f=0.165 and H_2O-fluid was extracted from the melt during its further evolution. Synchronous inversion of C vs. f behavior proves fluid enrichment with F, Cl, Nb, Zn, Pb, etc. (Fig. 1).

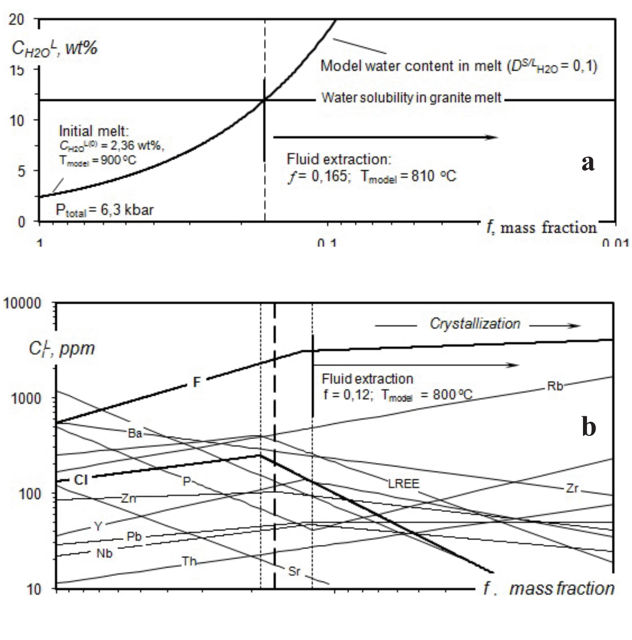

Fig.1. Results of geochemical modeling of the KP granitoid magmatic systems: **a** — segregation of aqueous fluid from the melt during its crystallization; **b** — concentrations of elements in residual melt of the magmatic system.

Modeling of the magmatic–hydrothermal system

Fluid/melt distribution coefficient

According to the "magmatic" model (Fig. 1), the behavior of each "inversion" element is described by two equations of Rayleigh type, which correspond to the sections of the magmatic evolution until ($f > f_{inv.}$) and after ($f < f_{inv.}$) inversion, which coincides with the beginning of the fluid segregation ($f_{inv}^{Nb}=0.123$ was accepted as the final $f_{inv.}$ value). Concentrations of elements in residual melt, which are calculated by the first and second equations, are rationally denoted as C^M and C^L, and efficient bulk distribution coefficients used in these cases — D and D' respectively. Both values are constant in the developed model (Table 1).

The final equation for calculation of inversion behavior elements fluid/melt distribution coefficient for any value of f_n was obtained (see Shnyukov et al. 2016 for explanations):

$$K^{F/L} = \frac{\Delta S_n (D' - D) + D' \Delta F_n}{\Delta F_n}, \qquad (1)$$

where ΔS_n and ΔF_n — the proportion of solid and fluid phases in the system, segregated during period Δf_n. For the elements with $D'=D$ this equation simplifies to the form $K^{F/L}=D$.

The volume of elements involved to magmatogenic–hydrothermal system

Developed model allows to estimate the *total elemental resource of the fluid* (Fig. 2), i.e. the total weight of each element, extracted from the melt by the aqueous fluid, which is segregated from the magmatic system during its evolution (R_F). Really, model provides data not only on the concentration of each element in the residual melt (C^L), and the value of its fluid/melt distribution coefficient ($K^{F/L}$), but also estimates the mass fraction of fluid segregated from magmatic system at any stage of evolution at $f < f_{inv.}$ (ΔF_n). Therefore:

$$\Delta R_{F_n} = \Delta F_n \cdot C_i^{F_n} \cdot M_{syst} / 10^6 , \qquad (2)$$

where ΔR_{F_n} — the fluid's resource, segregated from the magmatic system during the period Δf_n (billion tons);

$C_i^{F_n}$ — the concentration of the element i in the fluid (ppm) at the moment f_n; M_{syst} — the mass of the system (billion tons). The total fluid resource of the element i can be estimated using the expression:

$$R_F = \sum_{n=1}^{n} \Delta R_{F_n} \quad . \qquad (3)$$

In these equations the total mass of the parental magmatic system (M_{syst}) is an important input parameter but usually difficult for evaluation. In the case under consideration $M_{syst} \geq 200\,000$ billion tons was accepted. Due to the existing data this estimation is approximate, but realistic.

Additional, but important parameter in the elements behavior analysis during evaluation of ore-generating potential of magmatic–hydrothermal systems is *total elemental resource of the parent magmatic system* (R_M), i.e. the total weight of each element in the system. Its calculation is straightforward:

$$R_M = C_{i(0)} \cdot M_{syst} / 10^6 , \qquad (4)$$

where R_M — total resource of the parent magmatic system (billion tons); $C_{i(0)}$ — concentration of the element i in the initial melt (ppm) (see Table 1; M_{syst} — mass of the system (billion tons).

The model estimations obtained for KP are presented in Figure 2. They indicate that the fluid/melt distribution coefficient ($K^{F/L}$) is the most important factor that controls the total elemental resource of the fluid and ore-generating potential of magmatogenic–hydrothermal systems.

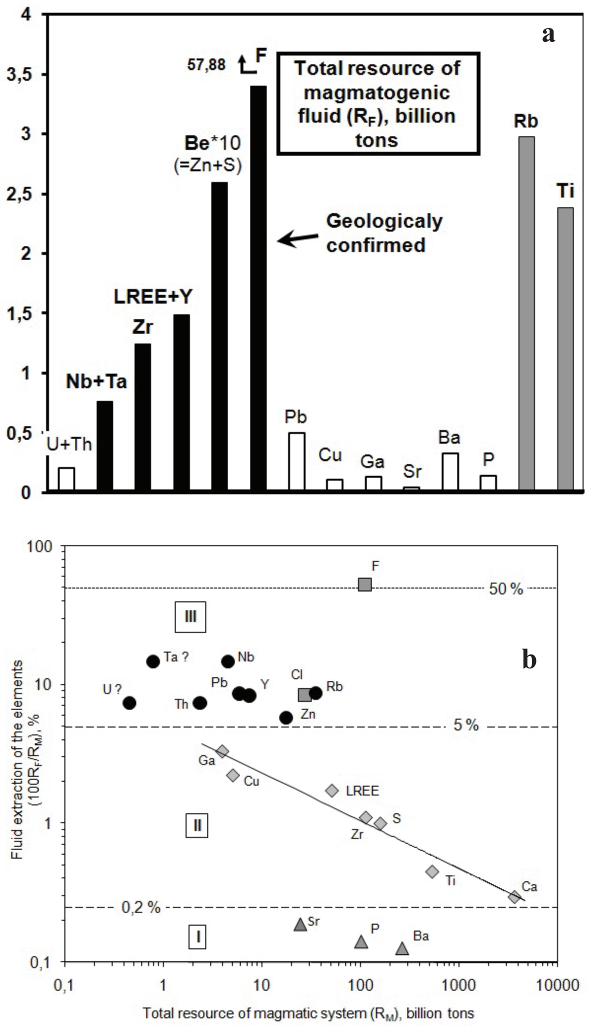

Fig. 2. a — Total elemental resource of the fluid as a criterion for the evaluation of ore-generating potential of magmatogenic–hydrothermal system. **b** — Extraction of elements with different total elemental resource of the magmatic system to the fluid.

Table 1: C_0 and D values calculated for selected elements on a base of C vs. f trends assuming that studied main Korosten granitoids rock types composition is as liquids (melts)

Element	Values calculated for various sections of C vs. f trends			
	Before inversion ($f > 0.1 \div 0.2$)		After inversion ($f < 0.1 \div 0.2$)	
	$C_0 = a$ (ppm)	$D = b + 1$	a	$D' = b + 1$
Zr	555.08	1.381	**	**
Sr	119.99	2.0564	**	**
P	497.04	2.172	9.4801	0.3058
Ti	2622.7	1.7251	**	**
Y	36.104	0.34	412.89	1.5363
LREE	251.6	0.7182	2381.3	2.0511
Rb	169*	0.5*	**	**
Ba	1289.8	2.2094	**	**
Zn	85.55	0.9	191.26	1.3368
Ga	19.314	0.9346	**	**
Th	11.428	0.5872	**	**
Nb	21.991	0.6341	81.164	1.258
Pb	28.841	0.7359	49.842	1.0001
Cu	24.789	1.1069	**	**
F	547.41	0.153	2492.5	0.8963
Cl	132.82	0.6315	2963.4	2.4732
S	780.15	1.418	**	**

Notes: (1) a and b are the parameters of the equations of $y=ax^b$ [$C(ppm)=af^{\,b}$] form obtained for each trace element; (2) * assumed values; (3) ** C vs. f trends demonstrate the monotonous behavior of these elements without inversion points; (4) LREE = La+Ce+Nd.

Conclusions

The method of fluid/melt distribution coefficients and total elemental resource of the magmatic fluids estimation was proposed based on geochemical modeling of parent magmatic systems. The model directly derives from the observed data of elements content in main rock types of magmatic complexes and mostly corresponds to the real conditions of the magmatic evolution. Obtained results allows to use methodology in the regional geological and metallogenic investigations.

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