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Geochemical modeling in the evaluation of ore-forming potential of magmatic-hydrothermal systems

Quantitative geochemical modeling possibilities of ore-bearing aqueous fluids separation process from a magmatic melt are considered. Suggested procedures allow calculation of fluid/melt distribution coefficient values for trace elements, their contents in a fluid, as well as its total resources in a genetically related metasomatically altered rocks. Application of this approach to the geochemical modeling of real ore-generating magmatic-hydrothermal system of the Korosten pluton granitoids (Ukrainian Shield), and associated hydrothermal-metasomatic formations (Suschano-Perzhanskaya area) has confirmed its efficiency. The purpose of present and future research is to obtain estimations of Ukraine and Kazakhstan regions mineral resources potential independent from a simple summation of previously conducted regional works.

Key words: metasomatites, granite, trace element, geochemical modeling, fluid/melt distribution coefficient, ore resources.

Introduction

Within such a huge and diverse geological regions as Ukraine and Kazakhstan mineral resource potential is largely determined by magmatic-hydrothermal and magmatogenic systems of various ages. Regardless from the later, as well as the declared mineragenous amount, important role in the evaluation of ore-generating potential of such systems had, have and will have such means as the geochemical modeling. They acquire a special role when in the first place there is the need for generalizing the data, independent in their reliability from results of a primitive summation which is regional, but routine research. At the same time, geochemical modeling, studying of the magmatic series and related magmatogenic-hydrothermal systems formation processes, which is the main problem of this article, solves next tasks [1, 2, etc.]:

- (1) determination of the leading magmatic series formation mechanism (fractional crystallization, partial melting, etc.);
- (2) determination of petrogenic and trace element behavior in the magmatic evolution processes;
- (3) evaluation of physico-chemical conditions of formation and functioning of magmatic systems;
- (4) evaluation of its ore-bearing fluids generation ability and to corresponding hydrothermal-metasomatic ore deposits formation;
- (5) Independent verification of the modeling results.

Theoretical basis and methodology of solving tasks (1) and (2) were developed in the works and are widely used in the study of magmatic complexes. As an organic supplement of this methodology for the tasks (3)–(5) we proposed [1, 2, etc.] complex use in modeling of petrogenic and trace elements distribution in the series of igneous rocks, experimental data of solubility in silicate melts of the common accessory minerals (CAM — Apatite, zircon, monazite, etc.) as well as the data on the distribution of trace elements in their associations. But the solution of the problem (4) should be considered as incomplete without a quantitative evaluation of the elements supply from the melt in magmatogenic-hydrothermal system amount during the magmatic evolution.

The importance of obtaining such «total resource of magmatogene fluid» evaluations is emphasized by the fact that they can be simultaneously considered as a value of the maximum mineralization potential magnitude, what allows to use them with the searching purposes. Such task solving principle is known for a long time, but given options still require the obligatory use of additional initial parameters, first of all independently (experimentally) obtained fluid/melt distribution coefficients for the large number of elements and wide range of physical and chemical conditions. That's why modern insufficiency of the experimental data significantly limited possibilities for quantitative calculations by proposed scheme.

The purpose of the work was to develop methods which allow to remove such limitations through the use of model fluid/melt distribution coefficients which correspond to the real specific magmatic evolution

systems conditions as they directly «derive» from the observed elements concentrations data in magmatic complexes petrotypes and from the results of geochemical modeling of their formation processes (1)-(5). Among the specific tasks of work, except for actual development of a model fluid/melt distribution coefficients calculation methodology and the supply amount of elements in magmatogenic-hydrothermal system, authors have also considered its experimental approbation.

Object of research

The main principles of the proposed approach practical application are reviewed at the example of the Precambrian (1.7 to 1.8 billion years) anorthosite-rapakivi-granite association Korosten Pluton (KP), one of the largest magmatic complexes of the Ukrainian shield (USh), localized in its Northern-Western part. The advantageous set of condition – good enough geological study and conservation level of the complex, a wide range of petrotypes (granitoid and mafic series), as well as the presence of well-studied igneous (Ti, P), pegmatitic (chamber pegmatites) and hydrothermal-metasomatitic (Li, Be, Nb, Ta, Zr, W, Sn, Mo, Zn, Pb, Cu, Bi, Cd) ore occurrences and deposits among the rocks of Pluton and its frame (Suschano-Perzhanskaya area — SPA), has allowed the authors earlier [2–4, etc.] to demonstrate ability to solve all the mentioned geochemical modeling problems. This justifies the rationality of the KPs use as an object of study during the process of previously described tasks solving.

Methodology of research

Initial data for work tasks solution. Previously proposed geochemical model of formation of the granitoid KP series, is described in detail in [2–4, etc.]. As the dominant mechanism of magmatic evolution for the current model was accepted deep magmatic chamber fractional crystallization of granitoid melt which was provided with sufficient evidence. Additional used data: 1) originally observed data on the distribution of petrogenic and trace elements in a granitoid series of KP; 2) experimental data on the solubility of apatite, zircon, monazite [5, 6] and H₂O [7] in granitoid melts; 3) temperature dependence [3] of the distribution of Y between paragenetic apatite and zircon. Trace elements behavior (Fig. 1) dependence on f (mass fraction of residual melt) was approximated by Rayleigh type equations. The model allowed to evaluate: P–T conditions and fluid mode of magmatic evolution; $f = f_{inv}$ value, which corresponds to the inversion in the behavior of trace elements caused by the fluid segregation (Fig. 1); the effective value of their combined crystallized fraction/melt distribution coefficients before ($f > f_{inv}$) and after ($f < f_{inv}$) inversion — D_i and D_i' respectively. The data which indicates genetic relationship between magmatic systems of the granitoid KP and ore-bearing hydrothermal-metasomatic formations of the SPA was also acquired [3, 4].

Model fluid/melt distribution coefficient calculation. The initial data which «magmatic model» and the cited works provide (Fig. 1), especially the beginning of the aqueous fluid segregation from the melt f value estimation ($f_{inv} = 0,123$) and effective D values in the range $f > f_{inv}$ and $f < f_{inv}$, allow calculate to values of the effective fluid/melt distribution coefficient (important parameter), for elements with «inversion» type of behavior (F, Cl, Nb, Zn, Pb, etc.), which regulates the load of ore-bearing magmatic fluid and its derivatives — hydrothermal-metasomatic formations. Inheriting approach that has been proposed in our previous works [3, 4], but modifying it, the following principle of calculation can suggested.

If the dominant factor in the magmatic system evolution is fractional crystallization, the trace elements behavior is described by the well-known Rayleigh equation provided their combined distribution coefficients are constant:

$$C = C_0 \cdot f^{(D-1)}, \quad (1)$$

where C — the concentration of the element in the residual melt; C_0 — the initial concentration of the element in the primary melt, D — the effective combined distribution coefficient of the element ($D = C^S / C^L$, C^S and C^L — concentration of the element in solid phase and melt respectively), f — mass fraction of liquid phase (residual melt) in the system. According to the «magmatic» model (Fig. 1, cited work), the magmatic system of KP granitoids represents exact case.

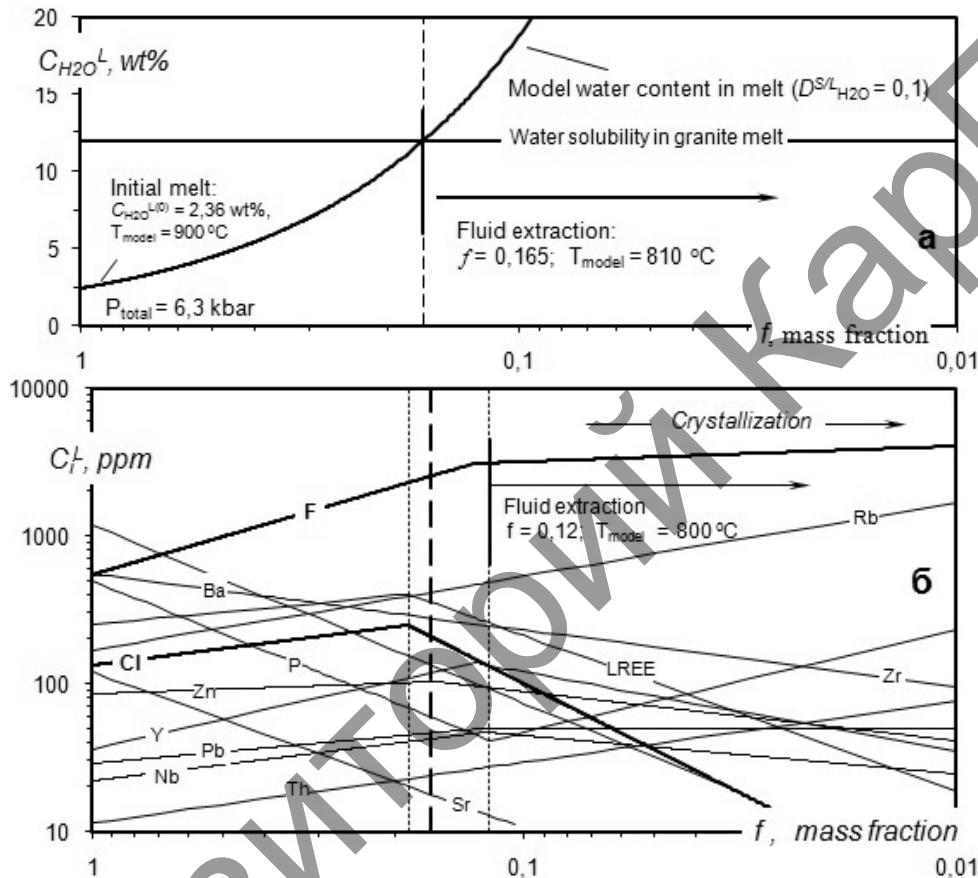
The f parameter of equation (1), before the emergence of the fluid component in the system, can defined as:

$$f = \frac{M^L}{(M^L + M^S)}, \quad (2)$$

where M^L and M^S — the mass of the liquid and solid phases of the system respectively. The equation for the combined distribution coefficient calculation of each of the elements under the same conditions as follows:

$$D = xk_i^X + yk_i^Y + \dots + zk_i^Z, \quad (3)$$

where x, y, \dots, z — the mass fraction of each mineral (X, Y, \dots, Z , respectively) which forms the solid phase of the system; $k_i^X, k_i^Y, \dots, k_i^Z$ — mineral/melt distribution coefficients of element i for these minerals ($k_i^X = C_i^X / C_i^L$, where C_i^X and C_i^L are the concentration of element i in these minerals and the melt respectively).



a — segregation of aqueous fluid from the melt during its crystallization conditions;
 b — concentrations of elements in residual melt of the magmatic system during its evolution shift

Figure 1. Results of geochemical modeling of the KP granitoids magmatic systems

According to the «magmatic» model (Fig. 1), the behavior of each «inversion» element is described by two equations of type (1), 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 (as the final $f_{inv.}$ value was accepted the Nb — element, segregated into a fluid phase last: $f_{inv.}^{Nb} = 0,123$). 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 combined distribution coefficients used in these cases — D and D' respectively. In the «magmatic model» for D and D' values are fixed constant [2, 3, etc.].

After emergence of the fluid component in system ($f < f_{inv.}$) the equation (1) retains valid, but on the condition that the equation (2) takes the form: $f = \frac{M^L}{(M^L + M^S + M^F)}$, where M^F is the mass of the fluid phase of the system. Certainly, D' is taking place of D , which values, similar to expression (3), are defined as:

$$D' = xD + yK^{F/L}, \quad (4)$$

where x and y are the mass fractions of the solid and fluid phases, respectively, in the system excluding the liquid phase ($x + y = 1$), a $K^{F/L}$ — fluid/melt distribution coefficient for element with inversion type of behavior ($K^{F/L} = C^F/C^L$, C^F и C^L — concentration of the element in the fluid and the melt, respectively). Since $x = 1 - y$, the final equation (4) becomes: $D' = D - yD + yK^{F/L}$. Hence:

$$K^{F/L} = \frac{D' - D + yD}{y}. \quad (5)$$

Consequently there is a necessity in y parameter estimation to calculate $K^{F/L}$. The given model of magmatic evolution provides such possibility (Fig. 1a, the works cited), which allows to estimate model water concentration value in the residual melt for any f and, upon reaching the solubility of water in it, to define the segregation of the aqueous fluid beginning moment (Fig. 1a). This gives the opportunity to estimate the «excessive» water concentration for the range of $f < f_{inv}$ ($\Delta C_{H_2O}^{f_n}$, wt%) — aqueous fluid formation resource, which segregates during any period Δf_n ($\Delta f_n = f_{n-1} - f_n$; $n = 1, 2, 3 \dots n$ — a number of conventional periods in the evolution of the system with the length of Δf from the beginning of the segregation of the aqueous fluid): $\Delta C_{H_2O}^{f_n} = C_{H_2O}^{f_n} - C_{H_2O}^L$, where $C_{H_2O}^{f_n}$ and $C_{H_2O}^L$ — respectively, model water concentration in the residual melt at the certain moment f_n and H_2O solubility in granitic melt (wt%) under current conditions, which is buffering its actual concentration for the range $f < f_{inv}$. Hence: $\Delta F_n = 0.01 \cdot \Delta C_{H_2O}^{f_n} \cdot \Delta f_n$, where ΔF_n — the proportion of the fluid phase in the system, segregated during period Δf_n .

The proportion of the solid phase in the system (S) for any moment f_n can be calculated by using the expression: $S_n = 1 - (f_n + F_n)$, where S_n, f_n, F_n ($F_n = \sum_{n=1}^n \Delta F_n$) — the fractions of solid, liquid and fluid phases in the system respectively. The quantity of solid phase formed during the period Δf_n can be easily estimated as: $\Delta S_n = S_{n-1} - S_n$. It is consequently easy to estimate y (mass fraction of fluid phase in the system excluding the liquid phase) for each period of the evolution of the system Δf_n :

$$y = \frac{\Delta F_n}{\Delta F_n + \Delta S_n}. \quad (6)$$

Substituting (6) into equation (5) and performing simple transformations, we obtain the final equation for calculation of inversion behavior elements fluid/melt distribution coefficient for any value of f_n :

$$K^{F/L} = \frac{\Delta S_n(D' - D) + D' \Delta F_n}{\Delta F_n}. \quad (7)$$

For the elements with monotonous behaviour, such as Ba, Sr, Zr and Th (Fig. 1), the expression (7) simplifies to the form $K^{F/L} = D$, their $D' = D$ a-priori.

The supply volume of elements into magmatogenic-hydrothermal system calculation. Developed and presented magmatic and magmatic-hydrothermal systems model of KP granitoids allows to estimate the total elemental resource of the fluid, 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. This opportunity is based on the fact that the proposed model provides data as about concentration of each element in the residual melt, so, using the fluid/melt distribution coefficients, in the fluid, model also estimates the mass fraction of the fluid segregated from magmatic system at any stage of its evolution:

$$\Delta R_{F_n} = \Delta F_n \cdot C_i^{F_n} \cdot M_{sist} / 10^6, \quad (8)$$

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_{sist} — the mass of the system (billion tons). The total fluid resource can be estimated using the expression: $R_F = \sum_{n=1}^n \Delta R_{F_n}$.

As it follows from the expression (8), important and usually difficult for quantitative evaluation initial parameter in such calculations is the total mass of the parental magmatic system M_{sist} . In this case, $M_{sist} \geq 200000$ billion tons was accepted the square of KP granitoids at the present level of erosion — 7800 km², the average density of 2.6 g/cm³, the prevalent depth of ≈ 10 km). According to the lack of data on KP and its frame deep structure, the authors consider this estimation to be approximate, but realistic.

Additional, but quite an important parameter in the elements behavior analysis during evaluation of ore-generating potential of magmatic-hydrothermal systems is *total resource of the parent magmatic system* (R_M), that is, the total weight of each element in the system at the beginning of its evolution. Its calculation, taking into account existing data, is straightforward:

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

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); M_{sist} — mass of the system (billion tons). Model estimations were used as the initial concentrations of the studied elements used in the initial melt of parent magmatic system of the KP granitoids.

The obtained results and their discussion

The calculation results obtained by the proposed approach, are presented in Figure 2. Thus, the total elemental resource comparison in the fluid, segregated from the magmatic system of the KP granitoids during the process of its evolution with a total resource of all parent magmatic system allows to confidently distinguish three groups, among these elements.

The first group of elements (P, Ba, Sr) is characterized by high magmatic system resource with a low fluid-resource, i.e., their total fluid extraction degree from the melt does not exceed 0.2 %.

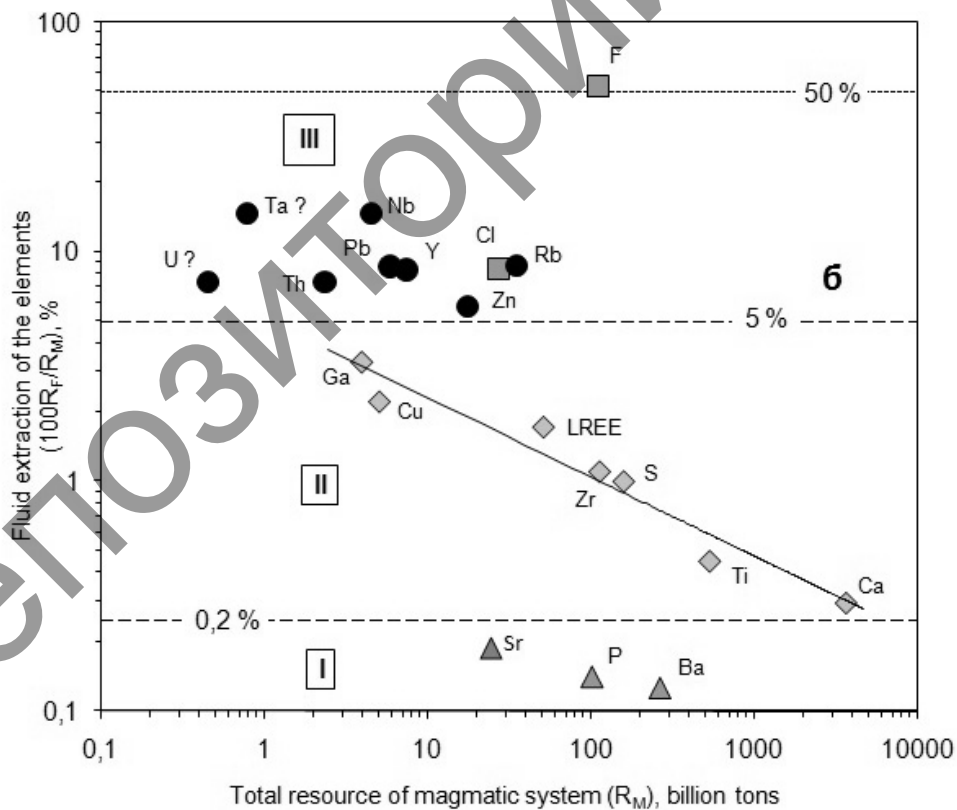
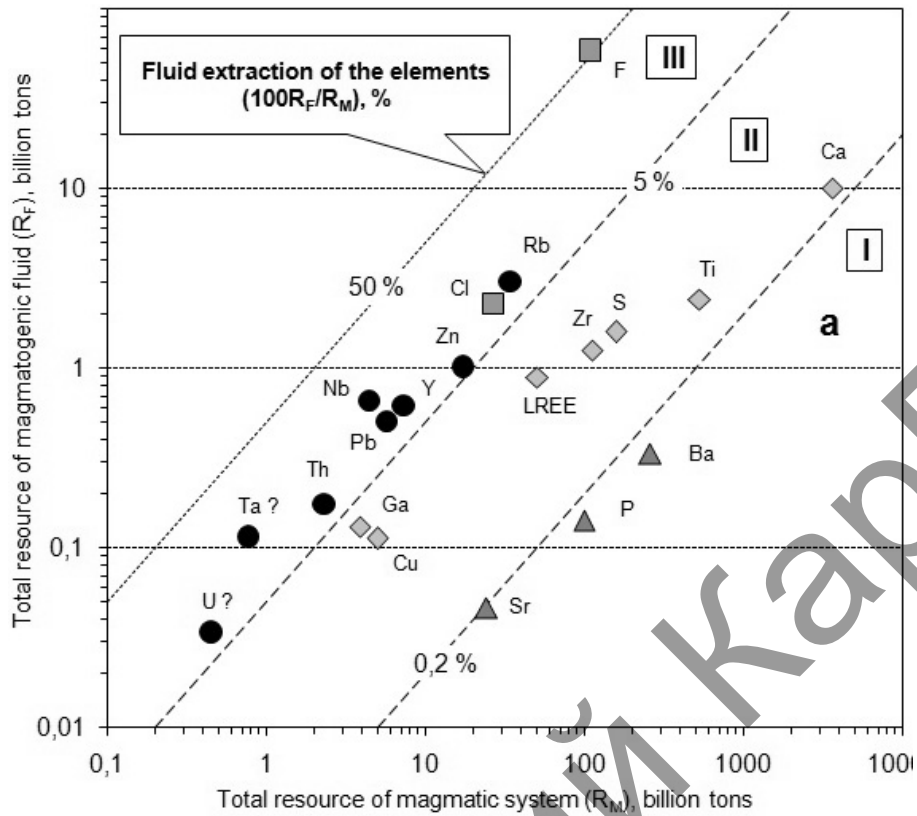
Besides, they behave as typically compatible elements in the process of magmatic evolution (Fig. 1), which results in their low concentrations in the residual magmatic system melt at the moment of the segregation of fluid (most of them «sealed» in the composition of crystallized material and are not available for extraction by the fluid). Therefore, despite the high overall magmatic system resource and relatively high values of the fluid/melt distribution coefficients (>2), P, Ba and Sr under no circumstances show large-scale concentrations in the form of ore-occurrences.

Opposite to the first, is the third group, which is composed of Th, Nb to Rb and F elements. All of them are characterized by a high extraction to the fluid (>5 %), because of their typically incompatible behavior in the process of crystallization differentiation. This grants their substantial accumulation in the residual melt rate and high concentration in the fluid efficiency even with moderate (<1) values of the fluid/melt distribution coefficients (F is also characterized by a high $K^{F/L}$ despite its inverse behavior). But as the total resource of a fluid, so the magmatic system resource vary for them within a wide range (more than tenfold).

The correlation of these parameters (Fig. 2 a) proves that both potential and scale of accumulation in industrial scale is dominant by primary concentration in the magmatic system (i.e. magmatic system resource).

Finally, the second group, which includes a number of elements from Ga to Ca, is transitional between the first and third groups. Regular decrease of the extraction to the fluid degree with increase of magmatic system resource (Fig. 2 b) demonstrates a wide variety of the influence of considered factors with preserved significant role of magmatic system resource as a factor that controls the potential of hydrothermal-metasomatic deposits formation.

At the same time, the obtained evaluations of the total magmatic fluid resource might be considered as a parameter that provides a maximum estimation of the mineralization likelihood potential extent of individual elements and their natural groups. Such evaluations might be only used as the premise of differentiated magmatic complexes potential ore-generation, because the possibility of its application is completely controlled by the geological conditions.



a — the comparison of the total elemental resource in fluid with the total elemental resource in a whole parent magmatic system; *b* — extraction of elements with different resource in the magmatic system to the fluid

Figure 2. The total element wise resource of magmatic fluid segregated from the magmatic system of the KP granitoids in the process of its evolution, and the extraction degree of elements from the melt (model evaluation). Explanations see in the text

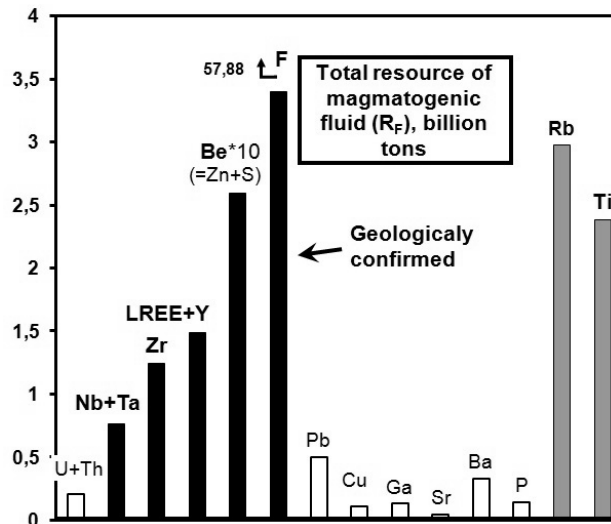


Figure 3. Total element wise magmatic fluid resource as a criterion for the maximum extent of potential mineralization evaluation (the total resource Be was evaluated for stoichiometry of genthelvite — SPZ dominant Be containing mineral). Black-filled bars correspond the elements which industrial mineralization presence is confirmed by geological exploration works. See explanations in the text

However it is supported by a rather positive correlation (Fig. 3) of the calculated (model) data obtained in this work results with existing information on real ore bodies that are discovered within the SPZ, application of such assessments, as long as the geochemical modeling, is able to greatly complement methodology of regional geological surveys.

Conclusions

The calculation methodology of the model fluid/melt distribution coefficients, which directly derives from the observed data on the contents of elements in magmatic complexes petrotypes and mostly corresponds to the real conditions of the magmatic evolution of specific magmatic systems, was developed. Element wise total magmatic fluids resource (supply of elements in magmatic-hydrothermal system volume) evaluation method based on geochemical modeling of parent magmatic systems was proposed. Obtained positive developed methodology approbation results, at the example of the Korosten Pluton and ore-bearing hydrothermal-metasomatic Sushano-Perganskaya area formations, allows to consider it as a promising way of regional geological surveys. Possibility of the further proposed methodology application requires additional development of proposed geochemical modeling means and their extended approbation at the example of geological objects such as Ukrainian shield etc. Kazakhstan also represents an object of a great interest as it possesses the huge fund of magmatic complexes of different age, formation conditions and metal-genetic specializations, which have been studied in detail in material aspect and are supported with the wide specter of ore deposits [8–10].

References

- 1 Шнюков С.Е. Распределение иттрия в апатит-цирконовых парагенезисах: зависимость от температуры и возможность ее использования в геохимическом моделировании магматических процессов // Кристаллогенез и минералогия: материалы междунар. конф. — СПб., 2001. — С. 352.
- 2 Шнюков С.С. Наскрізнні акцесорні мінерали в геохімічному моделюванні магматичних процесів // Збірник наукових праць УкрДГРІ. — 2001. — № 1–2. — С. 41–53.
- 3 Шнюков С.Е. Геохимические модели эволюции магматических систем и земной коры: потенциальный источник петрофизической и рудогенетической информации // Геофизический журнал. — 2002. — Т. 24, № 6. — С. 201–219.
- 4 Шнюков С.С., Лазарева І.І. Геохімічне моделювання в дослідженні генетичного зв'язку магматичних комплексів та просторово асоціюючих з ними гідротермально-метасоматичних рудних родовищ // Зб. наук. праць УкрДГРІ. — 2002. — № 1–2. — С. 128–143.
- 5 Harrison T.M., Watson E.B. The behavior of apatite during crustal anatexis: equilibrium and kinetic considerations // Geochim. et Cosmochim. Acta. — 1984. — Vol. 48, No. 7. — P. 146–147.
- 6 Holtz F., Johannes W., Tamic N., Behrens H. Maximum and minimum water contents of granitic melts generated in the crust: a reevaluation and implications // Lithos. — 2001. — Vol. 56. — P. 1–14.

7 Montel J.M. A model for monazite/melt equilibrium and application to the generation of granitic magmas // *Chemical Geology*. — 1993. — Vol. 110. — P. 127–145.

8 Серых В.И., Габов Ю.А., Новичкова А.П. и др. Минеральный и химический состав ультракислых гранитоидов Центрального Казахстана: сб. анализов. — Алма-Ата: Наука Каз ССР, 1976. — 195 с.

9 Серых В.И., Новичкова А.П., Егорычев Л.Г., Рыбалтовский Е.В. Балхашский сегмент. Петрология гранитоидов. (Минеральный и химический состав гранитоидов северной части Балхашского сегмента земной коры: сб. анализов.). — Алма-Ата: Наука КазССР, 1987. — 184 с.

10 Серых В.И. Геология, петрология и металлогения ультракислых гранитоидов Центрального Казахстана. — Караганда, 2009. — 315 с.

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Магматогенді-гидротермалды жүйелердегі кенжасаушы потенциалдарды бағалаудағы геохимиялық модельдеу

Мақалада магмалық балқымадан кенді су флюидін бөліп алу процесінің сандық геохимиялық модельдеу мүмкіндігі қарастырылған. Ұсынылған рәсімдер микроэлементтердің флюид/ерітіндіге бөлу коэффициентін, олардың флюидтегі санын, сонымен қатар оның элементтердің жиынтықтағы ресурсын есептеуге мүмкіндік береді. Геохимиялық модельдеу нақты кенқалыптастырушы Коростенск плутоны (Украин қалқаны) магмалы-гидротермалды жүйесіндегі гранитоидтар және онымен ассоциация болатын гидротермалды-метасоматикалық түзілімдер (Суцано-Пержанск аймағы) қолдануға ұсынылған тәсілдің тиімділігін растады. Осы кездегі өңірлік жұмыстардың қарапайым есебіне қарамастан, берілген жұмыстың қазіргі және болашақ зерттеулері мақсаты Украина мен Қазақстанның минералды-шикізат базасының әлеуеті болып табылады.

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Геохимическое моделирование в оценке рудогенерирующего потенциала магматогенно-гидротермальных систем

Рассмотрены возможности количественного геохимического моделирования процесса отделения рудоносного водного флюида от магматического расплава. Предложенные процедуры позволяют рассчитать значения коэффициента распределения флюид/расплав для микроэлементов, их содержание во флюиде, а также его суммарный поэлементный ресурс. Применение предложенного подхода к геохимическому моделированию реальной рудогенерирующей магматогенно-гидротермальной системы гранитоидов Коростенского плутона (Украинский щит) и ассоциирующих с ним гидротермально-метасоматических образований (Суцано-Пержанская зона) подтвердило его эффективность. Целью настоящих и будущих исследований является получение оценок минерально-сырьевого потенциала регионов Украины и Казахстана, независимых от простого суммирования уже выполненных региональных работ.

References

- 1 Shnyukov S.E. *Crystal genesis and mineralogy*: Materials of intern. conf., Saint Petersburg, 2001, 352 p.
- 2 Shnyukov S.E. *Coll. of sci. articles of UkrDGRI*, 2001, 1–2, p. 41–53.
- 3 Shnyukov S.E., *Geophysical journal*, 2002, 24(6), p. 201–219.
- 4 Shnyukov S.E., Lazareva I.I. *Coll. of sci. articles of UkrDGRI*, 2002, 1–2, p. 128–143.
- 5 Harrison T.M., Watson E.B. *Geochim. et Cosmochim. Acta*, 1984, 48(7), p. 146–147.
- 6 Holtz F., Johannes W., Tamic N., Behrens H. *Litos*, 2001, 56, p. 1–14.
- 7 Montel J.M. *Chemical Geology*, 1993, 110, p. 127–145.
- 8 Seryh V.I., Gabov Yu.A., Novichkova A.P. et al. *Mineral and chemical composition of Central Kazakhstan ultra-acid granitoids: analysis collection*, Alma-Ata: Nauka, 1976, 195 p.
- 9 Seryh V.I., Novichkova A.P., Egoroychev L.G., Rybaltoveckiy E.V. *Balhash segment. Granitoid petrology. (Mineral and chemical composition of the Balhashskij earth's crust segment northern part. Analysis collecrion*, Almma-Ata: Nauka, 1987, 184 p.
- 10 Seryh V.I. *Geology, petrology and metallogeny of Cantral Kazakhstan ultra-acid granitoids*, Karaganda, 2009, 315 p.