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Melt systems as the basis of paragenetic analysis of mineral assemblages in igneous rocks

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Abstract. The paper considers the simplified P_{H20} -T-projection and crystallization scheme of the *q-ne-kp-fo-mo-aq* system reflecting the process of the magmatic rock crystallization. The rocks are compositionally marginal between the normal series and the alkaline one, and from the normative quartz group to the normative montichellite one.

Аннотация. Представленные диаграммы в упрощенном виде отражают процесс равновесной кристаллизации (без фракционирования) магматических пород, которые по составу располагаются между рядом нормальной щелочности и щелочным. Групповая принадлежность может изменяться от кварцнормативной группы до монтичеллитнормативной.

Key words: melt systems, P_{H20}-T-projection, crystallization schemes Ключевые слова: расплавные системы, P_{H20}-T-проекция, схемы кристаллизации

1. Introduction

A deep insight into the relationship between mineral composition of rocks and their physicochemical formation conditions (chemical composition of initial rocks or magmas, temperature, pressure, and concentration of mobile components in solutions affecting the rocks) is the main objective of petrology. To solve this problem, the physicochemical diagrams more or less adequately reproducing natural processes are needed. Therefore, the development of physicochemical models simulating formation of paragenetic mineral assemblages is an important element of petrologic research based on experimental and theoretical studies concerning synthetic and natural mineral assemblages and properties of minerals, including the data on melting-crystallization of rocks.

The main achievements in petrology fell on the 20th century. The midst of this century was distinguished by especially vivid interest in physicochemical studies and application of their results to the geology, which progressively moved to the destination of exact natural science. As was emphasized by *Zharikov* (1976), the possession of intimate knowledge of physicochemical methods became necessary for each specialist dealing with formation of minerals, rocks, and mineral deposits. The preconditions were created for further progress in this field of research. Monographs by *Korzhinsky* (1957; 1973), *Zavaritsky, Sobolev* (1961), *Nikolaev, Dolivo-Dobrovol'sky* (1961), *Shinkarev* (1970), and others were published in the former Soviet Union. All they made a contribution to the advance in physicochemical petrology. Nevertheless, the current status of petrology leaves much to be desired.

2. Methods

Unfortunately, we have to state that even available physicochemical modeling diagrams do not find their application to solving petrologic problems, apparently due to insufficient education of geologists in physicochemical petrology. Objective reasons are related to the obstacles in the way of construction and application of phase diagrams for the systems containing more than four components. Therefore, the interest in the physicochemical methods that burst out in the first half of 20th century gradually waned in its second half, apparently because of low efficiency of the results based on using 3D isobars at 1 atm. Using three-component diagrams for solution of specific geological problems led either to uncertainties or to absurd conclusions. Precisely this circumstance generated doubts and even crisis in physicochemical petrology. On the one hand, the reliable physicochemical formation conditions of rocks and ores are possible to determine only by applying the corresponding phase diagrams, and no other ways do exist. On the other hand, the phase diagrams of three- and four-component systems do not satisfy completely the demand of the geology that deals with multicomponent systems. Nevertheless, the skilful application of even three- or four-component systems facilitates solution of many petrologic problems. In addition, some theoretical contrivances with isopleth sections reduce a number of components to four and allow working with such sections as with four-component diagrams. Other variants of isopleths are also possible. The projections from apices of excess and indifferent (separated) components are also widely used for visualization of phase diagrams for multicomponent systems (Korzhinsky, 1957; 1973; Zharikov,

1976; *Dubrovsky*, 1984; 1987). The methods of reducing a number of components in the studied systems expand possibilities of physicochemical petrology.

In many cases, when initial data (experimental results, thermodynamic properties of components) are insufficient for drawing an exact diagram, it can be substituted for a qualitative or semiquantitative scheme. For this purpose, it is enough to set the position(s) of nonvariant points and equation of the reaction of monovariant lines pertaining to them or to know their arrangement in the P-T projection established in experiments. The P-T projections are added by isobaric sections of the semiquantitative status. Such semiquantitative diagrams of the multisystems become an efficient tool for forecasting all possible equilibria in the given system deduced from limited data.

3. Discussion

The P_{H2O} -T projection and isobaric flow sheets of the *q-ne-kp-fo-mo-aq* system as juxtaposition of the basaltic *q-ne-fo-mo-aq* and the kamafugite-lamproite *q-kp-fo-mo-aq* expanded tetrahedra (*Dubrovsky*, 2006; 2007) are shown in Figs. 1, 2, and 3. Such a scheme can be obtained by transformation (recalculation) of the oxide SiO₂-Al₂O₃-Na₂O-K₂O-CaO-MgO-H₂O system with Al₂O₃ contents stoichiometric with respect to Na₂O + K₂O content, mol % into the subsystem of end members. To simulate formation of intermediate compounds with the end members undersaturated with silica, this end-member system is, in turn, subdivided into seven end-member subsystems, which differ in degree of saturation with silica and belong to the corresponding groups in the classification proposed by *Dubrovsky* (2002): (1) *q-ab-or-en-di-aq*, (2) *ab-or-en-di-fo-aq*, (3) *ab-or-en-di-fo-aq*, (4) *lc-or-ne-di-fo-aq*, (5) *lc-ak-ne-di-fo-aq*, (6) *lc-kp-ak-ne-fo-aq*, and (7) *kp-ak-ne-fo-mo-aq*. The construction of these diagrams was a rather sophisticated and long job which took 25 years.

One should remember that the complete 3D *P*-*T*-*X* diagram is possible to draw only for two-component systems. Therefore, various projections and sections are constructed for three- and four-component systems rather than complete phase diagrams. More or less full information on a phase diagram can be obtained from a *P*-*T* projection, isobaric *T*-*X* sections, and isobaric flow sheet taken together. All these diagrams are elaborated at the mutual control. It is impossible to present isobaric *T*-*X* sections for the systems having more than four components, and this significantly complicates reproduction of the rest elements of a phase diagram. Due to impossibility to display relationships between concentrations of five components, including H₂O, the nonvariant and monovariant equilibria were analyzed in detail in the particular subsystems with allowance for appearing hydroxyl-bearing phases at the liquidus and proceeding of certain reactions. At low P_{H2O} , the melt crystallization before appearance of hydroxyl-bearing phases and without fractionation will result in formation of the assemblage consisting of five minerals (combinations of end members) + H₂O.

With increase in $P_{\rm H2O}$, first phlogopite (Phl) and then amphibole (Am) appear at the liquidus of each end-member system, giving rise to the formation of nonvariant equilibria (points) and subdivision of end-member subsystems into modal-end-member subsystems. It should be kept in mind that the same-named mineral species in different systems differ in composition to a certain degree. The most significant distinctions, up to the change of species nomenclature, are characteristic of amphibole.

Further increase in $P_{\rm H2O}$ facilitates proceeding of exchange reactions Di + Kls = Fo + Ak + Lct and Di + Mo = Fo + Ak (*Yoder*, 1986), decomposition reaction Lct = Kfs + Klc, and formation of analcime in nepheline-normative subsystems. As a result, 18 nonvariant points appear in the considered system at 0-6 kbar and 650-1200 °C:

I ^{kp} _{phl} – Kls+Lct+Ne+Ak+Fo+Phl+V+L,
I ^{mo} _{phl} – Kls+Mo +Ne+Ak+Fo+Phl+V+L,
I_{am}^{mo} - Am+Mo +Ne+Ak+Fo+Phl+V+L,
I ^{anl} ₁ – Ab+Ne+Anl+Kfs+Di+Phl+V+L,
I ^{anl} ₂ – Ab+Ne+Anl+Am+Di+Phl+V+L,
I ^{anl} ₃ – Ab+Ne+Anl+Am+Fo+Phl+V+L,
I ₁ – Ak+Di+Kls+Lct+Ne+Phl+V+L,
$I_2 - Di+Mo+Ak+Fo+Am+Phl+V+L$,
I ₃ – Kfs+Lct+Kls+Ne+Di+Phl+V+L.

Eight lines of monovariant equilibria go out from each nonvariant point. The problem is to connect these lines into a single scheme. A P_{H2O} -T projection displaying crystallization of igneous rocks from various magmas in a simplified form is a result of solution of this problem. The composition of magma varies in degree of saturation with silica from quartz-normative to monticellite-normative. Its alkalinity must remain constant between normal and alkaline series with alkalinity index $K_{alk}^{al} = 1$ in the classification proposed by *Dubrovsky* (2002).



Fig. 1. Semiquantitative P_{H20} -T projection of the *q-ne-kp-fo-mo-aq* system; the mineral phases shown in parentheses do not participate in the given equilibrium and the underlined phases are indifferent



Fig. 2. Flow sheets complementary to Fig. 1 under low P_{H2O} before appearance of phlogopite at the liquidus



Fig. 3. Flow sheets complementary to Fig. 1 under 3-4 kbar $P_{\rm H2O}$

Difficulty in construction of the coherent P_{H2O} -T scheme is also related to inconsistent arrangement of non- and monovariant equilibria in some subsystems as compared with their ordering by the degree of saturation with silica. For example, phase transformations in the nepheline-normative system occur at a lower temperature than in the olivine-normative system, whereas the former occupies an opposed position by degree of saturation with silica. The same relationship is characteristic of the monticellite- and kaliophilite-normative systems.

The consecutive arrangement of phase transformations in the subsystems is shown in isobaric flow sheets depending on their degree of saturation with silica. Decrease in temperature in the subsystems of one

group is shown from the right to the left as in the P_{H2O} -T projection. The difference in temperature between the adjacent groups depends on existence or nonexistence of thermal barriers.

4. Conclusions

Thus, the presented diagrams reproduce in the simplified form equilibrium crystallization (without fractionation) of igneous rocks, whose compositions are bracketed between normal and alkaline series in degree of alkalinity and between quartz- and monticellite-normative groups in saturation with silica. The increase in Al_2O_3 content to $K_2O + Na_2O + CaO > Al_2O_3$ (molecular units) in the initial system transforms it in the system of normal alkaline system. Nevertheless, a number of minerals and their speciation remain the same after all phase transitions but their compositions change. In the first case, plagioclase varies in anorthite content, and in the second case, alkalinity of pyroxene is variable. Practically nothing is changed, when FeO is added to the system up to the 50 mol % FeO. After that amphibole first appears at the liquidus, and with FeO > 70 mol % the quartz + olivine assemblage appears, whereas amphibole and biotite disappear at the liquidus due to the low temperature of their breakdown. In addition, it should be kept in mind that multimineral assemblages without couples of minerals buffering silica activity may appear in all end-member subsystems. This complicates are almost always identified by their end-member composition.

The algorithm of using the constructed phase diagrams consists in determining mineral and endmember composition of the studied rock, selection of appropriate end-member system and then a level of water pressure corresponding to the real mineral assemblage. Various deviations of the real mineral assemblages from modeling ones make it possible to ascertain the factors that complicate and disturb the equilibrium process.

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