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The formation and differentiation of magmas

Bezmen N.I., Gorbachev P.N. Petrochemical types of layered magmatic complexes and modeling ore-forming differentiation trends.

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Abstract. As the main classification feature of igneous complexes, features of the intra-chamber cameral evolution of igneous melts were taken. The rocks of the stratified massifs are combined into differentiation trends, the combination and location of which on the petrochemical diagram determine the type of differentiation. Each differentiation trend corresponds to its own ore specialization. The number and location of array differentiation trends depends not only on the composition of the initial igneous melts, but also on the physicochemical conditions of formation, with the fluid components having a special role.

Keywords: melt, differentiation, experiment, gabbrosyenite, differentiation melts, contrast, cryptic.

Introduction. Many minerals are associated with massifs of magmatic origin, in particular sulfide copper-nickel ores, chromite and titanium-magnetite deposits, deposits of platinum group elements (PGE), etc. besides petrological, also economic value. In this article, petrochemical systematization of igneous complexes was developed, which formed the basis of the petrologometallogenic classification of differentiated intrusions with the separation of massifs that are promising for the content of ore mineralization.

Theoretical analysis. Method for constructing petrochemical diagrams. The whole range of rocks of stratified massifs (ultrabasic, basic, acidic, alkaline, and even ore) is compared in the diagram. It is based on the separation of the femic components, salic and silica. Since the role of calcium is dual: on the one hand, it is concentrated together with aluminum, binding in the composition of the main plagioclase, on the other hand, it accumulates together with iron in clinopyroxene, the total calcium content was divided by calculating:

$$Ca^{Pl} = 0.5(Al + Na + K), Ca^{Px} = Ca - 0.5(Al + Na + K)$$

The diagram $(Mg+Fe+Mn+C^{Px}+Cr+Ti+P) - (Na+K+Ca^{Pl}+Al) - Si$ (in at.%) clearly shows the petrochemical differences of the rocks, since all the main rock-forming elements are used.

Experimental technique. Some interesting trends in liquid nano-cluster differentiation were confirmed experimentally. As a rule, the fluid phase of the massifs contains water, hydrogen, fluorine and other fluid components; therefore, the experiments were carried out in a high-pressure gas equipment with controlled gas fugacity in the H-C-F-Cl system. It's the main components of magmatogenic fluid. The peculiarity of the experimental technique

was the direct dosing of hydrogen in the fluid by diffusing it through the walls of platinum ampoules using the improved Shaw membrane technique (Bezmen et al., 2016) and controlling the fugacity of other gases in the H-O-C system with buffer reactions involving carbon or Ni-Fe in the presence of hydrogen-containing wustite. The scheme of a hydrogen cell with a charged ampoule is described in detail in (Bezmen, 2001; Bezmen et al., 2016). As the initial silicate sample, a glass powder prepared from oxides was used, corresponding to the bulk composition of the trend rocks. In order to avoid diffusion of iron into the platinum ampoule from the melt during the experiment, the runs were carried out in glass graphite crucibles, or Ni-Fe alloy, which simultaneously were indicators of carbon activity or oxygen fugacity. Fluorine and chlorine were used in the form of an acid solution. The crucible was inserted into a platinum ampoule with a diameter of 8 mm and a height of 50 mm with a wall thickness of 0.2 mm. Then water was poured into the ampoule, the weight of which was determined by temperature and pressure. The presence of water in the reaction ampoule after the experiment was considered a prerequisite for the reliability of the experiment. The welded capsule was inserted into a Re-reactor, which was filled under a pressure of 100 atm with an argon-hydrogen mixture with a given molar fraction of hydrogen.

Methodological characteristics of experiences, received results and their discussion. Stratiform complexes. It was experimentally shown (Bezmen, 1992; Bezmen, 2001) that the composition of the fluid phase has a significant effect on the differentiation of melts. The presence in the fluid phase of carbon-containing gases, especially CH₄, stimulates the separation of ultrabasic melts in the upper parts of the sample. As an example, we present the results of experimental modeling of the basal zone of the Bushveld complex in South Africa. The

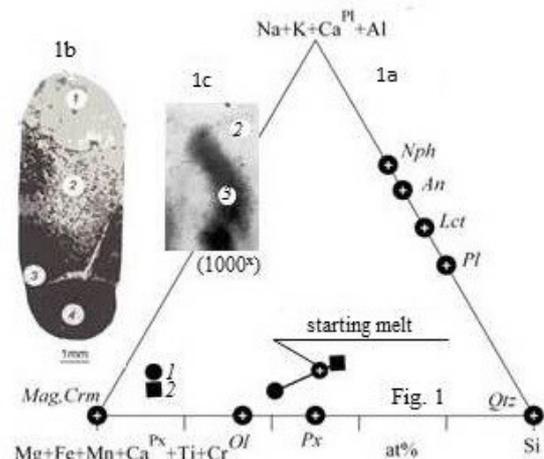


Fig.1.

Abstracts

main role in this part of the section belongs to the dunites and olivine bronzitites containing a small amount of plagioclase. The average composition of this zone (Fig. 1a) is close to plagioclase-containing olivine bronzitite. As the initial composition for experimental modeling glass of the following composition was synthesized from oxides in a high-temperature vacuum furnace at 1700°C (wt.%): SiO₂-49.1; TiO₂-0.2; Al₂O₃-7.56; Fe₂O₃-9.48; FeO-5.36; MnO-0.16; MgO-22.79; CaO-4.52; K₂O-0.11; Na₂O-0.71. The experiments were carried out under the pressure of complex gas mixtures of the H-O-C-S system at $P = 4$ MPa and $T = 1350^{\circ}\text{C}$. The mole fraction of hydrogen in the experiment was controlled by an argon-hydrogen mixture and was $X_{\text{H}_2} = 0.2$. The fugacity of other gases was determined by the presence of elemental carbon from which the crucible was made, and by the melt of pyrrhotite. The fluid phase at the parameters of the experiment had the following composition: $X_{\text{H}_2\text{O}} = 0.31$; $X_{\text{H}_2} = 0.2$; $X_{\text{H}_2\text{S}} = 0.003$; $X_{\text{CO}_2} = 0.077$; $X_{\text{CO}} = 0.19$; $X_{\text{CH}_4} = 0.218$; $\log f_{\text{O}_2} = -9.9$; $\log f_{\text{S}_2} = -3.71$. The specified parameters are as close as possible to the formation conditions of the Bushveld complex, in the rocks of which elemental carbon is present (Touyinhthiphonexoy et al., 1984), in gas-liquid inclusions of minerals recovered gases, including CH₄ (Ballhaus, Stuchfl, 1985). Besides, the redox conditions of rock formation are also close to natural (Elliott et al., 1982).

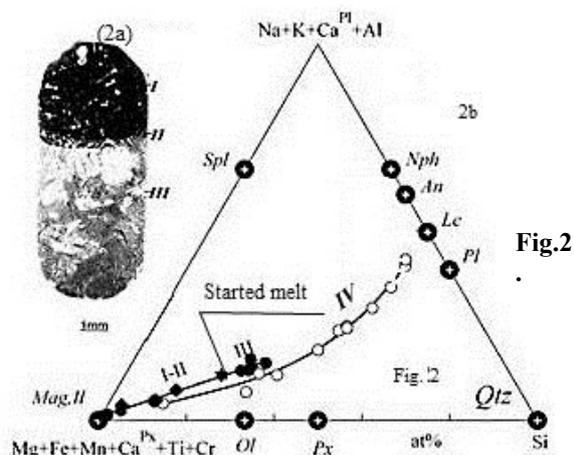
Under the pressure of hydrogen-containing fluids in the absence of a thermal gradient, the initial melt is stratified with accumulation of melt close to the dunite in the upper zone of the crucible, fig. 1b (1). The superliquidus temperatures were confirmed by experiments under pure water pressure ($P_{\text{tot}} = P_{\text{H}_2\text{O}} = 1200$ bar) equal to the partial pressure in mixtures ($X_{\text{H}_2\text{O}} = 0.31$). After 3 days of the experiment, the upper peridotite zone is represented by large (up to 1 mm) idiomorphic olivine crystals crystallized during quenching, between which there is not intergranular liquid. This zone has the following composition (wt.%): SiO₂ - 42.76; TiO₂ - 0.2; Al₂O₃ - 4.2; FeO - 17.41; MnO - 32.69; CaO - 2.14; K₂O - 0.007; Na₂O - 0.44. The lower zone, transparent glass, has a composition close to plagioclase bronzitite: SiO₂ - 50.80; TiO₂ - 0.2; Al₂O₃ - 9.99; FeO - 14.34; MnO - 0.15; MgO - 17.61; CaO - 5.78; K₂O - 0.18; Na₂O - 0.95.

In this zone (2), there is a new fluid separation in the form of packages or spheroids of clusters of macromolecules, Fig. 1b,c (3), which are gravitationally displaced to the bottom of the sample, where they form a liquid enriched with bronzite: SiO₂ - 51.09; TiO₂ - 0.2; Al₂O₃ - 9.37; FeO - 15.13; MnO - 0.15; MgO - 18.36; CaO - 4.71; K₂O - 0.17; Na₂O - 0.84. After quenching, it has a tangled fibrous characteristic structure of the devitrified

colloidal, macromolecular liquids (Strepikheev, Derevitskaya, 1976). The sulphide melt, fig. 1b (3) was used to determine the H₂S and S₂ fugacity. In general, the initial fluid in the experiment determined the antidromic type of differentiation. Antidromic differentiation is characteristic of the Ural-Alaskan type massifs, the Yelan-Vyazovsky and Podkolodnovsky massifs of the Voronezh crystalline shield, the Burpalinsky massif in Siberia. As a result of migration of volatile components to the upper part of the massif, the composition of the fluid changes, which affects the content and specialization of fluid components in melts of cluster shells (Bezmen, 2001). As a result, in some parts of the section of stratified complexes against the background of homodromic development of rocks, an anti-dromic type of differentiation may occur (for example, in the Khibinsky alkaline massif on the Kola Peninsula).

Gabbro-anorthosite, gabbro-granite and gabbro-syenite massifs. These massifs are characterized by close differentiation trends of plagioclase – alkaline ferrous gabbro – ilmenite - Ti-magnetite ores. They were formed in the zones of activation of the platforms in a relatively quiet tectonic setting and therefore they are contrast layered with separation of rich Ti-magnetite and ilmenite ores (up to 15 wt.% TiO₂). It was experimentally studied the stratification in the Novomirgorodsky (Ukraine) gabbro-anorthosite massif and gabbro-syenite one of the Northern Timan (Kola Peninsula).

Novomirgorodsky gabbro-anorthosite massif. The superliquidus nano-cluster laering of the ore-silicate gabbro melt containing anorthosite gabbro (33 wt.%) and ilmenite (67 wt.%) corresponding to the Novomirgorodsky massif rocks is shown in Fig. 2a Pyroxenites of this massif contain atomic carbon phenocrysts, which indicates the reducing environment for the formation of the selected association of the massif rocks. The experiments were carried out at 1250°C and at a pressure of 400 MPa. A weighed homogeneous powder of start composition (210 mg) was pressed into a glass carbon crucible that was placed in a platinum capsule



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of \varnothing 7 mm. Then a solution (150 mg) of acids (HF - 0.25 wt.%, HCl - 0.25 wt.%, H_3PO_4 - 0.15 wt.% and H_3BO_3 - 0.15 wt.%) was poured into the capsule and paraffin, C_nH_{n+2} (50 mg), was added. The composition of the fluid phase was controlled by molar fractions of hydrogen ($X_{H_2} = 0.18$) in the argon hydrogen cell of the reactor and atomic carbon of the crucible (Bezmen, Gorbachev, 2017). Within 3 days, the melt was stratified into three compositions: ilmenite (I), rutile (II) and anortosite gabbro (III). The obtained data (I-III) practically coincide with the natural trend of differentiation of the studied massif (IV).

Gabbro-Syenite Northern Timan massif. During the experimental interaction of magmatic fluid, which is close to the natural alkaline gabbro-syenitic melt of the Northern Timan massif, several stratified melts of different composition were formed, fig. 3 (2), which in the petrochemical diagram coincide with the trend of differentiation of rocks of the massif (1). *Ti-Mag* mineralization in the form of globules is confined to gabbro-pyroxenites (9.19 wt.% TiO_2) and syenite lenticular separations (5.03 wt.% TiO_2).

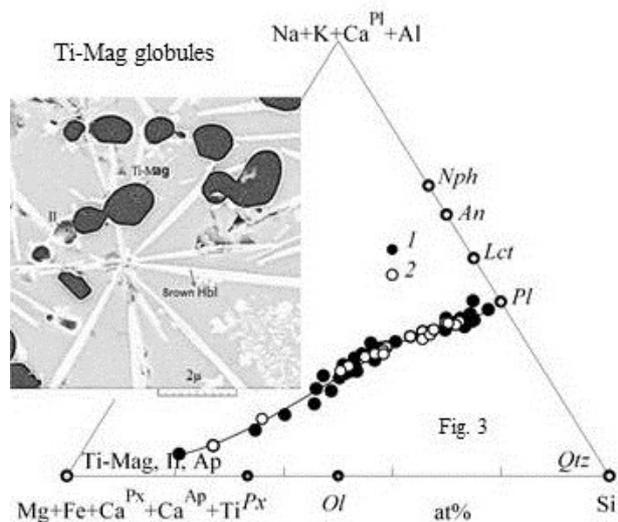


Fig.3.

Chromite ores of stratiform complexes. They are present at various combinations with ultrabasites in the section of massifs and reflect their heterogeneity due to magmatic fluid differentiation. Mineralization is represented by autonomous thick layers or packs of massive monomineral rocks. Very often, ores enter into rhythmic interbedding with basites (dunites, pyroxenites, and sometimes with anorthosites). In general, developing from the dunite-harzburgite ophiolite formations to the dunite-clinopyroxenite rift zones, and then to the stratiform magmatism of the platforms, mineralization changes from chromite to chromite-platinoid (native) and further to chromite-platinoid (sulphide).

An experimental study of the liquid separation of a chromite melt from a silicate melt in the presence

of platinum sulfide liquid was carried out at 1250°C under the pressure of a fluid of the H-O-C-S system. Homogeneous glass, fig. 4 (1) anortite-orthopyroxenite composition, $An_{80}Ab_{20}$ (30 wt.%) - $En_{75}Fs_{25}$ (70 wt.%), with an initial content of 0.5 wt. % Cr_2O_3 , which is close to the bulk composition of the Merensky Reef of the Bushveld Complex. The experiments were carried out in glass-graphite crucibles, i.e. with carbon activity equal to one. Pyrrhotite (3) was used as an indicator of sulfur fugacity.

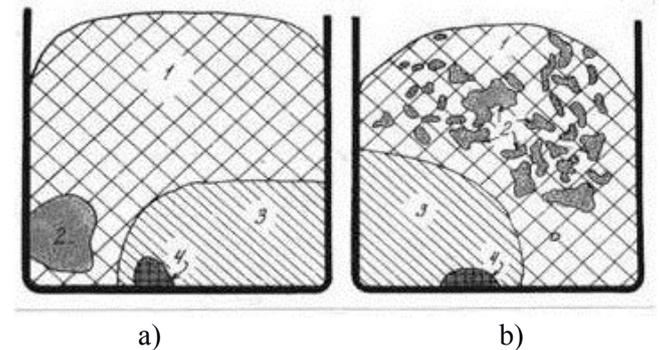


Fig.4.

In fig. 4, it can be seen that after 3 days of exposure, the chromite-liquid (17.85 wt.% Cr_2O_3) separated in the lower part of the capsule in the form of an oval-shaped brown glass, fig. 4a (2), or forms irregularly shaped clusters of glass (3.87 wt.% Cr_2O_3), unevenly distributed over the section of the silicate column (Fig. 4 b). Chromium-containing isolations are placed in a semi-transparent glassy matrix of silicate composition and enriched in sulfur (0.8 wt.%) relative to the silicate matrix (0.1-0.2 wt.%). Sulfide melts (3) are enriched with platinum and gold (4), however, the separation coefficients between silicate and chromitic liquids according to neutron activation analysis (Bezmen et al., 1994) are several orders of magnitude lower ($K_D = n \cdot 10^{-2}$) than for sulfide-silicate separation ($K_D = n \cdot 10^{-3} - n \cdot 10^{-5}$).

Conclusions. The supraliquidus nano-cluster differentiation of magmatic melts, crystallization of magmas at different levels of the section, separation of volatile, enriched ore components, and their interaction with the overlying magmas or rocks constitute a complex petrogenetic system of evolution of magmatic chambers. At various stages of this process, concentrations of fluids arise, leading to the separation of ore magmas, regularly associated with specific zones of the section of the massifs. Since the fluid components migrate both by themselves and simultaneously with the fluid-containing shells of the migrating nano-clusters, the effects of stratification further develop under the influence of fluids in the upper part of the magma chamber. In the lower parts of the magmatic chamber, the crystallization processes are activated

from bottom to top due to the formation of solidus temperatures as a result of the dissipation of fluid components from the melt.

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Bychkov D.A., Koptev-Dvornikov E.V. A high-precision algorithm for solving the problem of equilibrium minerals-silicate melt, not accumulating error during the computation process. UDC 552.111: 550.41

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Abstract. A new algorithm for finding the equilibrium mineral - melt has been developed. On the one hand, it is focused on the use of thermobarometers developed by us for rock-forming and ore minerals, on the other hand, it is independent of the specific type of thermobarometer. Its other advantage is the presence of a clearly defined objective function, which makes it possible to calculate the equilibrium without relying on the previous state of the system and, accordingly, without accumulating errors.

The sum of squared deviations of the current concentrations of the minerals from the concentrations of the minerals calculated using thermobarometers was chosen as the target function. Analysis of the shape of the surface of the objective function for a simplified system showed that it has a pronounced ravine character. An attempt to apply methods known from the literature to search for the optimum of the objective function in the complete system failed, apparently due to the appearance of local minima.

This forced us to develop our own algorithm for finding the optimum of the objective function.

Keywords: simulation, algorithm, thermobarometer, silicate melt, equilibrium

The main goal of our research is the reconstruction of the processes of formation of large stratified base-hyperbasite intrusives. This task is very relevant for modern petrology due to the fact that a large number of mineral deposits are associated with large stratified intrusions - EPG, sulfide polymetallic ores, chromite, magnetite and ilmenite. The largest of them are Bushveld, Stillwater, Great Dyke of Zimbabwe, Skayergaard, Volkovskoye field. In addition, the study of the formation of stratified intrusions can shed light on the problem of magmatic evolution. On the one hand, at present, there is no doubt that the leading process of magmatic evolution is crystallization differentiation. But the dynamics of this process remains acutely debatable.

In our opinion, the most promising way of reconstructing the processes occurring in the chambers of stratified intrusions is mathematical modeling. To build a consistent model of a magmatic object, a combination is needed:

- thermodynamic description of the mineral-melt equilibrium;
- algorithm for finding the phase composition of the magmatic system for a given composition, temperature, pressure and oxygen fugacity
- mathematical description of the flow of heat and matter in the crystallizing massif and its enclosing rocks.

At present, our scientific group has developed thermobarometers describing the composition of olivine, plagioclase, orthopyroxene, clinopyroxene, pigeonite, magnetite, ilmenite, and chrome spinelide in equilibrium with silicate melt (Aryayeva et al., 2016; Aryayeva et al., 2018; Koptev-Dvornikov, Bychkov, 2007; Chernyh, 2017). In addition, a thermobarometer was developed, which allows to determine the temperature and the content of sulfide sulfur in the melt during the separation of sulfide liquid from it (Koptev-Dvornikov et al., 2012). The existing thermobarometers combined with a realistic model (Aryayeva et al., 2016), built using the KOMAGMAT software package (Ariskin, Barmina, 2004), made it possible to accurately calculate the position of the cumulative chrome spinelide in the Burakovsky intrusion (Fig. 1).

Thus, on the one hand, the problem of thermodynamic description of the equilibrium mineral — melt for the main rock-forming and ore minerals can be considered solved. On the other hand, modern software known to us do not allow equilibrium to be found between mineral and melt with arbitrary thermobarometers.