

Glikin A.E. Crystallogenic specificity of multi-mineral systems (by the results of the experimental modeling in aqueous-salt systems)

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The substance of the modeling of mineral formation processes is a reveal of the laws connecting a composition, structure and shape of individual crystals or chemical-morphological features of aggregates with formation conditions. An application of such laws to concrete minerals and their associations requires model investigations at conditions made realistic in terms of the natural ones, that is traditional for the experimental mineralogy. However investigations of general laws are more effective with use of water-soluble salts at low temperatures due to a rapidity of the processes and a possibility of observations in situ. This is validated by a generality of crystallogenic mechanisms when a change of thermodynamic parameters has an effect on a ratio of their components only.

The traditional crystallogenesis is confined mainly to processes of single crystal growth in simple or binary systems. Meanwhile general cases of "multi-mineral crystallogenesis" in ternary and more complex systems are of the principal interest for interpretations of natural features. Really, one can see from the below short review of the data received at the Crystal Genesis Laboratory of the Crystallography Department in St. Petersburg University during the last 20 years, that joint growth of crystals of different phases, metasomatic replacement of crystal substances and aggregate recrystallization are characterized by inordinary combinations of familiar phenomena of single crystal growth and dissolution as well as by specific phenomena of a high novelty [1-10, etc.]. The specificity is determined by an interaction of crystals of different phases and/or of crystals of various isomorphic compositions.

Physicochemical interaction results in conjugated "metasomatic" effects of dissolving and growth; the most peculiar are formations of isomorphic mixed crystals, which form a separate group. The processes are explained on the base of both classical and modified Schreinemakers phase diagrams; the latter have been altered to suit systems with isomorphic salts.

Joint growth was investigated [1] using monocrystal seeds of KCl and NaCl in eutonic aqueous solutions of these salts including those containing MgCl_2 in a wide range of concentrations. A specificity of the process was analysed on the basis of the improved phase diagram of the system $\text{KCl-NaCl-MgCl}_2\text{-H}_2\text{O}$ that revealed substantially more complex features comparatively to the usual configurations, greatly increased an efficiency of our interpretations for multi-mineral media. Deformations of phase boundaries were revealed, that displayed unequally directed trajectories of different solution compositions at parameter variations and unequal dependence of a supersaturation on supercooling in different parts of the diagram.

Substantially, kinetic processes at the crystal surface cause a sharp difference between compositions of the diffusion layer and the rest of the solution even at small deviations from an equilibrium, at supercoolings in the range

1-2 °C. This is confirmed by an overgrowth of paragenetic microcrystals on a KCl or NaCl seed when they are absent in the bulk of the solution. This behaviour of the partner phase NaCl or KCl was observed in all the experiments. However a similar overgrowth of microcrystals of metastable carnallite $\text{KMgCl}_3\cdot 6\text{H}_2\text{O}$ is mostly impressive. It occurs at 12 wt. % MgCl_2 , i. e. out of the thermodynamic stability of carnallite that is higher 25 wt. % MgCl_2 . That is why media composition changes accompanying crystal formation occur in an uncertainly thin diffusion layer while bulk changes are negligible according to the experimental conditions.

The most important phenomena is a dissolution of NaCl seeds in supercooled solutions ($\Delta T=1$ and 2 °C) presented in the experiments by stages of 15-30 min in a general kinematic instability. The phenomena is connected with an advancing growth of NaCl causing a deviation of the solution composition into the stable field of KCl and an increase of a supersaturation of KCl. Further spontaneous formation of KCl microcrystals upon the seed surface is accompanied by the seed dissolving that compensates its advanced growth. The metastable dissolving at a supersaturation for both the phases indicates a metasomatic component of the joint growth of different phases. The component defines the kinetics of any polymineral crystallization to some degree being reflected in various trajectories of the figurative dot. It can cause the ultimate case of the complete metastable dissolving of one of the precipitated phases that we observed for instance in the eutonic system $\text{NaNO}_3\text{-Na}_2\text{S}_2\text{O}_3\text{-H}_2\text{O}$ [12].

A dissolving of KCl and NaCl crystals in a supercooled eutonic solution was also observed at MgCl_2 concentrations more 22 wt. %. As a whole the rates of growth of KCl and NaCl crystals increase, then drop to zero and to a dissolving with the increasing of MgCl_2 concentration at equal supercoolings. This is due to similar nature of dependences of both components supersaturation/undersaturation on MgCl_2 concentration at an equal supercooling resulting from the complicated shape of the phase diagram.

Hence, signs of a mineral replacement in magmatic and other rocks formed definitely by a direct crystallization can testify stages of a metastable dissolution, i. e. a revealed metasomatic component of the polymineral crystallization. Supersaturation is not a simple direct function of a supercooling (or a evaporation of a volatile substance). It varies in a complex fashion undetermined a priori. The correct analysis of a process is impossible without a sufficient information on the phase diagram shape.

Metasomatic replacement of crystals was investigated in about 200 systems [2, 3]. Under isothermal conditions the whole process known in chemistry as "salting-out" is represented by a set of interrelated synchronous sub-processes of a primary crystal dissolving and a secondary substance growth. This results in products having the shape either inherited from protocystal (pseudomorphs) or different from that (automorphs). The structure either remains monocrystalline or becomes polycrystalline: at an isomorphism between the substances or its absence respectively. A change of temperature results in additional processes of growth or dissolving interfering the replacement process, and in the case of salting-in systems there occur hollows in the aggregate, i.e. negative products are formed. Extent of preservation of the primary crystal shape is defined by the kinetic properties of the system: by

the ratio of the diffusion rates of the replacing and replaced substances as well as by the rate ratio of the primary crystal dissolution and a secondary substance precipitation. The product structure, volume effect, and the reaction rate depend upon the type of phase equilibrium the system possesses (isomorphic salting-out, non-isomorphic salting-in and non-isomorphic salting out), which is described by the Schreinemakers phase diagrams. Some diagrams features indicate a possibility of box-like pseudomorphs and poikilitic crystals.

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Recrystallization of aggregates was investigated in 20 systems; the most thoroughly studied was $K_2Cr_2O_7$ - $NaNO_3$ salt pair [4]. The process consists in a complex combination of the metasomatic replacement, growth and dissolving of individuals, and caused by temperature instability or heterogeneity of thermal field; the process proceeds in different manner in systems with salting-in and salting-out.

Prolonged oscillation of temperature in the systems with salting-in results in three stage gravitational redistribution of matter, the resulting two-phase aggregate thus acquiring stationary mineral-granulometric composition, while excess of one of the phases is separated into monomineral aggregate. In salting-out systems the aggregate does not undergo recrystallization. The difference gradually disappears with increasing the aggregate friability. The activity or passivity of the system results from the fact that physicochemical interaction of different phases involves correspondingly positive feedbacks stimulating a recrystallization, or negative ones inhibiting the process. Stability of the final aggregate appears to be determined by its orderliness that ensures stabilities of the local equilibria when temperature fluctuates.

Temperature gradients in any system result in formation of a cavity near the maximal temperature and local rearrangement of matter around the cavity.

Hence, the shape features of metasomatic products enable to outline the possession of the mineral formation media to the listed physicochemical types as well as to reconstruct kinetic conditions. The structure features of the recrystallization products contain also an information on the thermal regime, the degree of the completing of the process and the gravitational vector.

Formation of mixed crystals [5-8] is a combination of phenomena, considerable part of which does not fall under the classical theory restrictions. The replacement preserving monocrystallinity, which was described above, is divided into two types. Volume deficient replacement (relatively fast) is limited by diffusion within the solution and accompanied by inserting inclusions into the crystal body; the inclusions are filled by the solution in ternary media and they can be solid in fourfold or more complex media. Volume excess replacement (extremely slow) is limited by solid phase diffusion and accompanied by a crystal growth with autoepitaxial excrescence formation around the parts of an increased defectness. The process consists in random alternations of growth and dissolving of microspots on a

crystal surface. At the volume deficit replacement a part of dissolving microspots is transformed into the inserted canal-inclusions.

When temperature drops sharply (up to $>30^\circ C$ for $K_2(CrO_4, SO_4)$) metastable heterogeneous equilibrium of the solution is established; there exist two isomorphic crystalline phases enriched with ultimate components of the thermodynamic equilibrium composition. On certain cooling the replacement becomes negligible and normal crystal growth is observed. At this process according to the Ostwald rule, the system should pass over intermediate stages of metastable equilibrium, therefore a multi-modal distribution of crystals in a composition should arise at a spontaneous precipitation. Really, we observed bimodal and more complex distributions for the isomorphic series $(Co, Ni)(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $(Al, Cr)K(SO_4)_2 \cdot 12H_2O$.

These phenomena were discussed on the base of Schreinemakers phase diagrams modified in nomograms to display those compositions of crystals and solutions, which were in thermodynamic and heterogeneous metastable equilibria, as well as to show the composition trajectories for crystals and solutions at the equilibrium, quasi-equilibrium and extremely unequilibrium processes.

Hence, the specificity of mixed crystal formation admits a joint development of growth and dissolution forms on an individual or on crystals of the same mineral species. Also metastable coexistence of minerals of different isomorphic compositions of the same species is admitted. These impose restrictions on adoptions of well-known geothermobarometers as well as give a basis for some new models (for instance, the model of rapakivi formation [9]).

Mechanical interaction of crystals can be observed in their disorientation in epitaxial textures due to turns of crystal nuclei under the influence of growth layers of the substrate [10]. This process was investigated on the example of the epitaxial pair $K_2Cr_2O_7$ -KBr at a heterogeneous nucleation on a growing or dissolving substrate (both the substances were used for the substrates). It was displayed in a quantitative way that epitaxy becomes more perfect when a substrate growth rate decreases and a precipitate growth rate increases. We could outline from these dependencies a mechanical disorientation of precipitated crystals by climbing growth layers of the substrate or by a self-repulsion of precipitated crystals with their own layers (the self-repulsion is important for a precipitation on a dissolving substrate). A fast growth of a nucleus causes its sufficient bond with the substrate before an attack of a slowly climbing substrate layers (and opposite).

Electrostatic interaction can be observed in additional turns of crystal nuclei formed homogeneously to reach epitaxial position in the course of their adherence onto a substrate [10]. or through formation of peculiar adhesion textures. Some orientation features observed for the epitaxial pair KCl-NaCl can be explained by turns of crystal nuclei. However the oriented adherence of cleaved $CaCO_3$ micro-fragments from the aqueous suspension on $NaNO_3$ - and $CaCO_3$ -substrates should be considered as the decisive evidence of this process because the heterogeneous nucleation is ruled out. The epitaxial orientation of the particles is displayed clearly in such adhesive textures, moreover the sharp peak of the distribution is accompanied by of epitaxially oriented particles while such a peak of the distribution is accompanied by a minimizing of the amount of crystals within the adjacent range of the orientations, those were turned at the first.

Electrostatic long-range action is indicated by textures completed with crystals fastened to a substrate by edges or vertexes that was observed for the epitaxial pairs $K_2Cr_2O_7$ -KBr [10], and NaCl-KCl, $CaCO_3$ - $NaNO_3$, $CaCO_3$ - $CaCO_3$ [11]. The stability of such orientations is possible at an optimal combination of attractive and repulsive forces. Note; such orientation effects are caused by an anisotropy of the chemical bonds independently of a crystallochemical similarity of the substances.

The revealed effect of formation conditions on the orientation-disorientation degree for epitaxial and some other textures and the evidences of the relative mechanisms (including ideas by different authors since the Rower's times) permit to consider the results as a foundation of the general concept of epitaxy. The concept unites the crystallochemical, kinetic and adhesive factors of orientation-disorientation of crystals in the textures and determines the specificity of relationship between process conditions and an orientation degree. Owing to this approach the phenomena are moved from the series of "useless" mineralogical features to the field of perspective geospeedometric indicators.

The above examples allow some ideas on a possibility of modern approaches to investigations of the applicable problem aspects of mineralogy.

Thus, the displayed data can be used (or at least should be taken into account) at genetic reconstructions. The extension of crystallogenesis to the polymineral field causes a principally new view on mineral formation processes. A development of this field should establish a theory of the mineral typomorphism. The theory seems to become a barrier for speculative conceptions based on the idea of the obvious inadequacy of natural and laboratory processes of crystal formation.

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