Inhomogeneity of mixed crystal formed from aqueous solutions by direct growth and isomorphic replacement: studding by mCT

L.Yu. Kryuchkova¹, Yu.V. Plotkina², A.Glikin¹

¹ St.Petersburg State University, Crystallography Department, Lab of Crystal Genesis Universitetskaya emb. 7/9, St.Petersburg, 199034, Russia
² Institut of Precambrian Geology and Geochronology RAS, Makarova emb. 2, St.Petersburg, 199034, Russia

Aims
Crystallogenesis of solid solutions (mixed crystals) is a special field spread beyond an ordinary growth process that was found by means of experimental and theoretical elaborations with use of numerous soluble systems, optical microscopy, atomic force microscopy, X-ray microtomography, X-ray diffractometry, microprobe analysis and modified phase diagrams.

Mixed crystal formation is featured by a permanent exchange of isomorphic components between the crystal and solution that is the universal mechanism for an inherent regulation of a crystal composition. The exchange proceeds either in itself or in a combination with growth (or dissolution). It is realized by simultaneous acts of epitaxial growth and dissolution distributed along the surface chaotically in a form of spontaneously alternating micro-spots (compositional micro-mosaic), which sizes vary in the range of orders 0.1–100 micrometers. The spots walk randomly (including appearance and disappearance) all along the surface. The boundary solution acquires an inhomogeneity of a corresponding distribution and change. Overgrowths cover these surface mosaics protecting them from a homogenization. In their turn, the covers undergo the same micro-processes, and new covers bury them in a non-homogenized state, etc. A new layer masks it undergoing in turn the same exchange and so on. As a result the bulk acquires a chaotic isomorphic micro-inhomogeneity while the monocrystallinity is kept. The exchange process controls the total crystal composition.

The crystal-solution exchange runs in two the ways. A volume-deficit exchange runs if the solubility of the solid is higher than that of the dissolved substance. It is fast and causes implanting solution inclusions into a continuous crystal matrix (solid inclusions can penetrate too in quaternary systems). A volume-excess exchange runs if the solubility ratio is opposite. It is slow and causes excrescences onto the crystal surface. As a fundamental result, mixed crystals consist of coherent blocks, which compositions vary in wide ranges gravitating to discrete values determined by specific metastable equilibria.

We investigated mixed crystals inhomogeneity undergone isomorphic replacement and direct growth in aqueous solutions. Most of minerals and industrial substances are represented by isomorphic-mixed crystals, which formation is characterized by specific phenomena and mechanisms distinguished substantially from those for crystals with fixed composition [1].

Method
The samples [K(Br,Cl), K₂(Cr,S)O₄, K₂(Ni,Co)(SO₄)₂.6H₂O and (K,Rb)HC₈H₄O₄] were obtained in aqueous solutions at room temperature. In the course of direct growth, crystals were spontaneously precipitated from a solution saturated at 30°C in a Petri dish at the expense of the natural temperature decrease to room temperature and subsequent steaming through a loose plug over a period of 5–10 days.
During isomorphic monocrystalline replacement, monocrystals of one of the end-members of the solid solution underwent the influence of the saturated solution of the other end-member. The influence was long, in order to obtain volumetric samples of K$_2$(Cr,S)O$_4$, (NH$_4$)$_2$(Ni,Co)(SO$_4$)$_2$·6H$_2$O, (Fe,Co)(SO$_4$)$_2$·7H$_2$O, (Ni,Mg)(SO$_4$)$_2$·7H$_2$O, (Pb,Ba)(NO$_3$)$_2$, or short (first seconds), in order to obtain initial surface textures of K(Br,Cl) and (K,Rb)HC$_8$H$_4$O$_4$.

K(Br,Cl) precipitated crystals with a size of 2–5 mm were studied the most completely. Solutions with mole ratios of KBr/KCl > 2/1 and KBr/KCl < 2/1 are equilibrated with crystals enriched in KBr and KCl, respectively, in comparison with their concentration in solution; at KBr/KCl $\approx$ 2/1, the partitioning coefficient is 1 and the system is aliotropic [2]. Synthesis was performed at the ratios of KBr/KCl = 4.26/1, 2/1, and 1.56/1; in corresponding crystals it was 7.33/1–8.09/1 (core–periphery), 2.22/1 (bulk composition), and 0.39/1–0.54/1 (estimations are based on the known linear Vegard dependence by powder diffractograms, DRON-2 diffractometer, CuK$\alpha$ radiation, Si standard). Crystals had a cubic habit and were composed of practically parallel blocks (from single in Br-rich individuals to numerous in Cl-rich ones) and saturated by inclusions making marginal zones semitransparent and inner zones, nontransparent.

To study the crystal structure, we used the X-ray microtomography method (SkyScan 1172 and 1174) allowing us to work out a qualitative computer model of the volumetric element distribution and then obtain heterogeneity patterns for the given section.

Results
Mosaic inhomogeneity with domain sizes of ~10 $\mu$m is clearly observed in sections of crystal samples (Fig. 1a, b). Domains have different hues of gray color controlled by bromine content variations; the relations between light and dark domains change from core to periphery. The bromine concentration increases from core to periphery, which was revealed by bulk X-ray diffraction measurements in different zones of the crystals, as well as near edge trajectories in the peripheral zone. In the inner zone, domains of various compositions have unclear boundaries with each other being basically isometric. In the peripheral zone, domains are sharply separated and most of them are elongated towards the crystal surface (up to five-fold increase of length over width). Inclusions (black points) are predominantly located in the inner zones, being reflected on the visual image. The boundaries of zones and sectors of growth are significantly blurred, and crystal inhomogeneity increases as the composition of the solution recedes from the aliotropic point (Fig. 1a).

Analogous tomographic patterns were obtained for mixed crystals of the abovementioned compounds and some natural minerals. Note that the study of metasomatic replacement of mixed monocrystals allowed us to observe volumetric inhomogeneity of individuals using other methods, namely X-ray topography (H(K,Rb)C$_8$H$_4$O$_4$ [1, 3]) and optical microscopy (garnet of pyrope–grossular–almandine composition [4]).
The adequacy of the obtained patterns to real crystal structures is confirmed by several arguments. First, these patterns are clearly reflected in numerous synthetic and natural individuals and in all cases are similar in the morphology of domains and their zoned change. As this takes place, elongation of domains is observed in peripheral zones, which provides evidence for the inheritance of surface elements by them. Domains of the central zones most likely underwent evolution of the shape and composition at the expense of inclusion migration similarly to this process during deficit–volumetric metasomatic replacement [1, 3, 5]. Second, the discussed mosaic nature completely corresponds to the main distinguishing feature of mixed crystal genesis, namely the occurrence of the exchange reaction [1], which regulates the isomorphic composition of the crystal and leads to surface inhomogeneity revealed by the atomic force microscopy for (K,Rb)HCl$_2$H$_2$O$_4$ and K(Br,Cl) [5]. The discovery of the volumetric mosaic demonstrates that the surface of the mixed crystal does not relax to the homogeneous state because of continuous growth of new layers and the formation of a homogeneous crystal directly during the growth may not be possible. Third, the heterogeneity of mixed microcrystals by the composition in spontaneous sediment and the mosaic character of monocrystals have an analogous nature and result from the processes of “ensemble” selection of isomorphic materials in the three- and two-dimensional cases, respectively [5].

**Conclusion**

Mixed crystals formed in solution by different processes are inhomogeneous in composition. A mosaic character of mixed crystals we revealed for the first time is a principal importance for the knowledge on the growth specificity of such crystals. Growth front and adjacent solution layer have a coordinated heterogeneity which is of an extended lifetime. Therefore such inhomogeneity appears to be the immanent feature of mixed crystals. This should be urgently taken into account at reconstructions of the mineral origin and at growing of such crystals.

This work was supported by the Russian Foundation for Basic research 12-05-00876.

**References:**