SYSTEMATIZATION OF THE PROCESSES OF TRACE - ELEMENT UPTAKE BY MINERALS AND CHEMICAL TYPOMORPHISM OF MINERAL SURFACES

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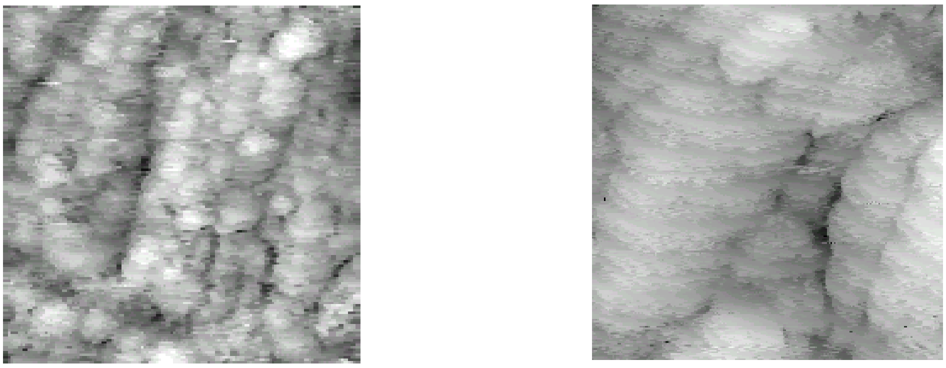
The principles of solid state geochemistry [1] and recently obtained experimental and surface analytical data [2-4] allow systematizing the processes of trace-element uptake by real crystals of mineral phases. The structural mechanism of impurity uptake involves the ion exchange and interaction of the trace element with intracrystalline crystal defects giving rise to such binding forms of the element as isomorphous admixture, clusters and associates of the impurity with point defects, impurity clouds around the dislocations and stacking faults. The nonstructural mechanism implies the interaction of trace element with crystal surface and its fixation in the forms of surface complexes, nonautonomous phases, and inclusions of the autonomous phases (including epitaxial phases). The first mechanism results in the phenomena of isomorphism and endocrypty, the second one results in the sorption, surface precipitation, and epitaxy. The most geochemical interest, especially for endogenous systems, is excited by the process of the formation of nonautonomous phases, particularly pre-phases, the precursors of separate bulk phase of trace element. The studies in nonautonomous phases need the genetic approach accounting for the correlation of these phases with the properties of initial surface of mineral because nonautonomous phases are often form by way of interaction of admixed component with the surface of already existing mineral phase. That is why they are genetically related to initial surface and depend on its composition, structure and crystallography; this dependence defines their nonautonomy. The considerable changes in the character of gold distribution under the influence of nonstoichiometric nonautonomous phase on pyrrhotite crystals were observed during their hydrothermal growth together with greenockite (CdS) at 450°C and 1 kbar. The metal-deficient phases containing up to 10 at. % of Cd are formed in the surface layer of several hundreds nanometer thick. In the system FeS-CdS the nonautonomous phases are more typical for the basal face of pyrrhotite crystals than for the prismatic one. The {0001} face image of pyrrhotite crystal $Fe_{0.98}S$ obtained with scanning tunneling microscope is shown in Fig.1. The surface phase is represented with ordered sphere-like fragments of tens and hundreds nanometers in size, in accordance with the data of surface study with Auger electron spectroscopy with ion etching.



2*2 µm 0.76*0.76 µm

Fig.1. Section of the basal face of pyrrhotite crystal $Fe_{0.98}S$ obtained in the system FeS-CdS. Image in scanning tunneling microscope SMM-2000.

The detailed study of trace-element uptake by minerals often reveals up to 4-5 binding forms observed even under the conditions far from saturation of the corresponding crystalline phase with the element, with the isomorphous form not always prevailing. These binding forms (species) correspond to the main mechanisms of trace-element uptake mentioned above. Fig.2 shows the spectrum of Cd thermoforms of galena crystals obtained under hydrothermal conditions at 400°C and 0.5 kbar. The four binding forms of the element can be determined, although its bulk content is 2 orders of magnitude lower than the incorporation limit of Cd in PbS under the conditions indicated above. Therefore, the study of geochemical processes on the base of physical-chemical regularities of interphase distribution of trace elements must be provided with quantitative diagnostics of their structural forms. Among the nonstructural forms of trace elements, the nonautonomous phases should prevail in endogenic conditions. Under hydrothermal conditions of crystal growth, the importance of sorption entrapment of trace element is low and becomes significant only under the activation of special mechanisms of element retention connected with the surface structure defects.

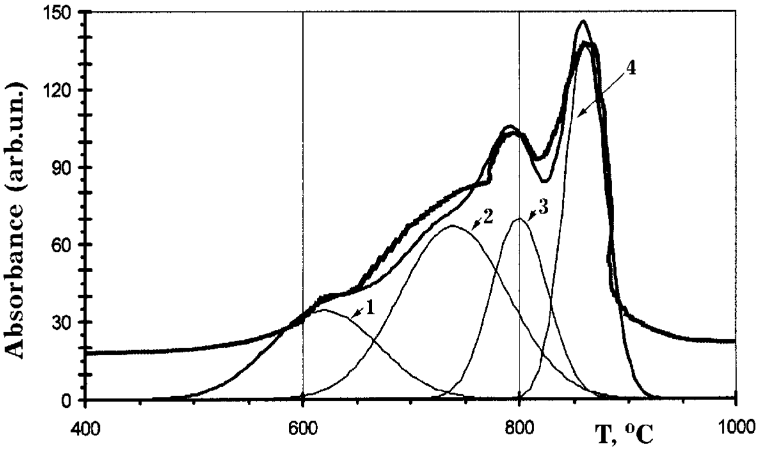


Fig.2. Cadmium binding forms in galena crystals containing 3x10^{-3} wt.% Cd in the bulk and synthesized under hydrothermal conditions at 400°C, 0,5 kbar, and log f_{S2}> -7,1 bar in 5% NH_4Cl solution, from the data of thermal atomic absorption analysis.

Experimental and smoothed curves of Cd release, and deconvolution of the thermal spectrum are shown (peaks 1-4: 1 – sorbed form, 2 – nonautonomous phase, 3 – dislocation-assistant form, 4 – isomorphous admixture).

The oxysulfide nonautonomous phases were observed under the study of the surface of the pyrite crystals, selected from the ore veins and metasomatites at gold ore deposits of Siberia and Far East of Russia. The methods of X-ray photoelectron spectroscopy and Auger electron spectroscopy accompanied with ion etching were used. The presence of such phases is the typical feature of the ore pyrites of epithermal deposits. These phases contain such elements as Tl, Ag, Cu, K, supposedly, in sulfide form. One seemed justified their formation on the pyrite surface as nonautonomous pre-phases because of the proximity of neighboring crystallization fields of chalcopyrite and metastable phases as $TlFeS_2$, $AgFeS_2$, $KFeS_2$.

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