

NON-AUTONOMOUS SURFACE PHASES UNDER SULFIDE MINERAL SYNTHESSES AND THEIR GEOCHEMICAL SIGNIFICANCE

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The surface layers of minerals can be changed in composition under alteration of the conditions of their occurrence. This is a consequence of surface relaxation, that is, the accommodation of a mineral to new conditions of its existence. A considerable change of sulfide mineral surfaces occurs under the action of non-oxidizing mineral acids. As a result, the non-stoichiometric, metal-deficient surface layer is formed. The mineral structure undergoes distortion to several tens or even more nanometers [1,2]. The chemically modified surface layers also appear under hydrothermal growth of sulfide crystals. Such layers can affect strongly the distribution coefficients of trace elements due to their unusual properties: other than in the bulk electronic structure and presence of S-S and S-O bonds.

Note that the surface layer actually represents a non-autonomous surface phase, as was defined by R.Defey and I.Prigogine. This means that such phase can exist only in the ensemble of other phases, particularly, the bulk phase of the same crystal [3]. Nevertheless, experimental evidence permits a more extensive treatment of non-autonomous phases. Taking into account the high concentrations of defects in the surface layer and their significance in adsorption of admixtures, we may suggest the formation of specific configuration of defects and adatoms giving rise to the formation of non-autonomous phase, which cannot be isolated from a given defect-assistant complex. The non-autonomous phases are thought to be crucially important although formerly ignored part of geochemical medium. Their significant role reveals obviously under the study of trace elements uptake by real sulfide mineral crystals.

The experimental procedure was recently described by the authors [4]. The experiments were performed at 400 and 450°C and 0.5 and 1.0 kb in NH_4Cl aqua solutions using thermal gradient method. The study of Cd speciation in galena by thermal atomic absorption analysis [5] shows that the adsorbed form at high sulfur fugacity is nearly lacking. Along with it, the thermal peak of mineral form and double peak of structural form were observed. The doublet has been previously designated as

dislocation-assistant form [5]. The distribution coefficient of Cd became several times higher when dislocation uptake observed, in accordance with theoretical prediction [3]. The appearance of the mineral form also elevates this coefficient. Thermal atomic absorption data for PbSO_4 shows that this form can be the sulphate one. However, the study by surface spectroscopy methods indicates its sulphate-chloride composition. Two facts allowed attributing this phase to the non-autonomous surface phase. First, the galena crystals are quite undersaturated with Cd admixture. Second, in the cases when the run produce the autonomous sulphate phase (mineral anglesite) this form was lacking. One seemed justified that the form under consideration is not directly deposited from the solution in the field of SO_4^{2-} predominance but appears by the way of interaction of Cd with oxidized galena surface alongside this field. Thus, the non-autonomous phases can actively participate the entrapment of trace elements by mineral crystals. The mechanism of admixture uptake by the process of the formation of non-autonomous phases is likely to be geochemically important. These phases are more stable as compared with ordinary surface complexes and therefore, can be used as a source of genetic information from mineral surfaces. Additional evidence in favor of this conclusion was obtained from the study of Cd admixture to pyrrhotite. This mineral was crystallized in association with ferrous greenockite (Cd,Fe)S. It seemed likely that the inclusions in pyrrhotite crystals should have corresponding composition and metal to sulfur ratio close to unity. Nevertheless, the detailed study of pyrrhotites of different composition using Auger spectroscopy and ion etching shows another picture. The investigation of crystals in depth revealed different compositions of surface and subsurface layers for the crystals of different morphology. Accordingly, the non-autonomous phases occupied crystallographically different planes. For instance, Figure shows the data for pyrrhotite of composition $\text{Fe}_{0.87}\text{S}$. Solid lines show the changes in stoichiometry, that is, the ratio of the sum of non-metals to the sum of metals (left-hand scale). Dotted lines show the Cd contents in the layers during ion etching of crystal surface with a rate of ~ 0.1 nm/s by the argon ions beam of 2 keV. In the nearly isometric crystals, Cd admixture either not determined (the case a – slightly magnetic type) or represented by the

inclusions with high Cd content (b – strongly magnetic type), that are close to stoichiometry MeS. In the crystal of plate-like form (c) the appearance of Cd in the layer of ~100 nm thick is accompanied with the change of composition from stoichiometric Me_4SO_3 to metal-deficient and again stoichiometric $\text{Me}_3\text{S}_3\text{O}_2$ when Cd content becomes zero (Figure). Therefore, Cd admixture is absorbed by the metal-deficient non-autonomous phase. It thought to be most important that this phase is buried inside of the oxidized surface layer. If this observation is true for natural conditions too, it may have an important value as a unique source of information about the history and mechanisms of the processes at mineral surfaces.

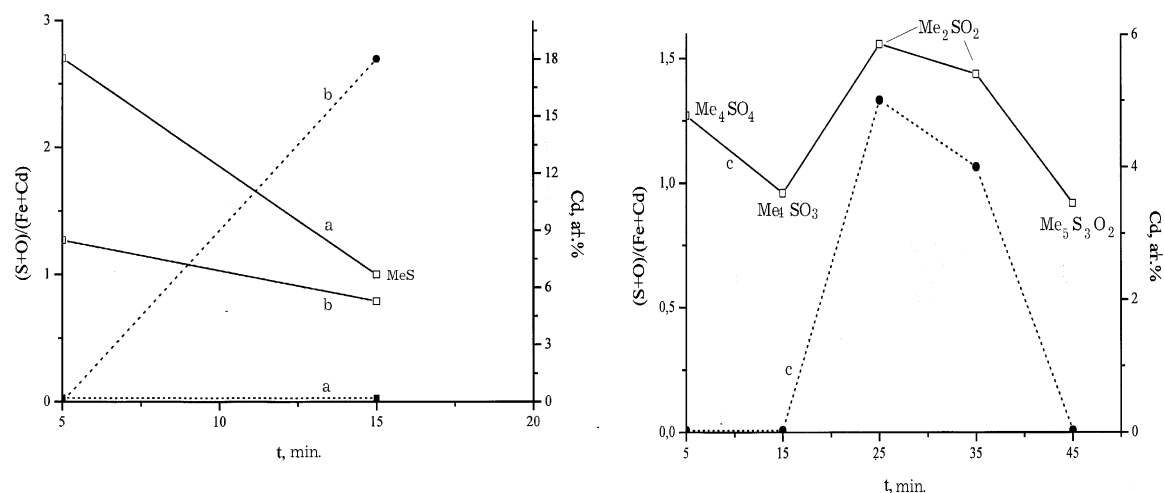


Figure. Changes of stoichiometry (solid lines) and Cd content (dotted lines) in the surface layers of pyrrhotite $\text{Fe}_{0.87}\text{S}$ crystals against the time of ion etching. The crystal types: a,b – isometric (prismatic), a – weakly, and b – strongly magnetic; c – plate-like. It can be seen that for isometric crystal the appearance of high Cd content falls on a near stoichiometric layer composition and more likely due to inclusion of equilibrium phase $(\text{Cd},\text{Fe})\text{S}$. In a plate-like crystal, the appearance of Cd in the layer of ~100 nm thick is accompanied by deviation of the layer composition from stoichiometry. Thus, Cd admixture is absorbed by a metal-deficient non-autonomous phase.

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