CHEMICAL TYPOMORPHISM OF MINERAL SURFACES

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Recent trends are toward increased studies on different aspects of physics and chemistry of mineral surfaces. Nevertheless, the genetic information is usually beyond the scope of such investigations. The reason is obvious so the surface reacts very sensitively to any change in ambient medium and generally not retains any traces of previous conditions. Purely sorption works that comprise a principal portion of investigations in this field consist of the construction of adsorption isotherms, mathematical description of the processes and their kinetics. In so doing it becomes clear that speculations on mechanisms of metal adsorption cannot be stated upon mathematical models of its elimination from the solution. Similarly, the kinetic models are impossible to use for prediction of the character of adsorption and its irreversibility beyond certain time interval possibly restricting to several months – a minute event in geological time scale. However, in the recent experimental works it has been shown that some phase-like forms occupy the reconstructed mineral surfaces representing thin-film islet-like precipitates, quasiphases or non-autonomous surface phases [1,2]. These forms are quite persistent and probably can exist under certain conditions during geological time. The surface tomography that is the layer-by-layer surface study can give information about the sequence of processes, specifically, about variations of chemical composition giving rise to the precipitation and distribution of such forms. We have performed a comparative study of natural and synthetic gold-containing pyrites using the methods of X-Ray Photoelectron Spectroscopy and Auger Electron Spectroscopy to estimate the mechanism of gold concentration by the processes of ore formation-assistant metasomatism.

The pyrite crystals were obtained in presence of Au and gold-accompanying elements (As, Se) by a standard procedure of hydrothermal synthesis at 450°C and 1 kbar. The experimental data allowed to evaluate the composition of the initial surface formed directly in the process of crystal growth. The analysis of differential Auger spectra shows that in the case of Se the surface layer of nearly 0.1 μm thick contains Fe oxides whereas in the system with As two kinds of crystals are formed: similar to the above-mentioned and sulphate-containing. In the latter case the oxygen compounds are found even after one hour of ion etching and the thickness of oxide film is comparable with that one for natural pyrite. In the experiments with Se, the oxide film is thinner and completely disappear in 20 min under 2 keV Ar ion bombardment. The results obtained show that the surface of hydrothermal or metasomatic pyrite is oxidized to depth of ~0.1-0.5 μm and the original (juvenile) surface contains about 10-20 at. % of oxygen incorporated into the oxide-sulfide surface layer.

The natural gold-bearing pyrites from the ore metasomatites of epithermal Au-Ag deposit «Dalnee»(North-East Russia) contained in the surface layer some lithophile elements (Si, Al, K). Iron was absent in the surface. The differential Auger spectra for different terms of ion bombardment are shown on fig.1. The composition of surface film is changed with depth (fig. 1A-C): Al and K leave the surface, Si is still retained and distinctive LMM triplet of iron appears. However, only after etching during one hour the picture of oxidized pyrite is observed that is similar to experimental samples (fig.1D). The covering layer is a ~0.5 μm thick. It should be taken into account that the specimen studied is characterized with an anomalous gold content represented by its evenly distributed, “invisible” form (up to 100 ppm in the fine fractions of pyrite crystals). The concentration of evenly distributed constituent of Au admixture correlates with the average specific surface area of crystal in statistical samples of different size fractions. This points clearly to the attribution of “invisible” gold to the surface, that is, the adsorbed nature of gold. We suppose that the concentration of dispersed gold on the surface of pyrite from ore-adjoined area took place under the action of alkaline ore solution. The deposition of gold was a consequence of neutralization of the solution under its interaction with “acidic” pyrite surface containing SiO_2 and iron oxides. This is the reason for gold deposition in ore-embedded rocks on the pyrite surface whereas in ore veins pyrite and gold are deposited simultaneously [3]. Thus, the surface composition makes possible to establish an important typomorphic criterion to differentiate between pyrite of ore veins and pyrite of ore-containing metasomatites. The changes in composition of the shell of the pyrite crystal in depth give evidence that the pyritization took place in excess of SiO_2 but next the formation of sericite and adularia occurred with possible participation of potassium introduced by ore solution. As a result, the shell with intermediate composition between adularia and sericite was formed.

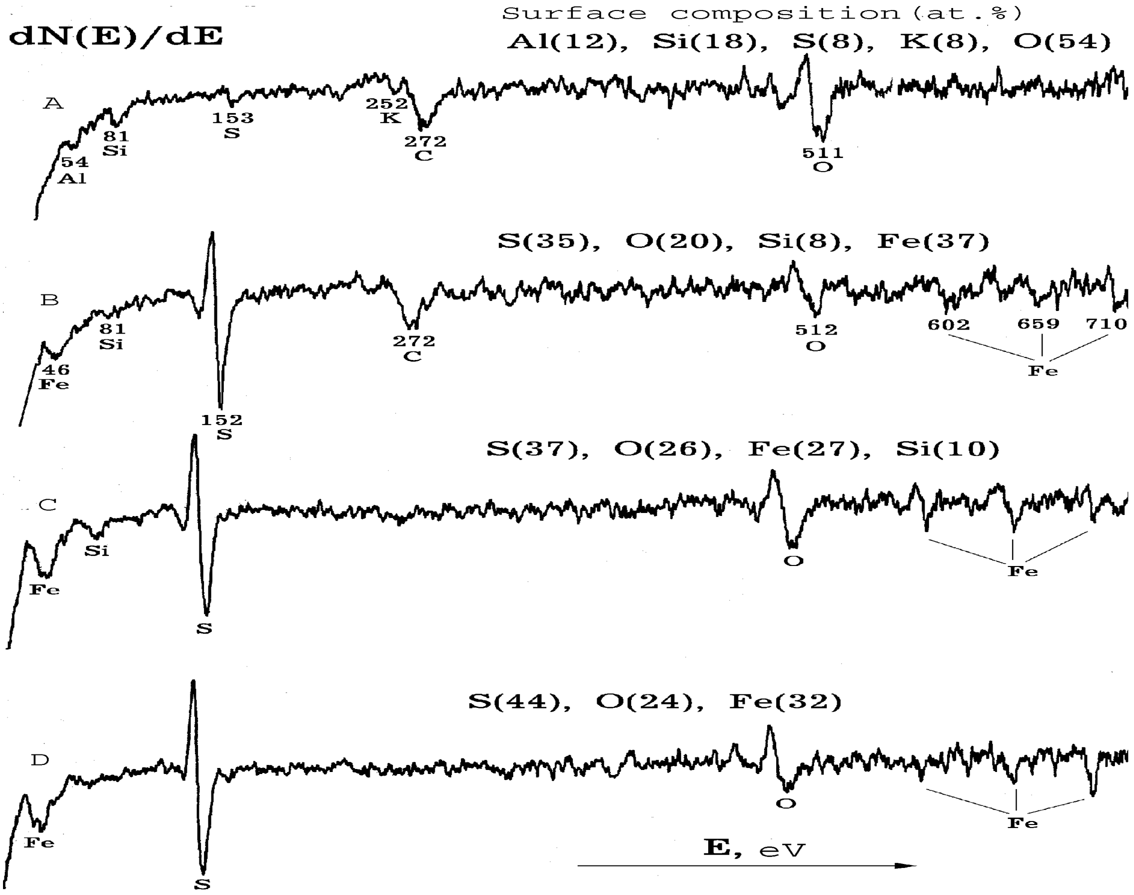

Fig.1. Differential Auger spectra of pyrite from ore metasomatites of epithermal deposit. **A**- initial sample with cleaned surface (5 min of ion etching); the lithophile elements (Al, Si, K) are present in the surface layer; **B** and **C** – 20 and 40 min of etching correspondingly; the pyrite oxidized surface exposed but Si is still present; **D**- 60 min etching, oxidized pyrite surface

The data obtained allow making two principal conclusions. First, the study of natural objects supports the experimental evidence of the significance of surface precipitates and non-autonomous phases for the mechanisms of uptake of incompatible elements such as gold in pyrite practically not incorporated into the pyrite structure [4,5]. Second, the comparison of natural and experimental data makes possible to estimate the composition of the original (juvenile) surface appeared during crystal growth process. This allows determining some benchmark (juvenile surface) above which the post-growth changes are imprinted in the composition of near-surface layers. Taking as an example the pyrite crystals of epithermal Au-Ag deposit we are able to show that the metasomatic processes can be marked in such a manner.

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