

Nonautonomous Phases As Potential Sources of Incompatible Elements

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The genesis of some deposits of noble and rare metals, which are extremely scarce in crustal and mantle rocks, attracts permanent interest of specialists in the field of ore formation. A new systematics of absorption of trace elements by real mineral crystals with participation of the so-called nonautonomous phases has been elaborated recently [1]. By definition, the nonautonomous phases cannot exist independent of crystal surface in contrast to the common (autonomous) phases, which can be separated from the system without a change of their composition and structure and alteration of related phases. The nonautonomous phases are formed by interaction of the surface with the surrounding medium or contacting phases. Moreover, a trace element may be absorbed by a crystal owing to its incorporation into nonautonomous phase as a result of interaction with the chemically and structurally modified surface layer of the crystal. The concentration of the trace element may be many times higher than its bulk content in the respective autonomous phase. In the polyphase continuum and at a lithostatic pressure of a few kilobars, each interphase boundary virtually represents a nonautonomous phase that provides excess partial thermodynamic potentials of the system. Relaxation of the excess may be provided by absorption of the trace element, if the absorption makes it possible to decrease the local thermodynamic potential of the system. In principle, the situation will not change if the second phase is a fluid. Moreover, in this case, absorption will not be restricted by the rate of diffusion, which is much faster in fluids (virtually, instantly in the geological scale of time) than in solids. Getting to other thermodynamic conditions, e.g., in the course of

change of fluid composition, the nonautonomous phases become unstable and they supply incompatible elements to a new fluid. Initially, these elements were quite compatible with structure and properties of nonautonomous phase. Thus, a nontraditional source supplies trace elements (including noble metals) to ore-forming fluids that percolate in the pore space and discontinuities (faults and fractures) of crustal rocks.

This communication furnishes evidence for the existence and stability of nonautonomous phases and their elevated absorption capacity with respect to trace elements. Possible mechanisms of nonautonomous phase formation in mineral systems are also considered. The experimental basis includes results of X-ray photoelectron and Auger electron spectroscopy [2] together with results of scanning tunnelling microscopy of pyrrhotite crystals synthesized under hydrothermal conditions in the Fe–S–CdS–NH₄Cl–H₂O–(Au, As, Se) system at 450°C and 1 kbar [2, 3]. Trace elements are shown in parentheses. The images of crystal surfaces have been obtained with a SMM-2000 scanning multi-microscope made in Russia. The measurements were carried out in the regime of atomic force microscopy (AFM) in a contact mode that provides resolution of a few angstroms on solid samples and in a regime of scanning tunnelling microscopy (STM) that yields a resolution of parts of angstrom on electroconducting samples.

The formation of a thin layer of polymorphic modification of substance, which is metastable in bulk phase but stable in minor particles or thin films, is a well-known process. For example, the sphalerite crystals growing from a relatively low-temperature hydrothermal solution bear a thin film of high-temperature ZnS modification (würtzite), which is stable above 1020°C [4]. The impurities dissolved in the nonautonomous phase of hexagonal würtzite more readily than in cubic sphalerite will be retained and accumulated in this film. First of all, this is actually recorded in the distribution of oxygen microimpurity, because ZnO has a würtzite structure [5]. Absorption of very high Au concentra-

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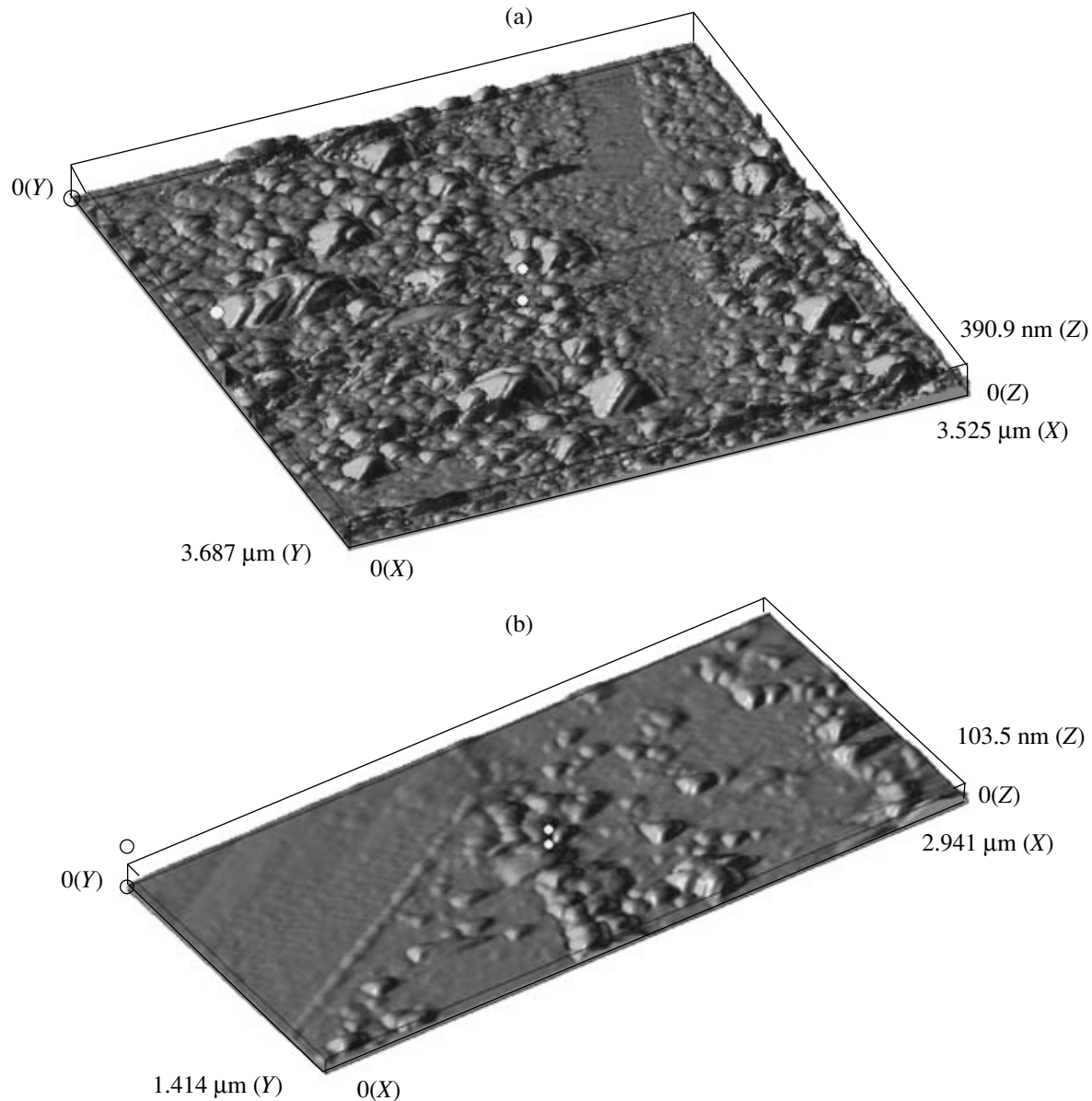


Fig. 1. AFM 3-D images of pyrrhotite crystal surface with a nonautonomous phase enriched in Cd and Au. (a) Nanoglobular structure, transitional forms between globules and tetrahedrons, and nanopyramids composed of tetrahedrons; (b) small, variously oriented tetrahedrons and their combinations adjoining the polished surface. Products of hydrothermal synthesis in the Fe–S–CdS–NH₄Cl–H₂O–(Au, As) system at 450°C and 1 kbar.

tions by As-bearing pyrite surfaces is extremely interesting and important for processing Au-bearing ores. As has been established in experiments, pyrite under equilibrium cannot contain more than 3 ± 1 g/t Au at 500°C and 1 kbar [6]. However, As- and Te-bearing pyrites from some epithermal and Carlin-type gold deposits contain as much as 500–700 g/t of structurally bound gold as has been established by modern analytical methods, such as PIXE with ion channeling, XANES, EXAFS, and SIMS [7–9]. Gold occurs as Au¹⁺ in contrast to the traditional scheme of isomorphism: $\text{Au}^{3+} \leftrightarrow \text{Fe}^{2+}$, $\text{AsS}^{3-} \leftrightarrow \text{S}_2^{2-}$. As has been men-

tioned in [10], the unusually high Au content is most likely related to the lamellas of As- and Au-bearing marcasite or Au-bearing arsenopyrite, in which Au occurs as a structurally bound species. The concept of nonautonomous phases could explain the effect of the superconcentration of structural gold in pyrite that is at least two orders of magnitude higher than equilibrium values. The crystallizing pyrite can bear a thin film of nonautonomous marcasite, which is unstable as a bulk phase. This provides strong surficial enrichment of crystal in both As and Au. A similar structure of marcasite and arsenopyrite, which, as is known, is mixed with a gold quasi-component AuS₂, though in a limited

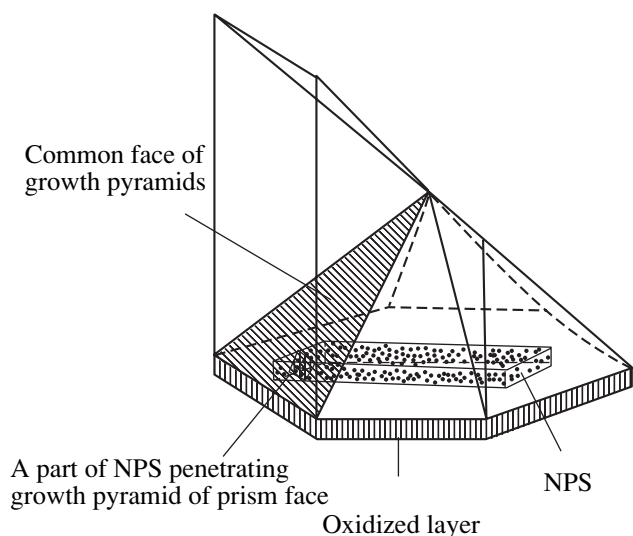


Fig. 2. A model of prismatic half-crystal of hexagonal pyrrhotite with nonautonomous phase segregation (NPS) in the plane of basal face that demonstrates the formation of sectorial zoning by element incorporated into the nonautonomous phase.

amount [11], may be a cause of this phenomenon. Thus, the enrichment of pyrite crystals in As and Au may be a surface effect related to the formation of nonautonomous phases. When the crystal continues to grow, marcasite and arsenopyrite, with high contents of structural Au, make up alternating nanophases in near-surface zones of As-bearing pyrite crystals.

Stability of nonautonomous phases through geological time and the cause of such stability is a pivotal question in respect to their genesis. One answer to this question has been given in [2]: a nonautonomous phase may be stabilized deep in an oxidized surface layer. The study of pyrrhotite crystal surface as a product of hydrothermal synthesis in the FeS–CdS system in the presence of some microcomponents led to another possible solution. Crystals of $\text{Fe}_{0.98}\text{S}$ turned out to be substantially enriched in Cd (as high as ~10 at %) at the surface, whereas equilibrium Cd solubility for this composition is $<10^{-3}$ at % [12]; i.e., the surficial enrichment attains more than 10^4 times. At the same time, the phase composition correlation to Au distribution is distorted, most likely, also due to gold absorption by a nonautonomous phase in the surface layer [3]. The study of the crystal surface with scanning tunnelling and atomic force microscopy revealed the areas with prevalent globular structure and the areas dominated by well-developed forms (tetrahedrons and their combinations) occasionally passing into pyramidal forms. The AFM images of the crystal surface (Fig. 1) demonstrate a multilevel (fractal) structure. The globules, ~10–100 nm in diameter (D) and slightly flattened along the Z axis, serve as a basis of this structure. Having reached $D > 100$ nm, the globules are transformed into nanopyramids, and eventually into pyramids with 400-nm edges

at a higher level of hierarchy. It is clearly seen that these pyramids consist of tetrahedral subindividuals. The morphological diversity of small pyramids, their orientation, the presence of globules nearby, and tracks of pyramids on polished surfaces indicate that the majority of these features cannot be formed by an AFM needle that cuts globules due to its pyramidal shape; i.e., the pyramids reflect the real surface structure rather than the result of the convolution of a probe needle function and the studied surface [13]. Such a fractal structure is observed for the first time. However, an ordered globular structure of similar dimensions was recorded with an AFM on hydrothermally grown hematite crystals ($\alpha\text{-Fe}_2\text{O}_3$) [14]. Judging by morphological features, the nonautonomous surface phase responsible for Cd and Au absorption is based on a cubic CdS form that is stabilized by Fe in minor crystalline particles and retained in the metastable state in the bulk phase. Stability of these particles may be controlled by a phase size effect [15]. To transform them into the hexagonal species that would grow further in the field of its thermodynamic stability, it is necessary to change the composition of nonautonomous phases. This is impossible to do, due to the phase size effect that puts specific structural and compositional features in correspondence with the certain dimensional parameter.

The preferential localization of nonautonomous phases on the face of certain crystallographic orientation and the effect of this localization on crystal morphology is one more interesting feature of nonautonomous phases. Because nonautonomous phases block up the normal growth of the respective face, it widens in the tangential direction at the expense of neighboring faces and becomes the best expressed in the crystal habit. In the case of pyrrhotite, such a face is represented by the basal plane $\{0001\}$ [2]. It is easy to show that this effect may lead to sectorial inhomogeneity in the distribution of a trace element. Figure 2 shows a model of a prismatic half-crystal of hexagonal pyrrhotite that bears a nonautonomous phase on the plane of its basal face. One can also see an oxidized surface layer with thickness varying from <30 to ~300 nm [2]. As is seen, the nonautonomous phase makes up a small protrusion to the locus of the prism face. The structure of this crystal will be sectorial. The element absorbed by the nonautonomous phase will be nonuniformly distributed by growth sectors and will largely be gained in the pyramid of the basal face. The cause of this inhomogeneity may be established only by surface analysis methods with a rather high resolution that would make it possible to record nonautonomous phases.

Thus, nonautonomous phases can absorb microelements with an enrichment coefficient of (in comparison with bulk content) $\sim 10^4$ and may serve as important and so far unaccounted sources of incompatible elements. They can retain a relative stability in natural mineral systems as a result of their capacity to be conserved inside the oxidized surficial layer and the phase dimen-

sional effect in thin surficial films. They can also affect crystal morphology and generate a sectorial zoning. Nonautonomous phases often are metastable in the bulk phase but stable in small particles and thin films of polymorphs of the same substance. The surface occupied by nonautonomous phases reveals fractal properties.

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