

Minerals of Rare Earth Elements in the Phosphate Fraction of Ferromanganese Crusts on Seamounts

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Ferromanganese crusts on seamounts are among the major forms of solid fossil minerals in the ocean. They contain a significant amount of nonore inclusions, including calcium phosphates that often represent the crust-underlying and closely associated substrate.

Phosphate is an undesirable impurity in ores, on the one hand, and an independent form of chemical raw material containing not only phosphorus, but also rare earth elements (REE) and several other valuable components, on the other hand. Preparatory works were started recently for the development of ferromanganese crusts on the Magellan Seamounts in the northwestern Pacific (see [1] for the description of the geology and ore potential of this region). Therefore, comprehensive investigation of ferromanganese crusts, in particular, their technological samples (including the phosphate fraction), has become a pressing issue. Such samples were taken during several cruises of research vessels of the Research and Design Institute of Geophysical Methods for the Exploration of the Ocean (Gelendzhik). Now, they are being processed in the Fedorovskii All-Russia Research Institute of Mineral Resources (Moscow) and other scientific organizations.

In order to carry out mineral investigations, we took phosphate rock fragments from an integral technological sample of crust with the following average composition (%): manganese oxides 21, iron oxides 19, and phosphate phase 10. According to previous investigations, such ferromanganese crusts can contain as much as 50% phosphates in some places [2, 3].

Mineralogy of the phosphate phase was analyzed using an analytical electron microscope (magnification up to 30 000–50 000). Fresh chips of samples were sputtered with carbon according to the method described in [4, 5] and examined with a BS-540 electron microscope (Czech Republic). Microdiffraction patterns of particles extracted on the carbon replica were recorded with a special device attached to the electron microscope and deciphered according to the method [5].

The results showed that the studied rock is primarily composed of aggregates of euhedral apatite crystals represented by hexagonal plates and short-prismatic prisms. The randomly distributed crystals vary from <1 to 2–4 μm in size. Minor gaps between crystals include a slightly crystallized phosphate material. One can see that the phosphate is associated in some places with differently crystallized calcium carbonate if the boundary between the phases is distinct. Moreover, the phosphate near the boundary is less crystallized. In some places, the carbonate material includes relicts of partly phosphatized coccoliths and foraminifers. Space between crystalline phosphate aggregates is often filled with a fine-dispersed hydroxide mass mainly represented by a vernadite composition. In some porous sectors, one can see rare halloysite fibers or their clusters up to tens of micrometers in size.

Sulfide minerals are abundant in ore crusts and associated phosphorites [5–10]. The studied phosphate fraction only contained cubic pyrite crystals (mainly, 0.2–0.3 μm across). One preparation also included barite crystal aggregates (up to 15 μm) of closely packed platy crystallites.

Minerals of REEs (hereafter, REE minerals) are of the greatest interest. In some places, faces of apatite crystals have a coating of fine-grained cerianite (Ce, Th)O₂ particles (0.0n μm). If the particles are closely packed, they make up a coating on the crystal surface (Fig. 1a). Fine pellicular segregations of another REE mineral—parisite (Ce, La)₂Ca(CO₃)₃F₂—are less common. This mineral is also associated with apatite crystallites

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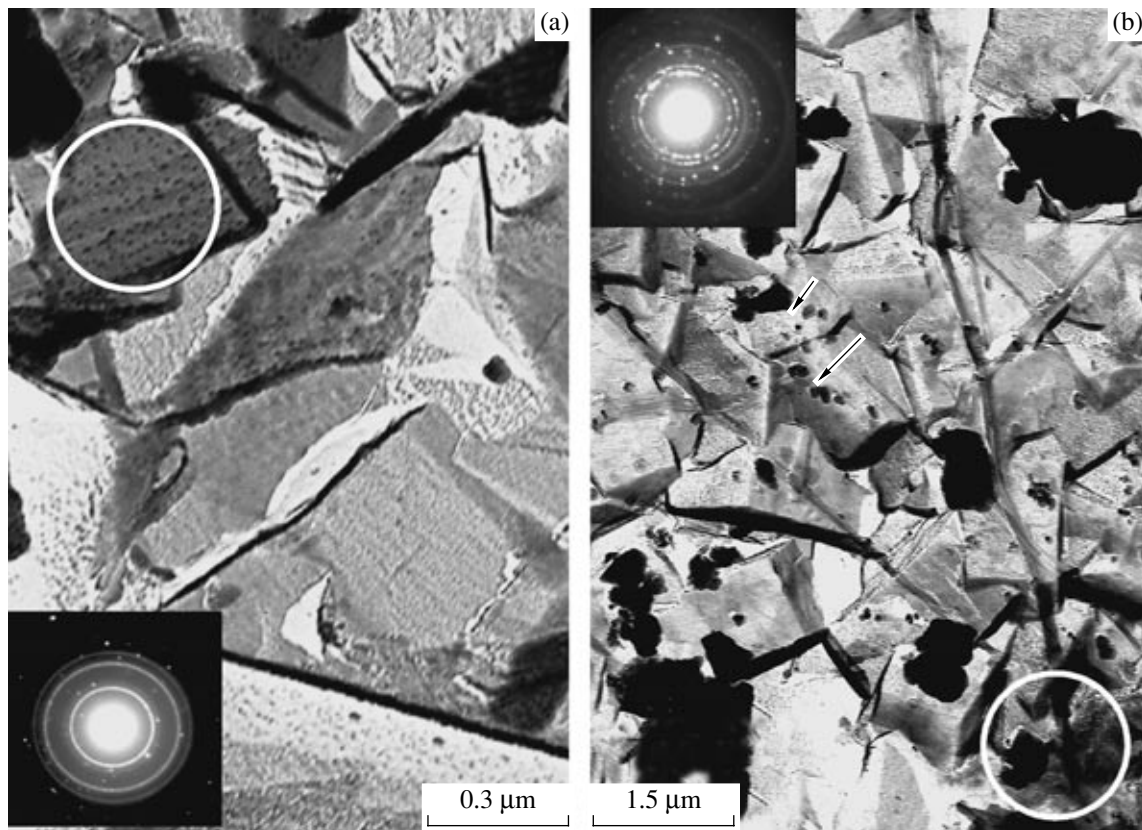


Fig. 1. Pellicular forms of REE minerals on the surface of apatite crystals. (a) Cerianite film (encircled) on the apatite crystal face and microdiffraction pattern of cerianite; (b) parisite film (encircled) in the fine-grained apatite and microdiffraction pattern of parisite. Arrows show cerianite microparticles.

(Fig. 1b). Both these minerals occur as random patches (islets) of separate round particles or their aggregates (up to $0.1 \mu\text{m}$ in size) among the crystallized phosphate mass (Fig. 2).

The data presented above suggest that the phosphate phase of ferromanganese crusts can play a significant role in the total budget of rare and trace elements concentrated in phosphorites, such as P, Ca, F, Sr, Ba, REE, Cd, and subordinate Ag and Au [10, 11].

The most important result obtained in our work is as follows. Rare earth elements are actively concentrated as independent mineral phases in the phosphate fraction of crusts and the purely phosphate sediments on seamounts [10]. Such mineral phases can play a crucial role in the total REE budget in ore crusts of a mixed (hydroxide-phosphate) composition.

Previous works have revealed that the REE content and composition in oceanic phosphorites and ferromanganese crusts show a wide range depending on the depth of ocean, hydrology and hydrochemistry of waters, age of sediments, sources of material, and so on. However, the mode of occurrence of REEs was not taken into consideration because of the lack of corresponding data. We obtained for the first time such data based on the study of nanomineralogy of shelf phos-

phorites [12, 13]. These data have been confirmed by analyses of the phosphate fraction of ore crusts. Therefore, they should be taken into consideration in the complex processing of crusts for the extraction of REEs.

Data on the marine geochemistry of REEs indicate that ore crusts of seamounts are characterized by a positive Ce anomaly, while phosphorites of seamounts display a negative Ce anomaly [2, 3, 10]. At the same time, correlation between REEs and phosphorus is rather weak in pelagic phosphorites, probably because the major portion of REEs (primarily Ce) is incorporated in cerianite rather than apatite. Precisely this factor can be crucial for the accumulation and distribution of REEs in seamount phosphorites. It should be emphasized that REE minerals have not yet been detected in ferromanganese phases of ore crusts by the methods used in the present work.

The conditions and mechanism of the formation of REE minerals in the phosphate phase of ore crusts need special investigation, probably including experimental simulation. According to [14], the reducing medium is favorable for the accumulation of present-day shelf phosphorites, but unfavorable for the accumulation of REEs. Their concentration in the phosphate material is related to the rewashing and redeposition of sedimentary

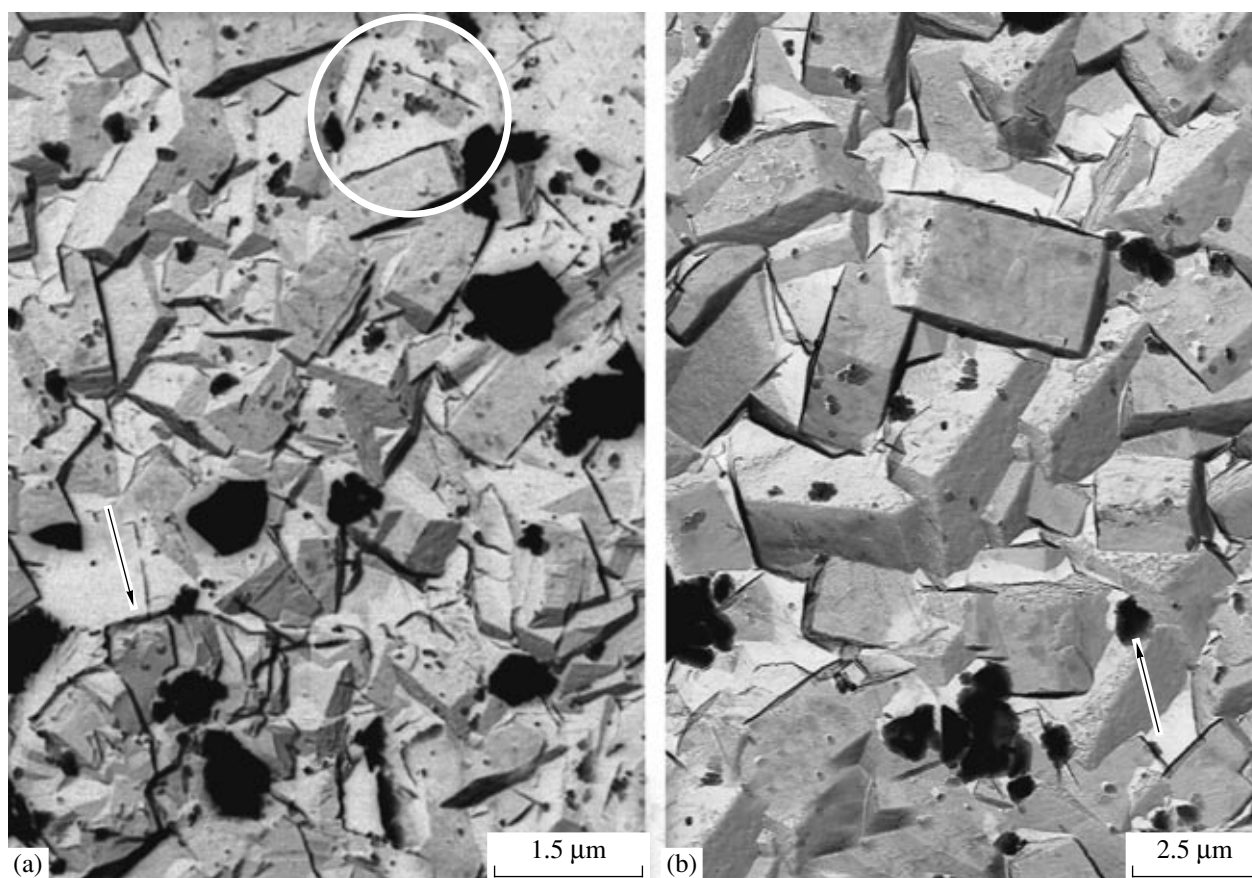


Fig. 2. Microparticles of REE minerals among apatite crystals. (a) Cerianite film (encircled) on the apatite crystal face (a relict of phosphatized coccolith is seen in the lower left-hand corner); (b) parisite film (shown by arrow) among apatite crystals.

material (slightly oxidizing environment). This process is associated with the formation of REE minerals as phosphates (monazite and xenotime) and the less common carbonate (bastnasite) in shelf phosphorites [13].

Phosphorites also accumulated initially in shallow-water zones of high bioproductivity and biogenic sedimentation on seamounts. The presence of pyrite indicates that the process mentioned above was accompanied by sulfate reduction in sediments. However, the REEs began to accumulate intensely in the phosphorites only in an oxidizing medium after replacement of shallow-water setting by the deep-water environment. This is evident from the REE composition corresponding to the parental water-mass level [15].

The exposure period of phosphate rocks on the seafloor could also influence the REE distribution in them. The input of REEs ceased after the coating of phosphates by ferromanganese crusts that played the role of REE-carriers.

Postvolcanic hydrothermal activity on seamounts [1] also could contribute to the concentration and composition of REEs in both phosphorites and ore crusts. This is suggested, in particular, by the positive Eu anomaly observed in the sediments in some places [3, 10].

Similar REE patterns in the seamount phosphorites and oceanic water indicate that precisely the postvolcanic hydrothermal activity served as the main source of REEs in the rocks.

The mechanism of the formation of REE minerals in the phosphate phase of ferromanganese crusts is unclear so far. However, it is remarkable that REE phosphates and carbonates are formed in shelf phosphorites [12, 13], whereas mainly REE oxide (cerianite) is formed in seamount phosphorites. Thus, the REE mineralization shows a distinct correlation with the facies environment. In addition, the initial accumulation stage of REEs can be related to their sorption by colloform phosphate from seawater. In the course of crystallization and the associated self-purification of the phosphate material, the REEs were removed from the crystal lattice of the mineral, resulting in the formation of authigenic REE minerals on the apatite crystal surface. The suboxic environment of the shelf fostered the formation of REE phosphates and carbonates, while the oxidizing environment of seamounts was more favorable for the formation of REE oxides. Hence, physicochemical properties played an essential role in the mineralogy of these elements.

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