

Forms of Gold and Platinum in Phosphorites on the Namibian Shelf

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Overview of works devoted to geochemistry of rare and trace elements in phosphorites has revealed that they cannot concentrate noble metals (Au, Pt, and PGM) [1–3]. This statement is also valid for phosphorites on the ocean floor [4, 5].

However, the presence of Au has been reported in [6–9]. For example, the content of native gold in the heavy fraction of phosphate sand from the Ukolov deposit (lower Santonian sediments, Kursk district) is as much as 36.4 mg/m³. The Au content based on phosphate nodule mass is three times higher (0.01–0.03 g/t). Gold occurs as nonrounded particles (up to 0.3 × 0.2 mm across) and coatings, suggesting the absorptional mechanism of their accumulation [8].

The ICP-MS analysis of different-aged phosphorites from the Voronezh anticline carried out at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (Moscow) detected the following noble metals (g/t): Au 0.37–4.7, Ag 1.1–8.4, and Pt 0.1–0.36 [9]. According to the authors of this work, the presence of noble metals and some other trace elements in the phosphorites is related to emanations from deep high-permeable zones of the Earth's crust.

In oceanic phosphorites, native gold associated with quartz was first discovered in the Agulhas Bank phosphorite at the submarine margin of southern Africa [10].

The presence of Pt in oceanic phosphorites has not been reported so far.

We continued the investigation of phosphorites from various regions of the World Ocean using several high-precision methods, including the ICP-MS. The results obtained indicate that shelf phosphorites generally contain a small amount of Au and Pt (<0.1 and <0.09 g/t,

respectively). However, the SEM and microprobe examination demonstrated the presence of characteristic lines of Au, Pt, and PGM on many energy-dispersive spectra of several samples (Fig. 1). The presence of these elements (~0.1–1 g/t) is also supported by the neutron activation data on some samples.

In order to decipher the mode of occurrence of noble metals in oceanic phosphorites, we used concretions recovered from the world's largest deposit of Pleistocene–Pliocene phosphate sand on the Namibian Shelf [5, 11, 12].

The concretions represent compact (gravel size) rounded, flattened, or irregular nodules scattered among phosphate grains of sand or silt dimension. They are composed of colloform and semicrystalline fluorocarbonate-apatite with a minor admixture of quartz, biogenic opal, and Ca–Fe carbonate [12]. Results of the chemical and physical analysis show that the nodules (1–2 cm across) have the following composition (wt %): P₂O₅ 32.75, CaO 47.7, SiO₂ 0.7, Fe₂O₃ 0.9, CO₂ 5.38, and C_{org} 0.9.

Examination of samples using the SEM equipped with an energy-dispersive analyzer demonstrated that the sectors enriched in colloform iron hydroxides include Pt, Os, and Ir. In some places, Fe is only associated with Pt. However, the SEM resolution is insufficient for deciphering the morphology of PGM segregations.

Material for the TEM analysis was extracted by spot replication from fresh chips of samples. In the case of excess extraction of material, the replica was successively etched with hydrochloric and sulfuric acids to obtain high-resolution images. After etching and washing in distilled water, the replica with heavy mineral phases was examined under the scanning electron microscope at a magnification ranging from 16 000 to 40 000.

The results (Fig. 2) show that PGM segregations represent finely dispersed vermicular (3–5 nm long and 1–2 nm across) and rounded (~1 nm across) particles. Microdiffraction images indicate that the particles rep-

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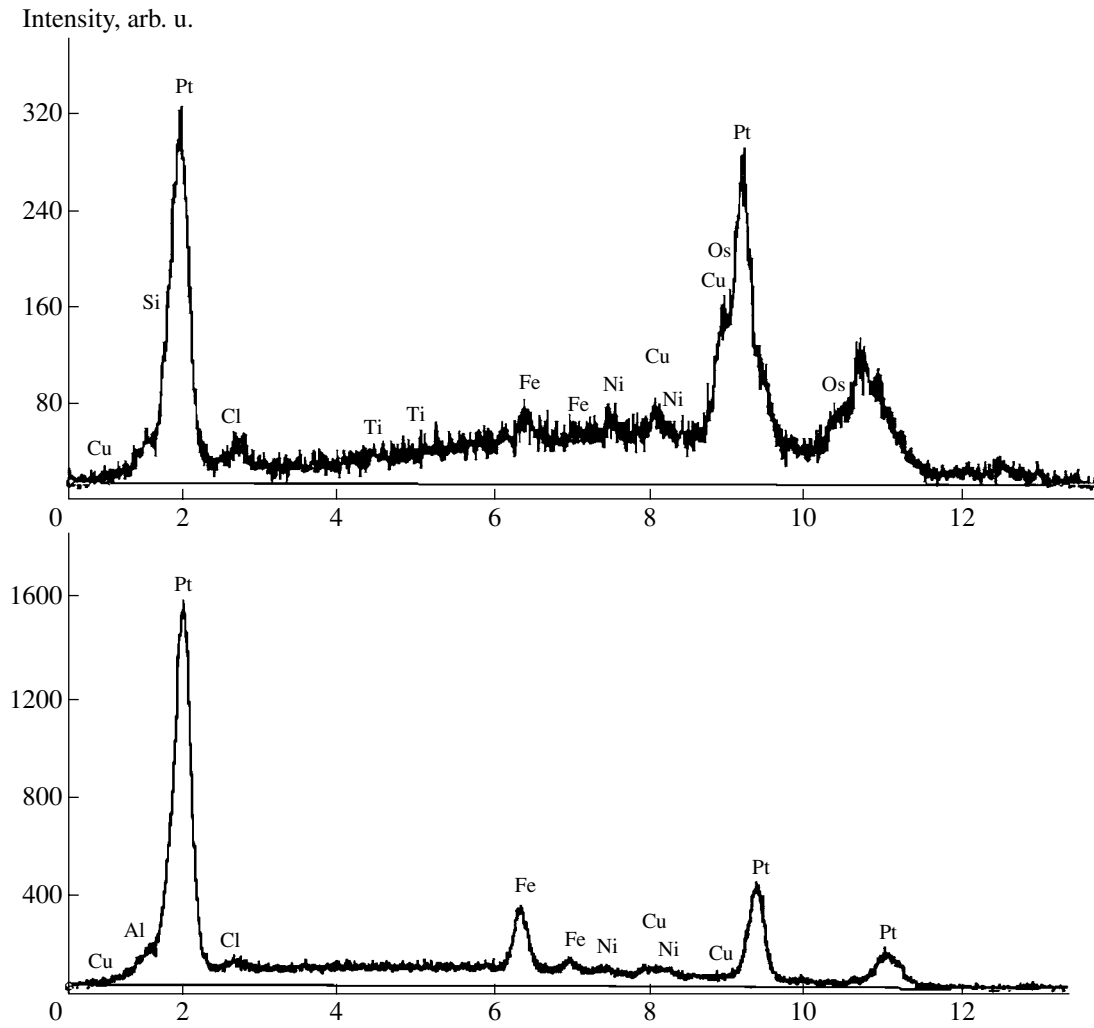


Fig. 1. Energy-dispersive spectra of phosphorite concretion from the Namibian Shelf.

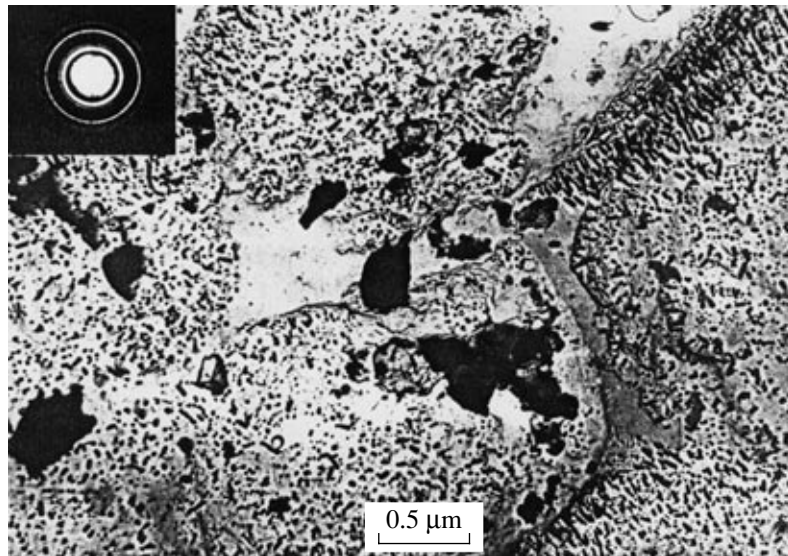


Fig. 2. Elongated and rounded platinum segregations (<1 μm) in the iron hydroxide groundmass of phosphorite concretion. The upper left corner shows the SAED image of PGM.

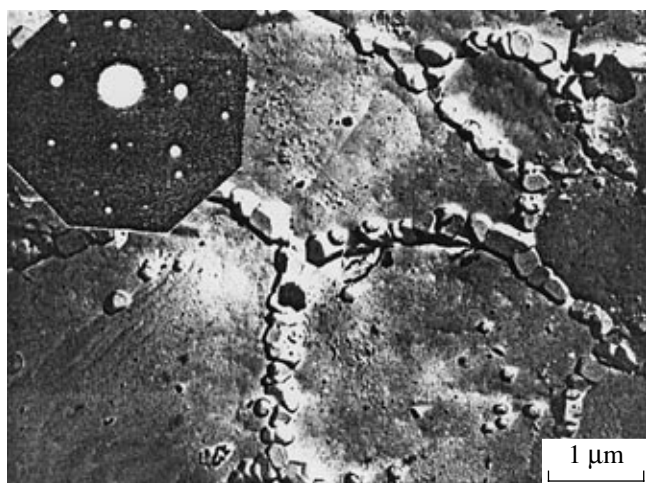


Fig. 3. Chain-shaped aggregate of native gold crystallites arranged along a crack in quartz grain inside the phosphorite concretion and SAED image of gold.

represent a mineral of cubic symmetry (Fm3m) with unit cell parameter $a = 3.81 \text{ \AA}$. These parameters fit two phases (OsIrPt and PtFe) that cannot be discriminated on the basis of microdiffraction data.

We used the SEM and TEM methods to investigate both gold and platinum in the phosphorites. In addition to the phosphate phase, allothigenic (silt size) quartz grains extracted under an optical microscope were also examined for the presence of Au. The joint SEM and microprobe investigation of samples demonstrated that gold is associated with quartz and pyrite. Quartz occurs as both crystalline and colloform varieties, while pyrite is only found as crystalline aggregates. Gold is developed as flaky and rounded particles of micrometer size.

The TEM investigation of replicas made it possible to outline three morphological types of gold: holocrystalline aggregates ($0.1 \text{ }\mu\text{m}$) arranged along quartz grain boundaries (Fig. 3); flakes confined to altered quartz zones; and clusters of bacterioform particles up to $1 \text{ }\mu\text{m}$ long.

Thus, the data presented above indicate that Pt and PGM are present in oceanic shelf phosphorites as ultradispersed traces. They are mainly associated with iron hydroxides included in the phosphorites at the

stage of redeposition of the older phosphate material. Variation in the redox state of the environment in this process was presumably related to the simultaneous precipitation of phosphates and iron hydroxides from seawater. According to this scenario, the mechanism of PGM introduction into the phosphorites is similar to that for ferromanganese nodules and crusts. Gold in the shelf phosphorites can be derived from various sources (terrigenous quartz or authigenic pyrite). In the latter case, gold is extracted together with other chalcophile elements from the enclosing rocks. According to an alternative scenario, gold can impregnate shells of marine bacteria that are present in oceanic sediments and, possibly, phosphorites as well.

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