

Nanogeochemistry of Ni, Co, and Cu in zoned marcasite-pyrite crystals

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ABSTRACT

This study describes the incorporation mechanism of Ni, Co, and Cu in zoned marcasite-pyrite (FeS₂) crystals from vein-type hydrothermal mineralization in the Sierra de Orihuela (Betic Cordillera, SE Spain). Single-spot analyses and X-ray mapping by electron probe microanalyzer (EPMA) of zoned marcasite-pyrite grains reveal positive correlations among Ni (up to 12.8 wt%), Co (up to 4.42 wt%), and Cu (up to 7.33 wt%), as well as a negative correlation between these elements and Fe. In contrast, nanoscale analysis using high-resolution transmission electron microscopy (HRTEM) reveals that these compositional variations arise from a combination of solid solutions and mineral nanoparticles of Ni, Co, and Cu. The cores of the zoned grains are marcasite, which is depleted in Ni, Co, Cu, and other trace metals. Cores are surrounded by zoned rims that contain inner portions with nanoscale zoning defined by alternating layers (~500 nm thickness) of pyrite (FeS₂) with catterite (CoS₂) and/or carrollite (CuCo₂S₄). This transitions to outer portions exhibiting *Pa*3 pyrite with frequent discrete mineral nanoparticles, including 80–120 nm sized cubic *Fd*3m carrollite (CuCo₂S₄), tetragonal *I*42d chalcopyrite (CuFeS₂), and cubic *Fd*3m violarite (FeNi₂S₄). The shift in the mode of Ni, Co, and Cu occurrence, from incorporation via solid solution to nanoparticles, reflects variations in the physicochemical conditions of the crystallizing system rather than the specific nature of the crystalline mineral matrix forming the zoned structure. The formation of the zoned structure begins with the initial crystallization of trace-element-poor cores of marcasite. This is followed by pyrite rims displaying an outward progressive enlargement of the crystal lattice due to the incorporation of Ni, Co, and Cu in solid solution, reaching characteristic *d*-spacings of carrollite and catterite. Finally, direct precipitation of pyrite and Ni-Co-Cu-rich nanoparticles occurs when pH increases and salinity decreases. Nanoscale insights from Sierra de Orihuela mineralization provide an unprecedented view of the partitioning of Ni, Co, and Cu into Fe-sulfides. These findings reveal mechanisms of metal enrichment in hydrothermal systems that are invisible to conventional tools used in the study of mineral deposits.

Keywords: Pyrite, marcasite, trace elements, zoning patterns, hydrothermal systems