American Mineralogist, Volume 108, pages 2086–2095, 2023

X-ray absorption spectroscopic study of Pd^{2+} on Ni site in pentlandite

Valeriya Brovchenko[1,*], Margarita Merkulova[2,†], Jonathan Sittner[2], Vladimir Shilovskih[3], Camelia Borca[4], Thomas Huthwelker[4], Sergey F. Sluzhenikin[1], and Veerle Cnudde[2,5]

[1]Institute of Geology of Ore Deposits Mineralogy, Petrography, and Geochemistry, Russian Academy of Sciences, Staromonetny per. 35, Moscow 119017, Russia
[2]PProGRess-UGCT, Geology Department, Ghent University, Krijgslaan 281, Ghent 9000, Belgium
[3]Centre for Geo-Environmental Research and Modeling, St. Petersburg State University, Ulyanovskaya ul. 1, St. Petersburg 198504, Russia
[4]Swiss Light Source, Paul Scherrer Institute, Villigen PSI 5232, Switzerland
[5]Department of Earth Sciences, Utrecht University, Princetonlaan 8a, Utrecht 3584, The Netherlands

Abstract

Norilsk sulfide ores are one of the largest known sources of Pd on Earth. Palladium in these ores is presented in platinum-group minerals (PGM) and base metal sulfides (BMS), especially in pentlandite [$(Fe,Ni)_9S_8$]. Although several studies demonstrated high concentrations along with heterogeneous distribution of Pd in pentlandites from Norilsk, the form of Pd in pentlandite has not been established. Here, we provide the first evidence for Pd incorporation in the structure of pentlandite from Norilsk ores using X-ray absorption near edge structure (XANES) spectroscopy, synchrotron-based micro-X-ray fluorescence (μXRF), and electron backscatter diffraction (EBSD). We present the first ever measured XANES spectra of Pd in pentlandite and atokite [$(Pd,Pt)_3Sn$] as well as in other common Pd minerals. Divalent Pd in pentlandite was detected by XANES. The Pd spectra in pentlandite show no similarities with Pd spectra in PGM, metallic Pd, PdS, $PdCl_2$, and $PdSO_4$ which signifies that Pd incorporates into the lattice of pentlandite. Substitution of Ni by Pd in the lattice of pentlandite is supported by negative correlations shown by μXRF and electron probe microanalysis (EPMA) and complies with the previous studies. The additional EBSD study demonstrates a resemblance in cell parameters of the Pd-rich and Pd-poor parts of the pentlandite grains and reflects that Pd incorporation into the pentlandite structure does not imply any notable structure distortion. The combination of analytical techniques used in the present study demonstrates the great potential of these methods for understanding the mechanisms of noble metal incorporation into ore minerals.

Keywords: Palladium, pentlandite, platinum-group minerals, XANES, μXRF, EBSD, EPMA