

The state of Pd in pentlandite from Norilsk and Lac-des-Îles ores

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Pentlandite ($\text{Fe,Ni}_9\text{S}_8$) is an important host of Pd in Ni and PGE deposits^[1]. There is some debate as to how Pd is incorporated into pentlandite, with some authors suggesting Pd substitutes via solid solution^[2,3] and some suggesting it is present as nano-sized clusters or inclusions^[4].

To study the formal oxidation state and local atomic environment of Pd in pentlandite, we performed XRF and XANES/EXAFS analyses at the LISA/BM08 beamline of the European Synchrotron Radiation Facility. To define the zones of interest, we performed XRF mapping of Pd-bearing pentlandite crystals at 26 keV. The Pd *K*-edge spectra were recorded in the various zones of the pentlandite grains from Norilsk and Lac-des-Îles deposits containing ~900 and 300 ppm of Pd respectively. Comparison of the Pd *K*-edge XANES spectra of pentlandites and references shows that the formal oxidation state of Pd is close to +2 (Fig. 1). The pentlandite structure^[5] contains tetrahedral (32f, ~90%) and octahedral (4b, ~10%) Wyckoff positions. The XANES spectra simulations and EXAFS spectra fittings demonstrated that Pd occupies the octahedral sites of the pentlandite structure. During the preliminary fittings, the attempts to introduce Se, As, Te, or Pd atoms in the vicinity of the absorbing atoms failed, meaning, the presence of Pd-bearing nano-sized clusters/ inclusions in these samples can be ruled out.

The Ni and Fe *K*-edge EXAFS spectra fittings suggest that Fe mostly occupies the tetrahedral sites in the pentlandite structure, whereas Ni occupies both tetrahedral and octahedral sites. Thus, the direct negative correlation between the contents of Ni and Pd observed in many natural pentlandites can be accounted for by the competition between Pd and Ni for the large octahedral sites of the structure.

References: [1] Mansur *et al.* (2021), *Min Dep* 56, 179-204; [2] Brovchenko *et al.* (2023), *Am Min* 108, 2086-2095; [3] Junge *et al.* (2015), *Min Dep* 50, 4-54; [4] Helmy *et al.* (2023), *Contrib Min. Pet* 178, 41; [5] Tenaillon *et al.* (2006), *Am Min* 91, 1442-1447.

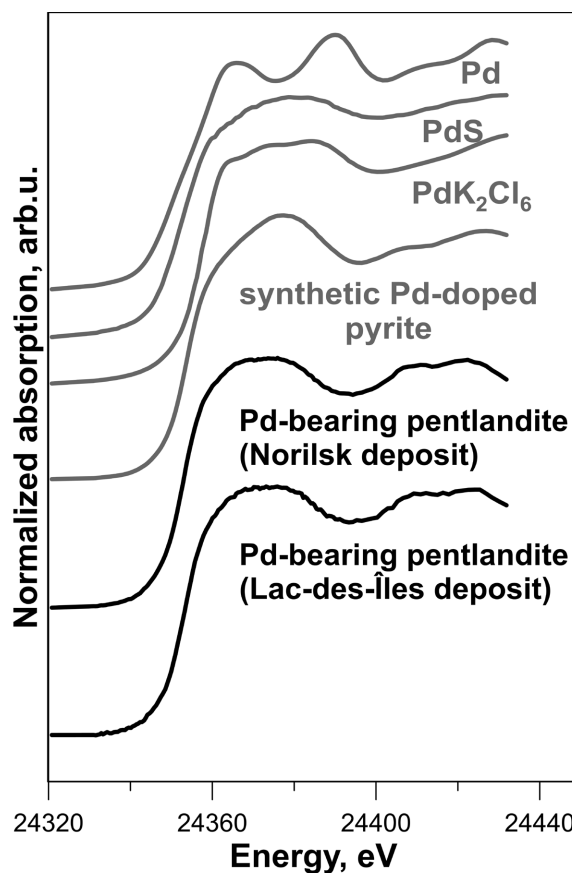


Fig. 1