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High-energy resolution X-ray absorption spectroscopy study of the state of Pt in pyrite

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Abstract

Pyrite (FeS_2) is a common host mineral of Pt in many types of deposits of late magmatic and hydrothermal origin, including the Aguablanca Ni-Cu ore deposit in southwestern Spain. Yet the exact state of Pt in the pyrite from Aguablanca, including its oxidation state and local atomic geometry, still lacks spectroscopic evidence. Here, we investigated the state of ~30 ppm of Pt in a natural pyrite sample from Aguablanca using the high-energy resolution fluorescence detection X-ray absorption near edge structure (HERFD-XANES) technique. Our analysis of the Pt L_3-edge HERFD-XANES experimental spectra and theoretical spectra simulations performed via the ab initio FDMNES code revealed that Pt is incorporated in the cationic subshell of the natural pyrite sample. The presence of Pt-bearing micro- or nano-sized inclusions disseminated in the pyrite matrix was ruled out. The Pt-S interatomic distance ($R_{Pt\text{-}S}$) of 2.34 ± 0.01 Å in the Aguablanca sample is almost identical to that in the Pt-doped synthetic pyrite sample ($R_{Pt\text{-}S}$ = 2.35 ± 0.01 Å). The Pt-S interatomic distance is ~3.5% larger than the Fe-S interatomic distance in the pure pyrite structure, primarily due to a 3% difference between the covalent radii of Pt and Fe, rather than differences in their ionic radii or electronegativities. The Pt "formal" oxidation state of +3.5 and partial atomic charge of +0.4 e in the natural sample substantially exceed those of Fe in the pure pyrite structure (+2 and +0.2 e, respectively). By employing available literature data on the solubility of Pt in synthetic pyrite samples, we demonstrated that the Pt enrichment of the natural pyrite specimen took place at a temperature above 360 °C.

Keywords: Isomorphous platinum, solid solution, natural pyrite, HERFD-XAS, X-ray absorption spectroscopy, solubility, Ni-Cu-PGE Aguablanca ore deposit, Spectroscopy in Geology: A Decade of Breakthroughs