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The crystal structure of a naturally occurring 5C pyrrhotite from Sudbury, its chemistry, and vacancy distribution

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ABSTRACT

The crystal structure of a naturally occurring pyrrhotite from the Copper Cliff North Mine, Sudbury, Canada, has been determined in the space group *Cmce* (formerly *Cmca*), and the positions and occupancy of the Fe and S atoms have been refined, together with their anisotropic atomic displacement parameters, to a conventional *R* value of 0.072. The summed occupancies of the Fe and Ni atoms [8.908 (Fe + Ni) per 10 S] are compared with the chemical composition, as determined by microprobe analysis, the latter giving a formula of $Fe_{8.892}Ni_{0.115}S_{10}$ or 9.007 (Fe + Ni) per 10 S.

The structure has cell dimensions of $a = 6.893(3)$ Å, $b = 11.939(3)$ Å, and $c = 28.63(1)$ Å. The S atoms are hexagonally close packed and adjacent Fe-S octahedra share faces that are perpendicular to the *c* direction. The Fe atoms in adjacent face-sharing octahedra also have the closest Fe-Fe interatomic distances. Some Fe atoms have partial occupancies, and together with the fully occupied sites, they add up to 71.26 (Fe + Ni) atoms per 80 S atoms in the unit cell, as compared with 72 atoms per 80 S atoms for Fe_9S_{10}.

The distribution of Fe in the partially occupied layers is different from that previously postulated for Fe_9S_{10}, with vacant sites present in two of the 10 layers. The partially occupied Fe sites are present in all the remaining cation layers, and there are therefore no cation layers containing completely filled atomic sites. Space group symmetry constrains the partially occupied cation sites to project on top of each other along the *c* axis, similar to the distribution of partially occupied sites in $Fe_{11}S_{12}$ (6C pyrrhotite).

Keywords: Pyrrhotite-5C, crystal structure, vacancy distribution, non-stoichiometry