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Fluorescent sphalerite from Montana, USA: Coupled substitutions of Cu, Ga, and W

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Polymetallic veins in the Philipsburg District, Granite County, Montana, contain sphalerite that fluoresces bright colors (red, orange, yellow, blue, green) under longwave UV (365 nm) light (fig. 1). The sphalerite (confirmed by XRD) coexists with enargite, tennantite, galena, quartz, and barite, and formed at temperatures between 200 and 250°C based on fluid inclusion geothermometry. Specimens from two mine shafts located 0.5 km apart show identical growth band patterns. Laser ablation ICP-MS analysis reveals that the sphalerite has very low Fe content (< 100 ppm in most cases), with high concentrations of Cu (up to 8500 ppm), Ge (up to 580 ppm), Ga (up to 5000 ppm), In (up to 2100 ppm) and W (up to 2800 ppm), as well as Ag (up to 100 ppm). Ablation profiles indicate all of these elements exist in solid solution within the sphalerite lattice, although some higher values of Ag are explained by micro-inclusions of other minerals. Covariance plots suggest the univalent metals (Cu, Ag) enter the sphalerite structure in combination with trivalent (Ga, In), tetravalent (Ge) and hexavalent (W) metals in such a way as to maintain overall charge balance and without the need of vacancies. Whereas numerous studies have discussed coupled substitution of Cu with Ga, In, and Ge in sphalerite, to our knowledge we are the first to suggest coupled substitution of Cu with W, by the following reaction: $4Cu^{+} + W^{6+} = 5Zn^{2+}$. Sphalerite bands with the deepest red fluorescence have the highest concentrations of Cu, W and Ga, whereas sphalerite with blue, green, or purple coloration have the lowest content of impurities and also display phosphorescence as well as triboluminescence. Divalent trace metals, such as Fe, Mn, Cd, and Hg, have nearly constant concentrations that show no variation across growth bands. The discovery of remarkably fluorescent sphalerite from Philipsburg should be an incentive to examine sphalerite from other deposits, as color patterns under UV light may give valuable information about trace metal content and paragenesis. A pre-requisite for deep coloration may be an unusually low Fe content, as Fe is known to inhibit fluorescence in other minerals.