

COPPER ZONING IN PYRITE FROM CERRO DE PASCO, PERU:
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In a recent article by Einaudi (1968) the occurrence of significant amounts of copper in pyrite from Cerro de Pasco, Peru, were reported (up to 1.4%). Electron probe analyses showed that the copper in pyrite from the above location and from Fiji (up to 10% Cu, Frenzel and Ottemann, 1967), occurs as an inclusion in the pyrite structure and not as a separate occluded phase. The analysis of the Peruvian pyrite showed an anomalously high As content when compared with pyrite from Elba. Also the copper-rich pyrite from Peru and Fiji are reported to occur with enargite mineralization (Cu_3AsS_4) rather than with arsenic poor copper sulfides, e.g. chalcopyrite. On this basis Einaudi (1968) concluded that pyrite crystallizing in the system Cu-Fe-As-S is more susceptible to solution of copper than it is in the system Cu-Fe-S.

These observations may be explained qualitatively by crystal field theory. The Cu^{2+} ion contains 9 *d*-electrons and when placed in a regular octahedral ligand field, e.g. the pyrite structure, becomes destabilized due to the Jahn-Teller effect (Orgel, 1965). The absence of one $d_{x^2-y^2}$ electron causes the Cu^{2+} nucleus to be less screened in discrete directions and ligands in these directions are attracted with a force equivalent to a larger apparent nuclear charge. The Cu^{2+} ion therefore is stabilized only in distorted octahedral sites (or in regular tetrahedral sites). For this reason Cu^{2+} generally does not enter pyrite in significant amounts, but crystallizes as a discrete phase involving tetrahedral coordination, e.g. chalcopyrite. If some As is substituted for S in pyrite, *d*-electrons of the metal must be used in bonding with the As atoms (Nickel, 1968), and the d^9 configuration of Cu would not be maintained. A resultant d^7 or d^8 Cu^{2+} ion would then be stabilized in a regular octahedral field because the Jahn-Teller mechanism would no longer be applicable. It is proposed that Cu^{2+} would be more likely incorporated into the pyrite structure if some As atoms were available for a coupled substitution.

Bravoite and villamaninite, disulfides of Cu, Ni, Co and Fe, are reported to crystallize in the pyrite structure with space group *Pa3* (Ypma, 1968). In these structures Fe varies from 23–55 mole percent total metals, Cu from 12–60 mole percent, Ni from 14–35 mole percent and Co from 3–11 mole percent. Although the pyrite structure is reported, Ypma (1968) notes that these phases exhibit optic anisotropy. This

implies distortion of the regular octahedral sites constituting the pyrite structure. The Cu^{2+} ion could therefore occupy these distorted sites without the necessity of a coupled substitution with As.

It is suggested that Cu^{+2} is incorporated stability into pyrite-like structures in two ways. In pyrite it occurs as a coupled substitution with As because the Cu^{2+} ion would not be influenced by the Jahn-Teller effect. In As-free phases (*e.g.* bravoite and villamaninite) the Cu^{2+} ion may be incorporated if there is sufficient distortion of octahedral site symmetry.

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