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COPPER ZONING IN PYRITE FROM CERRO DE PASCO, PERÚ: REPLY

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We would like to thank Dr. A. H. Clark for pointing out additional data on the problem of the inclusion of copper in pyrite. The hydrothermal experimental data described by Shimazaki (1969) suggest that there is extensive solid solution between CuS_2 and FeS_2 at 225°C. However, pyrite and chalcopyrite are common mineral associates yet cuprian pyrites are rare. As predicted from crystal field theory (Radcliffe and McSween, 1970), solid solution of CuS_2 and FeS_2 is essentially limited in the natural system.

Clark describes an arsenic-free cuprian pyrite (pyrite III, Ylöjärvi, Finland, 1969, above discussion) perhaps invalidating the coupled Cu-As substitution explanation of Radcliffe and McSween (1969). Clark also describes a "consistent sympathetic enrichment" of Cu and Se in the cuprian pyrite.

On the basis of crystal field theory, we maintain that the Jahn-Teller effect (Orgel, 1965) will oppose the stable inclusion of Cu into the regular-shaped octahedral sites of the pyrite structure unless there is a distortion of the symmetry of the octahedral sites or there is a coupled Cu-X substitution to effectively modify the 9 d-electron orbital symmetry of Cu^{2+} (Radcliffe and McSween, 1969). We suggest a Cu-As couple for Cerro de Pasco pyrite and the data of Clark may indicate a Cu-Se couple for Ylöjärvi pyrite III.

The analysis of pyrite crystals involving a coupled Cu-anion substitution need not show necessarily a stoichiometric proportion of Cu-X. Departure from stoichiometry could be indicated by (a) poor analytical precision error, (b) coexisting stable and unstable cuprian domains, (c)

the mineral itself may be nonstoichiometric, or (d) the substitution of small amounts of a larger ion (eg. Se) may cause enough distortion of octahedral site symmetry for stabilization of larger amounts of the Cu^{2+} ion.

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CHEMICAL REACTIONS IN CRYSTALS: CORRECTIONS AND CLARIFICATION

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Corrections

The following may be of some help to the baffled reader of my recent paper. Other, more obvious, misprints and lapses on my part have turned up, but the following includes those (at least the ones so far discovered) that appear most likely to cause trouble.

p. 345, equation (4): "Z_Q" not "Z_q"

p. 346, line following equation (5): "quantities" not "varieties"

p. 354, line following equation (30): "$\overline{G}_1^\circ$" not "$\overline{G}^\circ$"

p. 356, second line below caption: "univariant" not "invariant" [!]

p. 357, equation (40): "g_0" not "$g0$"

fourth line from bottom: T_{10} and T_{1m} [also true of T_{20} and T_{2m}]

p. 365, first two lines of text: The meaning would be clearer if the word "no" were entered before "symmetry," and the word "not" crossed out in the line below.

equations (47) and (49): "$g_{ss}s$" should be "$2g_{ss}s$" [!]. This error proliferates below.

line below equation (50): insert "numerical" before "subscripts"

third line from bottom: "W_{M3}" should be "W_{M2}"

p. 366, equation (52):