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COPPER ZONING IN PYRITE FROM CERRO DE PASCO, PERÚ:
FURTHER DISCUSSIONALAN H. CLARK, *Department of Geological Sciences, Queen's University,
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In their discussion of the paper by Einaudi (1968), Radcliffe and McSween (1969) have proposed, on the basis of crystal field theory, that solid solution of copper in pyrite is accommodated by a coupled substitution with arsenic. While the cuprian pyrites described by Frenzel and Ottemann (1967) and Einaudi (1968) both occur in enargite-bearing, arsenic-rich assemblages, analysis of pyrite from another locality indicates that some other mechanism must there have been responsible for the crystallization of copper-rich pyrite.

Three generations of pyrite, designated I, II, and III (Clark, 1965), have been distinguished in the Ylöjärvi copper-tungsten deposit in southwest Finland, and these differ markedly in their minor and trace element concentrations (to be discussed in detail in a paper in preparation). Selected compositional data for the three pyrites are presented in Table 1.

Of the generations, the strongly anisotropic pyrite I formed early in the development of the breccia pipe deposit, in part at least in equilibrium with arsenopyrite. This pyrite exhibits an unusual minor ele-

TABLE 1. SELECTED MINOR ELEMENT CONTENTS IN PYRITES, YLÖJÄRVI DEPOSIT, FINLAND

Pyrite generation	Cu	As	Sn	Se
	weight percent			
I	~0.001 ^a n.d. ^b	<0.1-2.2 ^b	nil-0.60 ^b	0.015 -0.022 ^c
II	0.001 -0.012 ^a n.d. ^b	n.d. ^a	n.d. ^a	0.011 -0.015 ^c
III	nil ^a -4.5 ^b	n.d. ^a	n.d. ^a	0.16 -0.97 ^c

n.d.—not detected.

^a Optical spectrographic analysis.^b Electron microprobe analysis of zones in individual grains.^c Spectrophotometric 3,3'-diaminobenzidine analysis.

ment array, and contains up to 0.60 weight percent Sn, and 2.2 percent As. The distributions of these elements in individual grains are unrelated. Pyrite I clearly crystallized before chalcopyrite and cubanite in the ore, in an essentially copper-free environment, and itself contains only traces of copper (~ 0.001 percent, by spectrographic analysis).

Pyrites II and III, both consistently isotropic, formed at a later stage in the hypogene paragenesis. The former developed predominantly as a replacement of pyrrhotite, and quantitatively inherited the minor element assemblages of that mineral, which is here poor in As and, generally, Cu. Although of approximately simultaneous formation, pyrite III has a radically different minor element make-up. Neither Sn nor As could be detected in this pyrite, but Cu attains concentrations of at least 4.5 percent, and the Se content approaches one percent in some specimens. The highly cuprian grains are erratically distributed in the deposit, and characteristically have a crudely concentric internal zonation, which is brought out by structure etching. Cu and Se are present in irregular annular rings in the cores of such grains, and show a consistent sympathetic enrichment, although Cu:Se ratios vary widely over very short distances within individual grains.

The presence of arsenic cannot have facilitated the entry of copper into pyrite III, which yields sharp, nondiffuse powder patterns and cell edges in the range 5.4174 to 5.4176 ± 0.0001 Å (four grain-aggregates, including one with an overall copper content of 0.3 percent). Shimazaki (1969) has recently demonstrated experimentally that extensive solid solution is possible along the $\text{FeS}_2\text{-CuS}_{-2}$ join, and that the cell edges of the intermediate members are functions of their Cu:Fe ratio, whether or not distorted octahedral sites are involved. The upper thermal stability of such solid solutions is not stated, but may fall at moderate temperatures. The absence of copper in pyrite I in the Ylöjärvi deposit might, therefore, have been due to its crystallization at a temperature above that at which the $(\text{Fe, Cu})\text{S}_2$ solid solutions are stable.

It should also be pointed out that not all pyrite occurring in enargite-rich ores is copper-bearing. Thus, hypogene pyrite, intimately associated with enargite in the El Guanaco deposit, Taltal, Chile (Clark, 1969), is non-cuprian.

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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 in 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)