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#### COPPER ZONING IN PYRITE FROM CERRO DE PASCO, PERU

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### INTRODUCTION

A review of 785 pyrite analyses (Fleischer, 1955) indicates that 75 percent contain more than 10 ppm copper, 10 percent contain more than 1 percent copper, and the maximum concentration reported is about 6 percent copper. The conclusion was reached that "it seems probable that most, if not all, of (the copper) is present as admixed chalcopyrite or other copper minerals" (*Ibid*, p. 1005). A review of the literature indicates that this is a widely held view. Analyses by all standard techniques are suspect, unless it can be shown that the material is inclusion-free. However, electron microprobe analysis, having a resolution of one micron, is ideally suited to the study of minor elements and their distribution. Probe analysis has recently confirmed the presence of significant amounts of copper held in solid solution in pyrite (Frenzel and Ottemann, 1967). The present note further documents this fact.

# Analytical Methods

The minor element content of sulfides from Cerro de Pasco, Peru, was studied by electron microprobe analysis (Applied Research Laboratories, EMX) of carbon-coated, polished sections. The analytical conditions were as follows: sample current, 0.03 microamps; accelerating voltage, 20 kV; probe diameter, 2 microns; and counting time, 40 seconds. Low counting rates obviated dead-time corrections. Drift and background corrections were applied to all data. Atomic number, fluorescence, and absorption corrections were not applied. Due to the low amounts of copper, these corrections would have little effect on the

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values. Chalcopyrite from Cerro de Pasco was used as standard for Cu K $\alpha$  radiation. No manganese or zinc was detected in this chalcopyrite by probe analysis, and it was assumed to contain 34.6 weight percent copper. Copper metal was used as a check against the chalcopyrite standard; the values obtained using copper metal as standard are lower by 10 percent of the amount present. A conservative estimate of the accuracy of the copper concentration is  $\pm 8$  percent of the amount present.

Semi-quantitative spectrographic analyses of pyrite were conducted on a Jarrell-Ash 3.4-meter Ebert Mark 4 grating spectrograph. A SA-1 plate was used. Samples were arced at 10 amps, with a slit width of 10 microns and a slit height of 2 millimeters. The grating (15,000 lines/inch) angle was set to get second order spectra. Standards were successive dilutions of SQ Jarrell-Ash standards in a  $Fe_2O_3$  base.

#### RESULTS

Preliminary scanning with the electron microprobe indicated detectable amounts of copper and manganese in some pyrites, though the



FIG. 1. Electron microprobe trace of Cu K $\alpha$  radiation along traverse A-B.

majority contained no detectable minor elements (detection limits were estimated to be: 0.03 wt% Mn, 0.10 wt% Cu). One sample from the northern portion of the pyrite-quartz body (4310 bench, McCune pit), near enargite-luzonite veins, was found to contain appreciable amounts of copper. The following remarks deal with this one sample.

The pyrite occurs as pyritohedrons up to 4 millimeters in diameter filling cavities in coarsely brecciated, silicified volcanics. Early, finegrained pyrite cements and partially replaces the breccia. No other sulfides are present in the hand specimen, and no inclusions of any kind were noted in the euhedral pyrite under oil immersion at  $1000 \times$ . No color, reflectivity, or anisotropism variations were noted. Etching with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> with KMnO<sub>4</sub> failed to bring out any zonal pattern.

The copper occurs in crystallographically oriented bands averaging 0.5 mm in width. The zonal pattern was delineated by means of fifteen probe traverses across an intergrowth of 10 crystals. One such traverse is shown in Figure 1. In addition, fourteen points were quantitatively analyzed, and the variation in copper content along the traverses related

### MINERALOGICAL NOTES



FIG. 2. Copper zonal pattern in an intergrowth of pyrite crystals as interpreted from 15 electron microprobe traverses. Traverse shown in Figure 1 is indicated A-B.

to them. The zonal pattern appears to be similar in all crystals (Fig. 2). It consists of a low copper core and rim, in which the copper content is less than 0.2 weight percent. The intermediate zone contains up to 1.5 weight percent copper. This zone can be traced across grain boundaries where it changes orientation according to crystal orientation. Figure 2 is intended to indicate the general location and distribution of copper. No attempt was made to determine if preferential solution of copper on any given form exists, as a more detailed knowledge of the growth zones would be required.

Preliminary X-ray data of material removed from the high-copper bands indicates that  $a=5.148\pm0.001$  Å. This value does not differ from published values of natural and synthetic pyrite.

Optical spectrographic analyses of euhedral pyrite from the same hand specimen indicated the presence of 0.1 weight percent copper and 0.05 weight percent arsenic. A sample of pyrite from Elba (Dana Collection

	Cerro de Pasco	Elba		
Mg	0.001	0.01		
Al	0.1	0.1		
Si	0.1	0.1		
Ti	0.001-0.01	0.01-0.1		
V	0.0001	0.0001		
Cr	0.0001	0.001-0.01		
Mn	0.0001	0.001-0.01		
Co	ND	0.3		
Ni	ND	ND		
Cu	0.1	0.01		
Zn	0.0001	ND		
As	0.05	ND		
Mo	0.0001	0.0001		
Ag	0.005	0.0005		
Sn	0.001	ND		
Au	ND	0.001		
Hg	ND	0.01		
Pb	0.005	0.0005		
Te	0.001	ND		

TABI	Е 1.	Spe	CTRO	GRAPHIC	ANA	LYSES	$\mathbf{OF}$	PYRITE	FROM	Cerro	DE	Pasco	AND
	Elb	A (I	)ANA	Collec	TION	NUME	BER	88092,	HARVA	ARD UN	IVE	RSITY)	

ND = not detected.

number 88092, Harvard University) was analyzed under identical conditions for comparative purposes. Both analyses are included in Table 1.

### CONCLUSIONS

It is now apparent that copper can enter the pyrite structure in significant amounts. The first conclusive evidence of this fact was published by Frenzel and Ottemann (1967). By electron probe analysis they show that optically zoned pyrite from Fiji contains up to 10 weight percent copper. The Cerro de Pasco pyrite, though less spectacular, also demonstrates copper zoning. Pyrite from both these localities occurs in areas of luzonite rather than chalcopyrite mineralization. It may be that pyrite in the system S-As-Fe-Cu is more susceptible to solution of copper than it is in the system S-Fe-Cu. It would be desirable to check synthetic pyrite from both these systems.

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ZINC-RICH MICAS FROM STERLING HILL, NEW JERSEY

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The occurrence of the zinc-mica hendricksite and of zincian and manganoan varieties of phlogopite at Franklin, New Jersey, has been described by Frondel and Ito (1966). The present note records similar



FIG. 1. Composition of the octahedral layer in trioctahedral micas from Sterling Hill (open circles) and Franklin (solid circles; data of Frondel and Ito, 1966).

<sup>1</sup> Mineralogical Contribution No. 455.