ELECTRON PROBE ANALYSIS OF MINUTE INCLUSIONS OF A COPPER-IRON MINERAL

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Abstract

An application of the electron probe x-ray microanalyzer to the analysis of extremely minute inclusions in minerals is described. Strongly birefringent grains about 0.03 mm. in size, which resemble what has been termed valleriite, occur in chalcopyrite from the Mackinaw mine, Snohomish County, Washington. These grains were found by the electron probe analysis method to contain about 55 per cent iron and less than 5 per cent copper; the composition was inferred to be approximately FeS. These results suggest that the mineral previously generally termed valleriite in high-temperature copper ores is distinct from the type of valleriite from Kaveltorp, Sweden, and is probably an undescribed sulfide.

Introduction

During a study of ores from the Mackinaw mine, Snohomish County, Washington (Milton and Milton, 1958), the problem arose of identifying an opaque, strongly birefringent mineral occurring as very fine grains, usually less than 0.03 mm. wide, enclosed in chalcopyrite, $CuFeS_2$ (Fig. 1. In the past such small grains in many other similar occurrences have been identified as valleriite ($Cu_{2-3}Fe_4S_7$), a platy mineral from Kaveltorp, Sweden (Ramdohr, 1955), although it had never been possible to remove the grains by drilling or other mechanical means so that chemical analyses could be performed. There are indications that the Kaveltorp valleriite and the Mackinaw "valleriite" are entirely different mineral species (Milton and Milton, 1958, p. 432, footnote). The problem seemed ideally suited for the recently developed electron probe x-ray microanalyzer (Castaing, 1951; Birks and Brooks, 1957) with which analysis can be performed on specific areas as small as one micron in diameter on a specimen surface.

Instrumentation

Several papers on the principles and operation of electron probe instruments have appeared in the literature (Castaing, 1956; Castaing, Philibert, and Crussard, 1957; Cosslett and Duncumb, 1957), therefore, only the briefest description will be given here.

An electron optics system somewhat similar to an electron microscope is used to form a beam of electrons only one micron in diameter. This

beam is allowed to strike a specimen and generate the characteristic *x*-ray spectra of the elements contained in the one-micron region. An accurate mechanical stage and an optical microscope allow the exact area of interest on the specimen to be positioned in the electron beam for analysis. The characteristic *x*-rays generated are analyzed by usual *x*-ray spectrochemical techniques (Birks and Brooks, 1955, 1958; Adler and Axelrod, 1957). That is, the wavelengths of the *x*-ray lines are used to identify the elements and the intensity of each line is related to the per cent composi-
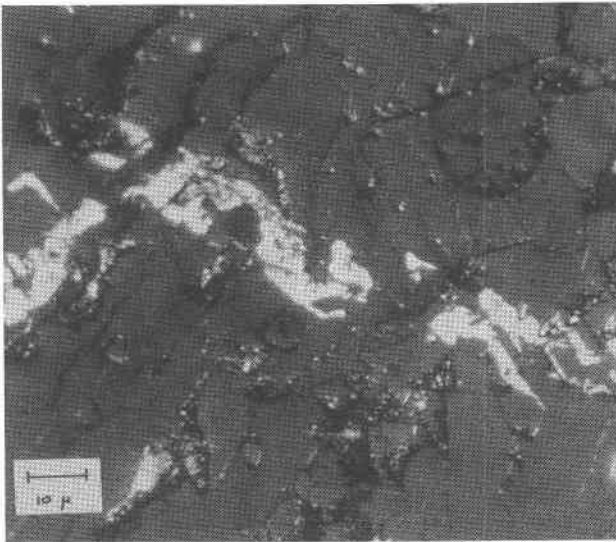

FIG. 1. Photomicrograph showing veins of unknown mineral in chalcopyrite matrix.

tion of that particular element by comparison with standards of known composition.

Figure 2 is a photograph of an electron probe instrument showing the electron optics column with the electron gun at the top, the viewing microscope in front, and several fixed, curved crystals and detectors on the left side (Birks and Brooks, 1955). The fixed crystals and detectors may be replaced by a scanning, curved-crystal spectrometer but for many applications, including the one described herein, it is desirable to measure simultaneously the variation of several elements as the specimen is translated past the electron beam; hence, the several fixed crystals.

Specimen Preparation

Examination in the electron probe requires that the specimen surface be flat, smooth, and electrically conducting. A metallurgical type of pol-
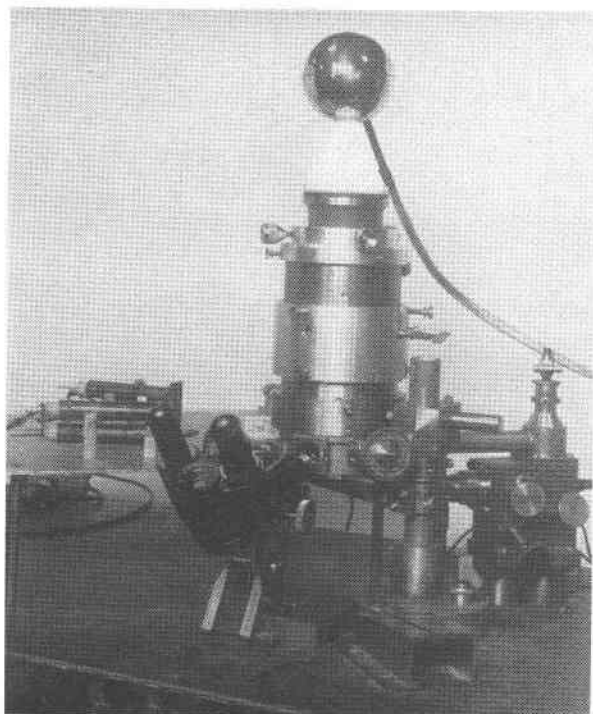
Fig. 2. Electron probe x-ray microanalyzer.

ishing was used to obtain the flat smooth surface on the chalcopyrite and it was made electrically conducting by evaporating a thin layer (100–200 Å) of manganese onto the polished surface. This thin manganese layer does not obscure the gross physical features of the specimen but it does not, of course, allow birefringent areas to be distinguished. Therefore, it was necessary to photograph the specimen in polarized light before the manganese was applied. This allowed the fine grains of interest to be located relative to the gross physical features so that they could be found and measured in the electron probe. Figure 1 shows a photomicrograph of the chalcopyrite mineral containing black gangue areas and the white, lightning-like streaks that are the unknown grains; Figure 1 was taken before manganese evaporation.

For the purpose of comparison, specimens of cubanite ($CuFe_2S_3$), valleriite ($Cu_{2-3}Fe_4S_7$?), and pyrite (FeS_2) were prepared in a similar manner. All the specimens were placed in the electron probe in a single specimen mount so that intensities from all specimens could be measured without changing any of the experimental conditions.

TABLE 1. ANALYTICAL RESULTS ON SOME CU-FE MINERALS

Name	Formula	Counts per second		Theoretical Weight per cent		Experimental Weight per cent	
		Fe	Cu	Fe	Cu	Fe	Cu
Chalcopyrite	$CuFeS_2$	126	160	30.4	34.6	Standard	
Cubanite	$CuFe_2S_3$	164	98	41.2	23.5	40*	22*
Valleriite (Kaveltorp)	$Cu_{2-3}Fe_4S_7$?	110	120	35.0–38.8	22.1–29.8	26.6*	26*
Pyrite	FeS_2	170	0	46.5	0	Standard	
Unknown (Mackinaw)	About FeS?	212	15–30			51*	0–5*
						58**	0–5**

* Values obtained by comparison with chalcopyrite.
** Values obtained by comparison with pyrite.

RESULTS

The iron and copper x-ray intensities were measured simultaneously by using two crystals and two detectors. Table 1 shows the measured intensities in counts per second for each of the minerals. Chalcopyrite and pyrite were used as standards and the per cent iron and copper in the other minerals calculated by comparison. The per cent concentration of the given element is determined from the relationship that the ratio of the concentrations is directly proportional to the ratio of the measured intensities in counts per second. The agreement of per cent iron and copper in cubanite as calculated from x-ray results and from the known formula is within 1.5 per cent and indicates the precision of the x-ray method. The formula for valleriite is not known accurately but the table shows the nature of the agreement between calculated weight per cent and x-ray measurements for two assumed formulas

The unknown grains may be compared with either chalcopyrite or pyrite and the weight per cent calculated. As shown in the table, the copper content is very low and corresponds to less than 5 per cent in either case. The iron content is 51 per cent if chalcopyrite is used as a standard or 58 per cent if pyrite is used. Because of the observed low copper content, it seems likely that the pyrite standard would be more accurate and that the iron content in the unknown is closer to 58 per cent. Without other evidence it is not possible to ascribe a definite chemical formula to the unknown. If it is assumed to be a sulfide of iron, the formula FeS would give 63.4 per cent iron or a formula of Fe_2S_3 would give 53.8 per cent iron. Since the ordinary Fe_2S_3 is unstable, a formula nearer FeS seems more probable. In fact if the small amount (near 5 per cent) of copper present

is considered as impurity, then a formula approximately FeS agrees rather well with the x-ray observations.

REFERENCES

ADLER, I., AND AXELROD, J. M. (1957), Reflecting curved-crystal x-ray spectrograph—a device for the analysis of small mineral samples: *Econ. Geology*, **52,** 694–701.

BIRKS, L. S., AND BROOKS, E. J. (1955), Applications of curved-crystal x-ray spectrometers: *Anal. Chemistry*, **27,** 437–440.

BIRKS, L. S., AND BROOKS, E. J. (1957), Electron probe x-ray microanalyzer: *Rev. Sci. Instruments*, **28,** 709–712.

BIRKS, L. S., AND BROOKS, E. J. (1958), X-rays lighten the analytical load: *Anal. Chemistry*, **30,** no. 10, 19A–30A.

CASTAING, R. (1951), Application of electron probes to local chemical and crystallographic analysis, Thesis, University of Paris.

CASTAING, R. (1956), Les récent développements de l'analyse ponctuelle par spectrographie-x: Laboratoires, no. 17, 7.

CASTAING, R., PHILIBERT, J., AND CRUSSARD, C. (1957), Electron probe microanalyzer and its application to ferrous metallurgy: *Jour. Metals* **9,** *An. Inst. Mine Metall. Engineers Trans.*, **209,** 389–394.

COSSLETT, V. E., AND DUNCUMB, P. (1957), A scanning microscope with either electron or x-ray recording; *in* Sjöstrand, F. S., and Rhodin, J., eds., Electron microscopy, Proceedings of the Stockholm Conference, September 1956: New York, Academic Press Inc., 12–14.

MILTON, CHARLES, AND MILTON, D. J. (1958), Nickel-gold ore of the Mackinaw mine, Snohomish County, Washington: *Econ. Geology*, **53,** 426–447.

RAMDOHR, PAUL (1955), Die Erzmineralien und ihre Verwachsungen, 2d ed., Berlin, Akademie-Verlag, 527–531.

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