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## Chapter D

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## SOLVING PROBLEMS IN PHOSPHATE MINERALOGY WITH THE ELECTRON PROBE

By CYNTHIA W. MEAD and MARY E. MROSE,  
Washington, D.C.

*Abstract.*—Qualitative and quantitative electron-probe analyses of nonconducting minerals, in conjunction with single-crystal and powder diffraction X-ray data, have been used successfully to solve several problems in phosphate mineralogy. The formulas of calcioferrite from Battenberg, Bavaria, and montgomeryite from Fairfield, Utah—minerals inferred to be isostructural on the basis of powder patterns—have been established by quantitative electron-probe analysis. Type zincian rockbridgeite from Maxedo, Portugal, has been shown to be a mixture of zincian lipscombite and zincian rockbridgeite. Electron-probe spectrometer traces, together with quantitative determinations of P and S, led to the identification of a mineral from Butte, Mont., as hinsdalite. Qualitative analysis of a white mineral from Västana (Westana), Sweden, confirmed that it has a composition similar to pink orthorhombic attakolite from the same locality and therefore is its monoclinic dimorph.

Qualitative and quantitative electron-probe analyses have been used in conjunction with single-crystal and powder diffraction X-ray data to solve several problems in phosphate mineralogy. Four such problems, presented in part at the First National Conference on Electron Probe Microanalysis, at College Park, Md., in 1966, are discussed in detail here.

### SAMPLE PREPARATION AND OPERATING CONDITIONS

All the samples were prepared by mounting tiny fragments of the minerals in epoxy resin. Rough polishing of the samples was done manually on a series of silicon carbide papers down to 600 grit. Final polishing was done on vibratory polishers using Linde A (0.3 micron  $Al_2O_3$ ) and Linde B ( $0.05\mu Al_2O_3$ ) as polishing compounds. The surfaces of the samples were coated with a layer of carbon to make them electrically conducting. The carbon coating was somewhat heavier than usual in order that the sample surfaces would not be damaged by bombardment with the electron beam. In order to insure further that the sample surface would not be damaged, operating voltages not greater than 20 kilovolts and specimen currents not greater

than 0.02 microamperes were used. A commercially built electron-probe having an effective take-off angle of  $41^\circ$  was used for the analyses.

### PROBLEMS AND THEIR SOLUTION

*Problem 1.*—The first problem involved the analysis of two extremely rare minerals: (1) type calcioferrite, a hydrated calcium ferric phosphate of uncertain formula, from Battenberg, Bavaria, and (2) montgomeryite, a hydrated calcium aluminum phosphate with questionable formula, from Fairfield, Utah. X-ray powder patterns indicated the minerals to be isostructural, but the quantities available were not large enough to permit even partial chemical analyses by conventional methods. The following mineral standards used in the analyses were selected on the basis of qualitative determinations by electron-probe spectrometer traces on the unknowns.

Mineral standard	Chemical analyses (in percent)			
	Fe	Al	Ca	P
Pyroxene.....	2.3	-----	17.6	-----
Väyrynenite.....	4.6	-----	-----	17.4
Albite.....	-----	11.0	1.9	-----

For the analyses of the unknowns, a LiF crystal was used for the determination of Fe, a KAP (potassium acid phthalate) crystal was used for the determination of Al and P, and a PET (pentaerythritol) crystal was used for the determination of Ca. The data are corrected for background and absorption. Results of the quantifications by electron-probe spectrometer traces on the unknowns.

Specimens	Electron-probe analyses (in percent)			
	Fe	Al	Ca	P
Calcioferrite.....	19.0	-----	10.0	14.8
Montgomeryite.....	-----	11.1	13.0	16.5

These data, together with crystallographic considerations, led to the following formulas for the two minerals:  $\text{Ca}_2\text{Fe}_2(\text{PO}_4)_3(\text{OH}) \cdot 7\text{H}_2\text{O}$ , for calcioferrite; and  $\text{Ca}_2\text{Al}_2(\text{PO}_4)_3(\text{OH}) \cdot 7\text{H}_2\text{O}$ , for montgomeryite. These satisfied the space-group criteria established by single-crystal X-ray work. The advantage of the electron probe for analyzing small samples is immediately evident.

*Problem 2.*—The second problem related to the use of the electron probe as the only means of conclusively determining the homogeneity and chemical composition of zincian rockbridgeite. X-ray powder diffraction patterns of type material from Viana do Castelo, Maxedo, Portugal, taken for the X-ray powder diffraction film files at the U.S. Geological Survey, suggested that the material represented a mixture of two minerals, rockbridgeite and lipscombite. Čech, Padera, and Povondra (1961) called attention to the fact that their X-ray powder data for a mixture of lipscombite and rockbridgeite from Otov I, near Domažlice (Bohemia, Czechoslovakia), are very similar to those published for zincian rockbridgeite by Lindberg and Fron del (1950). Therefore, the amount of ZnO reported in the chemical analysis for zincian rockbridgeite (Lindberg and Fron del, 1950) was considered attributable to the rockbridgeite phase, and (or) the lipscombite phase, or possibly to the associated sphalerite. Electron-probe analyses of carefully selected fragments, followed by supporting X-ray identification of these same fragments, seemed the most reliable approach to resolving this problem. Qualitative spectrometer traces were made first of two deep-blue-green microcrystalline aggregates. The traces showed that zinc was present in each fragment. These fragments were removed from the epoxy, and X-ray powder diffraction patterns taken of each proved to be identical with those of lipscombite, a hydrated ferrous-ferric phosphate. Lipscombite had not been reported previously from the Maxedo locality nor, to our knowledge, has a zinc-bearing lipscombite been recorded in the literature. Individual, very thin, greenish-brown laths, found sparingly in the type material, were selected for electron-probe analysis. Spectrometer traces showed that zinc was also present in these laths, in amounts comparable to that found in the deep-blue-green lipscombite fragments; a single-crystal X-ray study made of one of these zinc-bearing laths confirmed its structural identity to rockbridgeite. Electron-probe and X-ray diffraction studies proved beyond question that the material described as zincian rockbridgeite actually represents a mixture of zincian lipscombite and zincian rockbridgeite, both containing approximately equal amounts of zinc.

*Problem 3.*—The third study required a partial quantitative electron-probe analysis to permit positive

identification of minute, colorless to pale-yellow, hexagonal crystals that were found sparingly distributed on ore specimens from Butte, Mont. Single-crystal and powder diffraction X-ray study indicated that the mineral was either plumbogummite, a hydrated basic phosphate of lead and aluminum, or hinsdalite, a basic sulfate-phosphate of lead and aluminum. A spectrometer trace of the unknown compared with that for type hinsdalite showed them to be virtually identical and strongly suggested that the Butte mineral was hinsdalite. The following standards were used for the quantitative work:

Standard	Chemical analyses (in percent)	
	P	S
Type hinsdalite (Colorado)-----	6.4	5.7
Indium phosphide (InP)-----	21.2	-----
Pyrite-----	-----	53.1
Plumbogummite (Cumberland, England)-	8.2	-----

Four analyses were done on the Butte unknown, each using a different standard for the determination of P and S. A KAP crystal was used for the determination of P, and an ADP (ammonium dihydrogen phosphate) crystal was used for the determination of S. All data are corrected for background. The value for P obtained when indium phosphide was used as the standard is corrected for absorption, and the values for S and P obtained when pyrite and plumbogummite, respectively, were used as standards are corrected for atomic number. The results of the analyses are shown in table 1.

TABLE 1.—*Electron-probe analyses of P and S in the Butte mineral*  
[Quantities are in percent]

	Analysis and standard used			
	1 (type hinsdalite)	2 (indium phosphide)	3 (pyrite)	4 (plumbo- gummite)
P-----	6.4	6.2	-----	6.3
S-----	6.2	-----	6.2	-----

The electron-probe data verified that the Butte mineral contains appreciable sulfur and therefore is hinsdalite,  $(\text{Pb}, \text{Sr})\text{Al}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$ .

*Problem 4.*—In the fourth problem, spectrometer traces were used to show the relationship between pink orthorhombic attakolite from Västana (Westana), Sweden, described by Gabrielson and Geijer (1964) as a hydrous silicophosphate of Al, Ca, and Mn, and an adjacent white monoclinic attakolite-like mineral. The specimen bearing these two minerals is in the U.S. National Museum (USNM R5615). Single-crystal X-ray study of these two minerals show them to have closely agreeing cell parameters (table 2). Electron-probe spectrometer traces for the two minerals are vir-

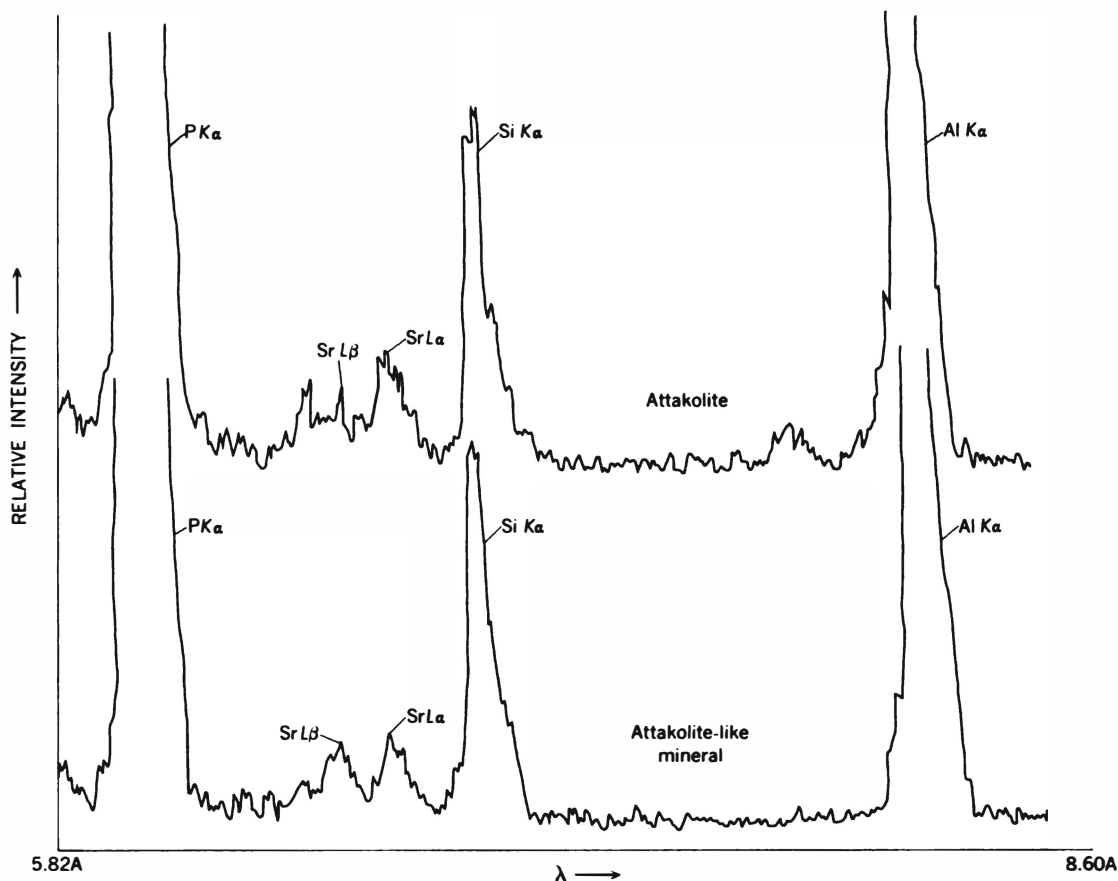


FIGURE 1.—Spectrometer traces ( $\lambda$ , 5.82–8.60Å) of attakolite and the attakolite-like mineral from Västana (Västana), Sweden. A KAP crystal was used.

TABLE 2.—Comparison of attakolite and an attakolite-like mineral from Västana (Västana), Sweden

[U.S. National Museum specimen R5615]

Crystallographic data	Attakolite <sup>1</sup> (pink)	Attakolite-like mineral <sup>2</sup> (white)
Symmetry.....	Orthorhombic.....	Monoclinic
Space group.....	$I^{***}$	$I^{*/*}$
Cell dimensions....		
$a$ .....	$11.46 \pm 0.01A$	$11.45 \pm 0.01A$
$b$ .....	$15.71 \pm 0.02A$	$15.69 \pm 0.02A$
$c$ .....	$7.28 \pm 0.01A$	$7.30 \pm 0.01A$
$\beta$ .....		$91^{\circ}30' \pm 05'$

<sup>1</sup> Data from von Knorring and Mrose (1967).

<sup>2</sup> Data from present report.

tually identical, as may be seen in figure 1, which shows the peaks for P, Sr, Si, and Al obtained with a KAP crystal. Traces made with a LiF crystal show peaks for Fe, Mn, and Ca. These traces, later supplemented by quantitative electron-probe analyses, verified that the

pink and white minerals have approximately the same composition; that they differ crystallographically indicates that the monoclinic attakolite-like mineral is dimorphous with orthorhombic attakolite and therefore is a new mineral species.

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