

## THE RELATIONSHIP BETWEEN BASIC FERRIC SULFATE AND PLUMBOJAROSITE

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### ABSTRACT

New  $x$ -ray diffraction data are provided for plumbojarosite ( $\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ ) and the basic ferric sulfate  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ . The values supplant incorrect data given in ASTM 5-0635 and 10-444. Unit cell dimensions are  $a = 7.315$ ,  $c = 33.758$  for plumbojarosite ( $R\bar{3}m$ ) and  $a = 7.356$ ,  $c = 17.010$  for the basic ferric sulfate ( $R3m$ ); these values are slightly larger than those given by Hendricks (1937). The compounds are readily distinguished from one another and from solid solutions between the above-mentioned end members by specific differences in the  $x$ -ray diffraction patterns.

Attempts to synthesize plumbojarosite by reacting lead sulfate with ferric sulfate solution produced solid solutions in all instances. These varied in lead content according to the preparative conditions and showed a gradual decrease in unit cell volume with increase in lead content. Under oxidative pressure-leaching conditions, however, galena and pyrite reacted to form (*inter alia*) a compound very similar to the mineral plumbojarosite. The implications of these results with regard to the mineral genesis of plumbojarosite are discussed.

### INTRODUCTION

In the course of oxidative pressure-leaching studies on pyritic lead sulfide concentrates, it was suspected that a basic sulfate of lead and iron, similar to the mineral plumbojarosite, was being formed, but the  $x$ -ray diffraction pattern for this mineral (ASTM 5-0635) could not be identified in the complex leach residues. Attempts were therefore made to synthesize the compound by reacting lead sulfate with ferric sulfate solution at  $140^\circ \text{C}$ . and subsequently extracting any unreacted lead sulfate from the solids with ammonium acetate solution. The product so obtained gave a characteristic  $x$ -ray diffraction pattern which was completely different from that listed for plumbojarosite by Kauffman (1950), although it closely resembled that for the basic ferric sulfate known as carphosiderite (ASTM 10-444). According to Hendricks (1937), however, carphosiderite and plumbojarosite are closely related members of the jarosite family and should be expected to yield similar  $x$ -ray diffraction patterns. To complicate matters further, van Tassel (1958) subsequently showed that carphosiderite from the type locality (USNMR-6266) does not possess the composition  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 7\text{H}_2\text{O}$  as given in ASTM 10-444, but is in fact natrojarosite.

In order to resolve these discrepancies, authentic samples of the mineral plumbojarosite were obtained and have been compared with our synthetic basic sulfate of lead and iron and with the compound

$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$  prepared by the hydrolysis of ferric sulfate solution at  $140^\circ\text{C}$ . All three compounds are shown to be closely related although they can be readily distinguished by specific differences in the x-ray powder diffraction patterns. The original data supplied by Kauffman for plumbojarosite is shown to be incorrect, and is now replaced by new data obtained by us on plumbojarosite from the type locality.

Also, because Van Tassel's findings discredit the data for basic ferric sulfate given in ASTM 10-444, we have supplied fresh data based on the compound  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$  obtained by hydrolyzing ferric sulfate solution at  $140^\circ\text{C}$ . As will be described in the sequel, our synthetic

TABLE 1. ANALYSES OF PLUMBOJAROSITE AND SYNTHETIC MATERIALS

|                                | Plumbojarosite mineral |                   |             | Synthetic plumbojarosite (solid solutions) |        |        |        |        | Basic ferric sulfate<br>$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ |
|--------------------------------|------------------------|-------------------|-------------|--|--------|--------|--------|--------|---|
|                                | A                      | B <sup>1</sup>    | Theoretical | C  | D      | E      | F      | G      |   |
| PbO                            | 19.90                  | 19.84             | 19.73       | 17.50                                      | 13.14  | 10.62  | 9.42   | 5.39   | —   |
| Fe <sub>2</sub> O <sub>3</sub> | 42.32                  | 42.37             | 42.44       | 43.41                                      | 44.14  | 45.35  | 45.70  | 47.87  | 49.82   |
| SO <sub>3</sub>                | 25.95                  | 27.06             | 28.29       | 28.40                                      | 29.90  | 31.01  | 31.08  | 31.96  | 33.30   |
| H <sub>2</sub> O <sup>1</sup>  | 10.40                  | 9.56              | 9.54        | 11.16                                      | 13.04  | 13.30  | 14.11  | 15.36  | 16.88   |
| (Na, K) <sub>2</sub> O         | 0.23                   | 0.38              |             |  |        |        |        |        |   |
| P <sub>2</sub> O <sub>5</sub>  | 0.58                   | —                 |             |  |        |        |        |        |   |
| Remainder                      | 0.62 <sup>2</sup>      | 0.94 <sup>2</sup> |             |  |        |        |        |        |   |
| Total                          | 100.00                 | 100.15            | 100.00      | 100.57                                     | 100.22 | 100.28 | 100.31 | 100.58 | 100.00  |

<sup>1</sup> Determinations by Australian Microanalytical Laboratory, Melbourne.

<sup>2</sup> By difference.

<sup>3</sup> Palache *et al.* (1951), p. 569.

“plumbojarosite” made from lead sulfate represents a solid solution between the end members  $\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ , and  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ .

#### MATERIALS

(a) Natural plumbojarosite was obtained from two sources. Sample A came from the Placa Mine, Laurion, Greece, and was supplied by the American Museum of Natural History; Sample B from the type locality (Cook's Peak, New Mexico, USNM-R6308) was obtained from the U. S. National Museum. Analyses are listed in Table 1 together with the theoretical values calculated from the formula  $\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ . Both minerals gave the same x-ray diffraction pattern (Table 2).

(b) Synthetic plumbojarosite was conveniently prepared by heating lead sulfate with ferric sulfate solution for 2 hours, usually at  $140^\circ\text{C}$ . in a glass-lined autoclave. In a typical reaction, 2 gm of lead sulfate

TABLE 2. POWDER PATTERNS FOR PLUMBOJAROSITE AND BASIC FERRIC SULFATE  
 Space groups (Hendricks (1937))— $R\bar{3}m$  (No. 166) and  $R3m$  (No. 160)  
 Symmetry—Rhombohedral, referred to hexagonal axes

| Plumbojarosite<br>$a = 7.31_5$<br>$c = 33.78_8$ |        |                  |        | Basic Ferric Sulfate<br>$a = 7.35_8$<br>$c = 17.01_0$ |        |                  |     |
|---|--------|------------------|--------|---|--------|------------------|-----|
| d(obs)  | d(cal) | I/I <sub>0</sub> | hkl    | d(obs)  | d(cal) | I/I <sub>0</sub> | hkl |
| 11.267  | 11.070 | 13               | 003    |   |        |                  |     |
| 6.232   | 6.232  | 34               | 101    |   |        |                  |     |
| 5.933   | 5.933  | 94               | 012    | 5.972   | 5.964  | 17               | 101 |
|   |        |                  |        | 5.683   | 5.667  | 36               | 003 |
| 5.063   | 5.063  | 3                | 104    | 5.110   | 5.098  | 97               | 012 |
| 4.619   | 4.628  | 6                | 015    |   |        |                  |     |
| 3.834   | 3.834  | 6                | 107    |   |        |                  |     |
| 3.657   | 3.660  | 31               | 110    | 3.678   | 3.678  | 9                | 110 |
|   |        |                  |        | 3.548   | 3.536  | 12               | 104 |
| 3.479   | 3.479  | 29               | 113    |   |        |                  |     |
| 3.114   | 3.114  | 46               | 202    | 3.131   | 3.131  | 97               | 021 |
| 3.066   | 3.068  | 100              | 116    | 3.087   | 3.087  | 100              | 113 |
|   |        |                  |        | 2.999   | 3.001  | 6                | 105 |
| 2.964   | 2.968  | 30               | 024    | 2.992   | 2.984  | 7                | 202 |
| 2.868   | 2.866  | 4                | 205    |   |        |                  |     |
| 2.812   | 2.813  | 3                | 00, 12 | 2.834   | 2.834  | 18               | 006 |
| 2.620   | 2.620  | 1                | 119    |   |        |                  |     |
| 2.531   | 2.531  | 18               | 208    | 2.549   | 2.551  | 18               | 024 |
| 2.389   | 2.389  | 9                | 211    |   |        |                  |     |
| 2.370   | 2.371  | 16               | 122    |   |        |                  |     |
|   |        |                  |        | 2.326   | 2.326  | 5                | 205 |
| 2.303   | 2.304  | 16               | 214    |   |        |                  |     |
|   |        |                  |        | 2.271   | 2.271  | 40               | 107 |
| 2.252   | 2.251  | 20               | 00, 15 |   |        |                  |     |
|   |        |                  |        | 2.245   | 2.246  | 5                | 116 |
| 2.145   | 2.145  | 12               | 217    |   |        |                  |     |
| 2.076   | 2.076  | 12               | 303    |   |        |                  |     |
| 1.976   | 1.979  | 45               | 036    | 1.989   | 1.989  | 38               | 303 |
| 1.954   | 1.954  | 1                | 21, 10 |   |        |                  |     |
|   |        |                  |        | 1.932   | 1.932  | 12               | 027 |
|   |        |                  |        | 1.890   | 1.890  | 8                | 009 |
| 1.829   | 1.829  | 70               | 220    | 1.839   | 1.839  | 36               | 220 |
| 1.807   | 1.806  | 3                | 223    |   |        |                  |     |
|   |        |                  |        | 1.750   | 1.750  | 16               | 223 |
|   |        |                  |        | 1.730   | 1.730  | 11               | 312 |
|   |        |                  |        | 1.632   | 1.632  | 11               | 134 |

was treated with 160 ml of neutral ferric sulfate solution (0.125M). The product was filtered, washed and subsequently digested with 10 per cent ammonium acetate solution (alternatively with a 10 per cent solution of diethylene triamine in water) to remove unreacted lead sulfate. The reaction sought by this procedure was as follows:



In practice, however, the product always contained unreacted lead sulfate, and the extracted material was consequently deficient in lead. This phenomenon persisted despite variations in the autoclaving time and temperature, in the relative proportions of lead sulfate and ferric sulfate used, and in the amount of free sulfuric acid added at the start of the reaction. Below 140° C., progressively less reaction occurred although some material giving the synthetic plumbojarosite diffraction pattern was still obtained at temperatures as low as 100° C. No reaction was observed at room temperature over a period of two weeks. Analyses for a variety of "synthetic plumbojarosites" (Samples C to G) are given in Table 1.

The basic ferric sulfate ( $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ) was prepared at 140° C. by the same procedure as described above, except that lead sulfate was omitted from the reaction mixture. Analyses of the product so obtained agreed with the theoretical composition given in Table 1.

Analyses for iron and sulfate were obtained by standard methods, although it was necessary to correct for lead in the barium sulfate precipitate. This was done either by determining the amount of lead recovered in the filtrate after precipitating barium sulfate or by direct determination of lead in the precipitate by *x*-ray fluorescence analysis. Lead was conveniently determined in the presence of impurities by atomic absorption spectrophotometry and checked, where necessary, by gravimetric determination as lead sulfate. Analyses for water presented some difficulties and the results provided in Table 1 were obtained by determining total hydrogen on solid samples dried at 110° C., using a microanalytical procedure. These values are somewhat higher than those obtained by alternative procedures and could account for the totals in Table 1 being slightly greater than 100.0.

#### X-RAY DIFFRACTION DATA

X-ray powder diffraction measurements were made with  $\text{CuK}\alpha$  radiation using both a Philips Geiger counter diffractometer and a Guinier type focusing camera. The Guinier camera was internally calibrated with KCl.

The lattice parameters of plumbojarosite, basic ferric sulfate and the

intermediate synthetic plumbojarosites were determined from the Guinier data by a least squares refinement method developed for the C.S.I.R.O. Elliot 803 computer by C. H. J. Johnson of these laboratories. They are probably accurate to 0.005 Å. All films were given 24 hour exposures and the line intensities were measured with a Joyce-Loebl double-beam microdensitometer.

The interplanar spacings for plumbojarosite (type sample from Cook's Peak) and basic ferric sulfate, measured with the Guinier camera, have been indexed using hexagonal axes and are listed in Table 2.

The results are summarized in Table 3 for comparison with those of Hendricks (1937). It is evident that the  $a$  and  $c$  dimensions given by

TABLE 3. COMPARISON OF RESULTS FOR PLUMBOJAROSITE AND BASIC FERRIC SULFATE

|                      | $a$               | $c$                  | Density |                   | Reference        |
|----------------------|-------------------|----------------------|---------|-------------------|------------------|
|                      |                   |                      | (calc.) | (obs)             |                  |
| Plumbojarosite       | 7.20              | 2×16.80              | 3.71    | 3.67              | Hendricks (1937) |
|                      | 7.31 <sub>5</sub> | 2×16.87 <sub>9</sub> | 3.60    | 3.64 <sup>1</sup> | Present study    |
| Basic ferric sulfate | 7.16              | 16.90                | —       | —                 | Hendricks (1937) |
|                      | 7.35 <sup>6</sup> | 17.01 <sub>0</sub>   | 3.00    | 2.94              | Present study    |

<sup>1</sup> Determined on mineral from Laurion, Greece (Sample A).

Hendricks are appreciably smaller for both compounds, a feature which is also observed if his values for the mineral jarosite are compared with the later results of Warshaw (1956), as given in ASTM 10-443. Since internal calibration was stipulated by both Warshaw and the present authors, the more recent results are preferred.

#### DISCUSSION

Although the powder patterns for plumbojarosite and basic ferric sulfate are closely related, they are readily distinguished by changes in intensity of the low-angle reflections. These are best observed in Fig. 1, which reproduces diffractograms for plumbojarosite mineral, synthetic plumbojarosite and basic ferric sulfate. The strong reflections from planes in basic ferric sulfate with  $d$  spacings of 5.68, 5.10 and 3.13 Å become progressively weaker in the plumbojarosite pattern, whereas the reflections corresponding to  $d = 5.97$  and 3.66 Å become much stronger.

The pattern for the synthetic material (sample F) shown in Fig. 1 is intermediate in nature, as would be expected for a solid solution between

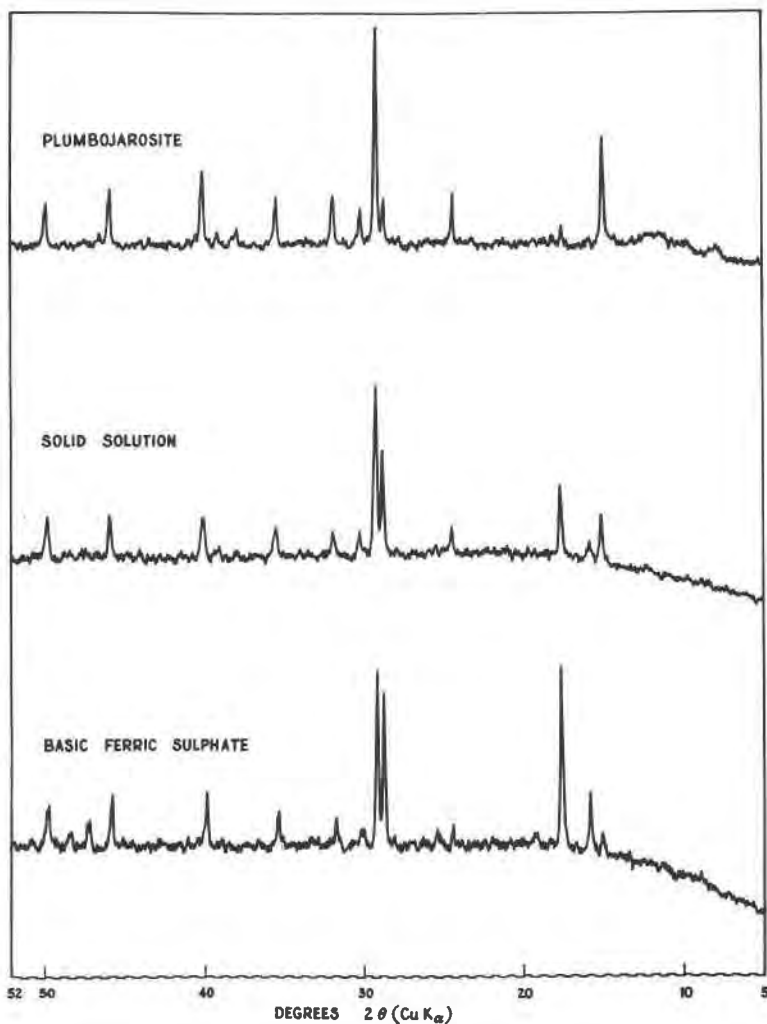


FIG. 1. X-ray diffractograms showing the relationship between plumbojarosite (Sample B in Table 1), solid solution (Sample F) and basic ferric sulfate.

the two end members, plumbojarosite and basic ferric sulfate. On the other hand, the pattern for a physical mixture of the end members (made to contain the same lead content as sample F) showed double peaks and was distinctly different from that for sample F.

By varying the methods of preparation (*q.v.*), synthetic plumbojarosites (or solid solutions as they should now be called) were made with

from 5 to 16 per cent lead (equivalent to 27 to 89 molar per cent of the plumbojarosite molecule). The corresponding x-ray diffraction patterns showed a slight but definite decrease in d spacings as the plumbojarosite content increased. Although this effect is not readily apparent in Fig. 1, it is clearly demonstrated in Table 4 by comparing the lattice parameters and unit cell volumes for different products. The relationship does not entirely satisfy Vegard's law, since the unit cell volumes for Sample C and the mineral plumbojarosite show a decrease greater than would be expected from the trend line for the solid solutions up to 66 per cent

TABLE 4. VARIATION OF PROPERTIES OVER THE RANGE  
PLUMBOJAROSITE—BASIC FERRIC SULFATE

| Sample                                | Plumbojarosite<br>B                           | Solid Solutions    |                    |                    |                    |                    | Basic<br>Ferric<br>Sulfate |      |
|---------------------------------------|---|--------------------|--------------------|--------------------|--------------------|--------------------|----------------------------|------|
|                                       |   | C                  | D                  | E                  | F                  | G                  |                            |      |
| Molar percentage of<br>Plumbojarosite | 100   | 88.7               | 66.5               | 53.9               | 47.8               | 27.4               | 0                          |      |
| Lattice constants                     |   |                    |                    |                    |                    |                    |                            |      |
| a                                     | 7.31 <sub>5</sub>                             | 7.32 <sub>5</sub>  | 7.33 <sub>9</sub>  | 7.34 <sub>3</sub>  | 7.34 <sub>2</sub>  | 7.35 <sub>3</sub>  | 7.35 <sub>6</sub>          |      |
| c                                     | 33.75 <sub>8</sub><br>(2×16.87 <sub>9</sub> ) | 16.83 <sub>6</sub> | 16.91 <sub>5</sub> | 16.93 <sub>2</sub> | 16.94 <sub>3</sub> | 16.99 <sub>0</sub> | 17.01 <sub>0</sub>         |      |
| V                                     | 26.08 <sub>8</sub>                            | 26.08 <sub>1</sub> | 26.29 <sub>8</sub> | 26.35 <sub>3</sub> | 26.36 <sub>3</sub> | 26.51 <sub>6</sub> | 26.57 <sub>4</sub>         |      |
| Ratio<br>by<br>Weight                 | $\frac{\text{Fe}_2\text{O}_3}{\text{SO}_3}$   | 1.565              | 1.53               | 1.475              | 1.46               | 1.47               | 1.49                       | 1.50 |

plumbojarosite. It has also been observed that the low angle reflection in the powder pattern of plumbojarosite (from planes at  $d=11.26 \text{ \AA}$ ) does not appear in any of the powder patterns of the synthetic material, which can all be satisfactorily indexed without doubling the  $c$ -axis dimension. These two observations taken in conjunction support the belief that the progressive substitution of  $\text{H}_3\text{O}^+$  by  $\text{Pb}^{2+}$  occurs in random fashion in the synthetic materials and that a higher degree of order, accompanied by a perceptible contraction in cell volume, only occurs when the lead content approaches that of the compound  $\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ . (This may possibly be due to an irregular coordination for the  $\text{Pb}^{2+}$  ion.) It is also worthy of note that Parker (1962) found some deviation from Vegard's law (again restricted to the  $c$  dimension) in the related alunite-natroalunite series.

According to the formulae of the two end members, the ratio by

weight,  $\text{Fe}_2\text{O}_3:\text{SO}_3$ , should remain constant at 1.50 throughout the series of solid solutions. However the ratios shown in Table 4 are generally lower than 1.50, except for the high-lead samples which show a higher ratio, reflecting some substitution of sulfate by hydroxyl ions. This phenomenon is probably connected with the departures from Vegard's law mentioned above and shows that the isomorphous substitution of hydronium ( $\text{H}_3\text{O}^+$ ) by lead is not as straightforward as would appear at first sight. In this connection it is relevant to note that Shishkin, Krogius and L'vovich (1958) demonstrated ion exchange between potassium and hydronium in the basic ferric sulfate ( $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ), whereas we have not been able to identify any plumbojarosite in diffraction patterns of basic ferric sulfate treated at  $140^\circ\text{C}$ . with concentrated solutions of lead nitrate. Apparently ion-exchange between hydronium and lead takes place with relative difficulty or very slowly, a feature which may have some bearing on the natural formation of plumbojarosite (*q.v.*).

#### CHEMICAL ASPECTS AND MINERAL GENESIS

In the present work, many attempts have been made to prepare a compound identical with the mineral plumbojarosite but without success. The highest lead content (Sample C—Table 1) was obtained by starting with a solution of ferrous sulfate and heating with lead sulfate in the presence of oxygen so as to produce ferric sulfate relatively slowly and to maintain thereby a substantial excess of lead sulfate throughout the experiment. Although Fairchild (1933) made a synthetic plumbojarosite by reacting lead chloride with an acid solution of ferric sulfate at  $110^\circ\text{C}$ ., no *x*-ray data or quantitative analyses are available for his product, which we were unable to reproduce from the available instructions. It was thought at first that our own preparations were simply contaminated with basic ferric sulfate but the *x*-ray diffraction patterns show no evidence of two phases and all reflections can be attributed to a single-phase solid solution. Further work showed that the latter phase (being less soluble) is always formed in preference to basic ferric sulfate and in fact extends the range over which the "jarosite" structure is stable in solution.

It would thus seem that the mineral plumbojarosite is not formed by the sort of reaction described above, especially as there is no record in the literature of any minerals having the composition of the solid solutions which formed so readily in our experiments. Furthermore, the basic ferric sulfate  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$  can hardly be a starting point for plumbojarosite formation since the evidence for its existence as a natural product has been discredited by Moss (1957) and Van Tassel (1958).



A more likely reaction is that between galena and pyrite under acid oxidizing conditions, which are commonly achieved in "the oxidized zone of lead mines in arid regions" where plumbojarosite is "widespread as a secondary mineral" (Palache *et al.*, 1951). As mentioned at the start of this paper, such a reaction has been under study by one of us (T. R. S.), and the presence of plumbojarosite in the residues had been suspected. Consequently, the residue from a leach at 140° C. was examined by *x*-ray diffraction methods and found to yield a pattern containing peaks identical with those for plumbojarosite. More importantly, the relative intensities of the peaks at 5.93 (vs) and 5.06 Å (vw) were such that the material could be identified as a high-lead plumbojarosite similar to sample B (Fig. 1) rather than a solid solution containing an appreciable amount of basic ferric sulfate (*e.g.* Sample C). In an attempt to make the identification more certain, a search was made for the characteristic peak at 11.2 Å (Table 1) on a Guinier film of the residue, but the peak could not be detected. This was not altogether surprising, considering that the reflection is not particularly strong even in the pure mineral, whereas the residue under examination contained only 5 per cent of plumbojarosite by chemical analysis. Nevertheless, the evidence is sufficient to support the view that plumbojarosite could be formed in nature by a reaction between galena and sulfides of iron. Although it is quite possible that the same reaction may proceed slowly at much lower temperatures than those used above, experimental verification has not been attempted because of the extended time scale required.

#### CONCLUSIONS

When solutions of ferric sulfate are heated at 100°–190° C. in the presence of lead sulfate for an hour or more, part of the lead sulfate is converted into a new compound, which is intermediate in composition between basic ferric sulfate ( $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ) and plumbojarosite ( $\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ ). This compound represents a single-phase solid solution and is always formed in preference to either of the end members of the series, despite wide variations in the experimental conditions used for its preparation. From *x*-ray diffraction data, it has been shown that the lattice constants for the solid solutions vary with the lead content, the unit cell volume increasing as the composition approaches that of  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ .

New *x*-ray diffraction data has been supplied for the mineral plumbojarosite and for the compound  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , since the data appearing in the literature for plumbojarosite (ASTM 5-0635) was incorrect and that supplied for the basic ferric sulfate (ASTM 10-444), was based on a mineral now known to be natrojarosite. In the course of this work,

material from a new locality at Laurion in Greece was shown to be authentic plumbojarosite, although it differed chemically from the type material (Cook's Peak, New Mexico) in containing less sulfate, which was in part replaced by phosphate and hydroxyl ions to balance ionic charges.

The data for plumbojarosite confirm the findings of Hendricks (1937), who found it necessary to index the mineral with a  $c$  dimension approximately twice that for any other members of the alunite and jarosite series. This difference is demonstrated by a low angle reflection (corresponding to planes at  $d=11.26 \text{ \AA}$ ) which does not appear in  $x$ -ray diffraction patterns of any of the synthetic solid solutions. It is concluded that this higher degree of order, accompanied by a marked contraction in cell volume, can only occur when the lead content approaches that corresponding to the ideal composition,  $\text{PbO} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$ .

By using the reaction between galena and pyrite in slightly acid solutions, in the presence of oxygen, and at temperatures over  $100^\circ \text{C}$ ., a compound has been formed which is less like the solid solutions referred to above and much more closely related to plumbojarosite as determined by  $x$ -ray diffraction patterns. It is therefore suggested that plumbojarosite is probably formed directly from these or similar minerals in a suitably-oxidizing geological environment, rather than by ionic substitution of lead in materials of the jarosite family. The latter process would tend to form solid solutions as described above, whereas no such minerals have so far been reported in the mineralogical literature.

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