

## THE OCCURRENCE OF JAROSITE IN UNDERCLAYS\*

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### ABSTRACT

Members of the jarosite family have been found intimately mixed with the clay minerals in underclays from southwestern Pennsylvania. The composition of these basic ferric sulfates has been determined by a combination of chemical and *x*-ray diffraction analyses. The powder patterns of these jarosites and of similar material from glauconitic sediments have been compared with indexed patterns of jarosites obtained from the U. S. National Museum.

### INTRODUCTION

Jarosite,  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ , has been identified in underclays from the southwestern part of Pennsylvania. This mineral occurs most commonly in the oxidized zones of ore deposits, but it has frequently been reported in sediments. Hutton (1950) has given representative examples of the variety of occurrences of jarosite. Briggs (1951) has shown that siltstones, glauconitic sandstones and diatomaceous shales in the Tertiary of California contain jarosite which has formed as a result of the oxidation of pyrite. Thus, the finding of jarosite in underclays which have a fairly high iron content is not surprising.

Most of the jarosite in underclays is intimately mixed with the clay minerals but some occurs as earthy yellowish patches resembling limonite. It was first noted during clay mineral studies on the supercentrifuged fractions, the equivalent spherical diameter being less than two microns. The differential thermal analysis (*DTA*) curve of the  $<0.3\mu$  fraction suggested the presence of a fair amount of lepidocrocite, but this was doubted since the samples were cream-colored. An *x*-ray diffraction pattern of the same material contained lines not attributable to the clays. Positive identification of the jarosite, which was too fine-grained for optical examination, was obtained by combining chemical and *x*-ray diffraction analyses.

The same mineral was also found in some glauconitic sandstones from Venezuela. It was concentrated in the  $<0.5\mu$  fractions of the clay minerals from the sandstones and seemed to be most plentiful in specimens which had yellowish material cementing the quartz and glauconitic grains. The yellow material was too fine-grained for optical identification and was studied concurrently with the underclays.

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## SOURCES OF SAMPLES

One underclay was from the Conemaugh formation in a road cut near the Youghiogheny Reservoir. A fresh sample of underclay was obtained from beneath the Upper Freeport coal in a mine at Creighton, Pennsylvania.

The glauconitic samples are from the upper member of the Cretaceous Temblador formation in the Greater Oficina area of Venezuela described by Hedberg et al. (1947). One is a well core sample from Tigre-1; the other is from Yopales-1.

## COMPOSITION OF UNDERCLAYS

The underclays from Pennsylvania consist of a mixture of disordered types of illite and kaolinite plus some quartz. In addition to the insoluble sulfate jarosite, the samples contain soluble sulfates of calcium and aluminum and perhaps free sulfuric acid. The soluble compounds were removed, and the clay was dispersed with a sodium oxalate solution. While only a minor amount of jarosite was detected by  $x$ -ray diffraction in the crude material, this mineral was so greatly concentrated in some of the supercentrifuged fractions that the clay minerals could not be identified before the removal of the sulfate with hydrochloric acid.

## X-RAY STUDIES AND THE IDENTIFICATION OF JAROSITE

The mineral which was later identified as jarosite gave a very distinctive  $x$ -ray diffraction pattern which agreed fairly well with the *ASTM*, pattern for coquimbite, but also showed some similarity to the *ASTM* patterns for jarosite and cyprusite, both basic ferric sulfates. When a jarosite-rich fraction was treated with hydrochloric acid and the residue  $x$ -rayed, it was found that the sulfate mineral had been dissolved, and the acid solution showed strong positive tests for ferric iron and sulfate. It was concluded that the mineral was more likely a basic ferric sulfate related to jarosite than the normal ferric sulfate coquimbite, since it was soluble in dilute acid but not in water. Proof that the sulfate was not coquimbite was obtained by  $x$ -raying two authentic samples of coquimbite donated by the U. S. National Museum. The diffraction pattern obtained from these samples was entirely different from the one given in the *ASTM* file for this mineral and likewise from the one obtained from the underclays. Moreover, the *DTA* curve of coquimbite differs greatly from the thermograms of the underclay samples, which agreed, at least below 600° C., with the *DTA* curves of jarosite given by Kulp and Adler (1950).

A fraction which contained a large amount of the ferric sulfate was treated with dilute hydrochloric acid, and a quantitative chemical analy-

sis was made of the solution. The ratio of ferric iron to sulfur trioxide was about the same as for jarosite, but the total alkalis were lower. Moreover, the sodium may have come entirely from the sodium-saturated clay. This analysis, No. 1 in Table 3, suggested that the mineral might be potassium-deficient jarosite. Therefore, samples of jarosite and karpfoserite, which is an alkali-free member of the jarosite family, were obtained from the U. S. National Museum for comparison.

TABLE 1. POWDER DIFFRACTION PATTERNS OF JAROSITES

(hkl)*	A			B			C		D		E	
	I	d(obs.)	d(calc.)	I	d(obs.)	d(calc.)	I	d(obs.)	I	d(obs.)	I	d(obs.)
101	3	5.94	5.93	3	5.93	5.93	1	5.95	1	5.94	1	5.95
003	2	5.74	5.74	3	5.56	5.56	1	5.73	2	5.72	1	5.65
012	4	5.09	5.09	4	5.05	5.05	2	5.10	3	5.59	2	5.10
110	1	3.65	3.65	1	3.66	3.66				3	5.10	
104	0		3.56	1	3.48	3.48						
021	6	3.11	3.11	8	3.11	3.11	2	3.120	4	3.115	3	3.115
113	10	3.08	3.08	8	3.06	3.06	3	3.085	4	3.080	3	3.075
202	1	2.97	2.964	2	2.96	2.963			4	3.065		
006	2	2.870	2.870	2	2.778	2.780	1	2.865	1	2.860	1	2.820
024	3	2.547	2.546	2	2.526	2.523					1	2.540
107	5	2.292	2.292	3	2.228	2.230	1	2.288	2	2.283		
									1	2.240		
									1	2.231		
033}												
303}	5	1.978	1.976	4	1.975	1.975						
027	2	1.941	1.940	1	1.905	1.905						
009	1	1.913	1.913	0		1.853						
220	5	1.823	1.823	4	1.830	1.830						
		several weak lines										
226	3	1.539	1.538	1	1.529	1.529						
02.10	3	1.512	1.512			1.476						
404	1	1.484	1.482	1	1.478	1.482						

NOTE:  $\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$ .

\* Hexagonal indices.

(A) Jarosite (U.S.N.M.-R6299).

(B) Karpfoserite (U.S.N.M.-R6266).

(C) Sulfate, Conemaugh underclay.

(D) Sulfate, Upper Freeport underclay.

(E) Sulfate, glauconitic sandstone.

The samples donated by the National Museum were portions of those which had been examined by Hendricks (1937) to determine the structure of jarosite. Jarosite (U.S.N.M.—R6299) from Meadow Valley Mine, Pioche, Nevada, and karpfoserite (U.S.N.M.—R6266) from Greenland were x-rayed in aluminum holders with the Norelco Wide Range Diffractometer using filtered copper radiation. Samples prepared by sedimenting the powdered minerals on glass slides were also x-rayed to determine whether these samples showed preferred orientation. Because of

its basal cleavage, the jarosite showed this effect, but the karpfoserite did not. Therefore, the samples were also  $x$ -rayed in powder cameras of 57.3 mm. radius in order to use a method of sample preparation which would give much less preferred orientation and permit better estimates of intensities. The  $d$  spacings greater than 1.48 Å were determined from diffractometer traces run at  $1/4^\circ$   $2\theta$  per minute. The powder patterns were indexed and the cell dimensions determined. These data are given in Tables 1 and 2.

The diffraction patterns of all the fractions from the underclay and glauconitic samples which contained appreciable amounts of basic ferric sulfate were examined to determine any minor differences which might be consistent for any one locality. Differences between fractions of the same samples were negligible. The major contamination was a mixture of kaolinite and illite in some fractions and quartz in others. Because of interfering diffraction lines from these impurities, the complete jarosite pattern could not be determined from any one fraction. The most en-

TABLE 2. LATTICE DIMENSIONS OF JAROSITES

Name	Formula	$a_0$	$c_0$	$c/a$
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	7.29	17.22	2.36
Jarosite*	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	7.22	17.03	2.36
$3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}^*$	$(\text{H}_2\text{O})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5(\text{H}_2\text{O})$	7.18	16.93	2.36
Natrojarosite*	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$	7.20	16.33	2.27
Karphosiderite	$\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5(\text{H}_2\text{O})$	7.32	16.68	2.28

NOTE: Dimensions of hexagonal cell are given in table;  $\lambda(\text{CuK}\alpha) = 1.5418$  Å. Those marked \* are from Hendricks (1937) and have been converted to Å.

Rhombohedral cell dimensions for powder patterns given in Table 1 are: jarosite,  $a_{rh} = 7.12$ ,  $\alpha = 61^\circ 35'$ ; karphosiderite,  $a_{rh} = 6.98$ ,  $\alpha = 63^\circ 15'$ .

riched fractions from each locality were  $x$ -rayed with the diffractometer at slow speed in order to determine accurate  $d$  spacings, given in Table 1. Like karphosiderite, none of these samples showed preferred orientation. The following in particular should be compared: the spacings of the (003), (006), and (107) reflections and the spread between the (021) and (113) reflections and their relative intensities.

The Conemaugh material gave the jarosite diffraction pattern while the Upper Freeport material appears to be jarosite mixed with a smaller amount of karphosiderite. The pattern of the sulfate from the glauconitic samples is intermediate between jarosite and karphosiderite, which suggests solid solution. The resolution observed in the pattern of the Upper Freeport material shows that it is possible to detect a mechanical mixture of jarosites.

The unit cell dimensions of jarosite (Table 2) do not agree with those determined by Hendricks (1937) on a single crystal, which may be due to variations among single crystals of jarosite. Such variation was suggested by Hendricks in order to explain the discrepancy that he found between the  $x$ -ray and morphological axial ratios. Hendricks' studies indicate that  $c_0$  is more affected than  $a_0$  by substitutions in the potassium position. Karphosiderite, in which this position is vacant, has a very much smaller  $c_0$  than jarosite, while the  $a_0$  dimensions are almost the same. Natrojarosite is also characterized by a smaller  $c_0$ . When water molecules fill the potassium position as in synthetic  $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ , the axial ratio is very similar to that of jarosite.

#### CHEMICAL STUDIES OF BASIC FERRIC SULFATES IN SEDIMENTS

The  $x$ -rayed fractions containing the water-insoluble sulfates were given a mild hydrochloric acid treatment, the results being shown in

TABLE 3. CHEMICAL ANALYSES OF SAMPLES CONTAINING JAROSITES

	Weight Per Cent			Molecular Equivalents		
Jarosite—Theoretical						
K <sub>2</sub> O		9.41			1.00	
Fe <sub>2</sub> O <sub>3</sub>		47.83			3.00	
SO <sub>3</sub>		31.97			4.00	
No. 1—Upper Freeport underclay <0.4 $\mu$ Fraction						
Na <sub>2</sub> O		1.11		0.39	}0.77	
K <sub>2</sub> O		1.61		0.38		
Fe <sub>2</sub> O <sub>3</sub>		24.54		3.31		
SO <sub>3</sub>		14.93		4.00		
	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Total Alk.
No. 2—Upper Freeport underclay 2-0.4 $\mu$ fraction	1.44	1.20	11.50	0.65	0.36	1.01
No. 3—Conemaugh underclay	1.08	0.72	4.19	1.33	0.58	1.91
No. 4—Glauconitic sandstone	0.9	0.64	4.02	1.16	0.54	1.70

Table 3. All the sulfate was assumed to be present as jarosite. Thus, the molecular equivalents of the alkalis are based on a figure of 4.00 for the molecular equivalent of SO<sub>3</sub>. The sulfates in the sediments are deficient in potassium. The highest percentage of sodium was found in a sample which contained more jarosite than some of the others. Thus, fractions which appear to give a karphosiderite  $x$ -ray pattern may ac-

tually contain natrojarosite. It is apparent from the lattice dimensions in Table 2 that natrojarosite must have a diffraction pattern more similar to karpfosiderite than to jarosite.

Soda and water determinations are of no value in determining the compositions of the jarosites in these samples because of the admixed clay minerals. The best that can be done is the estimation of probable compositions by considering both the *x*-ray diffraction patterns and chemical analyses for sulfate and potash.

The Upper Freeport underclay, which contains much less  $K_2O$  than the other samples, gives the diffraction pattern of a mixture of jarosite minerals. It contains relatively pure jarosite and either karpfosiderite or natrojarosite. If the latter is present, it must contain some vacant alkali positions in the structure since the total alkalis are lower than the theoretical amount. The jarosites from the Conemaugh underclay and the glauconitic sandstone, though very similar in chemical composition, give different *x*-ray patterns. Since the sulfate from the Conemaugh underclay gives a pattern of practically pure jarosite, many of the alkali positions may be filled with water molecules rather than sodium ions. The jarosite associated with the Venezuelan glauconite is a solid solution with only half of the alkali positions filled by potassium. It cannot be stated definitely whether the others are vacant or contain sodium, but the latter is probable since this particular sample was not appreciably contaminated with sodium saturated clay.

#### THERMAL STUDIES OF BASIC FERRIC SULFATES IN SEDIMENTS

Differential thermal analysis, carried out with apparatus described by McConnell and Earley (1951), first indicated that an unusual constituent

TABLE 4. THERMAL DATA FOR JAROSITES

	Endothermic Peaks		Exothermic Peaks
Jarosite (Kulp and Adler—1950)	470° C.	800° C.	590° C.
Upper Freeport underclay	430° C.	790° C.	490° C.
Conemaugh underclay	425° C.	770° C. ?	470° C.
Glauconitic sandstone	390° C.	—	425° C. ?

was present in these underclays. Before it was identified as jarosite, combined *x*-ray diffraction and differential thermal studies (Table 4) were carried out on fractions of the Conemaugh underclay and the glauconitic sandstones. The *x*-ray patterns remained unchanged up to the start of the first endothermic reaction, during which the color changes from light gray or cream to brown and the *x*-ray diffraction lines of the

sulfate mineral disappear. After the material has been heated for a longer time or at a higher temperature, it takes on a red color and gives the pattern of hematite. Most of the samples in Table 4 show no definite reaction attributable to jarosite at about 800° C. Apparently a large minimum percentage of jarosite is necessary for developing the characteristic thermogram given by Kulp and Adler (1950). Thus a small amount of jarosite in a sediment may be confused with lepidocrocite,  $\text{FeO}(\text{OH})$ , if the differential thermal method is used for identification. The peak temperatures found in this study differ from those of Kulp and Adler probably because of their faster heating rate (12.5° C. instead of 10° C. per minute) and the impurity of the jarosites concentrated from the sediments.

#### FORMATION OF JAROSITE IN SEDIMENTS

Merwin and Psonjak (1937) have discussed the chemistry of sulfate formation from the oxidation of pyrite in ore deposits based on their equilibrium studies in the system  $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  (Posnjak and Merwin, 1922). Complete oxidation of pyrite in the presence of sufficient water should yield the acid ferric sulfate rhomboclase,  $\text{HFe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , but the iron oxidizes more slowly than the sulfur and a mixture of ferrous and ferric sulfates and sulfuric acid results at first. The acid reacts with other minerals in the rock thus lowering the acidity of the solution. Alkalies and alkaline earths are easily introduced into the solution in this manner, especially if clays with exchangeable cations are present. When considerable dilution takes place, for example, when leaching and oxidation occur together near the surface of the ground, basic ferric sulfates may be precipitated. The jarosite type of basic sulfate occupies a large field below 170° C. in the central portion of the phase equilibrium diagram given by Posnjak and Merwin. The substitution of different alkalies in the jarosite structure should not greatly affect the general conditions of equilibrium. With considerable or continued dilution, the final product of the leaching and oxidation of pyritic rocks is goethite; however, once jarosites are precipitated, they are not readily dissolved.

The process described above should also apply under certain conditions to the oxidation of pyrite in sediments. Pyrite is very common in glauconitic sediments, coal beds, and other formations in which a reducing environment has been maintained. The occurrence of sulfates in any of these formations would be indicative of a considerable change in environment. Oxidation could occur more readily in sandstones and underclays than in sediments which contain fairly large amounts of organic matter. Dilution of the resulting acid solutions, which is also necessary for the deposition of basic ferric sulfates, could take place more readily

in porous sandstones than in clays or shales. On the other hand, sulfates might be completely leached out of sandstones and deposited elsewhere.

In most of the glauconitic samples, the jarosite was associated with kaolinite and relatively soluble calcium sulfate in the interstices between grains of quartz and glauconite. In some cases, it was concentrated in small lenses (a few inches in diameter) with kaolinite, fine-grained quartz and soluble calcium and aluminum sulfates which give an acid reaction with water. These lenses may have formed when percolating solutions became loaded with fine-grained material, clogged pores and deposited the mass of sulfates and clay in such a manner that further leaching could not occur. It is concluded that the jarosite found in the glauconitic sediments from Venezuela is merely a precipitate from the oxidation of pyrite and the dilution of the resulting solutions. The unaltered glauconite shows no evidence of replacement by jarosite like that observed by Briggs (1951) in California sediments.

Dilution probably is not as important in the deposition of jarosites in underclays as in sandstones. In fact, these underclays appear to contain free sulfuric acid and would be expected to contain soluble as well as insoluble sulfates. It is interesting, therefore, that soluble ferric iron was associated with the aluminum and calcium sulfates in the Upper Freeport underclay but not in the Conemaugh underclay, which had been exposed in a road cut.

#### SUMMARY

Members of the jarosite family of basic ferric sulfates have been found in underclays from the southwestern part of Pennsylvania. Because the particle size of the sulfates was less than one micron, they could not be separated mechanically from the clay minerals nor could they be identified optically. The probable composition was determined by a combination of chemical and  $x$ -ray diffraction analyses. Differential thermal analyses were also made.

$X$ -ray diffraction patterns of powdered samples of jarosite and karpfosiderite from the U. S. National Museum facilitated the identification of the basic ferric sulfates in the underclays. The powder patterns were indexed and lattice dimensions determined. The *ASTM*  $x$ -ray diffraction pattern for coquimbite was found to be a pattern of a member of the jarosite family.

The  $x$ -ray and chemical analyses indicated that jarosite is present in the underclays but that some of the potassium positions are probably filled with water molecules while others may contain sodium. One underclay sample, with less potassium in combination with the sulfate, contained a mixture of jarosite with natrojarosite or karpfosiderite. A basic



ferric sulfate in glauconitic sandstones from Venezuela was found to be a solid solution of jarosite and natrojarosite with a composition closer to the former member.

The formation of jarosites in pyritic sediments during concurrent oxidation and leaching processes is consistent with the phase equilibria studies in the system  $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  carried out by Posnjak and Merwin (1922). Both the iron and the sulfur are derived essentially from the pyrite, while the alkalis are derived from the other minerals of the sediments, particularly illite, by acid attack.

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