

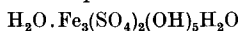
*The nature of carphosiderite and allied basic sulphates  
of iron.*

By A. A. Moss, B.Sc., Ph.D., F.S.A.

Department of Mineralogy, British Museum (Natural History).

[Read 24 January 1957.]

*Summary.* The composition of carphosiderite has been given<sup>1</sup> as



and like the jarosites is characterized by a ferric iron to sulphate ratio of 3:2. It is significant not only that this formula was worked out on artificial material but also that none of the analyses so far made supports it. The present investigation shows that there is little or no evidence for the existence of a mineral with the above composition and that carphosiderites are in reality either jarosite or natrojarosite. It has long been thought that certain other minerals, namely borgströmite, utahite, cyprusite, pastréite, raimondite, apatelite, and planoferrite, were similar to, if not identical with, carphosiderite and six of these are listed with carphosiderite in Dana, Syst. Min., 7th edn. These minerals with the exception of planoferrite and the possible exception of apatelite are also jarosite or natrojarosite.

CARPHOSIDERITE was reported in 1827 by A. Breithaupt<sup>2</sup> who wrote that the mineral occurred in mica-schist on the coast of Labrador, but that the exact locality was unknown to him. In Dana<sup>3</sup> the 'original' carphosiderite is said to come from the Upernivik District, Lango, Greenland. The fact of the matter is, of course, that no one knows where the type material came from, and Breithaupt introduced further complications when he reported, on the results of a qualitative chemical examination by E. Harkort, that the mineral was a basic iron phosphate, although it is clear from the account of the experiments made that the mineral was in fact a sulphate. The first analysis of a mineral supposed to be the type material was published by A. Pisani.<sup>4</sup> The mineral was contaminated by 9 % of gypsum and 10.78 % of sand, and after allowance had been made for these the composition was given as Fe<sub>2</sub>O<sub>3</sub> 49.88, SO<sub>3</sub> 31.82, H<sub>2</sub>O 18.30 %. Then, as now, analyses were frequently quoted without even the briefest description of the methods used to determine the constituents, but there can be little doubt that

<sup>1</sup> S. B. Hendricks, Amer. Min., 1937, vol. 22, p. 780 [M.A. 7-87].

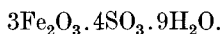
<sup>2</sup> Journ. Chem. Phys. (Schweigger), 1827, vol. 50, p. 314.

<sup>3</sup> Syst. Min., 7th edn., vol. 2, p. 566.

<sup>4</sup> Compt. Rend. Acad. Sci. Paris, 1864, vol. 58, p. 242.

the water content of this mineral was determined by difference. This is not surprising since an accurate determination of this constituent is not an easy matter owing to the ease with which these basic sulphates decompose on heating, releasing in the process not only water but sulphur trioxide as well. The second occurrence of carphosiderite was reported by A. Lacroix<sup>1</sup> from St. Léger, Mâcon, the analysis of which was given as Fe<sub>2</sub>O<sub>3</sub> 48.5, P<sub>2</sub>O<sub>5</sub> 2.72, SO<sub>3</sub> 30.18, H<sub>2</sub>O 18.48 %. Here again the water was taken by difference since an analysis of this specimen (see later) kindly supplied to me by Prof. J. Orcel gave the following figures: Fe<sub>2</sub>O<sub>3</sub> 48.8, P<sub>2</sub>O<sub>5</sub> 0.6, SO<sub>3</sub> 30.6, Na<sub>2</sub>O 1.3, K<sub>2</sub>O 6.9, H<sub>2</sub>O 10.8 %. It will be seen that, although there is reasonable agreement between the two analyses in the proportions of Fe<sub>2</sub>O<sub>3</sub> and SO<sub>3</sub>, part of that ascribed to water is made up of alkalis. The mineral is in fact jarosite. Lacroix realized his mistake some years later<sup>2</sup> and having learnt that this mineral contained alkalis also came to the conclusion that it was jarosite.

*Borgströmite.* This mineral from Otravaara, Finland, was first described by M. Saxen<sup>3</sup> in 1923. From the description of his experiments it is evident that alkalis were not looked for. Saxen gives the analyses of two specimens, an impure borgströmite containing limonite and a pure specimen to which, on the basis of his analytical results (Fe<sub>2</sub>O<sub>3</sub> 51.83, SO<sub>3</sub> 28.73, H<sub>2</sub>O 19.44 %), he ascribes the formula<sup>4</sup>



This material was later analysed by another author and found to contain 6 % K<sub>2</sub>O and accepted by Saxen to be jarosite.<sup>5</sup> His contention that the original impure material, none of which is now accessible, is indeed a new mineral, borgströmite, cannot be accepted in view of the fact that, as in the second analysis, no search was made for alkalis. As will be seen later, a specimen of borgströmite from the type locality analysed during the course of the present investigation proved to be a mixture of jarosite and limonite.

*Utahite.* A. Arzruni and A. Damour<sup>6</sup> first described this mineral from Eureka Hill mine, Tintic, Utah, and found it to have the following composition: Fe<sub>2</sub>O<sub>3</sub> 58.82, As<sub>2</sub>O<sub>3</sub> 3.19, SO<sub>3</sub> 28.45, H<sub>2</sub>O 9.35 %. Damour, who carried out the analysis, gave a brief account of his methods, from

<sup>1</sup> Bull. Soc. franç. Min., 1887, vol. 10, p. 142.

<sup>2</sup> Min. France, 1910, vol. 4, p. 145.

<sup>3</sup> Bull. Comm. Géol. Finlande, 1923, vol. 11, no. 65, p. 50.

<sup>4</sup> This is the formula for carphosiderite.

<sup>5</sup> M. Saksela [Saxen], *ibid.*, 1952, vol. 26, no. 157, p. 28 [M.A. 12-179].

<sup>6</sup> Bull. Soc. Min. France, 1884, vol. 7, p. 126.

which it is evident that he determined the water directly, but that, since he performed the rest of the analysis after fusion with potassium carbonate, he did not search for alkalis. A specimen in the British Museum from the same locality proved to be natrojarosite.

*Cyprusite*. This name was given by P. F. Reinsch<sup>1</sup> to a yellow earthy mineral found by him in Cyprus. Material was collected from the same spot and reported on by Deby<sup>2</sup> two years later. The analysis of the latter material, carried out by H. Fulton, gave, after allowing for some 17 % of insoluble matter (mainly diatoms), Fe<sub>2</sub>O<sub>3</sub> 49.68, Al<sub>2</sub>O<sub>3</sub> 3.89, SO<sub>3</sub> 35.34, H<sub>2</sub>O 11.06 %, figures which differ somewhat from those obtained by Reinsch, but to which Deby nevertheless gave the name cyprusite, believing presumably that Reinsch's analysis was unreliable.<sup>3</sup> This material of Deby is in the British Museum and has been shown on analysis to consist almost entirely of natrojarosite.

*Pastréite*. The history of this mineral is most unsatisfactory. It was collected at Saint Félix-de-Pallières (Gard), by a Dr. Normann, who named it after President Pastré in Marseilles and then sent it to Prof. C. Bergemann in Bonn for examination. Bergemann was of the opinion that it was a decomposition product of varying composition and that it would be unsafe to regard it as a new mineral.<sup>4</sup> In spite of this the name pastréite found its way into the textbooks and has since remained there, although L. Azema<sup>5</sup> has shown that a mineral collected from the type locality by Lacroix and thought to be the pastréite of Normann has, in reality, the same composition as jarosite.

*Raimondite* and *planoferrite*. It has not been possible to obtain either of these minerals. The claim of raimondite to be a mineral rests on an analysis carried out on behalf of A. Breithaupt by Dr. Ruhe some 90 years ago.<sup>6</sup> The results were given as Fe<sub>2</sub>O<sub>3</sub> 46.52 and 46.65, SO<sub>3</sub> 36.08 and 34.99, H<sub>2</sub>O 17.40 and 18.36 %. These figures do not correspond to any simple formula, and may well be wrong; furthermore, the description of the microscopic appearance of the mineral suggests that here again we are dealing with jarosite or natrojarosite.

It has been suggested that planoferrite is also carphosiderite. This

<sup>1</sup> Proc. Roy. Soc., 1882, vol. 33, p. 119.

<sup>2</sup> Journ. Roy. Microscop. Soc., 1884, ser. [2], vol. 4, pt. 1, p. 186.

<sup>3</sup> Rheinsch's analysis was given as oxide of iron (+Al<sub>2</sub>O<sub>3</sub>) 51.5, sulphuric acid 21.5, insoluble siliceous substance 25.0, hygroscopic water 2 %.

<sup>4</sup> C. Bergemann, Verhandl. nat. Ver. Rheinland, 1866, vol. 23, Sitzungsber. niederrheinisch. Gesell. (Bonn), p. 17.

<sup>5</sup> Bull. Soc. franç. Min., 1910, vol. 33, p. 130.

<sup>6</sup> Berg. hütten. Zeit., 1866, vol. 25, p. 149.

mineral was described by L. Darapsky<sup>1</sup> and sent by him to Munich, where it was many years later destroyed during the bombing of that town; it is, however, stated to be soluble in water by which it is subsequently hydrolysed, and is therefore undoubtedly a hydrated ferric sulphate.

*Experimental work.*

All specimens in the British Museum collection labelled 'carphosiderite', including a recent one from Boolcoomatta, South Australia, proved to be either jarosite or natrojarosite. The whereabouts of the type material not being known, an analysis was made of Lacroix's St. Léger material, supplied by Prof. J. Orcel, of the Musée d'Histoire Naturelle, Paris. Analyses were also made of borgströmite and utahite from the type localities, and of Deby's cyprusite. The X-ray patterns of these minerals showed that they are properly classified as jarosites.

The iron content was determined by precipitation as hydroxide and checked absorbtometrically (sulphosalicylic acid complex); phosphate also was estimated absorbtometrically (molybdovanado complex). Sulphate was precipitated as barium sulphate after removal of iron and ammonium salts. The alkalis were determined by the flame photometer after decomposition of the mineral with sulphuric and hydrofluoric acids followed by removal of ferric hydroxide by careful addition of ammonia. F. A. Gooch's method<sup>2</sup> was used to estimate the water content. The results are given in table I, together with the atomic proportions calculated on the basis  $(S,P)O_4 = 2$ .

TABLE I. New analyses of 'carphosiderite' and allied minerals.

	A.	B.	C.	D.		A'	B'	C'	D'
Insoluble (HCl)	0.7	1.1	0.5	1.5					
H <sub>2</sub> O—*	nil	1.1	<0.05	0.2					
H <sub>2</sub> O+*	10.8	12.6	10.7	11.1	OH	6.1	11.8	6.0	6.2
SO <sub>3</sub>	30.6	18.9	31.7	31.8	SO <sub>4</sub>	}	2	2	2
P <sub>2</sub> O <sub>5</sub>	0.6	nil	nil	tr.	PO <sub>4</sub>				
Fe <sub>2</sub> O <sub>3</sub>	48.8	61.2	51.0	49.1	Fe	3.1	6.5	3.2	3.1
Na <sub>2</sub> O	1.3	0.4	5.8	5.4	Na	0.22	0.11	0.95	0.87
K <sub>2</sub> O	6.9	4.8	0.6	1.2	K	0.75	0.86	0.06	0.13
	99.7	100.1	100.3	100.3	Na+K	0.97	0.97	1.01	1.00

A. Carphosiderite, St. Léger, Mâcon, France. B.M. 1956,353.

B. Borgströmite, Otravaara, Finland. B.M. 1923,406.

C. Utahite, Eureka mine, Tintic, Utah, U.S.A. B.M. 82743.

D. Cyprusite, Kynussa, Cyprus (35° N., 32° 30' E.) B.M. 67210.

A'-D'. Atomic proportions recalculated to a basis  $(S,P)O_4 = 2$ .

\* H<sub>2</sub>O— below and H<sub>2</sub>O+ above 105° C.

<sup>1</sup> Zeits. Kryst. Min., 1898, vol. 29, p. 213.

<sup>2</sup> Journ. Amer. Chem. Soc., 1880, vol. 2, p. 247.

*Discussion.* It will be seen from the table that the ratio of alkalis to  $\text{SO}_4$  is in every case near 1:2 as it should be in a jarosite, and that the iron and hydroxyl proportions in A, C, and D are also in agreement with the accepted formula for a jarosite,  $(\text{Na},\text{K})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ . The relative proportions of iron and hydroxyl in B show simply that borgströmite is a mixture of jarosite and limonite,<sup>1</sup> the presence of the latter having been recognized by Saxen in his first paper<sup>2</sup> (1923). It can also be seen from the table that carphosiderite from St. Léger is jarosite, whereas utahite and cyprusite are natrojarosite. There exists no evidence for a mineral of the composition  $\text{H}_2\text{O} \cdot \text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ , although Posnjak and Merwin have prepared a compound of such a composition artificially.<sup>3</sup> One of the important properties of these basic alkali ferric sulphates and all minerals previously described as carphosiderite, &c., is their insolubility in water. In the part of their paper that deals with 'carphosiderite' Posnjak and Merwin make no mention of its insolubility; in fact, in their description of their analytical methods they state that 'the weighed samples in most cases were dissolved in a suitable amount of water and a sufficient amount of the solution taken for analysis'. It is not possible, therefore, to deduce whether this artificial 'carphosiderite' is soluble or insoluble in water, although if it were even partly soluble, this fact would be evidence for the difference between the artificial product and the mineral that has so long gone under this name.

Finally a word about synonyms. Except in mineralogy, it has been customary to regard a synonym as a word identical in meaning with that of another known word. It is true that this custom has not always been ignored by mineralogists and some genuine synonyms have been incorporated in their literature. For example, the words sphalerite and blende, being in effect Greek and German renderings of the same idea, can be accepted as synonyms for cubic zinc sulphide without any misgiving, but the retention of, say, the carphosiderite mineral names as synonyms for jarosite is indefensible. In this instance these names have been invented by mineralogists only too eager to discover new minerals, and have, in fact, been introduced into the literature by false pretences, in so far as their compositions have been misrepresented, through errors or oversights in the analyses. We can indeed describe the names of the minerals forming the subject of this paper in the words of a writer<sup>4</sup> long

<sup>1</sup> From X-ray data, this was shown to be goethite.

<sup>2</sup> Loc. cit.

<sup>3</sup> E. Posnjak and H. E. Merwin, Journ. Amer. Chem. Soc., 1922, vol. 44, p. 1976 [M.A. 2-21].

<sup>4</sup> T. A. R[eadwin], Chem. News, 1875, vol. 31, p. 109.

since dead, namely that they are 'mineralogical orphans, fallen out of the ranks from unknown causes or weakness of constitution. Some of their parents and sponsors have been dead a very long while, and nobody appears to know where many of them came from. I don't care to keep an asylum for them any longer, but wish them to die a natural death, and to be sanitarily buried, or cremated (if preferred) clean out of sight and out of mind.'

---