

Hydronium Jarosite — $[\text{H}_2\text{O}] \text{Fe}_2 [(\text{SO}_4)_2 (\text{OH})_2]$

by

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Presented by A. HOLEWSKI on March 12, 1960

A. A. Moss [8] and R. Van Tassel [13] have questioned the existence of carphosiderite $(\text{H}_2\text{O}) \text{Fe}_2 (\text{SO}_4)_2 [(\text{OH})_2 \cdot \text{H}_2\text{O}] - 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, and of allied hydrated basic ferric sulphates. Their analyses, carried out on type material (holotypes), indicate that minerals named carphosiderite, cyprusite, utahite and bergströmite, are in reality (potassium) jarosites or natrojarosites. Research work of both A. A. Moss and R. Van Tassel proved to a satisfactory degree the error of ascribing to carphosiderite and allied minerals from the type localities, the chemical formula $(\text{H}_2\text{O}) \text{Fe}_2 (\text{SO}_4)_2 [(\text{OH})_2 \cdot \text{H}_2\text{O}]$. However, the analytic material proved too scanty to determine, whether a mineral of this chemical composition might not occur in natural conditions.

Investigations of jarosites hitherto undertaken by the author, as well as some other published results (Table) indicate that in nature, there exist minerals of the jarosite group whose analyses disclose an amount of alkalis which, when compared with the theoretical content, required for binding the total amount of SO_3 , is too small.

It must also be kept in mind that the amount of alkalis determined on basis of analyses presented in the Table is presumably too high and could be partly leached out of the accompanying minerals (most frequently illites and feldspars). The deficiency of alkalis in proportion to the amount of SO_3 in the analyzed material is usually attributed to the content of probable admixtures of other sulphates, or of free sulphuric acid. As a rule, such explanations lack actual evidence. The jarosite samples examined by the author were subjected to accurate leaching in water, in order to eliminate any water-soluble sulphates. In converting his analyses into molecular equivalents the author used as basis the content of SO_3 remaining after eliminating the amount bound as probable gypsum. This decision was prompted by phase examinations revealing that, apart from gypsum, these minerals are not accompanied as a rule by any sulphates insoluble in water. Analyses taken from literature (Table) have

TABLE

No.	Locality	Chemical formula	Weight %			Molecular equivalents						
			SO ₃	K ₂ O	Na ₂ O	PbO	CaO	SO ₃	K ₂ O	Na ₂ O	PbO	CaO
1 [1]	Kopeck, near Vodolka, north of Prague, Czechoslovakia	(K _{0.09} Na _{0.29} (H ₃ O) _{0.02})Fe ₃ [(SO ₄) ₂ (OH) ₄]	29.47	6.00	1.68			4.00	0.69	0.29		
2 [9]	St. Léger, Maçon, France (original carphosiderite)	(K _{0.76} Na _{0.22} (H ₃ O) _{0.02})Fe ₃ [(SO ₄) ₂ (OH) ₄]	30.6	6.9	1.3			4.00	0.76	0.22		
3 [8]	Otravaara, Finland (original bergströmite)	(K _{0.46} Na _{0.11} (H ₃ O) _{0.03})Fe ₃ [(SO ₄) ₂ (OH) ₄]	18.9	4.8	0.4			4.00	0.86	0.11		
4 [10]	Sinyak, Carpathians, USSR	(K _{0.41} Na _{0.13} (H ₃ O) _{0.04})Fe ₃ [(SO ₄) ₂ (OH) ₄]	26.17	4.70	1.80			4.00	0.61	0.15		
5 [11]	St. Felix de Pallières, France	(K _{0.42} Na _{0.09} (H ₃ O) _{0.00})Fe ₃ [(SO ₄) ₂ (OH) ₄]	32.02	7.75	0.55			4.00	0.82	0.09		
6 [13]	Greenland, USNM-R6262, (original carphosiderite)	(K _{0.01} Na _{0.90} (H ₃ O) _{0.09})Fe ₃ [(SO ₄) ₂ (OH) ₄]	31.4	0.01	5.5			4.00	0.01	0.90		
7 [11]	Chuquicamata, Chile	(K _{0.01} Na _{0.92} (H ₃ O) _{0.17})Fe ₃ [(SO ₄) ₂ (OH) ₄]	34.65	0.15	5.51			4.00	0.01	0.82		
8 [7]	Skopow, Carpathians, Poland	(K _{0.66} Na _{0.13} (H ₃ O) _{0.21})Fe ₃ [(SO ₄) ₂ (OH) ₄]	31.04	6.03	0.78			4.00	0.66	0.13		
9 [14]	underclay < 0.04 μ , Upper Freeport, Pennsylvania, USA	(K _{0.34} Na _{0.39} (H ₃ O) _{0.23})Fe ₃ [(SO ₄) ₂ (OH) ₄]	14.93	1.61	1.11			4.00	0.38	0.39		
10 [5]	"Polska" mine, Upper Silesia, Poland	(K _{0.07} Na _{0.70} (H ₃ O) _{0.23})Fe ₃ [(SO ₄) ₂ (OH) ₄]	34.33	0.67	4.64			4.00	0.07	0.70		
11 [7]	Borek Nowy, Carpathians, Poland	(K _{0.05} Na _{0.09} (H ₃ O) _{0.20})Fe ₃ [(SO ₄) ₂ (OH) ₄]	30.69	5.92	0.54			4.00	0.65	0.04		
12 [3]	Delatin, Carpathians, USSR	(K _{0.45} Na _{0.27} (H ₃ O) _{0.20})Fe ₃ [(SO ₄) ₂ (OH) ₄]	29.72	3.95	1.55			4.00	0.45	0.27		
13 [6]	"Marylda" mine, Upper Silesia, Poland	(K _{0.10} Na _{0.11} Pb _{0.57} (H ₃ O) _{0.29})Fe ₃ [(SO ₄) ₂ (OH) ₄]	22.74	0.45	0.17	9.13		4.00	0.07	0.04	0.57	
14 [7]	Kolaczyce, Carpathians, Poland	(K _{0.13} Na _{0.22} (H ₃ O) _{0.40})Fe ₃ [(SO ₄) ₂ (OH) ₄]	32.60	3.69	1.19			4.00	0.18	0.22		
15 [6]	"Orzel Biały" mine, Upper Silesia, Poland	(K _{0.10} Na _{0.20} Pb _{0.31} (H ₃ O) _{0.49})Fe ₃ [(SO ₄) ₂ (OH) ₄]	16.77	0.92	0.06	3.61		4.00	0.18	0.02	0.31	
16 [5]	Bezručowa, Carpathians, Poland	(K _{0.27} Na _{0.23} (H ₃ O) _{0.49})Fe ₃ [(SO ₄) ₂ (OH) ₄]	25.01	2.75	1.65			4.00	0.27	0.24		
17 [7]	Rudzińska, Rymanowska, Carpathians, Poland	(K _{0.43} Na _{0.06} (H ₃ O) _{0.50})Fe ₃ [(SO ₄) ₂ (OH) ₄]	33.34	3.58	0.53			4.00	0.1	0.09		
18 [9]	"Malka" mine, Caucasus, USSR	(K _{0.10} Na _{0.22} Ca _{0.27} (H ₃ O) _{0.59})Fe ₃ [(SO ₄) ₂ (OH) ₄]	32.74	1.22	0.64	1.58		4.00	0.12	0.10	0.27	
19 [6]	"Orzel Biały" mine, Upper Silesia, Poland	(K _{0.10} Na _{0.39} Pb _{0.03} (H ₃ O) _{0.70})Fe ₃ [(SO ₄) ₂ (OH) ₄]	32.29	1.56	1.09	0.86		4.00	0.19	0.20	0.05	
20 [9]	"Malka" mine, Caucasus, USSR**)	(K _{0.11} Na _{0.11} (H ₃ O) _{0.70})Fe ₃ [(SO ₄) ₂ (OH) ₄]	30.48	1.22	0.64			4.00	0.13	0.11		
21 [9]	"Staszic" mine, Holy Cross Mt., Poland	(K _{0.10} Na _{0.11} (H ₃ O) _{0.70})Fe ₃ [(SO ₄) ₂ (OH) ₄]	25.11	0.76	0.54			4.00	0.10	0.11		

*) unpublished data

**) after deducing SO₃ contained in gypsum, from analysis No. 18

been converted in an identical manner. Chemical formulae thus computed are but approximate; still, they illustrate with satisfactory accuracy quantitative proportions of the cation substituents. With this system of conversion it appeared that the majority of jarosites examined by the author, as well as some jarosites described in literature, fail to contain a sufficient quantity of alkalis, necessary for covering all cation positions of the structure. The conditions of crystallization of jarosites — strongly acid environment (pH 1—2) — suggested to the author that part of the cation positions might be occupied by hydronium ions $[H_3O]^+$, not by H_2O molecules as in carphosiderite^{*}). This supposition is also corroborated by X-ray data on the described minerals. The hydronium ions, present in large amounts in the acid environment are in many respects analogous with ions of alkalis and with the ammonium ion $[NH_4]^+$ (Grimm's hybride law).

Jarosites containing a hydronium ion should be looked upon as members of the isomorphic series: $KFe_3[(SO_4)_2(OH)_6] — H_3OFe_3[(SO_4)_2(OH)_6]$. Jarosite from the "Staszic" mine (analysis 21, Table), and probably likewise the calcium jarosite of Serdiuzhenko [9]**) (analysis 20, Table) occupy an end position in this series, while the plumbojarosites from the "Orzel Bialy" mine (analyses 15, 19, Table) and the jarosites from menilite shales (analyses 16, 17, Table) occupy an intermediate position. It seems probable that in nature the hydronium end member of this series occurs. However, in natural conditions its crystallization depends upon special conditions because, as a rule, the waters occurring in oxidized zones contain large quantities of potassium ions, or of other cations forming the jarosite lattice.

The hydronium character of the hydrated basic ferric sulphate $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O — [H_3O]Fe_3[(SO_4)_2(OH)_6]$ has been proved by Szyszkina [11]. He also experimentally demonstrated the existence of a connection between this sulphate, potassium jarosite [12] and ammonium jarosite [11]***) on synthetic material. Crystallization temperature of hydronium jarosites is lower than that of potassium jarosite. Fairchild [2] obtained jarosites only above $110^\circ C$; at lower temperatures ($90^\circ C$), he obtained

^{*}) It must be admitted that Hendricks [4] and, in his tracks, several further authors [9], [14] assume for carphosiderite the formula $Fe_3(SO_4)_2(OH)_3H_2O$ and imagine that the cation positions of its structure are not occupied: Dana [1], however, suggests the much more convincing formula $(H_2O)Fe_3(SO_4)_2\{(OH)_3 \cdot H_2O\}$.

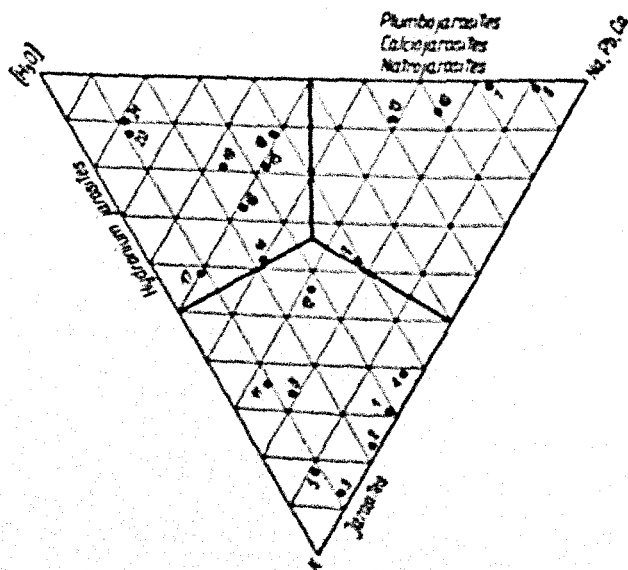
^{**}) Serdiuzhenko's calcium jarosite is, most probably, hydronium jarosite with an admixture of gypsum. Its analysis has been given in the Table twice, — once in the original (18) and, again, after elimination of its probable gypsum content (20).

^{***}) So far, Szyszkina's research work has found no echo among Russian mineralogists investigating jarosites [3], [9], [10]. Nor has this work been known before to the author of this paper.

compounds with an average content of $\text{SO}_3 = 33.5\%$, $\text{K}_2\text{O} = 7.24\%$, and molecular equivalents $\text{SO}_3 : \text{K}_2\text{O} = 4.00 : 0.73$, i. e. compounds of a chemical composition resembling that of average jarosites from the Carpathian menilite beds (analyses 11, 12, 14, 16, Table). On basis of Szyszkin's examinations, and according to results of the author's investigations of natural jarosites, carried out independently, jarosites may be considered derivatives of a basic ferri-hydronium sulphate in which the hydronium ion is isomorphically replaced by K, Na, Ag, NH_4 , Rb or by the bivalent Pb, Ca ions.

The name carphosiderite, applied to the presumable $(\text{H}_2\text{O})\text{Fe}_3(\text{SO}_4)_2((\text{OH})_2 \cdot \text{H}_2\text{O})$, or rather $\text{H}_2\text{OFe}_3((\text{SO}_4)_2(\text{OH})_2)$, has an old tradition and its place in handbooks.

This term, discredited by results of examinations made by A. A. Moss and R. Van Tassel, is no more justified than the names of related minerals such as bergströmite, utahite, cyprusite, apatelite*), planoferrite and raimondite. Owing also to its erroneous implication, a non-existent connection with siderite, this term should better be replaced by another one connected with the jarosite group.



*) The X-ray pattern of apatelite from Issy near Paris (collection of Wrocław University, made by the author, proved this mineral to be of jarosite structure.

The author suggests that minerals in which the molecule percentage of the $[H_3O]$ ion exceeds the molecule percentage of other cations (K, Na, Ag, NH_4 , Rb, Pb, Ca), should be called hydronium jarosites (Fig. 1).

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