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LONECREEKITE, SABIEITE AND CLAIRITE, NEW SECONDARY AMMONIUM FERRIC-IRON SULPHATES FROM LONE CREEK FALL CAVE, NEAR SABIE, EASTERN TRANSVAAL

by

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Abstract

Three new minerals from Lone Creek Fall Cave are described. They are supergene in origin and are formed by the interaction of pyrite with ammonia derived from decaying organic matter.]

Lonecreekite:	$NH_4Fe(SO_4)_2.12H_2O$ of the alum family cubic with $a = 12{,}302$ Å $Z = 4$ density 1,693 g/cm^3 colourless isotropic.
Sabieite:	$NH_4Fe(SO_4)_2$ hexagonal with $a = 4{,}822$ Å $c = 8{,}1696$ Å $Z = 1$ white.
Clairite:	$(NH_4)_2Fe_3(SO_4)_4(OH)_3.3H_2O$ triclinic with $a = 9{,}368$ Å $b = 9{,}150$ Å $c = 52{,}610$ Å $\alpha = 88{,}15^\circ$ $\beta = 90^\circ$ $\gamma = 118{,}36^\circ$ $Z = 8$ yellow $Nx = 1{,}595$ $Nz = 1{,}607$.

The three minerals are of supergene origin and are formed by the oxidation of pyrite, which interacts with ammonia produced from the decay of organic matter. Lonecreekite is likely to crystallize from this solution if the pH value is below one and clairite if the pH value is around 2. Sabieite derives from the dehydration of lonecreekite.

1. INTRODUCTION

Lone Creek Fall Cave is a shallow overhang situated about 20 m to the left of the well-known waterfall, a tourist attraction near Sabie in the eastern Transvaal. The cave ceiling consists of a chert breccia, which marks the base of the Pretoria Group and rests unconformably on the cherty dolomite of the Eccles Formation which is exposed on the walls and on the floor.

White and yellow saline efflorescences are growing on the ceiling and on the floor. X-ray and chemical tests show that the material on the floor is niter (KNO_3), whereas on the ceiling the efflorescences consist of tschermigite (ammonium alum) and three ammonium ferric-iron sulphate salts. Moreover, microprobe investigation revealed the presence of minor amounts of a nickel—copper—cobalt sulphate mineral which was not investigated. It was established that the ammonium ferric-iron sulphates were new species which have been named lonecreekite, after the place, sabieite, after the nearest town and clairite after the author's wife, Mrs Claire Martini. The International Mineralogical Association Commission on New Minerals and Mineral Names has approved the naming of the new minerals. Type material is housed in the Museum of the Geological Survey in Pretoria.

2. DESCRIPTION

2.1 LONECREEKITE

White sugary crusts and efflorescences, a few millimetres long, form several patches on the chert ceiling of the cave. Preliminary investigation showed that this material belongs to the alum family and contains ammonia, iron and aluminium. It appeared that the iron-aluminium ratio varies considerably from one patch to another. For instance, a sample collected in the central part of the cave contained essentially aluminium with only a small amount of iron and could consequently be considered as tschermigite. Material from the southern extremity of the cave proved to be more iron-rich (Sample LC 7). A microprobe investigation showed that the aluminium content varies within the same sample. In Table 2.1, Analysis No. 1 refers to Sample LC 7 in bulk, whereas Analysis No. 2 is for a selected iron-rich fraction of Sample LC 7, seperated in heavy media.

The empirical formula derived from Analysis No. 2 is: $(NH_4)_{0,99}(Fe_{0,79}\,Al_{0,16})_{\Sigma 0,95}\,S_{2,03}\,O_8.12,25H_2O$ on the basis of eight oxygens in the anhydrous part. If Al can be disregarded and if one defines lonecreekite as the ferric-iron end member, the ideal formula is

Table 2.1 – CHEMICAL ANALYSES OF SAMPLES LC 7, LC 2 AND LC 8

Analysis	1	2	3	4
Fe_2O_3	9,70*	13,04*	25,21*	31,42*
Al_2O_3	5,03*	1,69*	0,60*	0,10*
Mn_2O_3	–	–	–	1,23*
Na_2O	–	–	–	0,35+
K_2O	–	0,02*	0,62*	0,03+
$(NH_4)_2O$	4,78▵	5,34▵	7,20▵	6,97▵
SO_3	33,55¤	33,49▵	54,40*	43,86▵
H_2O	47,03▵	45,60▵	–	10,85▵
Insoluble in HCl	0,80¤	0,77¤	12,77¤	4,41¤
TOTAL	100,89	99,95	100,80	99,22

(1) Lonecreekite, bulk of Sample LC 7
(2) Lonecreekite, selected iron-rich fraction of Sample LC7
(3) Sabieite, residual from Sample LC 2
(4) Clairite, Sample LC 8

* From microprobe and loss on ignition
\+ By flame photometre
¤ From wet chemistry
▵ By gas chromatography

Analyst: H.H. Lachmann, National Chemical Research Laboratory

$NH_4Fe(SO_4)_2.12H_2O$. Analysis No. 2 shows that mineralogically the composition consists of 83 per cent lonecreekite and 17 per cent tschermigite. In Analysis No. 1 the theoretical values are 55 and 45 per cent respectively.

The powder diffraction pattern (Table 2.2, No. 1) is close to synthetic material (ASTM Card No. 7–5) and indexed as a cubic cell with a = 12,302 Å and Z = 4. There is no violation of the extinction rule for Pa3 which is given for tschermigite.

The mineral is colourless and transparent and the luster is vitreous. Xenomorph-granular crystals averaging 0,1 mm across, are visible under the microscope. The density measured by sink–float in a blend of tetrabromoethane and acetone is 1,693 g/cm^3. The calculated density after the normalized empirical formula is 1,691 g/cm^3. Lonecreekite is isotropic, with a refractive index of 1,483. The hardness of the mineral could not be measured, but it is obviously very soft. It is readily soluble in water, releasing brown ferric hydroxide due to hydrolysis.

2.2 SABIEITE

In some places, lonecreekite efflorescences are cloudy and yellowish white. This may be attributed to dehydration, as the same alteration occurs on the white transparent material if it is exposed to the air of the laboratory for several weeks. The X-ray diffraction pattern mainly shows alum lines with an additional reflexion at 8,2 Å, which can be attributed to an anhydrous ferric-iron sulphate (ASTM Card No. 3–35). As this compound is only slowly soluble in water, it was possible to dissolve the alum by quick leaching and separate about 20 mg of powdery residual on which chemical and X-ray diffraction investigations were performed (Table 2.1, No. 3).

The empirical formula derived from Analysis No. 3 is: $((NH_4)_{0,83}K_{0,04})_{\Sigma 0,87}(Fe_{0,94}Al_{0,04})_{\Sigma 0,98}S_{2,03}O_8$ on the basis of eight oxygens. The ideal formula is $NH_4Fe(SO_4)_2$.

The powder diffraction pattern is very near to synthetic material (J.C.P.D.S. Card No. 24–44) and can be indexed as a hexagonal cell with a = 4,822 Å, c = 8,1696 Å, Z = 1. After the synthetic material (P321), the system is trigonal.

Sabieite is a white powder of which hexagonal thin platelets (2 to 10 microns) are visible under the microscope. Neither the density nor the refractive indices could be measured. They can, however, be inferred as being high. The extinction is parallel to the outline.

2.3 CLAIRITE

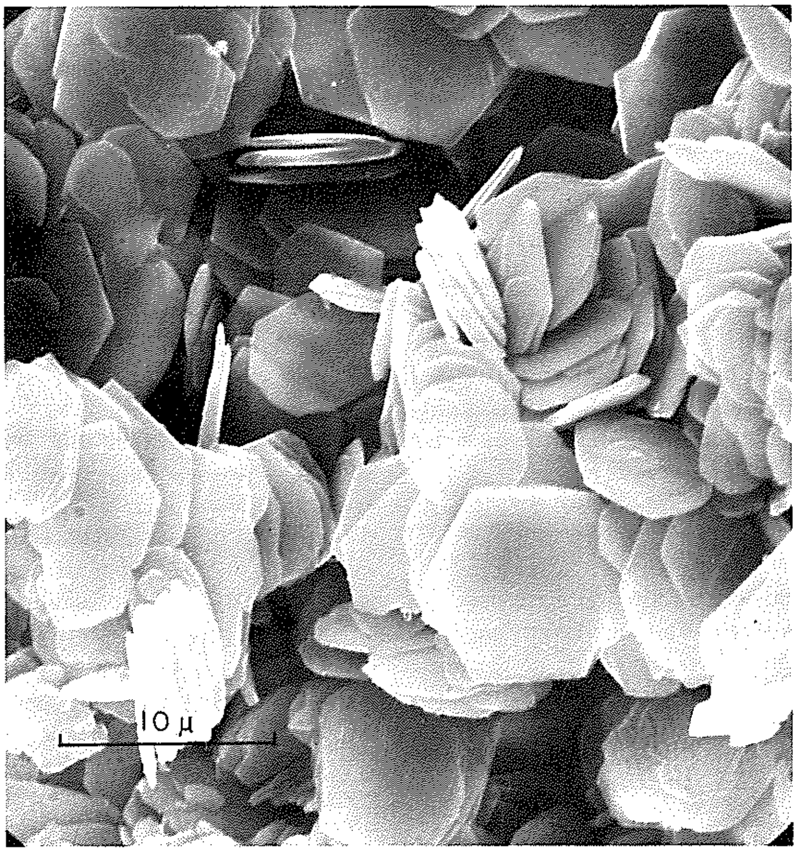
At the southern extremity of the rock shelter, a patch of lonecreekite efflorescences decays to an orange-yellow powdery material. The powdery material can easily be hand-sorted from alum. Examination under the scanning electron microscope showed that it is monomineralic with the exception of some quartz fragments, which were indicated as insolubles in the chemical analysis. The mineral forms aggregates of pseudo-hexagonal thin plates which are 5 to 50 microns across (Pl. 2.1).

Assuming that manganese is in trivalent form, the empirical formula derived from Analysis No. 4 in Table 2.1, on the basis of four sulphates, is: $((NH_4)_{1,95}Na_{0,08})_{\Sigma 2,03}(Fe_{2,87}Mn_{0,11}Al_{0,02})_{\Sigma 3,00}(SO_4)_4(OH)_{3,03}.2,88H_2O$ or ideally: $(NH_4)_2Fe_3(SO_4)_4(OH)_3.3H_2O$.

The X-ray pattern and general character of the mineral, show some similarities with metavoltine (Palache et al. 1957). Metavoltine bears the formula $K_5Fe_3(SO_4)_6(OH)_2.9H_2O$ and is hexagonal although synthetic material with a monoclinic or triclinic symmetry is known (Gossner 1936). The possibility of clairite being an ammonium equivalent to metavoltine can be ruled out as the proportions of the various elements in clairite differ considerably from those in metavoltine.

An X-ray single crystal study was not possible, because of the minute grain size. Due to the platy nature of the mineral an orientated preparation could be obtained by sedimentation in alcohol. After binding this loose material with a hair fixer, a fragment was mounted in a Debye-Scherrer camera in such a way that the platelets were orientated perpendicular to the axis of the camera. As the platelets were not perfectly orientated, the resulting image was crude but nevertheless good enough to index the first main lines of the diagram with some certainty. Moreover, taking into account the similarity to metavoltine, a triclinic cell was computed with a = 9,368 Å, b = 9,150 Å, c = 52,610 Å, α = 88,15°, β = 90°, γ = 118,36° and Z = 8.

The density measured by sink–float in a blend of tetrabromoethane and acetone is 2,31 g/cm^3. Calculated on the normalized empirical formula it is 2,32 g/cm^3. The cleavage (001) is perfect. Optically the mineral is birefringent but the optic sign and 2V could not be determined due to the minute grain size. The refractive indices are Nx = 1,595 and Nz = 1,607. The extinction is nearly parallel; α//c, X = pale yellow, Z' = dark yellow. Clairite is slowly soluble in water.



Pl. 2.1 — Scanning-electron microphotograph of clairite.
Aftaselektronmikrofoto van clairiet.

Table 2.2 – X-RAY PATTERNS OF LONECREEKITE, SABIEITE AND CLAIRITE.

No.	Lonecreekite (Sample LC 7)				Sabieite (Sample LC 2, leached)				Clairite (Sample LC 8)			
	I/I_{100}	$d_{obs.}$Å	$d_{calc.}$Å	*hkl*	I/I_{100}	$d_{obs.}$Å	$d_{calc.}$Å	*hkl*	I/I_{100}	$d_{obs.}$Å	$d_{calc.}$Å	*hkl*
1	70	7,12	7,103	111	100	8,19	8,169	001	100	17,5	17,525	003
2	50	5,505	5,502	210	20	3,72	3,718	101	100	8,78	8,762	006
3	25	5,027	5,022	211	10	2,910	2,920	102	20	8,23	8,242	100
4	100	4,356	4,349	220	10	2,718	2,723	003	10	7,76	7,774	012
5	60	4,107	4,101	221	30	2,409	2,411	110	5	7,63	7,616	$01\bar{2}$
6	40	3,710	3,709	311	10	1,865	1,859	202	10	7,31	7,291	$\bar{1}13$
7	65	3,289	3,288	321	10	1,806	1,805	113	10	7,18	7,186	$1\bar{1}3$
8	30	3,077	3,076	400	15	1,556	1,558	114	5	6,504	6,506	015
9	10	2,984	2,984	410	5	1,476	1,472	122	5	5,845	5,842	009
10	10	2,899	2,900	411	20	1,392	1,392	300	15	4,743	4,741	110
11	15	2,820	2,822	331	10	1,374	1,372	301	5	4,388	4,381	$00\underline{12}$
12	15	2,749	2,751	420	10	1,356	1,353	115	10	4,119	4,121	200
13	10	2,682	2,685	421					10	3,493	3,489	028
14	15	2,621	2,623	332					20	3,424	3,430	$\bar{2}28$
15	5	2,507	2,511	422					25	3,279	3,286	$00\underline{16}$
16	10	2,363	2,368	511					20	3,041	3,039	320
17	5	2,284	2,284	432					5	2,775	2,781	219
18	5	2,244	2,246	521					5	2,500	2,770	$\bar{1}38$
19	5	2,178	2,175	440					5	2,288		
20	5	2,139	2,142	522					5	2,218		
21	5	2,078	2,079	531					5	2,190		
22	5	2,050	2,050	600					5	1,947		
23	5	2,026	2,022	610					5	1,799		
24	5	1,994	1,996	611								
25	20	1,945	1,945	620								
26	2	1,833	1,834	630								
27	5	1,815	1,814	631								
28	5	1,723	1,723	711								
29	2	1,704	1,706	640								
30	5	1,643	1,644	642								
31	5	1,628	1,629	722								
32	5	1,602	1,602	731								

Philips diffractomer using cobalt Kα radiation, Fe filters and quartz as internal standard (lonecreekite, clairite and lines 1 and 2 of sabieite).
Debye-Scherrer camera, diameter 57,3 mm, quartz as standard, cobalt Kα radiation, Fe filters (sabieite).

3. GENESIS

The chert breccia above the cave presumably contains pyrite and possibly pyrrhotite which is oxidized by seepage water, forming sulphate and ferric ions. The most likely hypothesis is that the seepage water contains mainly sulphate and iron when it reaches the ceiling of the rock shelter and that ammonia is added from ammonia fumes produced from the soil of the cave. The ammonium is provided by the decay of organic matter in the form of excreta from animals (Hyrax) living in the cave or in the fissures above. It may be that the ammonium is already present in the seepage water when it enters the cave. Lonecreekite crystallizes by the evaporation of the seepage water.

Compared to aluminium alum, ferric alum is less stable. Therefore it seems likely that a strong deficiency in aluminium must be expected in the seepage water leaching the chert breccia, essentially constituted of silica.

As already mentioned, sabieite is formed by the dehydration of lonecreekite. It is interesting to note that the aluminium content in sabieite is lower than in lonecreekite. Presumably the ferric—aluminium alum dehydrates selectively, leaving the aluminium part as tschermigite, which does not lose water as easily at room temperature as lonecreekite.

The formation of clairite rather than lonecreekite is linked to the pH value of the solution. At a very low pH value and with an excess of sulphuric acid present, Fe^{3+} is the dominant cation (Garrel et al. 1965) and lonecreekite will crystallize. At a higher pH value, complexes like $Fe(OH)^{2+}$ are predominant and as the OH^- concentration increases, the formation of a brown-yellow hydroxyl compound like clairite is favoured. When pyrite is oxidized, the resulting solution contains an excess of sulphuric acid and therefore lonecreekite will form through the evaporation of such a solution. However, if this mineral is redissolved after having formed efflorescences, for instance by the condensation of water, a less acidic solution will form, buffered at about pH 2 due to hydrolysis. If evaporation occurs a second time, sulphate hydroxyl salts will crystallize. The previously-mentioned observation, that clairite seems to result from the decay of lonecreekite efflorescence, confirms this hypothesis.

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