

MBOBOMKULITE, HYDROMBOBOMKULITE AND NICKELALUMITE, NEW MINERALS FROM MBOBO MKULU CAVE, EASTERN TRANSVAAL

by

J.E.J. Martini, Dr. Sc. Geol.

Abstract

Three new cave minerals from the Mbobo Mkulu Cave, Eastern Transvaal, are described. The structure of these minerals, which is probably layered, is discussed and models are proposed.

Mbobomkulite, $\text{NiAl}_4(\text{NO}_3)_2(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$ is monoclinic with parameters $a_0 = 10,171$, $b_0 = 8,865$, $c_0 = 17,145 \text{ \AA}$, $\beta = 95,37^\circ$, $Z = 4$, density $= 2,30 \text{ g/cm}^3$ and optical properties $\alpha = 1,515$, $\gamma = 1,585$, maximum extinction $\alpha' \wedge$ perfect cleavage $\{001\} = 10^\circ$.

Hydrombobomkulite with composition $\text{NiAl}_4(\text{NO}_3)_2(\text{OH})_{12} \cdot 13-14 \text{ H}_2\text{O}$ is monoclinic (?) with parameters $a_0 = 10,145$, $b_0 = 17,155$, $c_0 = 20,870 \text{ \AA}$, $\beta = 90,55^\circ$, $Z = 8(?)$.

Nickelalumite, $\text{NiAl}_4\text{SO}_4(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$, is monoclinic with $a_0 = 10,175$, $b_0 = 8,860$, $c_0 = 17,174 \text{ \AA}$, $\beta = 95,95^\circ$, $Z = 4$, density $2,24 \text{ g/cm}^3$ and optical properties $\alpha = 1,532$, $\gamma = 1,543$, $\alpha' \wedge \{001\} = 30^\circ$.

The three minerals, of supergene origin, are microcrystalline, forming powdery pale-blue nodules in the soil of the cave and coatings on gypsum crystals. Mbobomkulite and nickelalumite are isomorphous to chalcoalumite and solid solutions exist between the three minerals.

1. INTRODUCTION

During the course of spelaeological investigations conducted by the South African Spelaeological Association, the author collected numerous mineral samples in Mbobo Mkulu Cave, situated on Goed Geluk 444 JT, Nelspruit District, Eastern Transvaal. Among the various species determined by X-ray diffraction, one sample produced unidentified lines. Additional sampling and further investigation led to the establishment of the three new species described in this paper. The minerals and the names mbobomkulite and hydrombobomkulite have been approved by the Commission on New Minerals and Minerals Names of the I.M.A. Nickelalumite has not been submitted to this Commission as the mineral could not be purified in such a way that completely reliable analyses could be obtained. Mbobomkulite is named after the cave, Mbobo Mkulu - "the big hole" - and hydrombobomkulite is the hydrated form of mbobomkulite. Nickelalumite is taken by analogy from chal-

coalumite, with which it is isomorphous, but containing nickel instead of copper. The type material is deposited in the Museum of the Geological Survey, Pretoria.

2. OCCURRENCE

The cave is developed immediately below palaeokarst residual breccia ("giant chert"), which marks the base of the Pretoria Group (Fig. 2.1). The dolomite in which the cave has formed is chert free and belongs to the Lyttelton Formation. One of the peculiarities of the cave is that it contains unusual spelaeothems - stalactites and stalagmites of haematite and goethite attaining lengths of several metres. Allophane forms spectacular blue draperies up to 10 m in length on the walls of the final chamber; the blue colour is due to small amounts of copper and nickel. Allophane, associated with halloysite, also forms transparent layers, 50 mm thick, on the floor, and is gelatinous, resembling jellyfish flesh in appearance; other minerals present in the cave include

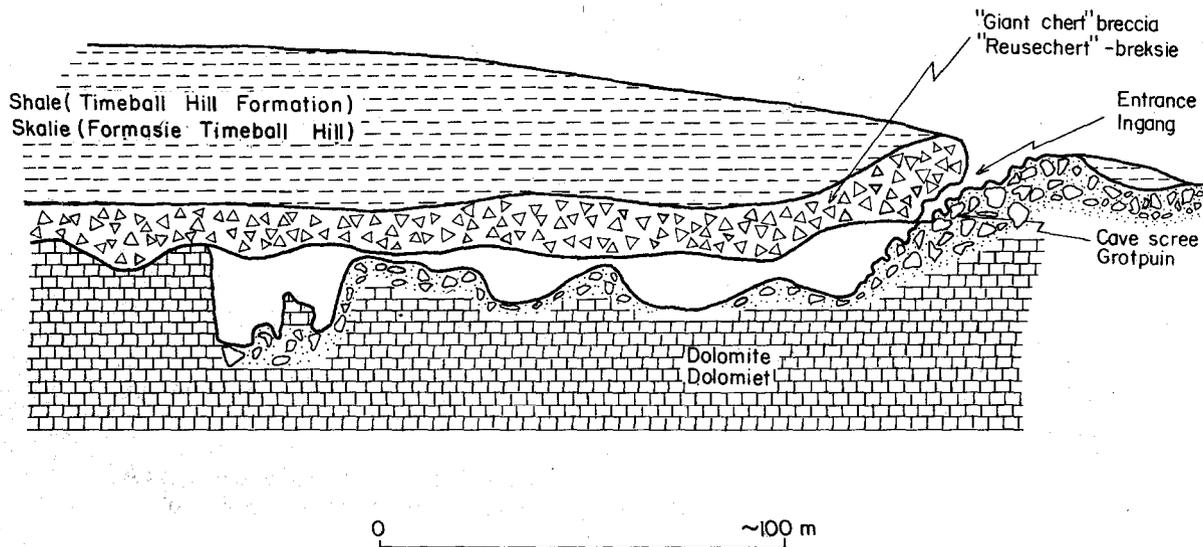


Fig. 2.1 — Schematic section through Mbobo Mkulu Cave.
Skematiese snit deur Mbobo Mkulu-grot.

opal (as a glaze coating blue allophane), alunite (as powdery pale-green nodules in the soil), aluminite (as white chalky efflorescences), jarosite (as yellow microcrystalline coating on haematite-goethite spelaeothems), atacamite (as a green staining in the soil), a potassium-rich sampleite (forming finely crystalline blue nodules in the soil), gypsum (as crystalline crusts on the walls), potash alum (forming granular oulopholites growing on the floor), sasaite (as white powdery nodules in the soil), and leucophosphite (as purple coatings on chert slabs).

The new minerals occur in two places in the third chamber of the cave. Mbobomkulite, hydrombobomkulite and nickelalumite occur as sky-blue, friable nodules in a matrix of powdery allophane, forming mounds on the floor. Nickelalumite, associated with chalcoalumite, is found at the second locality as thin, pale-blue coatings on gypsum crystals that form a crust on the ceiling.

3. DESCRIPTION

3.1 MBOBOMKULITE

Pale-blue nodules were sorted out from the allophane powder and carefully cleaned in order to obtain a material as pure as possible. It was dried in a silica gel desiccator prior to analysis. Carbon, nitrogen and hydrogen were determined by gas chromatography; the other elements were determined by wet chemical methods. The results appear in Table 3.1. Carbon is obviously due to organic matter because a residue is left after attack with HCl. The silica is due to impurities of allophane which may have the same composition as the matrix of the nodules. The matrix has the following composition: SiO_2 - 30,32 per cent, Al_2O_3 - 26,04 per cent, H_2O - 40,14 per cent. Microprobe investigations on various crystals indicate that the composition of mbobomkulite remains practically constant and that the only impurity present is allophane.

After deduction of Al_2O_3 and H_2O bound to allophane, the empirical formula is $\text{Al}_{3,93}\text{Ni}_{0,57}\text{Cu}_{0,29}(\text{SO}_4)_{0,25}(\text{NO}_3)_{1,50}(\text{OH}_{11,45}\text{F}_{0,02}) \cdot 1,59\text{H}_2\text{O}$ on the basis of a total valency of $\text{NO}_3 + \text{SO}_4 = -2$. When the mineral is removed from the desiccator, it takes up about 5 per cent of its original mass by absorbing moisture from the atmosphere, which would give the formula a number of H_2O very close to 3. These variations of the water content are not marked by any change in the XRD pattern.

X-ray single-crystal studies could not be made on account of the very fine grain size of the material. The powder diffraction pattern (Table 3.2) is, however, very close to that of chalcoalumite ($\text{CuAl}_4\text{SO}_4(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$), a mineral which has been indexed by Weissenberg photographs and which is monoclinic ($a_0 = 10,221$,

$b_0 = 8,915$, $c_0 = 17,090 \text{ \AA}$, $\beta = 95,88^\circ$) - Williams and Khin 1971. Using these indices for chalcoalumite, the cell dimensions could be computed and yielded the following results: $a_0 = 10,171$, $b_0 = 8,865$, $c_0 = 17,145 \text{ \AA}$, $\beta = 95,37^\circ$ and $Z = 4$.

Macroscopically mbobomkulite is a powdery, very finely grained, pale sky-blue mineral. Under the microscope it is colourless. It forms pseudohexagonal, very thin plates about 10 microns across, piled up along the c axis as well as forming rosettes (Plate 3.1a). The cleavage $\{001\}$ is perfect. Optically it is birefringent but the optical sign and $2V$ could not be determined on account of the minute grain size. Refractive indices measured in natural light are $\alpha = 1,515$ and $\gamma = 1,585$. The maximum extinction angle $\alpha' \wedge \{001\}$ is about 10° . The hardness could not be measured but is certainly very low. For material dried in room atmosphere, the density (g/cm^3) measured by sink-float in tetrabromoethane diluted with acetone is 2,30 (calculated after the formula $\text{Ni}_{0,66}\text{Cu}_{0,34}\text{Al}_4(\text{NO}_3)_{1,50}(\text{SO}_4)_{0,25} \cdot 3\text{H}_2\text{O}$, the density is 2,344).

3.2 HYDROMBOBOMKULITE

If the blue nodules described in the previous section are removed from the cave and protected from desiccation, the X-ray powder pattern is entirely different from mbobomkulite. When freshly sorted material is exposed to the atmosphere, it loses water and is entirely transformed into mbobomkulite within a few hours. This transformation seems to be irreversible. Mbobomkulite was kept in water for two months after which it was X-rayed again but showed no sign of reversal. The name hydrombobomkulite is proposed for the more hydrated phase.

According to the X-ray pattern of the material analysed it is composed mainly of hydrombobomkulite with approximately 10 per cent mbobomkulite, which is only detectable by its four strongest lines. By progressive dehydration the lines of hydrombobomkulite disappear and at the same time the lines of mbobomkulite increase in strength. The loss in mass (H_2O) when placed in a desiccator, was 32,10 per cent. If the data are added to the chemical analysis of mbobomkulite (Table 3.1), the empirical formula of hydrombobomkulite will be identical except that the number of H_2O molecules increases from 1,59 to 13,48. It is therefore suggested that the small percentage of mbobomkulite present in the original material is more or less compensated by a slight excess of moisture. However, the real number of water molecules is not known accurately but must certainly be included in the numbers from 12 to 15.

As it seems logical that mbobomkulite has a layered structure, it may be expected that hydrombobomkulite has a similar structure but with the difference that it

Table 3.1 — CHEMICAL ANALYSES

	SiO ₂	Al ₂ O ₃	NiO	CuO	SO ₃	N ₂ O ₅	H ₂ O	C	F	-O=F ₂	Total
1. Mbobomkulite (blue nodules in allophane)	1,91	39,42	7,98	4,28	3,81	15,23	27,90	0,26	0,07	0,03	100,83
2. Nickelalumite (blue nodules in allophane)	8,95	39,30	6,59	2,35	10,28	4,70	28,53	<0,30	-	-	100,70
3. Nickelalumite (crust on gypsum)	-	41,65	10,08	0,93	13,53	-	-	-	-	-	-
4. Chalcoalumite (crust on gypsum)	-	35,67	2,32	8,63	13,75	-	-	-	-	-	-

Nos 1 and 2 by wet chemistry. Carbon, N₂O₅ and H₂O determined by gas chromatography (analyst: H.H. Lachmann, National Chemical Research Laboratory).

Nos 3 and 4 — electron microprobe analyses.

contains more water and that a cell could be derived from that of mbobomkulite simply by increasing c_0 . However, several attempts in this direction failed. It was possible to find a cell for indexing the lines of hydrombobomkulite (Table 3.2) only after substantial modifications of $2b_0$ of mbobomkulite: $a_0 = 10,145$, $b_0 = 17,155$, $c_0 = 20,870 \text{ \AA}$, $\beta = 90,55^\circ$. As the density could not be measured, Z is not known, but could possibly be eight.

The thermal data obtained on 25 mg of purified material consist of poorly resolved endothermic reactions from 60 to 100 °C (32 per cent loss in mass) and at 160 °C (5 per cent loss), a strong endothermic peak at 280 °C (24 per cent loss), and a small endothermic peak at 800 °C (3 per cent loss).

Macroscopically the mineral looks very similar to mbobomkulite. Under the microscope it forms aggregates of very fine grains showing no discernible crystallographic outlines or cleavages. It appears to be weakly birefringent but no other optical characteristics could be measured. During the dehydration process, it is possible to observe that the cleavage of mbobomkulite appears by the exfoliation of the grains which fall into loose tiny pseudo-hexagonal plates.

3.3 NICKELALUMITE

A second sample containing similar pale-blue nodules was collected at a different spot on the mound of allophane powder. The composition differs from that of mbobomkulite as a result of a much higher SO_4/NO_3 ratio (Table 3.1). The material analysed is unfortunately impure as it contains more allophane and other impurities such as opal. Microprobe investigations showed that the chemical composition of various grains remains constant and that the sulphur content is always much higher than in mbobomkulite. By analogy with chalcoalumite and mbobomkulite and using the Ni/Cu and SO_4/NO_3 ratios, it is possible to establish the following exact formula for nickelalumite: $\text{Ni}_{0,75}\text{Cu}_{0,25}\text{Al}_4(\text{NO}_3)_{0,5}(\text{SO}_4)_{0,75}(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$.

Under the microscope the morphology is very similar to mbobomkulite but the crystals show more regular outlines (Plate 3.1). The extreme refractive indices could be determined as $\alpha = 1,532$ (2) and $\gamma = 1,543$ (2). The birefringence is therefore much lower than for mbobomkulite, and is the easiest test to distinguish these minerals from each other. The maximum extinction angle $\alpha' \wedge \{001\}$ is about 30°.

The powder X-ray diffraction pattern (Table 3.2) is very similar to that of mbobomkulite but does show some minor differences. The reflections 112 and $1\bar{1}\bar{2}$, present in nickelalumite, are for instance, absent in mbobomkulite and the line 022 is only present in mbobomkulite. The cell parameters are very close to those obtained

for mbobomkulite and chalcoalumite: $a_0 = 10,175$, $b_0 = 8,860$, $c_0 = 17,174 \text{ \AA}$, $\beta = 95,95^\circ$, $Z = 4$. The density (g/cm^3) calculated from the exact formula indicated previously is 2,28; the density measured by sink–float in tetrabromoethane diluted with acetone, is 2,24 g/cm^3 . The thermal properties of the material analysed (containing about 30 per cent allophane) are comparable to mbobomkulite with the exception that the endothermic reaction at 750 °C is much more pronounced and represents a larger loss in mass (12 per cent = loss of SO_3).

In the other occurrence of nickelalumite in the cave, the mineral forms thin blue coatings on gypsum crystals which developed on the ceiling of the cave. The mineral takes the shape of radially orientated blades (Plate 3.1c) on which microprobe analyses were conducted (Table 3.1). The detectable elements have been quantitatively analysed with reference to metal standards for Cu and Ni, corundum for Al and celestite for S. The mineral could not be polished to a high degree as it is very soft and brittle, therefore the results are semiquantitative only. However, it is obvious that the sulphur content is such that practically only sulphate is present and that nitrate, which was not detectable, must be very low. The results show that the Ni/Cu ratio varies considerably. At the base the mineral is a fairly pure nickelalumite ($\text{Ni}_{0,92}\text{Cu}_{0,08}$), and grades into chalcoalumite ($\text{Ni}_{0,22}\text{Cu}_{0,78}$) at the extremity of the blades. The small grain size of the coatings on the gypsum crystals did not allow for mechanical separation for X-ray diffraction analyses. However, the bulk of the coatings analysed with a Debye-Scherrer camera gave a spectrum comparable to that of nickelalumite–chalcoalumite.

Fresh material from the blue nodules proved, by X-ray analysis, to consist essentially of nickelalumite. However, it contains a minor amount of a phase comparable to hydrombobomkulite, which disappeared completely on exposure to the room atmosphere. Due to its dilution with nickelalumite, it is represented only by a restricted number of diffraction lines which are almost identical to that of hydrombobomkulite. It is not possible to obtain more information about this phase. However, this strongly suggests the existence of "hydronickelalumite".

4. GENESIS

Most of the minerals found in Mbobo Mkulu Cave, including the new minerals described here, may be classified as "orebody-derived cave minerals" after Hill (1976). They are the products of oxidation and leaching of sulphide minerals contained in the roof. It is known that the breccia of the giant chert is very weakly mineralised over a wide area. Other caves in a similar stratigraphic position also show blue spelaeothems (Foster et al. 1979). Primary mineralisation in the shaly matrix of the breccia, consisting essentially of pyrite and

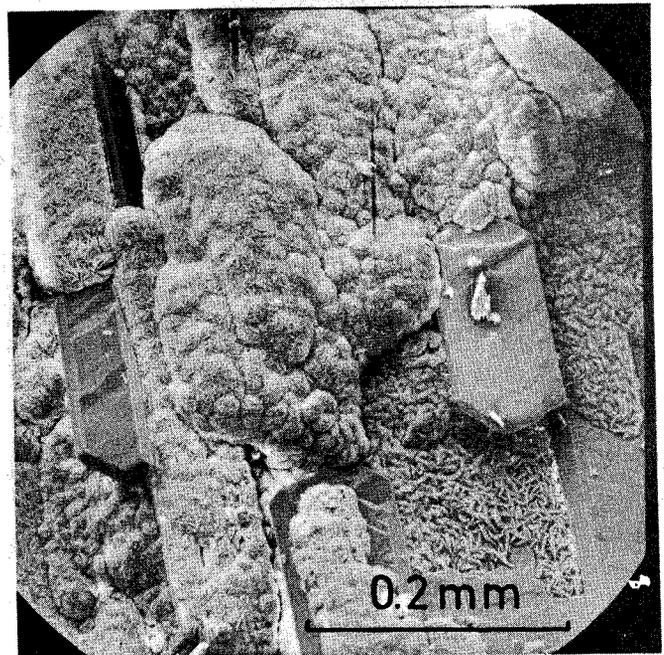
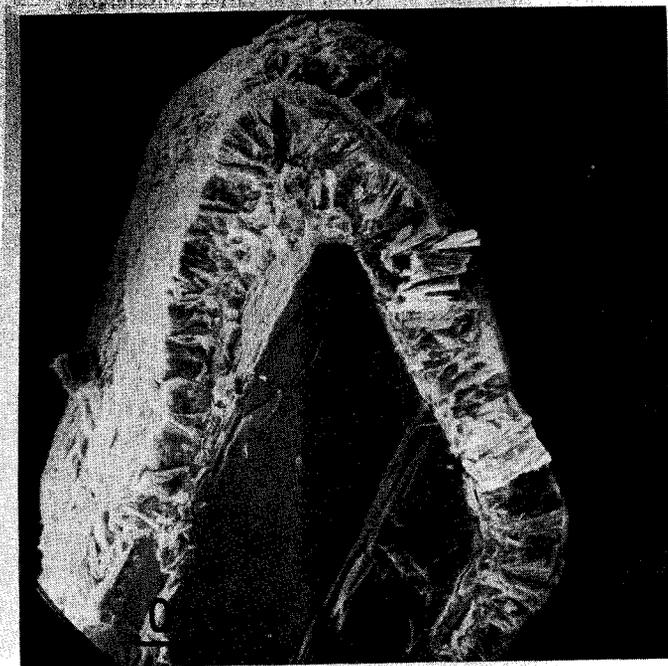
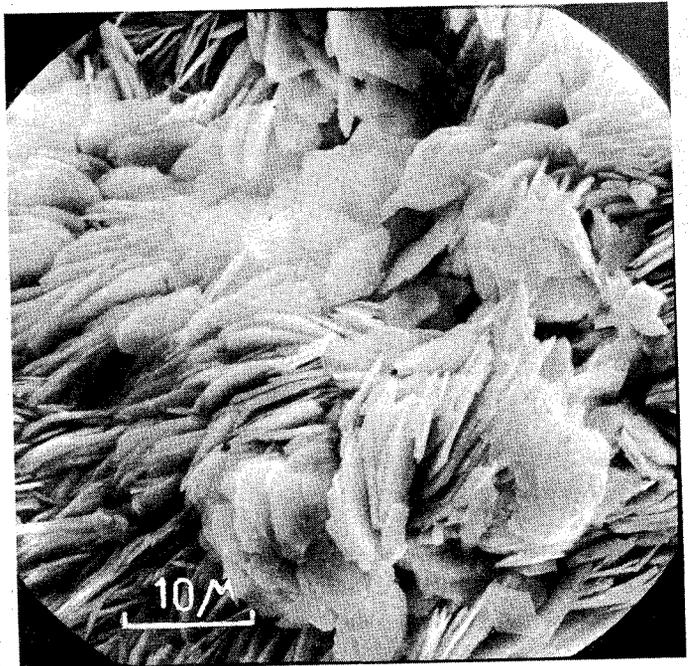
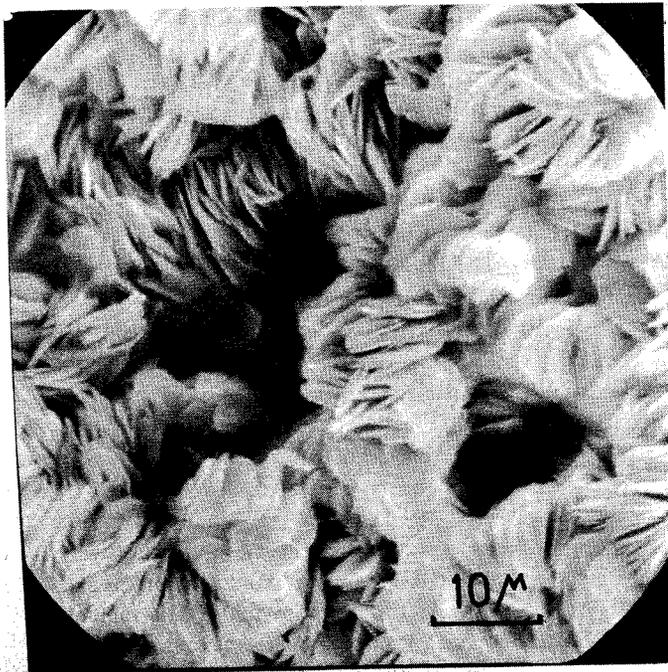


Plate 3.1 — Scanning-electron micrographs:

(a) Mbobomkulite, blue nodule, (b) nickelalumite, blue nodule — note pseudo-hexagonal flakes, (c) chalcoalumite-nickelalumite on gypsum crystal — the base of the fibro-radiated blades, against gypsum, is nickel rich, the top is copper rich, (d) the same as (c).

Plaat 3.1 — Skandeerelektronmikrofoto's:

(a) Mbobomkuliet, blou knol, (b) nikkellumiet, blou knol — let op die pseudobeksagonale skilfers, (c) chalkoalumiet-nikkellumiet op gipskristal — die basis van die radiale veselle teen die gips is nikkelryk, die top is koperryk, (d) dieselfde as (c).

Table 3.2 — X-RAY PATTERNS OF THE MINERALS OF THE CHALCOALUMITE FAMILY

Chalcoalumite (after Williams and Khin)				Nickelalumite				Mbobomkulite				Hydrombobomkulite								
No.	$1/\lambda_{100}$	d obs. Å	d calc. Å	hkl	No.	$1/\lambda_{100}$	d obs. Å	d calc. Å	hkl	No.	$1/\lambda_{100}$	d obs. Å	d calc. Å	hkl	No.	$1/\lambda_{100}$	d obs. Å	d calc. Å	hkl	
1	100	8,502	8,500	002	1	100	8,543	8,541	002	1	100	8,550	8,535	002	1	100	10,45	10,44	002	
2	22	7,898	7,895	011	2	20	7,877	7,865	011	2	15	7,870	7,867	011	2	5	7,290	7,309	102	
3	9	6,705	6,703	110	3	5	6,667	6,666	110	3	1	6,676	6,670	110	3	10	6,233	6,238	121	
4	6	6,393	6,385	111	4	5	6,364	6,359	111	4	1	6,348	6,347	111	4	50	5,229	5,217	004	
5	8	6,103	6,097	111	5	5	6,073	6,071	111	5	1	6,080	6,087	111	5	10	4,899	4,918	201	
6	8	5,445	5,446	112	6	5	5,431	5,438	112	6	5	4,778	4,788	013	6	5	4,849	4,864	210	
7	13	5,100	5,098	112	7	5	5,095	5,089	112	7	15	4,549	4,545	202	7	1	4,739	4,747	211	
8	22	4,786	4,782	013	8	10	4,778	4,790	013	8	40	4,271	4,267	004	8	1	4,359	4,366	220	
9	9	4,573	4,574	202	9	10	4,577	4,566	202	9	1	4,050	4,045	212	9	10	4,172	4,174	005	
10	6	4,314	4,312	021	10	60	4,267	4,270	004	10	5	3,935	3,934	022	10	1	4,055	4,059	133	
11	91	4,250	4,250	004	11	10	4,179	4,168	202	11	1	3,723	3,721	122	11	1	3,815	3,795	230	
12	23	4,178	4,178	202	12	2	3,332	3,336	213	12	1	3,621	3,624	213	12	5	3,651	3,654	204	
13	3	3,849	3,836	014	13	5	3,177	3,188	015				3,618	203					3,651	043
14	5	3,705	3,704	114				3,179	222	13	1	3,337	3,350	213	13	30	3,485	3,478	006	
15	6	3,501	3,504	023	14	10	3,044	3,048	311				3,335	220	14	5	3,343	3,343	301	
16	5	3,335	3,342	213	15	5	2,718	2,714	132	14	15	3,179	3,186	015					3,341	233
17	9	3,177	3,177	015	16	2	2,623	2,622	033				3,173	222	15	5	3,195	3,192	135	
18	9	3,059	3,062	311	17	15	2,507	2,509	133	15	15	3,054	3,055	311	16	10	3,129	3,119	242	
19	5	2,822	2,826	131	18	15	2,289	2,286	126	16	1	2,999	2,998	124	17	1	3,070	3,077	053	
20	8	2,726	2,728	132				2,285	305	17	1	2,920	2,912	031					3,064	126
			2,723	224	19	5	2,208	2,214	135	18	1	2,873	2,878	312	18	1	2,958	2,956	243	
21	8	2,633	2,632	033	20	1	2,098	2,095	226				2,867	313	19	5	2,921	2,911	330	
22	7	2,585	2,585	215	21	1	2,027	2,029	240	19	5	2,812	2,810	131	20	5	2,885	2,880	331	
23	11	2,520	2,519	133				2,024	333	20	5	2,709	2,713	132	21	10	2,793	2,798	332/235	
					22	20	1,997	1,995	235				2,710	224	22	5	2,740	2,738	252	
					23	1	1,899	1,898	208	21	5	2,625	2,622	033	23	1	2,704	2,707	127	
								1,895	415	22	1	2,573	2,566	133/125					2,701	046
					24	1	1,855	1,852	340/341	23	15	2,512	2,513	133	24	1	2,610	2,615	305	
					25	5	1,810	1,813	336	24	1	2,387	2,392	134					2,606	146
					26	10	1,720	1,719	209				2,387	206	25	1	2,560	2,561	155	
					27	1	1,560	1,562	239	25	10	2,294	2,295	305					2,560	207
												2,290	126						2,557	163
										26	5	2,279	2,283	306	26	15	2,489	2,491	260	
												2,273	404						2,490	254
										27	5	2,209	2,211	135					2,488	411
										28	1	2,179	2,185	332	27	5	2,467	2,470	402	
										29	1	2,105	2,101	226	28	1	2,374	2,375	403/261	
										30	1	2,030	2,030	240					2,374	344
												2,029	333						2,373	038/422
										31	15	2,004	1,999	235	29	1	2,341	2,343	352/255	
										32	5	1,989	1,990	501					2,341	263
												1,986	406	30	5	2,308	2,312	073		
										33	1	1,904	1,904	208					2,311	208
												1,903	415						2,308	218
										34	1	1,879	1,880	037					2,306	431
										35	1	1,853	1,853	340	31	5	2,271	2,272	404	
												1,852	341						2,271	353
										36	5	1,808	1,807	336					2,270	414
										37	5	1,726	1,724	209	32	1	2,232	2,233	345	
										38	1	1,709	1,710	523					2,231	228
												1,708	434	33	5	2,210	2,212	424/742		
										39	1	1,631	1,633	613					2,209	660
										40	1	1,561	1,558	239	34	5	2,083	2,086	219	
										41	1	1,537	1,538	418					2,080	355
												1,536	445	35	5	2,066	2,067	175		
														36	5	2,028	2,029	500		
																			2,028	451
														37	5	1,850	1,851	374		
														38	5	1,826	1,827	463/408		
																			1,826	541
														39	5	1,800	1,801	534/069		
																			1,800	418
														40	1	1,643	1,644	287		
																			1,643	295
														41	1	1,618	1,619	482		
																			1,617	546
														42	1	1,590	1,590	296		

Plus 14 additional
lines to 1,191 Å

Philips diffractometer using cobalt K_{α} radiation, Fe filters and quartz as internal standard (not applicable to chalcoalumite)

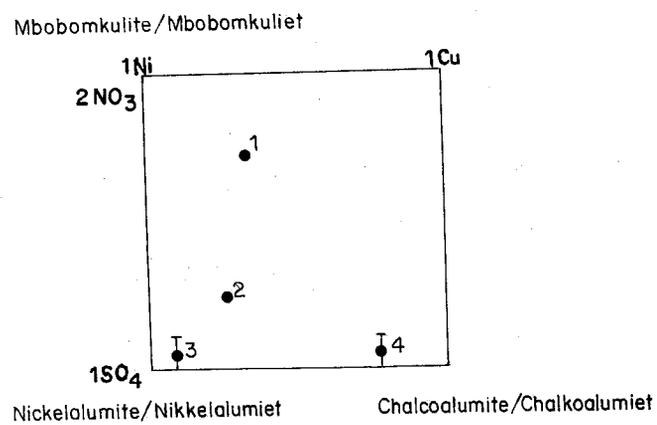


Fig. 5.1 — Chemical variations in the chalcoalumite family:

- (1) Mbobomkulite, blue nodule in allophane
- (2) Nickelalumite, blue nodule in allophane
- (3) Nickelalumite from crust on gypsum
- (4) Chalcoalumite from crust on gypsum.

Chemiese variasies in die chalkoalumietgroep:

- (1) Mbobomkuliet, blou knol in allofaan
- (2) Nikkelalumiet, blou knol in allofaan
- (3) Nikkelalumiet afkomstig van kors op gips
- (4) Chalkoalumiet afkomstig van kors op gips.

pyrrhotite with minor amounts of chalcopyrite and pentlandite was found in cores from boreholes drilled through a thick cover of shales of the Pretoria Group; the grade is usually a few hundred parts per million only. Leaching creates strongly acid conditions and the solutions not only contain the elements from the sulphides (SO_4^{2-} , Fe^{3+} , Ni^{2+} , Cu^{2+}) but also K^+ , Al^{3+} and silica released by the attack of phyllosilicates of the shaly matrix. When by slow seepage these solutions enter the cave, minerals are precipitated as a result of an increase in pH caused by the reaction with an excess of shale matrix or with dolomite, or by evaporation. The minerals resulting entirely from this process are opal, allophane, halloysite, goethite, haematite, jarosite, alunite, alunite, potash alum, gypsum, atacamite, chalcoalumite and nickelalumite. Other minerals are of mixed origin, partly formed by the leaching of the sulphides and reactions with the country rock, and partly by obtaining nitrate and phosphate from the bat guano. This category includes sampleite and mbobomkulite.

5. DISCUSSION

Mbobomkulite, nickelalumite and chalcoalumite are closely related to one another and are members of the chalcoalumite family. They can be considered as end members between which a continuous solid solution exists, as suggested by their very similar cells. A fourth end member, containing only nitrate and copper, can be predicted, although so far it is not known to occur. The composition of the various samples is shown in Figure 5.1. The general formula of the family is consequently $\text{Ni}_{1-y}\text{Cu}_y\text{Al}_4(\text{NO}_3)_{2-2x}(\text{SO}_4)_x(\text{OH})_{12}\cdot 3\text{H}_2\text{O}$, where x and y vary from 0 to 1.

This close structural relationship between these minerals is somewhat surprising as it is known that the elements acting as variables show differences in co-ordination: nickel and copper are both hexa co-ordinated, but the latter element often displays strong distortion of the octahedron; sulphur as sulphate is tetra co-ordinated whereas nitrogen as nitrate is tri co-ordinated. However, the substitution of $2(\text{NO}_3)$ for SO_4 is seen in another case: a solid solution between connellite ($\text{Cu}_{19}\text{SO}_4\text{Cl}_4(\text{OH})_{32}\cdot 3\text{H}_2\text{O}$) and buttgenbachite ($\text{Cu}_{19}(\text{NO}_3)_2\text{Cl}_4(\text{OH})_{32}\cdot 3\text{H}_2\text{O}$) was suggested (Palache et al. 1957).

There is partial similarity between the minerals described in this paper and carrboydite (Nickel and Clarke 1976), a nickel aluminium hydrated sulphate containing a large number of hydroxyls, also characterised by a layered structure, but with less aluminium. The X-ray pattern of carrboydite (hexagonal) shows much less lines than the minerals described here, but the 001 lines are very similar to those of hydrombobomkulite. Moreover, by heating to above 60°C the basal spacing of carrboydite ($10,4 \text{ \AA}$) collapses to $8,6 \text{ \AA}$, a value which is close to

002 of the minerals of the chalcoalumite family. Consequently it is possible to imagine a structure for mbobomkulite analogous to that proposed for carrboydite (Nickel and Clarke 1976), which comprises three layers of oxygen, hydroxyl and large anions, and two layers of cations (Ni, Cu, Al) in between. Water separates these double layers of octahedrons. In the case of the minerals of the chalcoalumite family, this double octahedron layer should be repeated twice in order to fill the basal spacing ($17,2 \text{ \AA}$) and the cell should accommodate one layer of water.

However, it is possible that the similarity between carrboydite and mbobomkulite is purely fortuitous. Moreover, in the chalcoalumite family, the ratio (Ni,Cu)/Al seems constant and the Al^{3+} are exactly equilibrated with OH^- , whereas Ni^{2+} and Cu^{2+} are equilibrated with NO_3^- and/or SO_4^{2-} . It is therefore tempting to propose another structure consisting of two layers of aluminium hydroxide octahedrons, each one alternatively separated by layers of water and nickel or copper sulphate/nitrate. It is of interest to point out the similarity between the cell dimensions of mbobomkulite and gibbsite: $a_o(\text{mbobomkulite}) \cong 2b_o(\text{gibbsite})$ and $b_o(\text{mbobomkulite}) \cong a_o(\text{gibbsite})$. This fact is in favour for the presence of $\text{Al}(\text{OH})_3$ layers in the structure of the minerals of the chalcoalumite family.

The structure could be composed of seven layers of oxygen, each containing 12 atoms in the case of mbobomkulite. In the case of nickelalumite or chalcoalumite, one third of the oxygen sites of the Ni-Cu layer would be unoccupied due to the replacement of 2NO_3^- by SO_4^{2-} . Because of their difference in co-ordination, S^{6+} and N^{5+} cannot occupy the same sites, which has apparently little effect on the X-ray pattern due to their small amount in these minerals.

Any discussion about the structure of hydrombobomkulite would be mere speculation; it may differ from that of the chalcoalumite family by a larger number of water layers.

ACKNOWLEDGMENTS

Mr. C.P. Venter assisted in the computer work. Mr. H.H. Lachmann of the National Chemical Laboratory did the gas chromatography determinations. Dr. R.A. Edge analysed the fluorine content in mbobomkulite and Mr. J. Trojak its carbon content. Mr. M.D. Köhler analysed qualitatively a few specimens by X-ray fluorescence. Mr. E.A.W. Peters and J.N. Dunlevey assisted in the X-ray diffraction work. The skill of Ms S.C. Greeff who took scanning microscope photographs is greatly appreciated.

REFERENCES

- FOSTER, C., MARTINI, J. and MIGNAT, J-P., 1979. Jewel Cave - Eastern Transvaal: Bull. S. Afr. Speleol. Ass., 1977, p. 15-17.
- HILL, C., 1976. Cave Minerals: Speleopress, Austin, Texas, 138 p.
- NICKEL, E.H. and CLARKE, R.M., 1976. Carrboydite, a hydrated sulphate of nickel and aluminium: a new mineral from Western Australia: Am. Miner., 61, p. 366-372.
- PALACHE, C., BERMAN, H. and FRONDEL, C., 1957. The system of mineralogy: Vol. II, J. Wiley and Sons, New York, 1 124 p.
- WILLIAMS, S.A. and KHIN, B-S., 1971. Chalcoalumite from Bisbee, Arizona: Miner. Rec., 2, p. 126-127.