A new occurrence of the hydrated aluminium sulphate zaherite, from Pofadder, South Africa

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ABSTRACT. A new occurrence of zaherite is reported from a sillimanite quarry 65 km west of Pofadder, Bushmanland, South Africa. It occurs as earthy white to light bluish-green cryptocrystalline material in narrow veins, in close association with natro-alunite and hotsonite, a new hydrated aluminium phosphate–sulphate. Scanning electron micrographs show an orientated wavy texture and tubular fibres. The optical and physical properties agree with those of the type material described from Pakistan, and it can be added that the mineral is biaxial positive with a moderate $2V$ and length-fast orientation. The new chemical analysis yields an ideal formula of $Al_{12}(SO_4)_5(OH)_{26} \cdot 20H_2O$, which is identical to that of the type material. The white and light bluish-green varieties are identical in major element composition but yielded trace Cu values of 1281 and 2408 ppm respectively. The X-ray powder diffraction pattern fits a triclinic symmetry (a 5.55, b 9.74, c 18.43 Å, α 99.71°, β 89.13°, γ 94.97°), and is dominated by one intense reflection at 18.12 Å, representing 001. The most important of the weak lines are (d, I, hkl): 9.56, 5, 010; 9.08, 4, 002; 4.82, 6, 0$\bar{2}$1; 4.61, 8, 110; 4.56, 4, 0$\bar{2}$2; 4.44, 4, 021; 3.61, 4, 1$\bar{2}$1; 3.22, 8, 015. The differential thermal properties are characterized by endothermic peaks at 190, 470, and 685 °C and a duplex at 880 and 910 °C. The infrared absorption spectrum is characterized by absorption bands centring about 905, 960, 985, 1150, 1700, and 3600 cm^{-1}.

ZAHERITE was first described by Zaher (1969) and Ruotsala and Babcock (1977) from the Salt Range, Pakistan, where it occurs as veinlets in a kaolinite–boehmite rock. During the investigation in 1982 of aluminous metamorphites in an abandoned sillimanite quarry on the farm Hotson 42, located 65 km west of the town of Pofadder, in Bushmanland, South Africa, the two senior authors sampled peculiar veins and encrustations of very fine-grained material. On closer inspection in the laboratory, the veins were found to consist of zones of various aluminous minerals,* one of which proved to be a new hydrated aluminium phosphate

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* Schoch, A. E. and Beukes, G. J. (in prep.). A natro-alunite–zaherite–hotsonite paragenesis from Pofadder, South Africa.

sulphate, hotsonite (Beukes *et al.*, in press). Because a few kilograms of pure zaherite was obtained the known physical and chemical properties could be refined, and are presented in this paper. Slight differences between the material from Pofadder and zaherite from the Salt Range, Pakistan, will be indicated, and may be of mineralogical significance.

Occurrence. The mineral occurs as veins up to 2 cm wide in close association with natro-alunite and hotsonite. It is derived from primary sillimanite but alters to encrustations of hotsonite. The sillimanite occurs as large irregular lenses with size ranging from several metres to hundreds of metres. Field relations suggest that the formation of hotsonite and associated minerals was controlled by weathering, local structure, geographical topography, and the mineral composition of the country rocks (Schoch and Beukes, in prep.). The mineral occurs in an arid region with an average rainfall of less than 3 inches per annum. The mode of occurrence suggests that the zaherite from Pofadder is an intermediate mineral in the alteration of natro-alunite to hotsonite, the former originally deriving from sillimanite.

Optical and physical properties. The mineral occurs as sheaves of chalk-white to light bluish-green material orientated perpendicular to the walls of the veins. When observed under a magnification of 500 × the zaherite proves to be extremely fine grained, forming elongated flakes of densely packed aggregates.

Under this high enlargement it is colourless, micro- to cryptocrystalline, and optically anisotropic with a mottled and irregular extinction. Fragments of the flaky aggregates are slightly elongated and consistently yield a length-fast orientation. The zaherite is anisotropic, biaxial positive with a moderate $2V$, and has an extremely low birefringence of 0.001. The refractive indices are difficult to determine accurately by means of the immersion method, because of the earthy nature of the substance. The best values that could be

obtained, using monochromatic Na light (Fraunhofer D), are α 1.498 ± 0.001 and γ 1.499 ± 0.001.

The aggregate hardness is Mohs' 3.5. The density was determined by the micropycnometer method (May and Marinenko, 1966), and checked with the suspension method with heavy liquids (Embrey, 1969). The average of six determinations on separated samples is respectively 2.008 and 2.011.
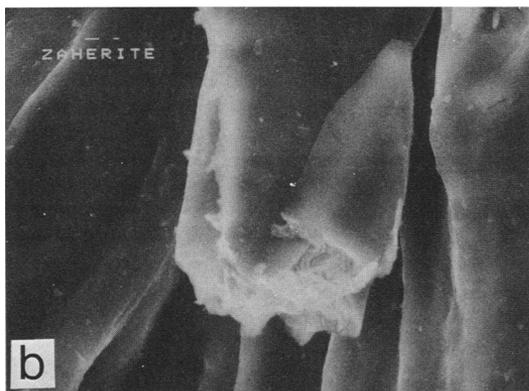
Fig. 1. Scanning electron micrographs of zaherite. (*a*) Wavy microstructure of zaherite with minute crystals (white) of hotsonite. The longer of the three bars in the upper left-hand corner represents 10 μm. (*b*) Curled tubular structure of zaherite. The short right-hand bar in the upper left-hand corner represents 1 μm.

Electron optical investigation confirms that the material is not a mixture of minerals. A pronounced orientated wavy texture proves at high resolution to be constituted of tubular fibres (fig. 1).

Chemical composition. The chemical analysis was carried out in quadruplicate on different samples by means of wavelength-dispersive X-ray fluorescence spectrometry, on a Philips PW 1410 spectrometer, using the Norrish method. The sample was diluted

with pure silica in order to prevent unwanted physical reactions with the flux. The SiO_2 was determined on undiluted pressed powder briquettes. Sulphate values were independently checked by means of classical gravimetric analysis (Vogel, 1968; Kolthoff *et al.*, 1969). The essential constituents are Al_2O_3, SO_3, and H_2O; all other components are very minor and assumed to be contaminants, difficult to identify mineralogically at this stage owing to the cryptocrystalline nature of the material. The total water content was determined by the modified Penfield method (Kolthoff *et al.*, 1969, 577–8), and agrees with the values calculated from loss on ignition. The results are presented in Table I. The ideal formula was calculated to be $Al_{12}(SO_4)_5(OH)_{26} \cdot 20H_2O$ or $6Al_2O_3 \cdot 5SO_3 \cdot 33H_2O$, which is identical to the previously reported formula of Ruotsala and Babcock (1977) for the type material.

TABLE I. *Chemical analysis of zaherite*

	a	b	c	d
SiO_2	0.11	—	—	—
Al_2O_3	37.85	38.41	38.08	37.79
Fe_2O_3 (T)	0.08	—	—	—
MnO	0.01	—	—	—
MgO	0.19	—	—	0.01
CaO	0.21	—	—	0.09
Na_2O	0.08	—	—	0.03
K_2O	0.01	—	—	0.01
P_2O_5	0.06	—	—	0.02
SO_3	24.63	25.00	24.92	24.87
H_2O (T)	36.05	36.59	37.00	36.55
Total	99.28	100.00	100.00	100.00

a. Analysis (wt. %) for zaherite from Pofadder, South Africa.

b. Recalculated to 100 after deducting the values attributed to contaminants.

c. Analysis calculated from proposed formula.

d. Analysis of zaherite from Salt Range, Pakistan, reported by Ruotsala and Babcock (1977).

The white and light bluish-green varieties of zaherite are identical in major components, but differ in the content of Cu and Pb, namely 1281 and 40 ppm respectively for the former and 2408 and < 20 ppm for the latter.

X-ray diffraction data. The zaherite was examined by X-ray diffraction, using a Philips PW 1051 diffractometer with Ni-filtered Cu-Kα radiation. A single crystal study was precluded by the fine-grained nature of the material and all investigations were on powdered zaherite. Debye-Scherrer films

TABLE II. *X-ray powder pattern of zaherite*

	a			b		c	
hkl	I	d_{meas}	d_{calc}	I	d_{meas}	I	d_{meas}
001	100	18.12	18.16	100	17.9	100	18.1
				2	12.6		
				2	11.9		
010	5	9.56	9.561	5	9.5	5	9.6
002	4	9.08	9.084	4	9.1	3	9.1
				1	6.1		
100	1	5.52	5.531				
101	3	5.28	5.292	3	5.3		
0$\bar{2}$1	6	4.82	4.827	5	4.82	4	4.85
						4	4.80
110	8	4.61	4.620	7	4.61	4	4.60
				7	4.58		
0$\bar{2}$2	4	4.56	4.55	7	4.56		
						2	4.50
021	4	4.44	4.443	4	4.44		
				3	4.27		
1$\bar{1}$2	1	4.22	4.210				
				3	4.14		
103	1	4.08	4.085	1	4.08		
1$\bar{1}$3	1	4.03	4.022	1	4.03		
				1	3.87		
1$\bar{2}\bar{2}$	1	3.67	3.667				
1$\bar{2}\bar{1}$	4	3.61	3.606			4	3.60
113	2	3.54	3.538	6	3.55		
12$\bar{1}$	2	3.49	3.491	3	3.51		
120	1	3.47	3.473	3	3.46		
1$\bar{2}$3	2	3.42	3.418	3	3.44		
015	8	3.22	3.222	8	3.22	5	3.22
032	2	3.18	3.179				
				1	3.10		
				1	3.06		
006	1	3.03	3.028	1	3.02		
11$\bar{5}$	1	2.97	2.975				
12$\bar{4}$	1	2.94	2.937				
				1	2.888		
				1	2.612		
210	1	2.60	2.598				
131	1	2.59	2.585	2	2.579		
				1	2.339		
042	1	2.22	2.222				
138	1	1.62	1.620	1	1.618		
				2	1.608		

a. Zaherite from Pofadder, South Africa.

b. Zaherite from Salt Range, Pakistan. Type Specimen (Ruotsala and Babcock, 1977; JCPDS 29.90).

c. Zaherite from Salt Range, Pakistan. Hydrated form (Ruotsala and Babcock, 1977).

Operating Conditions: 40 kV, 20 mA; 1° 2θ/min. scan speed; $\frac{1}{2}$ inch/min. chart speed; Cu-$K\alpha$ radiation, λ 1.54178 Å. Intensities estimated visually.
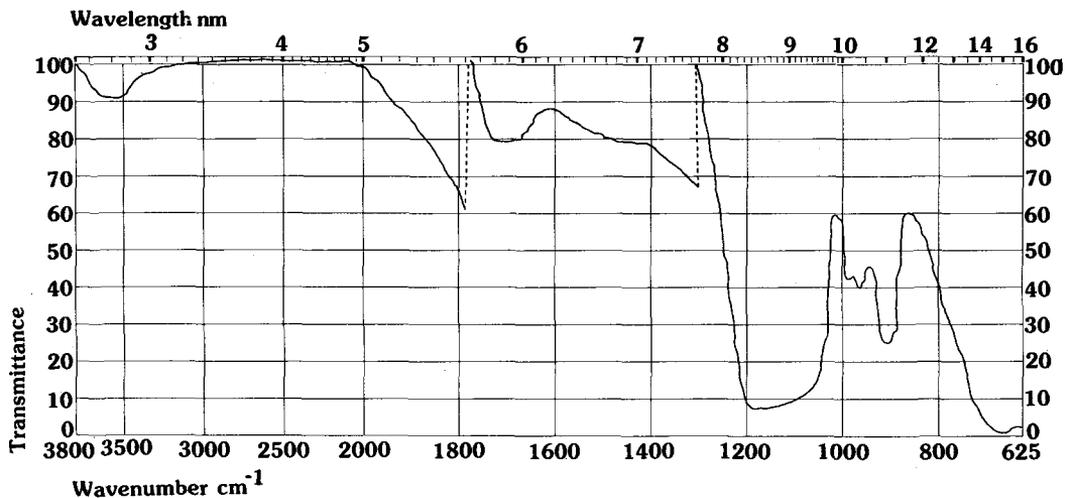
FIG. 2. Infra-red absorption spectrum of zaherite.

(114.6 mm diameter) and diffractometer patterns were obtained. The *d* spacings, *hkl* values and relative intensities are given in Table II. It should be noted that the pattern obtained agrees well with the values given by Ruotsala and Babcock (1977) for the hydrated variety of zaherite, but faint additional lines correspond with the type material from Salt Range, Pakistan (JCPDS 29.90). Indexing according to the method of Appleman *et al.* (1972) indicates that the mineral belongs to the triclinic crystal system with *a* 5.552, *b* 9.736, *c* 18.431 Å, α 99.71°, β 89.13°, γ 94.97° and cell volume 978.315 A^3. It should be noted that the reflections are often broad and asymmetrical, indicating poor crystallinity.

Differential thermal data. A differential thermo-gram is shown in fig. 2. These results are broadly similar to those given by Ruotsala and Babcock (1977). A pronounced and well-defined endo-thermic peak appears at 190 °C and is attributed to the loss of water. A very small peak at 470 °C and a broad endothermic peak with a median value of 685 °C appear in the place of the peak at 360 °C reported by Ruotsala and Babcock, which was interpreted by them to represent loss of hydroxyl. An endothermic duplex at 880 and 910 °C probably indicate loss of sulphur compounds. This duplex was also reported by Ruotsala and Babcock.

Infra-red absorption data. An infra-red absorption spectrum (fig. 3) was obtained with a Pye-Unicam SP 1000 double beam infra-red spectro-photometer, using the KBr disc method. The
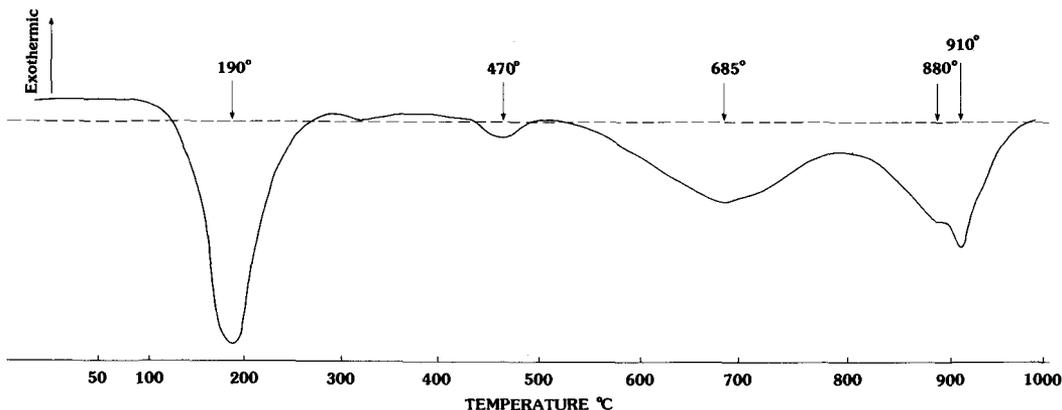
FIG. 3. Differential thermogram of zaherite.

zaherite was mixed with KBr in the ratio 1:100. The determinations were carried out on three different samples, yielding identical results.

A medium-intensity absorption band has a well-defined value of 905 cm^{-1}, followed by two weaker but narrower bands at 960 and 985 cm^{-1}. A strongly developed and broad maximum with a median value at 1150 cm^{-1} is attributed to the sulphate absorption band. A broad medium intensity peak with a minimal turning-point at 1700 cm^{-1}, is interpreted as the manifestation of structural water. The last, broad peak with maximum intensity at 3600 cm^{-1} is regarded as representing a hydroxyl stretching band.

The zaherite absorption spectrum is remarkably similar to that of hotsonite (Beukes *et al.*, in press), with the exception of the three absorption bands at 905, 960, and 985 cm^{-1}. The reason for this difference must have structural implications which can probably only be evaluated if and when single crystals become available for diffractometric studies.

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