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Hotsonite, a new hydrated aluminum-phosphate-sulphate from Pofadder, South Africa

GERHARD J. BEUKES, AYLVA E. SCHOCH, WILLEM A. VAN DER WESTHUIZEN,
LOUIS D. C. BOK, AND HENDRIK DE BRUIYN

Department of Geology
University of the Orange Free State
Bloemfontein, South Africa

Abstract

Hotsonite, with the provisional formula $Al_{11}(PO_4)_2(SO_4)_3(OH)_{21} \cdot 16H_2O$, is a new hydrated aluminum-phosphate-sulphate from a sillimanite quarry on the Hotson farm, 65 km west of Pofadder, South Africa. The mineral occurs as white compact masses with a dull to silky luster and earthy fracture. Scanning electron micrographs show that the mineral consists of tabular microcrystals. The aggregate hardness on the Mohs scale is 2.5 and the specific gravity is 2.06. The mineral is anisotropic with a very low birefringence and refractive indices of $\alpha = 1.519$ and $\gamma = 1.521$. The dominant lines of the X-ray powder diffraction pattern are (d(Å), intensity): 10.05(100), 8.45(40), 5.20(10), 5.01(10), 4.63(20), 4.43(10), 4.34(7), 3.91(7), 3.67(10). Indexing according to the method of Visser (1969) based on the method of Ito, shows that the mineral is triclinic with values (Å) of 11.23, 11.66 and 10.55 for a, b and c respectively and angles of 112° 32′, 107° 32′ and 64° 27′ for α, β and γ. The infrared absorption spectrum is characterized by absorption bands centering about 950, 1150, 1700 and 3600 cm^{-1}. The differential thermal properties are characterised by endothermic peaks at 110°C, 520°C and 840°C. Hotsonite occurs as an alteration product of zaherite in an arid environment.

Introduction

During the investigation of aluminous metamorphic rocks in an abandoned sillimanite quarry in 1982, the two senior authors sampled peculiar veins and encrustations of cryptocrystalline fine-grained white material. On closer investigation in the laboratory, the veins proved to consist of zones of various aluminous minerals, one of which exhibited chemical and X-ray diffractometric properties which could not be matched to any known mineral. The suggested name is derived from the farm Hotson 42, located 65 km west of the town of Pofadder, in Bushmanland, northwestern Cape Province, South Africa. This is an arid region with an average rainfall of 3 inches per annum.

The name has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (July 1983). The type material has been deposited in the National Museum, Bloemfontein (specimen number K2359).

Occurrence

The mineral occurs in close association with zaherite, ($Al_{12}(SO_4)_5(OH)_{26} \cdot 20H_2O$, Ruotsala and Babcock, 1977), and natro-alunite, as secondary encrustations on zaherite derived from primary sillimanite. The sillimanite occurs as large irregular lenses with size ranges on the order of several meters to hundreds of meters. Field relations suggest that the formation of hotsonite and associated minerals is controlled by weathering, local structure, topography and the mineral composition of the country rocks. The paragenetic aspects will be fully reported in a later paper when investigations currently in progress are completed, but preliminary results indicate that sillimanite is locally altered to natro-alunite and zaherite, which is in turn transformed to hotsonite.

Optical and physical properties

Hotsonite exhibits optical and physical properties which are similar to those of other hydrated aluminous sulphates and phosphates discussed at the end of this paper. The mineral occurs as white chalk-like material with a dull to silky luster and earthy fracture. It has a flaky appearance when observed under magnification of 500 times.

Under this high enlargement it is colorless, micro-to crypto-crystalline, optically anisotropic with a mottled and irregular extinction, and a very low birefringence of less than 0.003. Because of the small grain size and the irregular extinction it was not possible to determine complete optical properties. However, fragments of the

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flaky aggregates are slightly elongated, and consistently yield a length-fast orientation.

Electron optical investigation confirms that hotsonite is not a mixture of minerals but that it is composed of crystals of a single substance (Fig. 1). The tiny crystals prove to be lathlike with average dimensions of 1 to 15 μm.

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 $\alpha = 1.519$ and $\gamma = 1.521$.

The aggregate hardness is Mohs' 2.5. The density was determined by the micropycnometer method (May and Marinenko, 1966), and checked with the suspension method with heavy liquids (Embrey, 1969). The values are respectively 2.060±0.005 and 2.068±0.005.

Chemical composition

Point analyses by EDX of 20 grains indicated that the major components of the mineral are Al, P and S. The material undergoes rapid damage owing to loss of the volatile elements S, P and H when subjected to focussed electron beams, even at low accelerating voltages, precluding quantitative microanalysis. The chemical analysis was carried out in quadruplicate on different powdered samples each weighing 0.5 g by means of wave-length 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 and phosphate values were independently checked by means of classical gravimetric analysis (Vogel, 1968, p. 462–465; Kolthoff et al., 1969, p. 647–649), yielding values of 17.1±0.44 ($2s/\sqrt{n}$) for SO_3 and 9.25±0.58 for P_2O_5. The latter value is considered to be low owing to incomplete dissolution and precipitation. The essential constituents are Al_2O_3, SO_3, P_2O_5 and H_2O; all other components are very minor and assumed to be contaminants, difficult to identify minerologically at this stage owing to the cryptocrystalline nature of the material. The total water content was determined by the modified

Table 1. Chemical analysis^x of hotsonite

Oxide	(a)	(b)	(c)
SiO_2	0.35 (0.03)	-	-
Al_2O_3	39.15 (0.17)	39.50	39.48
Fe_2O_3(T)	0.03 (0.01)	-	-
MgO	0.28 (0.09)	-	-
CaO	0.24 (0.06)	-	-
Na_2O	0.21 (0.07)	-	-
K_2O	0.00	-	-
P_2O_5	9.85 (0.09)	9.94	9.99
SO_3	16.80 (0.08)	16.95	16.91
H_2O(T)	33.30 (0.60)	33.60	33.61
Total	100.21	99.99	99.99

^{x}(a) Average of four independent analyses (weight per cent). The standard error of the mean is given in brackets ($2s/\sqrt{n}$).

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

(c) Analysis calculated from proposed formula.

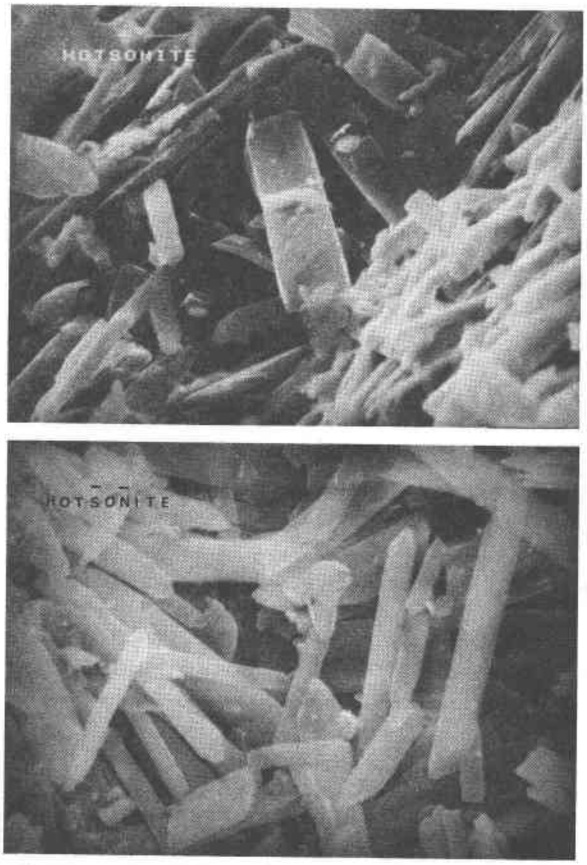

Fig. 1. Scanning electron micrographs of hotsonite. The longer of the two bars in the upper left hand corner represents 1 μm.

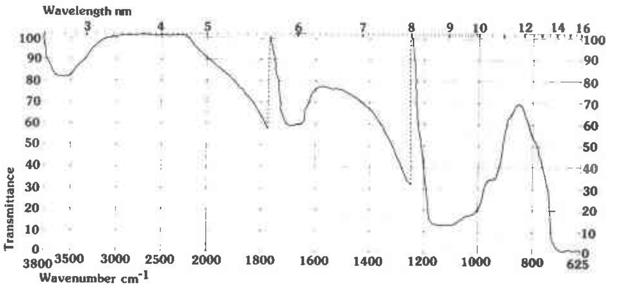

Fig. 2. Infrared absorption spectrum of hotsonite.

Table 2. Powder diffraction data for hotsonite

d(obs)	d(calc)	(hkl)	I/I_o
10.05	10.05	010	100
	10.05	$0\bar{1}0$	
8.45	8.42	$11\bar{1}$	40
6.13	6.11	011	1
	6.11	$0\bar{1}\bar{1}$	
5.48	5.50	111	1
5.20	5.19	$11\bar{2}$	10
5.01	5.03	020	10
	5.03	$0\bar{2}0$	
4.97	4.97	$1\bar{1}\bar{1}$	2
4.77	4.76	$20\bar{1}$	2
4.63	4.64	$10\bar{2}$	20
4.43	4.43	220	10
4.34	4.34	$21\bar{2}$	7
3.91	3.91	012	7
	3.91	$0\bar{1}\bar{2}$	
3.67	3.67	$2\bar{1}\bar{1}$	10
3.62	3.63	$2\bar{1}1$	2
	3.63	$1\bar{1}\bar{2}$	
3.46	3.46	$1\bar{2}\bar{1}$	6
3.30	3.31	$22\bar{3}$	1
3.13	3.14	$33\bar{2}$	3
3.08	3.08	311	2
2.97	2.97	$30\bar{2}$	1
	2.97	$2\bar{2}1$	
2.87	2.87	$24\bar{1}$	2
	2.87	$3\bar{1}0$	
2.83	2.83	$1\bar{2}\bar{2}$	2
2.75	2.75	222	1
	2.75	$41\bar{1}$	
	2.75	$1\bar{1}\bar{3}$	
2.68	2.68	$34\bar{1}$	1
2.58	2.60	$22\bar{4}$	1
	2.60	$11\bar{4}$	
2.56	2.56	$04\bar{2}$	1
	2.56	$0\bar{4}2$	
2.47	2.47	430	1
	2.47	$2\bar{1}3$	
2.41	2.41	411	1
	2.41	$2\bar{3}0$	
	2.41	$3\bar{2}0$	
2.34	2.34	241	1
	2.34	$0\bar{4}3$	
	2.34	$04\bar{3}$	
2.32	2.32	$20\bar{4}$	1
	2.32	$3\bar{2}\bar{1}$	
2.28	2.28	$2\bar{3}2$	1
2.25	2.25	$34\bar{4}$	1
	2.25	$15\bar{2}$	
2.23	2.23	$35\bar{1}$	1
	2.23	$25\bar{3}$	
2.17	2.17	$51\bar{1}$	1
2.14	2.14	303	1
	2.14	520	
2.11	2.11	510	1
	2.11	313	
2.06	2.06	$41\bar{4}$	1
	2.06	$54\bar{1}$	
2.01	2.01	050	1
	2.01	$0\bar{5}0$	
1.984			1
1.944			2
1.921			1
1.900			1
1.867			1
1.844			1
1.782			3
1.687			1
1.682			1
1.665			1
1.585			2
1.539			1
1.526			1
1.495			1
1.462			1
1.449			1
1.407			1
1.378			1
1.368			1

Unit cell parameters (standard errors): a_o= 11.228(0.059)Å b_o=11.658(0.060)Å c_o=10.550(0.067)Å α=112° 32.22'(2.93') β=107° 31.73'(2.84') γ=64° 27.06'(2.90') V = 1135.33(0.70) Å³

Operating conditions: 40 kV, 20mA; 1° 2θ/min. scan speed; ½"/min. chart speed; Cu K_α-radiation, λ=1.54178 Å. Intensities estimated visually.

Penfield method (Kolthoff et al., 1969, p. 577–578), and agrees with the values calculated from loss on ignition which were 32.40±0.05 (2s/√n). The results are presented in Table 1. The ideal formula was calculated to be $Al_{11}(PO_4)_2(SO_4)_3(OH)_{21} \cdot 16H_2O$ or $5.5Al_2O_3 \cdot P_2O_5 \cdot 3SO_3 \cdot 26.5H_2O$.

X-ray diffraction data

Hotsonite was examined by X-ray diffraction, using a Philips PW 1051 diffractometer with nickel-filtered Cu$K\alpha$-radiation. A single crystal study was precluded by the fine-grained nature of the material, and all investigations

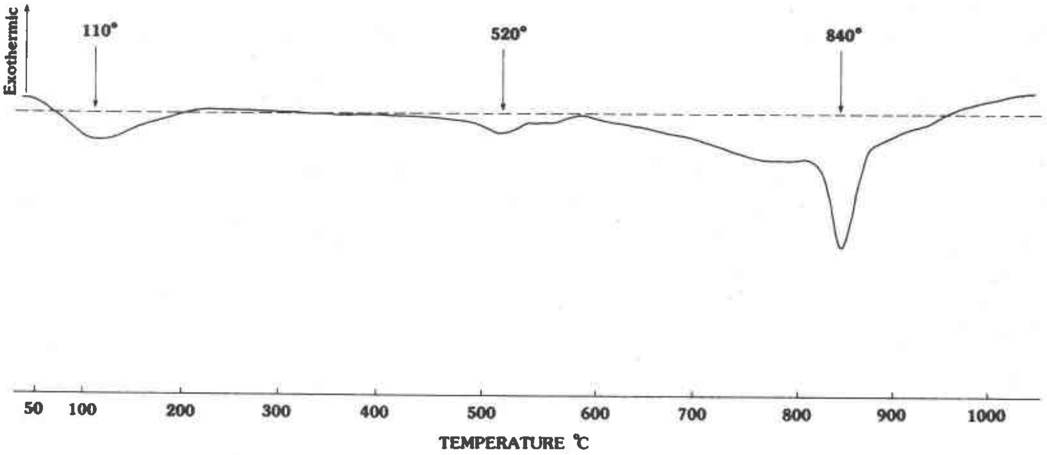

Fig. 3. Differential thermogram of hotsonite.

were done on powdered hotsonite. Debye-Scherrer films (114.6 mm diameter) and diffractometer patterns were obtained. For the films more than twenty different samples were used employing the small sample method (Hiemstra, 1956). All yielded practically identical results which also agreed with the more than ten diffractometer patterns, indicating the homogeneity of the material. The only peak not attributable to hotsonite, encountered in three samples, is the 18Å peak (I/I_o = 100) of zaherite, which appeared with a very low intensity ($I/I_0 < 2$). The *d*-values and relative intensities are given in Table 2. Preliminary indexing according to the method of Visser (1969) based on the method of Ito (1950), refined by the least squares program of Appelman *et al.* (1972), indicates that the mineral belongs to the triclinic crystal system, and this deduction is partly illustrated by the scanning electron micrographs (Fig. 1).

Infrared absorption data

An infrared absorption spectrum (Fig. 2) was obtained with a Pye-Unicam SP 1000 double beam infrared spectrophotometer, using the KBr disc method. Hotsonite was mixed with KBr in the ratio 1:100.

A medium-intensity shoulder appears at 950 cm^{-1}. A strongly developed and broad maximum at 1000 to 1180 cm^{-1} is attributed to the sulphate absorption band, which probably incorporates the less strongly developed phosphate absorption band as well. 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.

Differential thermal data

A differential thermogram is shown in Figure 3. A low and broad endothermic peak with a median value of 110°C is interpreted to represent loss of water, while a similar peak at 520°C may be attributed to hydroxyl. The relatively strong and well defined peak at 840°C is taken to represent the loss of sulphur compounds.

Relationship to other minerals

Chemically hotsonite is related to the other known hydrated aluminum-phosphate-sulphate minerals sanjuanite, $Al_2(PO_4)(SO_4)(OH) \cdot 9H_2O$ (De Abeledo et al., 1968), and kribergite, $Al_5(PO_4)_3(SO_4)(OH)_4 \cdot 2H_2O$ (Du Rietz, 1945). In both these minerals, however, the phosphate content is substantially higher than in hotsonite.

The X-ray diffraction pattern of hotsonite resembles the pattern for sanjuanite (De Abeledo et al., 1968; JCPDS 20-47), but is clearly different from that of kribergite (De Abeledo et al., 1968; JCPDS 20-48). The *d*-values for many hotsonite lines are unique, and the relative intensities of the lines that match sanjuanite are quite different. The infrared absorption spectrum of hotsonite is in a broad sense very similar to the absorption spectrum of sanjuanite (De Abeledo et al., 1968).

Hotsonite differs from sanjuanite and kribergite in optical and physical properties.

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