

# A HIGH-ALUMINOUS CHLORITE-SWELLING CHLORITE REGULAR MIXED-LAYER CLAY MINERAL

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**ABSTRACT:** One of the alteration products of a deuterically altered beryl is a high-aluminous chlorite-swelling chlorite regular mixed-layer clay mineral. An attempt was made to calculate the structural formula, and the results of X-ray, differential thermal and electron diffraction analyses are given.

During an investigation of the alteration products of beryl from the Dernburg pegmatite, Karibib, South West Africa (Roering & Heckroodt, 1964), a mineral with a 30 Å spacing was detected in the fine fraction. The responses of reflections, attributed to this mineral, to treatment with organic liquids indicated that the mineral is of an expanding lattice type. The fine fraction was subsequently beneficiated in an attempt to obtain a pure sample for a detailed investigation.

The altered beryl occurs in a pegmatite located in quartzites of the Damara System. It has been mined for beryl, amblygonite, and tantalite. Replacement bodies consisting of lithium-bearing mica and albite also occur, with or without cleavelandite-rich borders. The altered beryl occurs where these cleavelandite-rich borders abut against the beryl in the central zone of the pegmatite. From field relationships it would appear that this alteration was caused by deuterically altered pegmatite solutions intimately associated with the formation of the lithium mica-bearing replacement zones and their cleavelandite-rich margins.

## PREPARATION OF SAMPLE

Two small specimens of highly altered beryl were crushed in an iron pestle and mortar, and any contaminating iron was removed by means of a strong magnet. The crushed sample was dispersed in a 'Waring Blendor' for 20 min to facilitate the separation of the clay particles adhering to other mineral grains and to disintegrate the clay aggregates. The fraction less than 5  $\mu$  was then obtained by sedimentation methods. The water of sedimentation was removed by means of a membrane filter.

## CHEMICAL ANALYSIS

The chemical analysis is given in Table 1, column 1. The sample contained various amounts of impurities, and an attempt was made to adjust the analysis by subtracting from the constituents appropriate portions for allocation to the impurities.

TABLE 1. Chemical analysis of the fraction less than 5  $\mu$ 

	1	2	3	4	5	6
SiO <sub>2</sub>	38.24	7.26			30.98	39.05
Al <sub>2</sub> O <sub>3</sub>	33.95		0.24		33.71	42.49
TiO <sub>2</sub>	0.20				0.20	0.25
MgO	1.73				1.73	2.18
FeO	0.54				0.54	0.68
CaO	1.75			1.75		
Na <sub>2</sub> O	0.07			0.07		
K <sub>2</sub> O	0.07			0.07		
MnO	0.05			0.05		
Li <sub>2</sub> O	1.00		0.06		0.94	1.18
BeO	6.05	6.05				
P <sub>2</sub> O <sub>5</sub>	0.64		0.64			
CO <sub>2</sub>	0.63			0.63		
H <sub>2</sub> O <sup>+</sup>	12.40	1.09	0.08		11.23	14.17
H <sub>2</sub> O <sup>-</sup>	2.80			2.80		
Total	100.12	14.40	1.02	5.37	79.33	100.00

Columns: 1, Total analysis (iron determined as Fe<sub>2</sub>O<sub>3</sub> = 0.60% and CO<sub>2</sub> by micro-analytical methods); 2, bertrandite; 3, amblygonite; 4, other impurities; 5, constituents attributed to the clay mineral; and 6, column 5 recalculated to 100%.

Analysts: P. J. Fourie and C. E. G. Schutte, Chemical Services Division, Department of Agriculture, and CO<sub>2</sub> micro-analysis by Miss A. F. Hogg, C.S.I.R., Pretoria.

Bertrandite [Be<sub>4</sub>(OH)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>] could still be detected as a minor constituent in the X-ray diffraction patterns, and in column 2 the amounts of SiO<sub>2</sub> and H<sub>2</sub>O calculated from the amount of BeO are given.

The small amount (1.02%) of amblygonite [LiAl(F,OH)PO<sub>4</sub>] was calculated from the P<sub>2</sub>O<sub>5</sub> present in the analysis (column 3). Amblygonite could not be detected by X-ray diffraction analysis, and the probable presence of this impurity is inferred from the presence of P<sub>2</sub>O<sub>5</sub>, as well as from the environmental conditions.

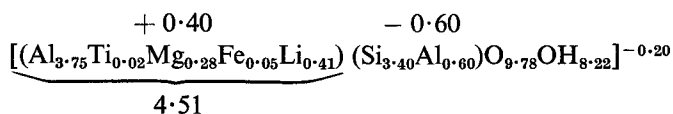
In column 4 all the other constituents not normally present in chlorites are grouped together. MnO may be present due to tantalite-columbite, the alkalis and some CaO may represent adsorbed or exchangeable cations, and H<sub>2</sub>O<sup>-</sup> is adsorbed water.

The cation exchange capacity of the material was determined as 26 m-eq/100 g sample dried at 110° C. The exchangeable cations were not determined, but the

above base exchange capacity could account for all the Na<sub>2</sub>O and K<sub>2</sub>O as well as 0.62% CaO as exchangeable cations. The CO<sub>2</sub>, determined by micro-analytical methods, could account for a further 0.80% CaO as CaCO<sub>3</sub>.

The Li<sub>2</sub>O could not be allocated to lithium–mica, as no mica could be detected in the sample by X-ray diffraction analysis.

In column 5 the constituents to be attributed to the clay mineral are given, and in column 6 the values are recalculated to 100%. From this estimated analysis the structural formula (half cell) was calculated on the basis of the determined H<sub>2</sub>O<sup>+</sup> (Foster, 1962) as follows:



The lattice charge of  $-0.20$  will be balanced by the exchangeable cations. The recalculated cation exchange value for the clay mineral is 33 m-eq/100 g dried clay.

#### X-RAY ANALYSIS

A Noreclo X-ray diffractometer was employed using Co K $\alpha$  radiation (Fe filter). The goniometer was calibrated with a silicon standard, and diffraction patterns were recorded at a speed of  $\frac{1}{2}^\circ 2\theta/\text{min}$ . Divergence and scatter slits of  $1^\circ$  and a receiving slit of 0.003 in was used. The specimen size was 10 × 20 mm and 1.5 mm thick.

The  $d$ -values obtained on the fraction less than 5  $\mu$  are listed in Table 2, as well as the strongest reflections of bertrandite and beryl. The random orientation of the sample was obtained by mixing with an equal part by volume of less than 100 mesh cork powder, and side-loading this mixture into an aluminium specimen holder (von Engelhardt, 1955). The orientated specimen was prepared by allowing a Mg<sup>+</sup> saturated suspension of the fine fraction to dry on a microscope glass-slide (Kittrick, 1961).

Beryl has its strongest reflections at 2.867, 3.25, and 7.98 Å. As there are no reflections corresponding to the latter two in the diffraction pattern of the fraction less than 5  $\mu$ , it appears that any remaining beryl is well below the limit of detection. The X-ray pattern indicates that a certain amount of fine bertrandite is still present. Most of the reflections given in Table 2 must therefore be ascribed to the clay mineral. The 30 Å reflection suggests that the clay mineral is of a mixed-layer type. From Table 2 it is apparent that the 4.78 Å reflection is characteristic of the clay mineral, and that it must be a 00 $l$  reflection. Indexing this line as 006, the  $d$ -values of the other 00 $l$  reflections were calculated according to Ito's method (Azároff & Buerger, 1958), and compared with the observed values in Table 3. As an integral series of basal reflections exists, the clay mineral is of the regular mixed-layer type (MacEwan *et al.*, 1961).

TABLE 2. X-ray data of the fraction less than 5  $\mu$ 

Random orientation		Preferred orientation (Mg <sup>+</sup> saturated)		Bertrandite* (strongest lines)		Beryl† (three strongest lines)	
<i>d</i> -value (Å)	Intensity	<i>d</i> -value (Å)	Intensity	<i>d</i> -value (Å)	Intensity	<i>d</i> -value (Å)	Intensity
Not resolved		30	M				
15	VS	14.44	VS				
		9.68	VW				
7.2	M	7.20	M	7.56	1	7.98	93
4.79	S	4.78	S				
4.47	S			4.38	10		
4.41	M						
4.20	M						
3.95	W			3.94	4		
3.84	VW			3.80	0.7		
3.58	M	3.58	S				
3.18	W			3.19	9	3.254	95
2.86	M	2.86	M	2.88	1	2.867	100
2.71	VW						
2.56	S						
2.52	S			2.54	8		
2.33	S						
2.29	W	2.29	W	2.28	6		
2.22	VW			2.22	6		
2.03	W			2.02	0.5		
1.98	W			1.983	2		
1.65	W			1.650	1		
1.49	MS			1.491	0.2		
1.47	VW			1.465	3		
1.45	VW						
1.43	VW						

\* Vernon &amp; Williams (1960)

† Swanson *et al.* (1960).TABLE 3. Agreement of computed and observed  $Q_{00l}$  values of the Mg<sup>+</sup>-saturated clay mineral  
 $Q_{00l} = 1/d_{00l}^2$ 

<i>d</i> <sub>obs</sub>	I*	00 <i>l</i>	$Q_{00l}$		Difference (obs-comp)	<i>d</i> <sub>calc</sub>
			Computed	Observed		
30	W	001	0.00122	0.00111	-0.00011	28.68
14.44	VVS	002	0.00486	0.00480	-0.00006	14.34
9.68	W	003	0.01094	0.01067	-0.00027	9.56
7.20	S	004	0.01945	0.01929	-0.00016	7.17
4.78	VS	006	—	0.04377	—	4.78
3.58	S	008	0.07781	0.07803	+0.00022	3.585
2.86	M	00,10	0.12157	0.12226	+0.00069	2.868

\* Intensities as for an orientated specimen.

The responses of the 00 $l$  reflections of the fine fraction to various treatments are given in Table 4. Regular mixed-layer minerals showing similar responses to these treatments are a mixed-layer chlorite–swelling chlorite, reported by Stephen & MacEwan (1951), corrensite from Zaisersweiher (Lippmann, 1954), some minerals from the Jura described by Martin Vivaldi & MacEwan (1957), and a swelling chlorite mineral (1:1 chlorite–swelling chlorite interstratification) reported by Sutherland & MacEwan (1960).

The medium–strong reflection at 1.49 Å was indexed as 060 and the  $b$ -parameter is therefore 8.94 Å.

TABLE 4. Response of 00 $l$  reflections to various treatments

00 $l$	Untreated*				Heat-treated				NH <sub>4</sub> <sup>+</sup> saturated				
	Observ- ed	Calcu- lated	Ethylene glycol†	Glycerol‡	300° C§	500° C¶							
001	30	W	28.68	31	M	32	W	30	VW	—	—	—	—
002	14.4	VS	14.34	15.0	VS	15.7	S	14.3	VS	13.64	VS	14.2	VS

\* Mg<sup>+</sup> saturated.

† Mg<sup>+</sup> saturated, then treated with ethylene glycol vapours (Walker, 1958).

‡ Mg<sup>+</sup> saturated, then treated with 10% glycerol solution (Kittrick, 1961; Walker, 1958).

§ Natural sample orientated and heated to 300° C for 1 hr.

¶ Mg<sup>+</sup> saturated sample orientated and heated to 500° C for ½ hr.

## ELECTRON DIFFRACTION

Single crystal electron diffraction was used to confirm the  $b$ -parameter of the clay mineral. In the discussion of the identification of clay minerals by single crystal electron diffraction, Brindley & de Kimpe (1961) pointed out some limitations of this method. Using an internal standard, however, they suggested that the  $b$ -parameter can be accurately determined, and that such data can help in the partial identification of clay minerals.

The electron diffraction pattern of the mineral shows the typical pattern of hexagonal symmetry commonly obtained from clay minerals lying flat on the basal substrate (Brindley & de Kimpe, 1961). Gold was employed as an internal standard, and the apparatus used was a Siemens Emiskop I Electron Microscope. Unfortunately the [0 $k$ 0] zone of reflections could not be identified. Three zones occurring at 120° to each other may well represent the [0 $k$ 0] zone, but all gave a  $b$ -value of 8.94 ± 0.02 Å. This result confirms the  $b$ -value obtained by X-ray diffraction methods.

## DIFFERENTIAL THERMAL ANALYSIS

The differential thermal analysis (d.t.a.) curve of the fraction less than  $5\ \mu$  is given in Fig. 1. The material was dried at  $74^\circ\text{C}$  for  $1\frac{1}{2}$  hr, and cooled in a desiccator prior to analysis. The d.t.a. apparatus was calibrated with pure quartz, and the maximum temperature error was  $5^\circ\text{C}$ .

Two weak endothermic reactions occur at  $100$  and  $200^\circ\text{C}$ , a major reaction at  $555^\circ\text{C}$  and another weak reaction at about  $850^\circ\text{C}$ . Exothermic reactions occur at  $880$ ,  $915$ , and  $1020^\circ\text{C}$ . The curve resembles those obtained for pseudo-chlorites (Caillière & Hénin, 1957), and for some swelling chlorites described by Honeyborne (1951).

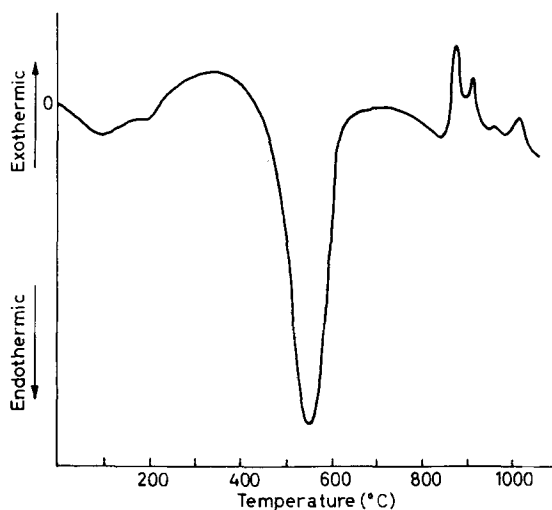


FIG. 1. Differential thermal analysis curve of the fraction less than  $5\ \mu$ . Heating rate:  $12^\circ\text{C}/\text{min}$ .

## DISCUSSION

From the X-ray data it is clear that the mineral is of the regular mixed-layer type consisting of alternate layers of swelling and non-swelling  $14.4\ \text{\AA}$  units. The  $b$ -parameter is  $8.94\ \text{\AA}$ .

Unfortunately the sample contained about 20% of impurities, and considerable correction of the chemical analysis was necessary to calculate the structural formula. This is similar to that of a dioctahedral chlorite described by Brydon, Clark & Osborne (1961) in that the total of octahedral cations is 4.5 in both minerals. They also have a high alumina content of the same order. A further similarity between these two minerals is the d.t.a. endothermic peak at  $550$ – $555^\circ\text{C}$  and the exothermic peak at  $910$ – $915^\circ\text{C}$ . Other examples of aluminous dioctahedral chlorites are given by Müller (1963) in his discussion of the sudoite members of the sudoite-chlorite

group. Sudoite is characterized by a basal reflection of approximately 14.2 Å which is not influenced by glycol treatment, and by a *b*-parameter of 8.95–9.06 Å.

The presence of lithium in the structural formula also suggests a similarity to the Li-chlorite, cookeite, ideally  $[(\text{LiAl}_4)(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8]$  (Brammall, Leech & Bannister, 1937) with a *b*-parameter of 8.92 (Radoslovich, 1962). Cookeite is a leptochlorite (Brown, 1955) with one dioctahedral and one trioctahedral layer. The ratio of octahedral to tetrahedral cations is 5 : 4 while in the mineral described in this paper this ratio is 4.5 : 4. The possibility that the mineral is a leptochlorite with a deficiency of cations in some of the octahedral layers, which caused the swelling of alternate 14.4 Å units with glycol, should therefore not be overlooked.

The mineral is thus a high-aluminous chlorite–swelling chlorite regular mixed-layer clay mineral and could be either dioctahedral or di-trioctahedral with some octahedral cation deficiency.

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