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Reyerite

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Summary. Reyerite from the original locality in Greenland has been re-examined using chemical analysis, infra-red absorption, X-ray powder and single-crystal diffraction, and thermal weight-loss curves. The unit cell is trigonal with *a* 9·74, *c* 19·04 Å, and the space group is probably $P\bar{3}$. The unit cell contents are probably best represented as $KCa_{14}(Si_{24}O_{60})(OH)_5.5H_2O$, with some minor replacements. The molecular water is lost reversibly below 400° C. There are indications that the crystal structure is based on Si_6O_{18} rings resembling those in beryl, but linked into sheets by additional tetrahedra.

Reyerite closely resembles truscottite, a mineral found originally in Sumatra, but there are distinct differences, especially in the infra-red pattern. It is not yet certain whether or not the two minerals should be considered as distinct species. Synthetic preparations examined resembled truscottite more closely than reyerite.

REYERITE is a calcium silicate mineral of micaceous appearance. The original specimen was collected at Niakornak, Greenland, by Giesecke in 1811, and was first studied by Cornu and Himmelbauer (1906) and independently by Bøggild (1908). It was later studied also by Flint, McMurdie, and Wells (1938), Strunz and Micheelsen (1958), and Meyer and Jaunarajs (1961). These studies have indicated a composition approximating to $3CaO.5SiO_2.2H_2O$ with small amounts of alumina and alkalies, and have also provided optical, unit-cell, and other data.

At least two other minerals have been described that are closely related to reyerite. The first of these, gyrolite, has been found in many localities and has generally been assigned the idealized formula

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$2CaO.3SiO_2.2H_2O$. Bøggild (1908) originally regarded the Niakornak specimen as an abnormal gyrolite, but later (Bøggild, 1953) accepted the view that it was a distinct species. Flint, McMurdie, and Wells (1938) concluded from X-ray powder photographs that the two minerals were identical. However, the compositions are distinctly different, and the unit-cell parameters, though related, are also quite distinct (Strunz and Micheelsen, 1958). There seems little doubt that reyerite and gyrolite are distinct species.

A second mineral similar to reyerite was found in Sumatra by Hövig (1914), who named it truscottite. The principal subsequent studies on this specimen were made by Grutterink (1925), Mackay and Taylor (1954), and Strunz and Micheelsen (1958). The unit-cell parameters are close to those of reyerite. The composition has variously been reported as $2CaO.4SiO_2.H_2O$ (Hövig, 1914; Mackay and Taylor, 1954) and as $2(Ca,Mg)O.3SiO_2.2H_2O$ (Grutterink, 1925). Strunz and Micheelsen (1958) concluded from X-ray single crystal studies that truscottite was identical with reyerite and was thus discredited as a species. It will, however, be shown in the present paper that this conclusion may not be correct and the name truscottite will therefore be provisionally retained for the Sumatra specimen.

Synthetic materials can be prepared hydrothermally that resemble reyerite or truscottite (Buckner, Roy, and Roy, 1960; Harker, 1960; Meyer and Jaunarajs, 1961; Funk, 1961). Meyer and Jaunarajs, and also Funk, concluded from their experiments that their products had the composition $2CaO.4SiO_2.H_2O$, but Harker concluded that the composition was $3CaO.5SiO_2.1\frac{1}{2}H_2O$.

Strunz and Micheelsen (1958) considered that the idealized formula of reyerite was $Ca_{9/2}(Si\,O_{18})(OH)_3$ (this is apparently a misprint for $Ca_{9/2}(Si_6O_{15})(OH)_3$). Ca/Si ratios ranging from 0·50 to 0·75 have thus been proposed for reyerite or truscottite. The objects of the present work were to establish the composition and ionic constitution of the type reyerite, and to examine more fully its relationships with truscottite and the synthetic materials.

Reyerite from Greenland: experimental methods and results

Optical examination and density. The specimen used (USNM 4016) was from the original locality at Niakornak, Greenland, and was kindly provided by the U.S. National Museum. Crushed material consisted of flakes with (0001) cleavage. Optical examination showed no impurities other than calcite, which was widely dispersed between the reyerite lamellae. The refractive indices, and also the density, were determined, the latter by suspension in bromoform–benzene mixtures, care being taken to select transparent flakes free from calcite and to remove trapped air by boiling the liquid under reduced pressure. Slight variability was found in both refractive indices and density. The results agreed closely with those reported by earlier investigators (Table I).

TABLE I. Optical properties and specific gravities

		Reyerite (Greenland)			
	Cornu and Himmelbauer (1906)	Bøggild (1908)	This investigation	Truscottite (Sumatra) This investigation	Synthetic preparation B This investigation
Optic sign	negative	negative	negative	negative	?
Refractive indices ω	1·564	1·5645	1·563	1·546	mean
Refractive indices ϵ	n.d.	1·5590	1·558	?	1·538
Specific gravity or density (gm/cc)	2·499–2·578	2·463–2·578	2·51–2·54	2·47*	?

* Mackay and Taylor (1954).

Purification of material for analysis. Because of the intimate admixture with calcite, the material is difficult to purify. Attempts using heavy liquids were unsuccessful, and acid extraction of the calcite was rejected because it was found that even very dilute acid attacks reyerite. Hand picking was resorted to. About 60 mg of material was thus collected, which from microscopic examination appeared to contain only a few percent of calcite. The crystals were crushed to pass a 60-mesh sieve (further crushing was thought inadvisable because of the possible danger of CO_2-attack or change in water content), and representative portions used in the chemical analysis and for a weight-loss curve. It was found desirable to make several redeterminations of the weight-loss curve, and for this purpose further samples were purified in the same way.

Chemical analysis. Table II, column A, gives the results. It was assumed that the CO_2 was present as calcite, and in column B the results have been corrected on this assumption. The values in column B agree closely with the incomplete data of Cornu and Himmelbauer (1906; column C), and mean of the two (column D) was taken as a basis for further calculations. Bøggild's (1908) analysis, given in column F, shows more SiO_2, Al_2O_3, and H_2O, and less CaO and Na_2O. It was made on material that had been washed with dilute acetic acid. This procedure might well have leached out small proportions of the more basic constituents.

In the present work, it was found that the Al_2O_3 content varied throughout the sample; a preliminary analysis, made on material containing a higher proportion of calcite, showed no Al_2O_3 at all. This variation could perhaps be correlated with those in refractive indices and specific gravity, but not enough material was available to investigate this.

TABLE II. Chemical analyses of reyerite from Greenland

	A.	B.	C.	D.	E.	F.
SiO_2	51·7	53·2	53·31	$53{\cdot}2_5$	$53{\cdot}2_5$	54·83
Al_2O_3	3·8	3·9	3·72	3·8	3·8	4·58
CaO	33·2	32·3	32·22	$32{\cdot}2_6$	$32{\cdot}2_6$	31·15
Na_2O	2·2	2·3	n.d.	2·3	2·3	1·74
K_2O	1·6	1·6	n.d.	1·6	1·6	n.d.
CO_2	1·4	—	n.d.	—	—	n.d.
H_2O^{-400}	4·0	4·2	6·73	4·2	3·4	8·14
H_2O^{+650}	2·3	2·6		2·6	2·6	
	100·2	100·1	95·98	100·0	99·2	100·44

A. This investigation; analyst, R. A. Chalmers.

B. Column A after deducting CO_2 as $CaCO_3$ and normalizing; value for H_2O^{+650} based on the mean of several determinations of the weight-loss curve (see text and Table III).

C. Cornu and Himmelbauer (1906).

D. Mean of columns B and C.

E. Column D after deducting 0·8 % of H_2O, assumed to be uncombined.

F. Bøggild (1908); analyst, C. Christensen. Also: fluoride, nil; H_2O includes 2·45 % lost at 100°.

Weight-loss curves. Several determinations were made, using a quasi-static heating technique. The sample (usually 20–30 mg) was placed in a platinum microboat, which was heated at successively higher temperatures in a silica tube furnace through which a current of CO_2-free N_2 was passed. After each heating, the boat was rapidly cooled on a stainless steel block, and weighed on a microbalance. At each temperature, the sample was reheated and reweighed until the weight had become constant to 0·01 mg before going on to the next temperature. Each run took 1–3 weeks.

Samples which had been heated at temperatures below 400° C regained weight rapidly while on the balance. For each weighing, an initial reading was completed exactly 1 minute after the specimen had been removed from the nitrogen atmosphere of the furnace. Further readings were then taken at 30-second intervals, and the weight extrapolated back to the time of removal from the nitrogen atmosphere. For all temperatures above 300° C, the boat was left for 1–2 minutes out of the hot part of the furnace, but still in the nitrogen atmosphere, before being placed on the block.

Buckle (1959) showed that under conditions similar to those used here, calcite decomposes at 450–600° C. A typical curve obtained in the present work (fig. 1) showed three steps. The first, at 30–400° C, and the third, at 600–850° C, were attributed to the loss of water present in the reyerite as molecules and as hydroxyl ions respectively. The second, at 400–600° C, was attributed to decomposition of the calcite; this was confirmed by optical and X-ray examinations of heated samples.

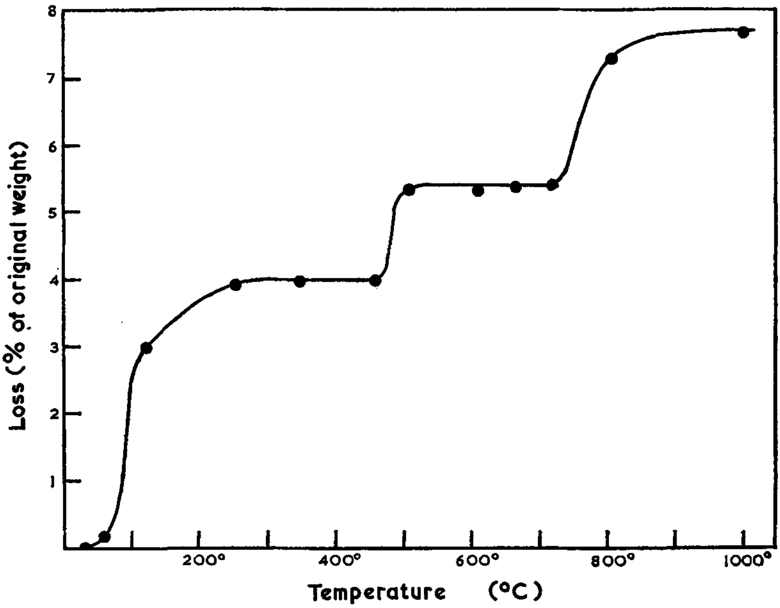

FIG. 1. Quasi-static weight-loss curve for reyerite from Greenland; sample heated in a stream of CO_2-free nitrogen.

Five separate determinations were made. From the results (Table III), the mean values of 4·2±0·2 % for the loss below 400° C and 2·6±0·1 % for the loss above 650° C were obtained. These are the values obtained after correction for the presence of calcite and are the ones used in column B of Table II.

X-ray single-crystal examination. X-ray single crystal oscillation, rotation, and Weissenberg photographs were made about the *a* and *c* axes, using filtered copper radiation. They confirmed the trigonal symmetry reported originally by Bøggild (1908); no evidence was found to support the view of Meyer and Jaunarajs (1961) that reyerite is monoclinic and only pseudo-trigonal. The value of *a* was found from measurements of row line positions on a *c*-rotation photograph, and that of *c* from the layer line spacings on a *c*-rotation, and also from the positions of the 000*l* reflections on an 0*kil* Weissenberg photograph. The results so obtained were *a* 9·74±0·01 Å, *c* 19·04±0·02 Å. The cell volume calculated from these values is 1563 Å.^{3}

TABLE III. Weight-loss data for reyerite.

Run no.	Loss below 400° C	Loss at 450–650° C	Loss at 650–950° C	% calcite*	% H_2O lost below 400° C†	% H_2O lost above 650° C†
1.‡	4·0 %	1·4 %	2·3 %	3·2	4·1	2·4
2.‖	4·0	2·7		Probably < 1·0	4·0	< 2·7
3.	4·2	1·4	2·6	3·2	4·3	2·7
4.	3·7	1·2	2·8	2·7	3·8	2·9
5.§	3·5	10·3	$1{\cdot}9_5$	23·4	4·6	2·5
Mean	—	—	—	—	4·2	2·6

* Calculated from loss at 450–650° C, assumed to be CO_2.

† After correcting for $CaCO_3$.

‡ Run carried out on a representative portion of the sample used for the analysis (Table II, column A).

‖ Run carried out without passage of N_2; CO_2 and H_2O^{+650} not distinguished.

§ Run carried out on a 110 mg sample of unpurified material.

Examination of the oscillation and Weissenberg photographs limited the possible space groups to $P3$ and $P\bar{3}$. The essential difference between these space groups is that $P\bar{3}$ has a centre of symmetry while $P3$ has not. Bøggild (1908) showed, from goniometric studies together with etch figures and percussion figures, that the crystal class was $\bar{3}$, which is centrosymmetric; this indicates the space group $P\bar{3}$. In an attempt to obtain additional evidence, the intensities of about 400 non-equivalent 0*kil* reflections and about 100 non-equivalent *hki*0 reflections were estimated from Weissenberg photographs, F^2 values calculated, and the statistical method of Howells, Phillips, and Rogers (1950) applied. With the *hki*0 projection a centre of symmetry was indicated; with the 0*kil* projection an inconclusive result was obtained, but this can perhaps be explained by absorption. The balance of the evidence favours the centrosymmetric space group, $P\bar{3}$.

It will be shown later that the relative intensities of the 000*l* reflections are of diagnostic value, and these are therefore reported (fig. 2).

X-ray powder investigation. X-ray powder data (Table IV) were obtained from 6 cm and 11·46 cm diameter powder cameras and also from a diffractometer, in all cases with filtered copper radiation. It was not found possible to eliminate preferred orientation with the diffractometer. The pattern was indexed, for *d*-spacings above 1·45 Å, mainly by direct comparison of the 6 cm powder pattern with the *c*-rotation photographs obtained using the same type of camera. Due account was taken of relative intensities as well as spacings.

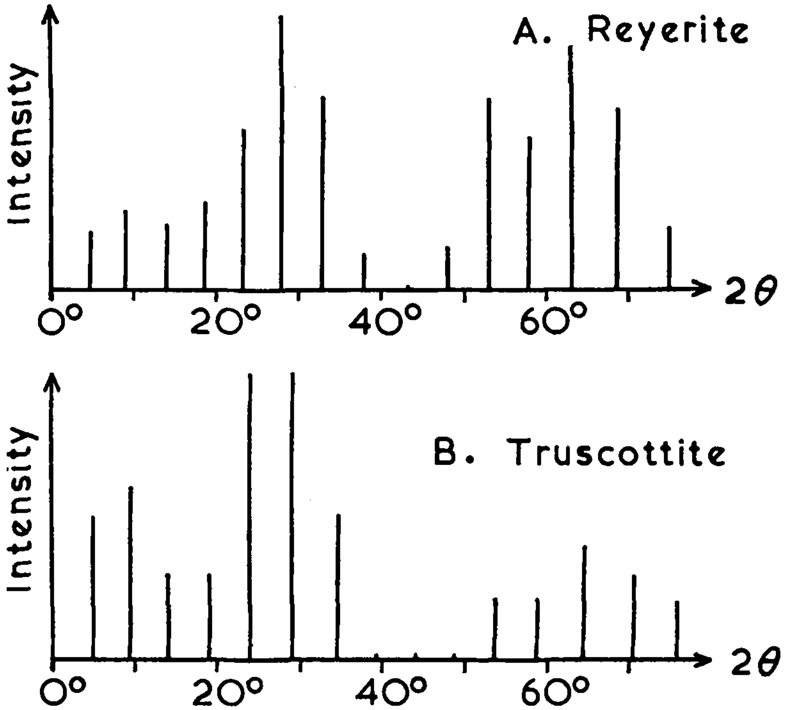

FIG. 2. Relative intensities of the first fifteen 000*l* reflections for (*a*) reyerite from Greenland, and (*b*), truscottite from Sumatra, estimated visually from Weissenberg photographs in each case. No Lorentz, polarization, or other corrections have been made.

X-ray examination of heated crystals. Single crystals were heated to various temperatures, allowed to cool, and then examined by oscillation or rotation photographs. Those heated at 400° C or below were unchanged (almost certainly, the water lost on heating was largely

TABLE IV. X-ray powder data for reyerite (from Greenland) and for synthetic truscottite. Cu-Kα radiation, $\lambda = 1{\cdot}542$ Å.

Reyerite				Truscottite			
Observed			Calc.	Observed			Calc.
d (Å)	*I*	*hkil*	*d* (Å)	*d* (Å)	*I*	*hkil*	*d* (Å)
19	vw	0001	19·04	19	*s*	0001	18·71
9·56	mw	0002	9·52	9·4	m	0002	9·355
7·65	vw	$10\bar{1}1$	7·712	7·78	mw	$10\bar{1}1$	7·677
6·33	vw	0003	6·347	6·11	mw	$10\bar{1}2$	6·257
		$10\bar{1}2$	6·313			0003	6·237
5·07	vvw	$10\bar{1}3$	5·071	4·89	vw	$10\bar{1}3$	5·011
4·77	vvw	0004	4·760	4·65	mw	0004	4·677
				4·23	s	$11\bar{2}2$	4·313
4·23	ms	$20\bar{2}0$	4·218			$20\bar{2}0$	4·209
4·15	vvw	$10\bar{1}4$	4·145			$10\bar{1}4$	4·089
3·84	mw	$11\bar{2}3$	3·864	3·85	m	$11\bar{2}3$	3·833
		0005	3·803	3·78	m	0005	3·742
3·52	m	$20\bar{2}3$	3·513	3·47	m	$20\bar{2}3$	3·489
3·47	w	$10\bar{1}5$	3·470			$10\bar{1}5$	3·419
3·17	vs	0006	3·173	3·12	vs	$21\bar{3}1$	3·137
		$21\bar{3}1$	3·144			0006	3·118
3·035	m	$21\bar{3}2$	3·023	3·018	w	$21\bar{3}2$	3·012
3·004	w	$11\bar{2}5$	3·000			$11\bar{2}5$	2·965
2·970	w	$10\bar{1}6$	2·970	2·823	ms	$10\bar{1}6$	2·924
2·855	s	$21\bar{3}3$	2·849			$21\bar{3}3$	2·834
2·720	vw	0007	2·722				
2·659	s	$11\bar{2}6$	2·659	2·637	m	$21\bar{3}4$	2·631
		$21\bar{3}4$	2·649			$11\bar{2}6$	2·625
2·587	vw	$10\bar{1}7$	2·589	2·515	vvw	$20\bar{2}6$	2·506
2·540	vw	$20\bar{2}6$	2·536	2·424	w	$22\bar{4}0$	2·430
2·449	w	$21\bar{3}5$	2·445			$21\bar{3}5$	2·424
2·347	vvw/b	$11\bar{2}7$	2·375	2·333	vvw	$31\bar{4}0$	2·335
		$31\bar{4}0$	2·339			$31\bar{4}1$	2·317
2·294	vw/b	$10\bar{1}8$	2·291				
		$20\bar{2}7$	2·286				
2·256	mw	$31\bar{4}2$	2·272	2·219	mw/b	$31\bar{4}2$	2·265
		$21\bar{3}6$	2·249			$21\bar{3}6$	2·227
2·191	vw	$31\bar{4}3$	2·195			$31\bar{4}3$	2·186
2·103	w	$31\bar{4}4$	2·100	2·090	w	$31\bar{4}4$	2·089
2·072	mw	$21\bar{3}7$	2·069	2·044	w	$21\bar{3}7$	2·047
		$22\bar{4}5$	2·051	1·913	vw	$32\bar{5}0$	1·931
1·945	vw	$11\bar{2}9$	1·940	1·884	vw	$21\bar{3}8$	1·884
1·900	vw	$21\bar{3}8$	1·907			$31\bar{4}6$	1·869
1·860	vvw	$1.0.\bar{1}.10$	1·857	1·834	ms	$41\bar{5}0$	1·837
1·846	s	$41\bar{5}0$	1·841			$41\bar{5}1$	1·828
1·812	m	$41\bar{5}2$	1·807	1·800	vw	$41\bar{5}2$	1·802
1·766	mw	$41\bar{5}3$	1·768	1·759	w	$41\bar{5}3$	1·762

TABLE IV (*cont.*)

Reyerite				Truscottite			
Observed			Calc.	Observed			Calc.
d (Å)	*I*	*hkil*	*d*(Å)	*d*(Å)	*I*	*hkil*	*d*(Å)
1·762	mw	$21\bar{3}9$	1·763	1·747	w	$21\bar{3}9$	1·740
1·732	vvw	0.0.0.11	1·731	1·710	vvw	$41\bar{5}4$	1·710
1·704	vvw	$22\bar{4}8$	1·702				
1·661	vw	$41\bar{5}5$	1·657	1·642	w	$41\bar{5}5$	1·649
1·636	vw	$2.1.\bar{3}.10$	1·635	1·613	vvw	$2.1.\bar{3}.10$	1·613
1·596	w	$41\bar{5}6$	1·592	1·590	w/b	$42\bar{6}0$	1·591
1·572	w	$31\bar{4}9$	1·569			$41\bar{5}6$	1·583
						$33\bar{6}3$	1·568
1·550	vvw	$42\bar{6}3$	1·546	1·540	w	$42\bar{6}3$	1·541
1·519	vw	$42\bar{6}4$	1·512	1·512	w	$42\bar{6}4$	1·506
1·502	vvw	$32\bar{5}8$	1·501				
1·472	vw	0.0.0.13	1·464	1·459	vw	$42\bar{6}5$	1·464
1·435	vvw			1·437	vw	$51\bar{6}4$	1·439
1·419	w						
1·409	vw			1·403	w		
1·377	vvw						
1·352	vw			1·348	vw		
1·328	vw			1·316	vw		
1·296	vvw			1·287	vvw		
1·273	vvw			1·271	vvw		
1·248	vvw			1·238	vvw		
1·229	vvw			1·222	vw		
1·200	vw			1·195	vw		
1·166	vw			1·163	w		
1·149	vvw						
1·120	vw			1·122	vvw		
1·112	vw			1·102	vvw		
1·093	vw						
1·073	vvw						
1·056	vw			1·055	vvw		
1·048	vw			1·047	vw		
1·012	vvw						
0·9986	vvw						
0·9687	vvw			0·982	vvw/b		
0·9543	vw			0·958	vvw/b		
0·9426	vw			0·936	vvw		
0·9258	vvw						
0·9103	vw			0·907	vw		
0·9018	vvw						
0·8943	vvw						
0·883	vw/b			0·888	vvw		
0·871	vw/b			0·878	vvw		
0·8602	vvw			0·856	vvw		

re-absorbed even before the exposure was begun). A crystal heated to 800° C showed α-CaSiO$_3$ as the only crystalline product. The α-CaSiO$_3$ showed marked preferred orientation, with $(0001)_{\alpha\text{-CaSiO}_3} \parallel (0001)_{\text{reyerite}}$ and the normal to $(11\bar{2}0)_{\alpha\text{-CaSiO}_3} \parallel$ the normal to $(21\bar{3}0)_{\text{reyerite}}$; α-CaSiO$_3$ is here referred to a pseudohexagonal cell with a 6·85, c 19·65 Å. This is the same orientation relationship as was found by Mackay and Taylor (1953) in the dehydration of gyrolite.

Infra-red examination. Infra-red absorption spectra were recorded using a NaCl prism with 2 mg and 0·33 mg samples each contained in a 12·7 mm diameter KBr disk. The effects of heating the samples to 250° C in the disk, to drive off the low-temperature water, and of allowing them to rehydrate in moist air, were also studied. Fig. 3 gives the results for the original (curve C) and heated samples (curve D). The rehydrated sample gave a curve closely similar to that of the original material. The spectrum of the original hydrated form was also recorded in the 650–400 cm^{-1} region using a KBr prism (fig. 4c, 0·33 mg in a 12·7 mm disk). Hydroxyl groups coordinated only to calcium give rise to a sharp absorption band near 3600 cm^{-1} in curves C and D. This band was resolved into two components under grating resolution, showing then a principal peak at 3639 cm^{-1} with a much weaker subsidiary one at 3612 cm^{-1}. This does not necessarily indicate that these hydroxyl groups occupy two different kinds of site: such splitting can also arise by coupling between symmetrically equivalent hydroxyl groups. The broad shoulder at about 3000 cm^{-1} and the band at 1640 cm^{-1} can be attributed to molecular water. This assignment is confirmed by the loss of these bands on heating the disk to 250° C (curve D). Absorption of hydrogen bonded Si–OH groups possibly underlies the water absorption at 3000 cm^{-1}, but there is little evidence of such absorption in the spectrum of the heated sample; if such groups are present, they must dehydrate at a low temperature, or their absorption must be very weak. Bands at 1429 and 877 cm^{-1} can be attributed to carbonate ions present in the calcite impurity. The remaining bands can be attributed to the Si–O bond vibrations of the reyerite. The fact that the centre of the main complex of absorption bands at 900–1200 cm^{-1} lies at about 1050 cm^{-1}, and not at some value nearer to 900 cm^{-1} indicates that the anion is highly condensed: the range of absorption is in fact close to that of kaolinite (Launer, 1952). The occurrence of subsidiary bands at 600–850 cm^{-1} is also indicative of Si–O–Si bonds. In the pattern of the heated material (curve D), not only have the bands attributed to molecular water disappeared, but

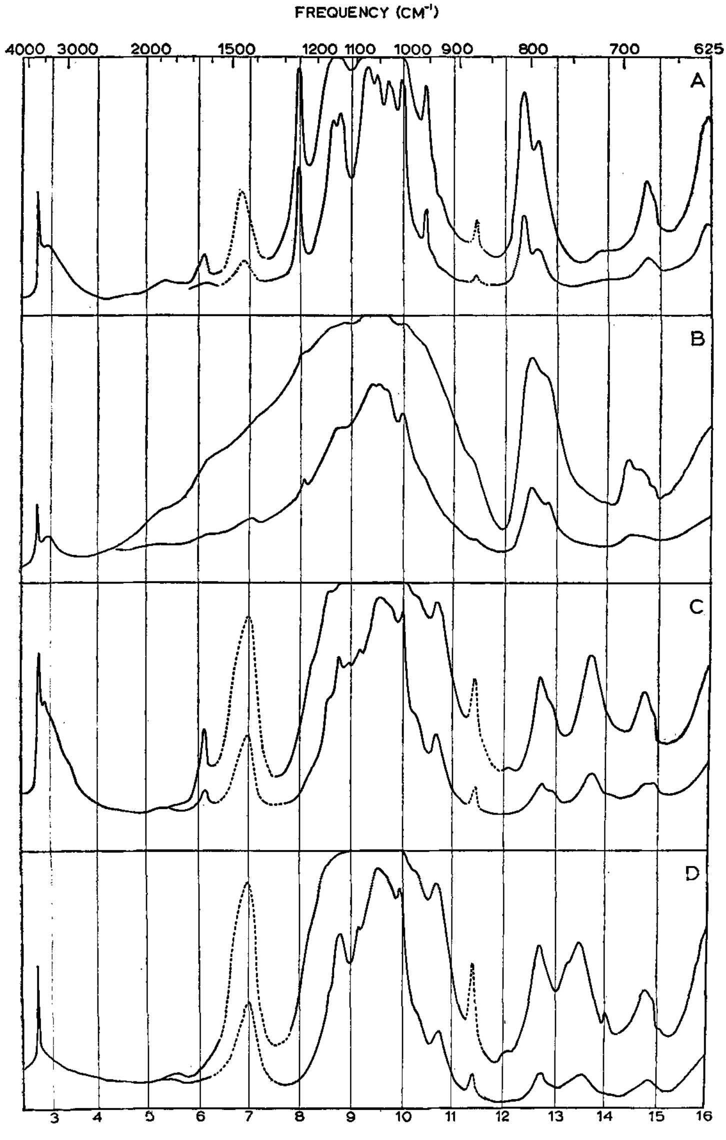

FIG. 3. Infra-red spectra (4000–630 cm^{-1}) of truscottite and reyerite: (A) synthetic preparation, (B) natural truscottite from Sumatra, (C) natural reyerite from Greenland, normal hydrated form, and (D) natural reyerite from Greenland, after heating to 250° in the disk. Carbonate absorption bands are dotted. Spectra recorded at sample concentrations of 2 mg and 0·33 mg in 12·7 mm KBr disks.

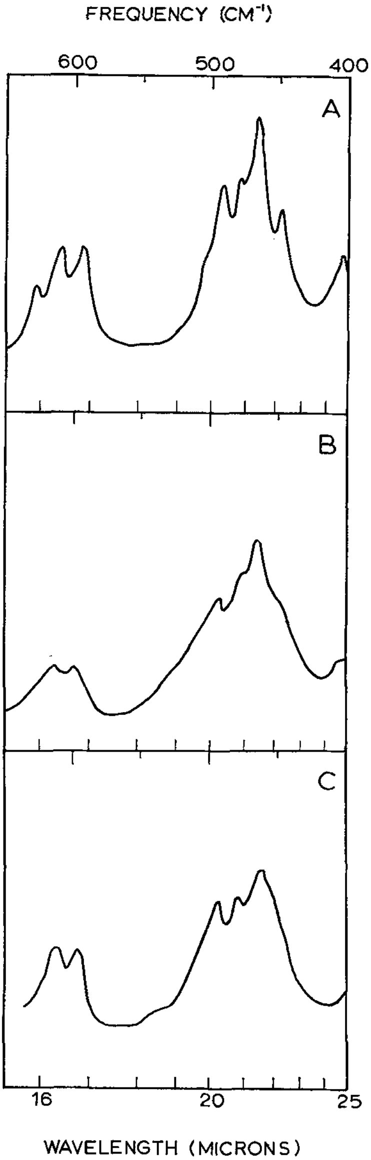

FIG. 4. Infra-red spectra (650–400 cm^{-1}) of truscottite and reyerite: (A) synthetic preparation, (B) natural truscottite from Sumatra, and (C) natural reyerite from Greenland, normal hydrated form.

there are also distinct changes in the Si–O bands, particularly near 1100 cm^{-1}, and in the position of a band which moves from 730 cm^{-1} to 738 cm^{-1}.

Reyerite from Greenland: discussion of results

The low-temperature water. Before the chemical analysis can be interpreted, it is necessary to decide whether the water lost below 400° C is contained in the crystal structure, or whether it is uncombined. Two lines of evidence show that at least a part of it is in the structure:

The changes that occur in the infra-red pattern can only be explained if at least a part of the low-temperature water is contained in the structure; if this water were uncombined, its loss would not affect the Si–O bands. Recent X-ray studies on zeolites (Smith, 1962) have shown that loss of loosely held, molecular water can cause marked distortion of a silicate framework, and the present evidence suggests that this happens here.

The density of a calcium silicate mineral can be calculated from the mean refractive index, assuming the composition to be known, by an adaptation of the Lorentz–Lorenz equation (Howison and Taylor, 1957). In the present case, if all the water is assumed combined, this calculation gives a value of 2·54 gm/cc, which agrees with the value directly determined in the present investigation. If the low-temperature water is assumed to be entirely uncombined, the calculated value is 2·61 gm/cc, but the observed value (after correction for the water as an impurity) is 2·71 gm/cc.

Bøggild (1908) reported that the purest crystals he examined had a specific gravity of 2·578, lower values being apparently due to the presence of liquid inclusions. If the value of 2·54 observed by us is assumed to be low because of this, 0·8 % of the low-temperature water would have to be considered as unbound, and the density calculated from the refractive index would become 2·56 gm/cc. It is difficult to decide whether to make this correction, since the assumption that the lowering of the density is caused by liquid inclusions may be wrong; no definite indications of such inclusions were observed in the present work. On balance there is probably a case for making the correction, the results of which are shown in Table II, column E. If the correction is not made, the interpretation of the analysis that follows is not changed in essentials, although the content of molecular water rises to approximately 5·5 per unit cell.

Unit-cell contents. Using the corrected analysis given in Table II, column E, and taking the density as 2·578 gm/cc and the unit cell volume as 1563 Å^3, the unit cell contents given in Table V, column A are obtained. It was assumed that water lost below 400° C was molecular and water lost above 650° C was hydroxyl.

The numbers of Na and Al atoms in the cell are equal, and the sum of (Si+Al) approximates to 24, a number which could easily be reconciled with the trigonal symmetry. This suggests that, ideally, there are 24 Si atoms in the cell, and that in the actual mineral some of these are replaced by Al with introduction of Na into otherwise empty sites. The sum of (Si+Al) is, however, significantly below 24; if it is arbitrarily set at 24, the X-ray density becomes 2·63 gm/cc, which is well above the observed value. Perhaps the most likely assumption is that replacement of Si by 4H occurs, as this would cause the idealized formula of the silicate anion to become $Si_{24}O_{60}$ (columns B and C). This formula for the anion is consistent with a sheet structure and is the same as that found for gyrolite (Mackay and Taylor, 1953). The replacement of Si by 4H might occur by simple substitution of SiO_4 by $(OH)_4$, as in the hydrogarnets, or in some less obvious way, such as that suggested for serpentine minerals by Deer, Howie, and Zussman (1962).

TABLE V. Atomic cell contents for reyerite from Greenland.

		A.	B.	C.
Si	21·7		23·5	24
Al	1·8			
Ca	14·1	14·0	14·0	14
		0·1		
K	0·8	0·8	0·9	1
Na	1·8		1·8	—
H_2O	4·6		4·6	5
OH	7·1	5·1	5·1	5
		2·0		
O (other than H_2O and OH)	58·0	58·0	60·0	60

A. Calculated from experimental data.
B. Column A interpreted as described in the text.
C. Idealized values.

The unit-cell contents are thus probably best represented as $KCa_{14}(Si_{24}O_{60})(OH)_5 . 5H_2O$, with small replacements of Si by NaAl and by H_4, though other possibilities, such as $KCa_{14}Si_{24}O_{59}(OH)_7 . 5H_2O$, cannot quite be excluded. An X-ray structure determination is needed to establish the ionic constitution with certainty.

Crystal structure and behaviour on dehydration. The good basal cleavage of reyerite, together with the empirical formula Si_2O_5 of the anion, suggests a sheet structure. The trigonal symmetry and the length of the *a*-axis (9·74 Å) suggest the occurrence of Si_6O_{18} rings similar to those known to exist in beryl and other minerals. The anion in reyerite may therefore be composed of Si_6O_{18} rings linked together into sheets by additional tetrahedra. As well as these sheets, the idealized structure contains Ca^{2+}, K^+, and OH^- ions and H_2O molecules. These last are not essential to the structure's stability.

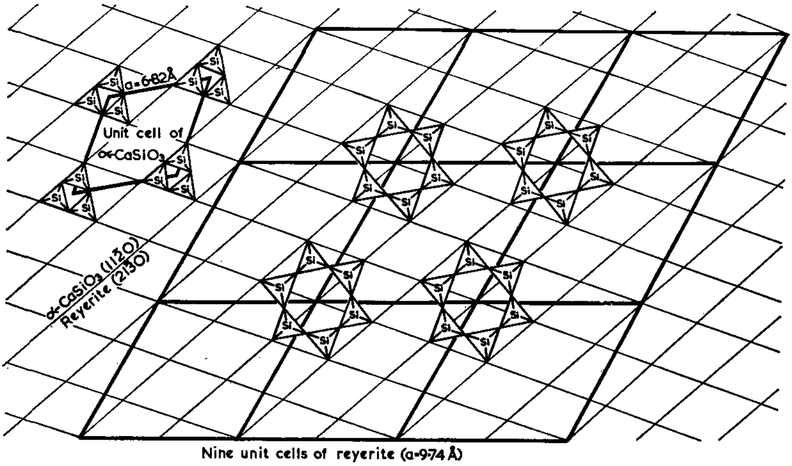

FIG. 5. Reyerite and α-$CaSiO_3$ lattices in the observed relative orientation, viewed along the common *c*-direction. Only four of the Si_6O_{18} rings believed to occur in the reyerite sheet are shown; it is assumed that these rings are linked together by additional tetrahedra to give a sheet of empirical composition Si_2O_5.

The hypothesis of sheets based on Si_6O_{18} rings would also explain the formation of α-$CaSiO_3$ on dehydration, and its orientation relative to that of the reyerite. Fig. 5 shows the reyerite and α-$CaSiO_3$ cells in the observed relative orientation (reyerite (0001) → α-$CaSiO_3$ (0001) and reyerite (21$\bar{3}$0) → α-$CaSiO_3$ (11$\bar{2}$0)). The thin lines in fig. 5 define a lattice that is common to both structures. α-$CaSiO_3$ has a structure based on Si_3O_9 rings, which are arranged in layers parallel to (0001) (Hilmer, 1958, 1962). One of these layers is shown (in a somewhat idealized form) superimposed on the common lattice of thin lines in the top left-hand corner of fig. 5; the peripheral oxygen atoms of the Si_3O_9 rings lie on the points of the lattice. In the main part of fig. 5, nine cells of reyerite are outlined, and four Si_6O_{18} rings have been drawn in such an orientation that their peripheral oxygen atoms also lie on the points of the common lattice. The resulting orientation of the Si_6O_{18} rings relative to the unit cell edges of the reyerite is identical with that found in beryl. The orientation relationship could therefore be explained if it is assumed that rings of this type and orientation are present in reyerite, and that the dominant tendency during the dehydration reaction is for the sheets of oxygen atoms which form their upper and lower surfaces to persist with little or no disturbance.

Studies on other hydrated calcium silicates that dehydrate at 650–850° C (e.g. xonotlite, foshagite) suggest that migration of Si^{4+} occurs freely at these temperatures, with consequent destruction and rebuilding of the Si–O parts of the structure (Dent and Taylor, 1956; Taylor, 1960). The existence of Si_3O_9 rings in α-$CaSiO_3$ therefore provides no evidence either for or against the presence of such rings as the linkages between the larger Si_6O_{18} rings within the Si_2O_5 sheets in reyerite. In the dehydration reactions of xonotlite and foshagite, the Ca–O parts of the structures undergo relatively little change, and one might expect that this would be true also with reyerite. However, the number of Ca^{2+} ions per unit volume is nearly twice as high in α-$CaSiO_3$ as in reyerite, and it seems almost certain that considerable movement of Ca^{2+} must occur. It does not therefore appear profitable to make any predictions about the positions of the calcium ions in reyerite on the basis of the present evidence.

The hypothesis of Si_6O_{18} rings linked into sheets by additional tetrahedra was also proposed for zeophyllite (Chalmers, Dent, and Taylor, 1958); in that case the anion appeared to have the empirical composition Si_3O_8. An anion of this composition does not, however, appear consistent with the chemical evidence in the case of reyerite. Moreover, the *a*-axis of zeophyllite, which is pseudohexagonal, is appreciably shorter (9·34 Å) than that of reyerite. Several possible modes of linkage of the rings in reyerite that would form a sheet of empirical formula Si_2O_5 have been considered but it has not so far been found possible to decide definitely which is correct. Some preliminary calculations based on 000*l* intensities have been made. These strongly support the assumption made here that most, and perhaps all, of the SiO_4 tetrahedra are oriented with one edge approximately parallel to the *c*-axis. This provides further support for the assumption that linked Si_6O_{18} rings occur.

Reyerite, truscottite, and synthetic preparations

Materials, optical data, and densities. A few new observations have been made on a sample of truscottite (BM 1925,1044) from the Lebong

Donok mine, Benkulen, Sumatra, which was kindly provided by the British Museum. Two synthetic preparations were also examined. These were prepared hydrothermally from mixtures of $Ca(OH)_2$ and SiO_2 gel, under the following conditions:

Preparation	Ca : Si ratio of starting materials	Hydrothermal treatment		
		Temp. (°C)	Pressure (kg/cm²)	Time (days)
A	0·60	255	225	27
B	0·57	222	23	19

Optical, X-ray powder, and electron microscope investigations of both these preparations showed that they consisted almost entirely of reyerite or truscottite. No unreacted silica gel was found in either preparation. Electron micrographs of specimen A showed a very small proportion of short laths, possibly xonotlite. Chemical analysis of this preparation showed 0·7 % of CO_2, but there were no definite indications of calcite under the optical or electron microscopes. Some optical and density data for preparation B and for natural truscottite are included in Table I.

Infra-red examination. Infra-red absorption spectra were determined as for reyerite, using both unheated samples and ones that had been heated in the KBr disk at 250° C. Figs. 3 and 4 include the results for one of the synthetic preparations (curves A) and for the natural truscottite (curves B), in each case before heating. The other synthetic preparation gave a closely similar curve to that shown (figs. 3A and 4A), which agrees well, in contour, with one reported by Meyer and Jaunarajs (1961) for a synthetic preparation described as reyerite.[1] Curve B agrees substantially with one reported by Hunt (1962) for truscottite from the same locality: this material is contaminated with a small proportion of quartz, which gives an absorption band at 694 cm^{-1}, and contributes to the truscottite absorption at 800 cm^{-1}.

There is a clear analogy between the spectra of the natural truscottite (curves B) and of the synthetic preparations (curves A), although the absorption bands of the natural material are slightly displaced from those of the synthetic preparations, and are much more poorly defined, perhaps owing to the substitution of a small amount of Al for Si in the natural mineral. The differences between the spectra of natural reyerite from Greenland (curves C), and the other two are so great as to suggest a marked difference in structure. There are appreciable differences in

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[1] There is an error in fig. 5 of Meyer and Jaunarajs' paper; the curves they give for gyrolite and synthetic reyerite have clearly been interchanged at wavelengths shorter than 4 μ. Further, the curve for synthetic reyerite appears to be displaced relative to the wavelength scale in the 7 to 13 μ region.

the Si–O bands, especially at 600–850 cm^{-1}: these absorption bands are associated with Si–O–Si linkages, and are sensitive to changes in Si–O–Si bond angles. Moreover, the Greenland reyerite appears to be richer in molecular water, and whereas the loss of this water caused distinct changes in its Si–O bands, this was not the case with the truscottite or synthetic preparations. With these specimens, the bands attributed to molecular water were lost on heating at 250° C, but there were no other changes at all in the spectrum of truscottite, and only a reversal of the relative intensities of the bands at 1159 and 1142 cm^{-1} in the spectrum of the synthetic preparations. On the other hand, the Greenland reyerite does have features in common with natural truscottite and the synthetic preparations, particularly in the 400–600 cm^{-1} region, and the absorption of their ionic hydroxyl groups occurs at identical frequencies, although that of natural truscottite is weaker and broader than the others.

The synthetic preparations showed bands at 1460 and 874 cm^{-1}, attributable to CO_3^{2-} ion. The position of the first of these bands differs significantly from that of all the known forms of $CaCO_3$ (Baron *et al.*, 1959), and the carbonate ions are presumably either adsorbed on the surface or contained in the structure of the material.

X-ray studies. X-ray powder photographs and diffractometer traces were obtained for the natural truscottite and the synthetic preparations, using the same experimental techniques as for the reyerite. The patterns agreed with each other but differed slightly from that of the reyerite. The results for one of the synthetic preparations, which gave the sharpest pattern, are included in Table IV. The pattern was indexed, for spacings above 1·43 Å, mainly by direct comparison with *c*-rotation photographs of natural truscottite. The results are essentially the same as those given previously for natural truscottite (Mackay and Taylor, 1954) but are more complete.

The differences between the pattern of truscottite or synthetic material and that of reyerite are partly attributable to a difference in cell parameters, which were found to be *a* 9·72, *c* 18·71 Å for truscottite as compared with *a* 9·74, *c* 19·04 Å for reyerite. There are also distinct intensity differences; in truscottite the line at 3·018 Å, in particular, is weaker relative to its neighbours than is the corresponding group of lines in reyerite.

Differences between truscottite and reyerite are also apparent on single-crystal photographs. The relative intensities of the 000*l* reflections were measured from Weissenberg photographs in the case of the natural truscottite and are compared in fig. 2 with the corresponding intensities for reyerite.

Mackay and Taylor (1954) reported that crystals of truscottite that had been heated to 770° C gave a weak and unidentified X-ray pattern with only slight preferred orientation; they did not give oriented α-$CaSiO_3$ in the same way as gyrolite (Mackay and Taylor, 1953) or reyerite. In the course of the present work, Mackay and Taylor's original X-ray photographs from the heated truscottite were re-examined. Their conclusion was incorrect; the pattern given by truscottite after heating at 770° C is of α-$CaSiO_3$, the orientation of which is the same as in the other cases.

Specimens from Japan and from Scotland. Two further natural specimens of reyerite or truscottite have been found, although neither has yet been described in the literature. Infra-red absorption spectra of each of these were determined. The first was from Biriyama vein, Toi mine, Toi town, Tagata-gun, Shizuoka, Japan, and was kindly provided by Professor R. Sadanaga. It gave a spectrum essentially identical with that of the Sumatra truscottite. The second was from Scotland (specimen 2294 from the collection at the Department of Mineralogy and Petrology, Cambridge), and was kindly provided by Dr. J. R. Cann and Dr. E. J. McIver. It gave a spectrum close to that of the Greenland reyerite, although the absorption bands were not quite as sharp. With both minerals, X-ray and optical studies gave results consistent with those obtained from the infra-red examination.

Discussion. The above results show that the truscottite from Sumatra and the synthetic preparations examined are closely similar to each other, but that they differ appreciably from the type reyerite from Greenland. The most marked differences are in the infra-red pattern, but there are differences also in refractive indices, density, length of *c*-axis, and relative intensities of various X-ray reflections. There may also be significant differences in composition, though this cannot be considered certain until better data have been obtained for natural truscottite and the role of the CO_3^{2-} ion in the synthetic preparations clarified. The latter preparations do not contain potassium; this may be an essential difference between truscottite and reyerite. For the present, it seems necessary to leave the question open as to whether truscottite should be regarded as a distinct mineral species.

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