

SYNTHESIS AND CRYSTAL CHEMISTRY OF
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ABSTRACT

Phase equilibria in the system $\text{CaSiO}_3\text{-SiO}_2\text{-H}_2\text{O}$ have been determined by using hydrothermal techniques. These experiments combined with dehydration studies of pure compounds have shown that reyerite has a composition $\text{Ca}_2[\text{Si}_4\text{O}_9(\text{OH})_2]$. Attempts to synthesize pure gyrolite were unsuccessful due to a gradual transformation of gyrolite to reyerite. During this inversion mixed-layer gyrolite-reyerite phases have been observed. On the basis of selected area electron diffraction patterns and (000 l) diffraction intensities it is concluded that both minerals must be composed of the same structural elements which probably have trigonal symmetry. These structural elements are stacked in a perfect way to form reyerite ($c=18.7 \text{ \AA}$). Due to a 60° rotation of successive layers the expanded gyrolite lattice ($c=22.1 \text{ \AA}$) is obtained. Gyrolite having the composition $\text{Ca}_2[\text{Si}_4\text{O}_9(\text{OH})_2]\cdot 3\text{H}_2\text{O}$ cannot be transformed into reyerite by dehydration. Therefore it has to be assumed that the elementary layers are undulating sheets. In gyrolite the layers are separated due to an improper fit so that molecular water penetrates between the sheets.

Electron microscopy and diffraction indicate that tobermorite appears as flaky and fibrous crystals.

INTRODUCTION

The mineral gyrolite was first described from Skye (Scotland) by T. Anderson in 1851. Chemical analysis indicated the mineral to be a hydrated calcium silicate with approximate composition, $2\text{CaO}\cdot 3\text{SiO}_2\cdot 3\text{H}_2\text{O}$. Gyrolite has since been found in other localities. In their comprehensive study of a natural gyrolite sample from Bombay (India), Mackay and Taylor (1953) concluded that the chemical formula of gyrolite is $2\text{CaO}\cdot 3\text{SiO}_2\cdot 2\text{H}_2\text{O}$. Their x -ray single crystal examination showed that the mineral is hexagonal with $a=9.72 \text{ \AA}$ and $c=132.8 \text{ \AA}$ ($=6\times 22.13 \text{ \AA}$). On being heated gyrolite loses water in two distinct stages. After heating to 450° C. about 75% of the water content is lost without appreciable changes in the crystal structure. The second dehydration stage is observed between 550° and 850° C. , where the rest of the water is lost. This step is accompanied by complete destruction of the structure. According to Mackay and Taylor (1953) the gyrolite crystal is thereby transformed in an ordered way to pseudowollastonite and to amorphous silica.

The mineral reyerite was discovered by Giesecke in 1811 in Greenland and was described and named by Cornu (1907). In 1914 Hövig described a hydrated calcium silicate mineral having the chemical composition $\text{CaO}\cdot 2\text{SiO}_2\cdot \frac{1}{2}\text{H}_2\text{O}$, which was named truscottite. The identity of this mineral and its relationship to reyerite was in doubt for many years until Strunz and Micheelson (1958) established that reyerite is identical

with truscottite. Although truscottite is a well established mineral name, the name reyerite actually has priority and will be used exclusively in this paper. Mackay and Taylor (1954) demonstrated that truscottite (=reyerite) from Benkulen (Sumatra) is a distinct mineral species, though one closely related to gyrolite. They confirmed Hövig's chemical formula and showed that reyerite has trigonal symmetry. The unit cell dimensions were found to be $a=9.72 \text{ \AA}$ and $c=18.7 \text{ \AA}$. Dehydration characteristics of this mineral are similar to those of gyrolite. About 50 per cent of the water is lost upon heating to 450° C. , apparently without affecting the crystal structure. The second dehydration step ends at about 850° C. , when the remainder of the water is lost. According to Mackay and Taylor (1954), this stage is connected with the formation of an unidentified, unoriented phase. After prolonged heating at 1000° C. the main products are wollastonite and cristobalite with a little pseudo-wollastonite.

Both reyerite and gyrolite have a trigonal or hexagonal unit cell with identical a -parameters ($a=9.72 \text{ \AA}$). Significant differences exist in the chemical composition, in the c -axis dimension, which is 18.7 \AA for reyerite and 132.8 \AA ($=6 \times 22.13 \text{ \AA}$) for gyrolite, and in the dehydration characteristics. Mackay and Taylor (1954) observed that 000 l reflections occur in strong and weak bands at similar θ values for both minerals. This and the identical a -parameters suggest that gyrolite and reyerite may have the same structural layer units. In a recent discussion by Mamedov and Belov (1958) of the crystal structures of mica-like calcium silicates the unit cell dimensions of gyrolite and reyerite reported by Mackay and Taylor (1954) were accepted. Strunz and Micheelson (1958) in a report on their study of calcium phyllosilicates indicated that gyrolite is a water-expanded reyerite. This hypothesis was reflected in the chemical formulas of the two minerals. Reyerite was assumed to have a CaO/SiO_2 ratio of 0.75 which leads to the idealized formula $\text{Ca}_{9/2}[(\text{OH})_3\text{Si}_6\text{O}_{15}]$. Gyrolite presumably has the same structural units separated by molecular water ($3\text{H}_2\text{O}$ per formula unit).

Flint, McMurdie and Wells (1938) attempted a synthesis of these compounds. They reacted mixtures of lime and silica under saturated steam pressures at 250° C. for 40 days and obtained gyrolite. From x -ray powder patterns they concluded that both species were identical. Peppler's experiments (1955) led to the conclusion that gyrolite was metastable with respect to xonotlite ($6\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$) and quartz. He did not observe reyerite as reaction product. Assarsson (1957) synthesized gyrolite under saturated steam conditions at temperatures between 160° and 220° C. , but found no reyerite in these samples. Most synthetic preparations of these authors were carried out in short periods of time only. Therefore, it

is probable that equilibrium was not attained, since hydrothermal reactions in the system $\text{CaSiO}_3\text{-SiO}_2\text{-H}_2\text{O}$ are frequently very sluggish. Due to this fact one cannot deduce the exact chemical composition of gyrolite from short hydrothermal runs. The synthesis of reyerite was recently reported by Buckner, Roy and Roy (1960) in their studies in the system $\text{CaSiO}_3\text{-H}_2\text{O}$. However, the stability range and composition of reyerite or gyrolite was not discussed.

In order to study the synthesis, stability and composition of gyrolite and reyerite, a systematic investigation of the phases in the system $\text{CaSiO}_3\text{-SiO}_2\text{-H}_2\text{O}$ was undertaken. The reactions were carried out mainly at saturated steam pressures for periods of time ranging from 24 hours to 4 months. Some runs were made under supersaturated steam conditions (up to 20,000 psi). The reaction products were examined using x -ray powder diffraction, electron microscope, electron diffraction, dehydration and infrared absorption methods. On the basis of the results obtained some conclusions have been reached about the relations between the synthetic compounds gyrolite and reyerite, and their relationship to the natural minerals. This relationship has great bearing on the chemical composition of gyrolite and reyerite.

SYNTHESIS AND IDENTIFICATION OF SAMPLES

Preparation of samples

Many substances which might be used as sources for silica are not suitable for hydrothermal reaction studies, either due to their low reactivity (e.g. pulverized quartz) or to undesirable impurities (diatomaceous earths). For these experiments silicic acid (Mallinckrodt, Special Bulky) was found to be sufficiently reactive and pure. It was used for most syntheses. A few runs were made using the much less reactive tripoli in order to duplicate several reactions reported by Flint, McMurdie and Wells (1938).

Calcium oxide, which was freshly prepared by igniting c.p. grade CaCO_3 at 1000°C . for about four hours, and c.p. grade Ca(OH)_2 , furnished the calcium for these reactions.

The two components at the desired CaO/SiO_2 ratios were thoroughly dry mixed in sealed containers before they were used for the reactions. After addition of 35 ml. distilled water to the dry-mixed starting materials the slurry was reacted in stainless steel vessels of 70 ml. capacity. The ratio of solid to liquid was varied between 1:3 and 1:20 in order to find the most reactive conditions. The reaction vessels were placed in a constant temperature oven equipped with a fan. A few high pressure reactions were made using equipment similar to that described by Tuttle (1948) which has separate controls for pressure and temperature. Sealed

platinum tubes containing the sample-water mixture were placed in stainless steel bombs for the reaction.

Several experiments were made using a Morey bomb of 20 cc. capacity in the temperature range of 340° to 425° C. and pressures up to 5000 psi. These runs were designed to determine the upper stability limit of reyerite. The starting material for these preparations was a well crystallized synthetic reyerite.

After reaction the products were removed from the vessel, immediately filtered, washed with acetone and dried in a CO₂-free atmosphere at 105° C. for one hour.

Composition of samples

Seven ternary phases are known to exist in the system CaSiO₃-SiO₂-H₂O. Six of these are natural minerals or mineral groups: gyrolite (2CaO·3SiO₂·2H₂O), reyerite (CaO·2SiO₂·½H₂O), okenite (CaO·2SiO₂·2H₂O), nekoite (CaO·2SiO₂·2H₂O), xonotlite (6CaO·6SiO₂·H₂O), and the tobermorite group (4-5CaO·5SiO₂·nH₂O). A synthetic ternary phase of variable composition has been called CSHI; it is related to the tobermorite group minerals (Heller and Taylor, 1951), but can be distinguished from tobermorite on the basis of its x-ray pattern. Okenite and nekoite have never been reported as synthetic phases.

Mixtures of CaO and SiO₂ having C/S ratios* from 0.5 to 1.0 were subjected to hydrothermal treatment. A list of significant runs is given in Table 1. In order to attain equilibrium rapidly, temperature or time must be increased, or a lower solid-to-liquid ratio may be used. The effects of these variables can be easily studied because the reactions are quite sluggish at lower temperatures. Attempts to increase the rate of reaction by employing high-pressure techniques were not successful (Table 2). A number of runs which were made to establish the upper stability limit of reyerite are also listed in Table 2.

Reaction products were obtained from samples with C/S ratios 0.5, 0.67, 0.74, 0.8, and 1.0, which were treated hydrothermally at temperatures between 145° and 320° C. The experiments were frequently extended over long periods of time in order to test the stability of a particular phase. If equilibrium is reached, the mineralogical composition is indicative of the chemical composition of the phases.

METHODS OF IDENTIFICATION

Since most phases formed under these conditions are extremely fine-grained, x-ray diffraction, differential thermal analysis, electron micros-

* Lime-to-silica molar ratio.

TABLE 1. LIST OF REPRESENTATIVE RUNS

Run No.	CaO/SiO ₂	Temp. ° C.	Press. psi	Time days	Solid/liquid	Starting Materials	Phases Present
1	0.50	170	114	6	1:3	CaO+silicic acid	CSHI (G)
2	0.50	180	145	7	1:9	CaO+silicic acid	G
3	0.50	188	174	3	1:9	CaO+silicic acid	G
4	0.50	220	336	14	1:3	CaO+silicic acid	G (R)
5	0.50	220	336	14	1:9	CaO+silicic acid	G, G+R
6	0.50	220	336	42	1:3	CaO+silicic acid	R, (G)
7	0.50	220	336	42	1:9	CaO+silicic acid	R+G
8	0.50	220	336	112	1:9	CaO+silicic acid	R
9	0.50	250	576	5	1:8	CaO+silicic acid	G
10	0.50	270	797	7	1:10	CaO+silicic acid	R (G)
11	0.50	282	958	7	1:10	CaO+silicic acid	R
12	0.50	300	1245	5	1:19	CaO+silicic acid	R
13	0.50	300	1245	30	1:30	CaO+silicic acid	R (X, α)
14	0.50	320	1600	8	1:10	CaO+silicic acid	R (α)
15	0.50	320	1600	7	1:10	Sample 14	R (α, X)
16	0.50	320	1600	17	1:10	Sample 15	R, X, α
17	0.55	300	1245	30	1:10	CaO+silicic acid	R (X, α)
18	0.60	300	1245	30	1:10	CaO+silicic acid	R (X, α)
19	0.60	320	1600	8	1:10	CaO+silicic acid	R
20	0.60	320	1600	8	1:10	Sample 19	R (α)
21	0.60	320	1600	15	1:10	Sample 19	R (α, X)
22	0.60	320	1600	25	1:10	Sample 19	R, X
23	0.66	220	336	14	1:6	CaO+silicic acid	CSHI, (G+R)
24	0.66	220	336	42	1:9	CaO+silicic acid	G+R
25	0.66	220	336	112	1:9	CaO+silicic acid	R+G
26	0.66	250	576	5	1:8	CaO+silicic acid	G
27	0.66	250	576	21	1:10	CaO+silicic acid	R, (R+G)
28	0.66	250	576	40	1:20	Ca(OH) ₂ +tripoli	X, R, T, Q
29	0.66	250	576	40	1:20	CaO+tripoli	Q, X, (T)
30	0.66	250	576	40	1:20	Ca(OH) ₂ +silicic acid	R (T, X)
31	0.66	250	576	40	1:20	CaO+silicic acid	R (R+G)
32	0.66	270	797	7	1:10	CaO+silicic acid	R (R+G)
33	0.66	300	1245	5	1:19	CaO+silicic acid	R (X)
34	0.67	300	1245	30	1:10	CaO+silicic acid	R, X
35	0.74	220	336	14	1:3	CaO+silicic acid	G (X)
36	0.74	220	336	42	1:9	CaO+silicic acid	R, G, (X)
37	0.74	220	336	112	1:9	CaO+silicic acid	X, G, R
38	0.8	220	336	14	1:9	CaO+silicic acid	X, (G)
39	0.8	220	336	42	1:9	CaO+silicic acid	X (G)
40	0.8	220	336	112	1:9	CaO+silicic acid	X (G)
41	0.8	250	576	5	1:8	CaO+silicic acid	X
42	0.8	270	797	7	1:10	CaO+silicic acid	X
43	0.8	300	1245	5	1:19	CaO+silicic acid	X (R)
44	1.0	90	Atmos	6 hr	1:9	CaO+silicic acid	CSHI
45	1.0	170	100	1 hr	1:9	Sample No. 33	CSHI, (T)
46	1.0	170	100	3 hr	1:9	Sample No. 33	CSHI, T
47	1.0	170	100	4 hr	1:9	Sample No. 33	CSHI, T
48	1.0	170	100	20 hr	1:9	Sample No. 33	T, (CSHI)
49	1.0	170	100	8	1:4	CaO+silicic acid	T, (CSHI)
50	1.0	250	576	5	1:8	CaO+silicic acid	X, CSHI, Ca(OH) ₂
51	1.0	300	1245	5	1:19	CaO+silicic acid	X

Abbreviations: G=Gyrolite
 R=Reyerite
 T=Tobermorite
 α=α-Cristobalite

X=Xonotlite
 R+G=Reyerite-gyrolite mixed layer material
 ()=minor amount present

TABLE 2. DATA ON HIGH PRESSURE OR HIGH TEMPERATURE RUNS

Run No.	CaO/SiO ₂	Temp. ° C.	Press. psi	Time hrs.	Solid/Liquid	Starting Materials	Phases Present
52	0.50	425	4000	192		Sample 2 (R)	R, α, X, W
53	0.50	420	4000	67		Sample 2 (R)	R
54	0.50	365	3500	192		Sample 2 (R)	X, R, α
55	0.50	367	3500	38		Sample 2 (R)	R
56	0.50	362	500	12		Sample 2 (R)	R
57	0.50	340	3000	240		Sample 2 (R)	X, R, α
58	0.5	210	20,000	30	1:2.3	CaO+silicic acid	(G)
59	0.5	220	20,000	4	1:2.3	CaO+silicic acid	(G)
60	0.5	220	20,000	7	1:2.3	Sample No. 2	G
61	0.5	230	20,000	6	1:2.3	Sample No. 2	G
62	0.5	240	20,000	3	1:2.3	Sample No. 2	G
63	0.5	265	15,000	15	1:2.3	Sample No. 2	R

Abbreviations: R = Reyerite
 X = Xonotilite
 α = α-Cristobalite
 W = Wollastonite

copy and diffraction, infrared spectroscopy and thermobalance methods were employed for identification.

X-ray powder diffraction

All phases which appear in the system CaSiO₃-SiO₂-H₂O can be identified by x-ray powder diffraction methods. A list of powder diffraction patterns of calcium silicates, which was found to be very accurate, has been collected by Heller and Taylor (1956). Due to the fact that gyrolite and reyerite have the same *a*-parameter, all (*hki*0) reflections have identical spacings. Differences between the two phases are most apparent in their (000*l*) reflections. It was found that tobermorite and CSHI can be distinguished on the basis of their strongest diffraction line, which has a spacing of 3.03 Å for CSHI and 3.07 Å for tobermorite. Kalousek (1958) used the same criterion. All other phases in this system have distinct powder patterns.

X-ray powder diffraction methods were used to study all reaction products. The results of this investigation have been incorporated in Table 1. Since it is quite difficult to detect minor components with this method, electron diffraction and microscopy were used to study samples, which were close to the ideal composition of the phases.

Electron diffraction and microscopy

Grudemo's examination of the synthetic phases formed in the system CaO-SiO₂-H₂O at low temperatures demonstrated the value of a combined electron microscopy-selected area diffraction study for a mineralogical characterization of reaction products. Such compounds are

frequently very fine-grained, and electron microscopy allows a morphological study of these phases. Many of the compounds which were investigated in the course of this work have similar habit; gyrolite, reyerite, and tobermorite always appear as thin hexagonal flakes, fibrous "tobermorite" and xonotlite as fibers. CSHI is present as "crumpled foils." In order to distinguish phases of similar morphology an identification of the crystals by selected area diffraction methods is absolutely necessary.

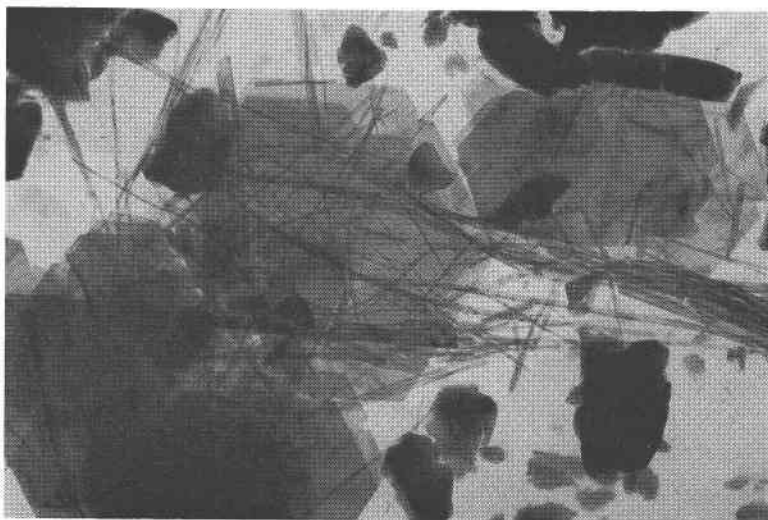


FIG. 1. Electron micrograph of synthetic tobermorite (24,000 \times)
Hydrothermal treatment of 0.8 C/S mixture at 170°C.

A typical electron micrograph of synthetic tobermorite is shown in Fig. 1. Selected-area electron diffraction of the platy phase (Fig. 2) gave a sharp ($hk0$) pattern of tobermorite ($a=11.2 \text{ \AA}$, $b=7.3 \text{ \AA}$). These crystals, always lying on (001) show strong pseudo-halving of b . The strong reflections can be indexed in terms of a pseudo-cell with $a=5.6 \text{ \AA}$ and $b=3.65 \text{ \AA}$. The weak reflections are elongated into streaks parallel to a^* while the maxima on these streaks appear in positions which are indexable on the basis of the larger unit cell. Similar features have been observed by Gard, Harrison and Taylor (1959) on their synthetic materials. It is interesting to note that the $00l$ spacing as determined by x -ray diffraction is 11.0 \AA and does not shift upon heating. A selected area diffraction pattern of the fibrous phase is shown in Fig. 3. It consists of strong arcs, which suggest a b -spacing of 7.3 \AA parallel to the fiber axis. A positive identification of this phase is not possible because the spacings

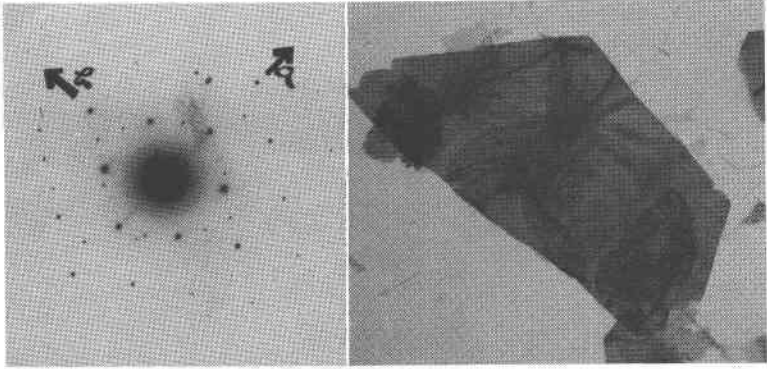


FIG. 2. Selected area diffraction pattern and corresponding micrograph (12,000 \times) of a platy tobermorite crystal. (C/S 0.8, 170°C.)

of the strong arcs correspond to either tobermorite or xonotlite. Some electron micrographs seem to suggest that the platy tobermorite breaks up parallel to its b -axis into these small fibers. Kalousek and Prebus (1958) and Gard *et al* (1958) have published such micrographs. Materials consisting exclusively of crinkled foils never give clear electron diffraction patterns. Their x -ray diffraction patterns always show a broad peak at 3.04 Å which is characteristic for CSHI.

Synthetic reyerite always consists of thin flakes. Selected area electron diffraction of this crystal gives a sharp, hexagonal pattern with $a = 9.7$ Å (Fig. 4). Intense peaks are indexed as $(20\bar{2}0)$, $(21\bar{3}0)$ and $(41\bar{5}0)$. A similar pattern is obtained from a synthetic gyrolite. Since natural reyerite was found by single crystal x -ray diffraction methods to have trigonal symmetry (Mackay and Taylor, 1953) which is in contrast to the present

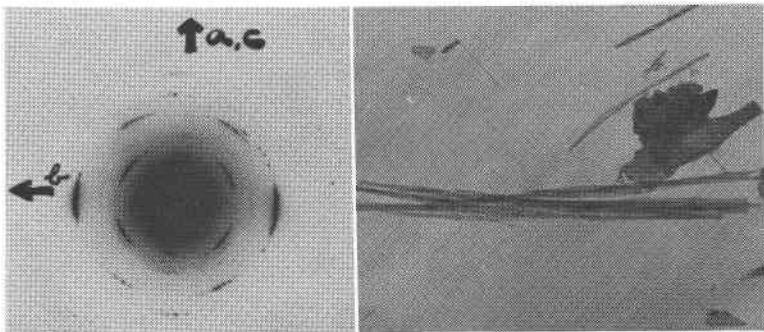


FIG. 3. Selected area diffraction pattern and micrograph (12,000 \times) of a bundle of tobermorite fibers (C/S 0.8, 170°C.)

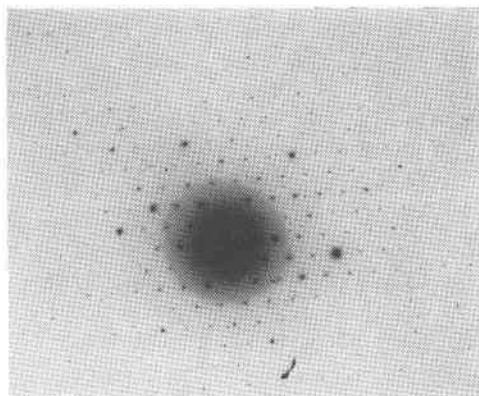


FIG. 4. Selected area diffraction pattern of synthetic reyerite (C/S 0.5, 300°C.) showing a sharp hexagonal pattern with $a=9.7 \text{ \AA}$.

findings on synthetic material, natural minerals were also investigated in the course of this study. Selected area diffraction patterns of gyrolite from Bombay, India (AMNH No. 12587) and of reyerite from Niakornak, Greenland (USNM No. 4016) were similar to the pattern in Fig. 4, in that both minerals have hexagonal Laue symmetry. A preliminary single-crystal x -ray study revealed that reyerite from Greenland is actually monoclinic, pseudo-trigonal. It is quite clear that gyrolite and reyerite are structurally related because the intensities and spacings of $(hki0)$ peaks are very similar. This similarity of the $(hki0)$ patterns is the reason why the two mineral species cannot be distinguished by selected area diffraction methods.

Xonotlite appears under the electron microscope as a bladed mineral. Electron diffraction methods always give $(hk0)$ Laue patterns with b as fiber axis.

Thermal dehydration characteristics

Differential thermal analysis and thermobalance curves were obtained from the synthetic phases gyrolite, reyerite, tobermorite, xonotlite and CSHI. X -ray powder diffraction methods were used to interpret the phase changes at elevated temperatures.

Upon heating to 200° C. gyrolite loses about 7% water, which corresponds to about two-thirds of its total water content. No structural changes were observed. The rest of the water is lost between 600° and 800° C. (about 4%). In the course of this reaction the gyrolite lattice is completely destroyed. After an exothermic reaction at 825° C., diffraction lines of wollastonite (β -CaSiO₃) appear and are strengthened by heat

treatment at higher temperatures. A trace of pseudo-wollastonite is frequently observed.

Reyerite experiences a water loss of about 1% at 200° C. without changes in crystal structure. The rest of the water (about 4%) is driven off between 600° and 800° C. In this temperature range the (*hki*0) reflections of reyerite, which are more stable than the (000*l*) diffraction peaks, slowly fade away while faint lines of pseudo-wollastonite (α -CaSiO₃) appear. After an exothermic reaction at 835° C. reyerite has been completely destroyed. Pseudo-wollastonite is now the major component. Often a small amount of wollastonite is detected.

Due to the fact that gyrolite and reyerite have a C/S ratio of less than 1.0, silica must be present in the high temperature phases. It was not detected, however, as a crystalline compound by *x*-ray diffraction methods. The present findings disagree with the observations on natural crystals by Mackay and Taylor (1953), who found that gyrolite is converted to pseudo-wollastonite and reyerite to wollastonite upon heating to 1000° C. It is possible that the difference between the high-temperature products of natural minerals and synthetic materials may be due to the grain size. A small crystal size could favor a rapid inversion of the initially formed pseudo-wollastonite to the stable wollastonite.

Synthetic tobermorite shows a partial dehydration if heated to about 500° C. This dehydration is not accompanied by a one-dimensional lattice shrinkage. At about 810° C. an exothermic reaction takes place during which the material is transformed to wollastonite. The synthetic material seems to correspond in that respect to the tobermorite from Loch Eynort, Scotland (Gard and Taylor, 1957).

Synthetic xonotlite is converted to wollastonite at about 800° C. This reaction is connected with the loss of hydroxyl groups.

Differential thermal analysis or thermobalance methods are not sensitive enough to detect mixtures of several components. A proper identification of such mixtures must be made by other means.

Infrared spectroscopy

A Perkin Elmer 12C spectrometer was used to obtain spectra in the range of 2 to 15 micron wavelengths. The samples were dispersed in mineral oil on sodium chloride sample plates. The resulting spectrograms were corrected for radiation curve, mineral oil, atmospheric water vapor, carbon dioxide and back scattering.

Infrared absorption spectra of xonotlite and tobermorite were discussed extensively by Kalousek and Roy (1957). Since our patterns corresponded closely to the ones presented by those authors, only gyrolite and reyerite curves will be presented here (Fig. 5).

The infrared absorption spectrum of synthetic reyerite (curve 1) shows that the stoichiometric water in this sample consists of hydroxyl ions (peak at 2.7 microns). In synthetic gyrolite (Fig. 5, curve 2) two kinds of (OH) can be distinguished; hydroxyl ions (peaks at 2.7 microns) and non-ionic (OH) groups (peak at 2.9 microns). The large amount of hydrogen bonding suggests that these non-ionic (OH) groups are present as water. This water is tightly bound, because the (OH) arm neither flexes nor rotates (no 6.7 micron peaks). A similar arrangement is found in layer silicates, such as vermiculite.

The main region of silicon-oxygen vibrations (between 8 and 12 micron

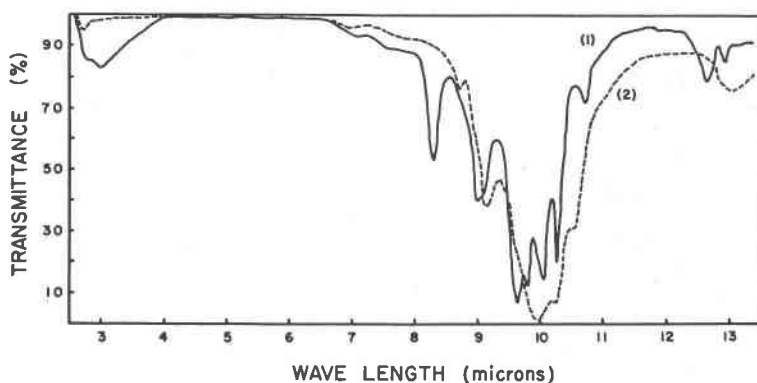


FIG. 5. Infrared absorption spectra of synthetic reyerite (curve 1) and gyrolite (curve 2).

wavelength) shows several absorption peaks. Synthetic gyrolite as well as the natural mineral exhibits broad overlapping peaks (curve 2). The natural mineral reyerite is characterized by a similar pattern. The broad absorption zones, which are indicative of gyrolite, are resolved into sharp peaks in synthetic reyerite (curve 1). The appearance of these sharp peaks suggests a perfection of the structural building plan. Since no shifts in the peak wavelengths, which would indicate changes in the effective bond strength, can be observed in the case of the most intense peaks, it has to be assumed that the structures of gyrolite and reyerite are indeed closely related.

Since gyrolite and reyerite have excellent basal cleavage, preferred orientation spectrograms were obtained. Such a method has been used by Serratosa and Bradley (1958) to determine the orientation of the OH-bond axis in some layer silicates. The present investigation showed that oriented and unoriented gyrolite gave the same absorption spectrum.

RESULTS

The composition of the samples, the reaction time and temperature, the solid-to-liquid ratio, and the phases as identified by *x*-ray diffraction methods, of significant experiments are listed in Table 1. A reasonable approach to evaluate such a number of experiments is achieved if the effects of temperature and time upon the course and rate of reaction are considered. In this way the stability of a phase or a phase assemblage can be critically studied; however, it is impossible to draw conclusions as to the chemical composition of the individual phases. Therefore the review of stability ranges will be followed by a brief discussion of the effects of varying C/S ratios upon the stable phase assemblages.

Samples with C/S=0.50

CaO and silicic acid are reacted at 320° C. (saturated steam pressure) for eight days. Reyerite is the major component together with a trace of α -cristobalite. After fifteen days the amount of α -cristobalite has increased and a trace of xonotlite is observed, while reyerite is still the main constituent. A prolonged treatment results in a decrease of the amount of reyerite and in a corresponding increase of the xonotlite and α -cristobalite content.

At temperatures between 270° and 300° C. and saturated steam pressures, CaO and silicic acid react to form first CSHI, then gyrolite and finally reyerite. Short runs at 300° C. (several hours) leads to a mixture of reyerite and gyrolite. After seven days only reyerite is found. After reacting the mixture for thirty days at 300° C., reyerite is the major component together with xonotlite and α -cristobalite. At lower reaction temperatures the time for a gyrolite-reyerite inversion becomes very important. At 220° C. (saturated steam pressure) pure reyerite is obtained only after a reaction period of four months. It is of interest to note that the transition of gyrolite to reyerite is characterized by the appearance of a mixed-layer phase (gyrolite-reyerite) in which the 000 l reflections become broad. This random-interlayered phase always shows fairly strong, non-integral diffraction effects which are characteristic of one-dimensional disorder. The (*hki*0) peaks always remain sharp. Below 220° C. the transformation time is appreciably increased. It should also be pointed out that a decrease in solid-to-liquid ratio speeds up the reaction. The lower limit of gyrolite synthesis is about 145° C.

In order to increase the rate of conversion from gyrolite to reyerite several samples were reacted at temperatures between 210° and 265° C. and at pressures between 15,000 and 20,000 psi. Samples, which were prereacted under saturated steam conditions at 180° C. for ten days, were subjected to high pressures. The results of this study listed in Table 2 indicate that the rate of conversion increased slightly. It is evident, however, that temperature is a much more important factor.

Samples with C/S=0.55

A hydrothermal reaction of CaO and silicic acid at 300° C. for thirty days led to the formation of reyerite with small amounts of α -cristobalite and xonotlite.

Samples with C/S=0.60

The phases obtained by reacting CaO and silicic acid at 320° C. after eight days are reyerite, after sixteen days reyerite plus a trace of α -cristobalite, after thirty-three days reyerite, α -cristobalite and xonotlite. At 300° C. and saturated steam pressure reyerite, α -cristobalite and xonotlite are detected after thirty days.

Samples with C/S=0.67

The phases obtained by reacting CaO and silicic acid under saturated steam conditions at 300° C. are reyerite and a small amount of xonotlite. At lower temperatures reyerite-gyrolite mixed-layer phases are very common. Short reactions lead to the formation of gyrolite, which is transformed to a mixed layer phase if the experimentation time is prolonged. Xonotlite was not observed in the low temperature reaction products. Electron micrographs reveal the presence of fibrous components, which were too small for selected area diffraction studies.

Several samples having a C/S ratio 0.67 were prepared using tripoli as the source of silica and Ca(OH)₂ or CaO as the source of calcium. These samples were reacted for forty days at 250° C. (saturated steam pressures). The results of these experiments listed in Table 1 indicate that tripoli is much less reactive than silicic acid. In fact, quartz (unreacted tripoli) is a major constituent of the reaction product, which consequently contains hydrated calcium silicates with a higher C/S molar ratio (xonotlite, tobermorite) in addition to reyerite. In comparison CaO and silicic acid formed mainly reyerite and a small amount of interlayered material. If Ca(OH)₂ is used, the resulting products are reyerite and small amounts of xonotlite and tobermorite. The formation of tobermorite seems to be favored by use of Ca(OH)₂ as starting material. These experiments clearly show that tripoli is not a suitable material for phase equilibria studies. The stable phases at 250° C. and forty days reaction time are reyerite and small amounts of xonotlite.

Samples with C/S=0.74

Mixtures of CaO and silicic acid were reacted only at 220° C. for extended periods of time. After 2 weeks gyrolite and a small amount of xonotlite appear. Reyrite and gyrolite were the major components after six weeks. A four months' reaction resulted in the formation of xonotlite, reyerite and gyrolite.

Samples with C/S=0.8

Hydrothermal reactions of CaO and silicic acid, which were carried out between 220° and 300° C., led always to the formation of xonotlite as main constituent. Above 250° C. reyerite is the minor component; below that temperature it is gyrolite.

Samples with C/S=1.0

Samples having this C/S molar ratio reacted above 180° C. to form pure xonotlite. Below this temperature tobermorite was the main component of long reactions. Short reaction times resulted in the formation of CSHI. A distinction of these phases was discussed earlier.

Reactions with synthetic reyerite (C/S=0.5)

A pure sample of reyerite was reacted in a Morey bomb in order to obtain some information concerning the upper stability limit of this material at relatively low pressures. The reactions are listed in Table 2. The results combined with previous experiments show that reyerite is transformed into xonotlite and α -cristobalite at saturated steam pressures above 300° C. The reaction is however quite sluggish. At 425° C. and 4000 psi wollastonite was also observed.

DISCUSSION OF SYNTHESIS

The results of the hydrothermal reactions lead to several important conclusions concerning the mineralogical relationship between reyerite and gyrolite.

The experiments carried out at 300° and 320° C. show conclusively that reyerite cannot have a C/S ratio larger than 0.6. At higher ratios xonotlite appears in the products indicating the presence of excess lime. On the basis of hydrothermal runs, it is, however, impossible to pinpoint the lime/silica ratio of reyerite, which may vary between 0.5 and 0.6. Since no crystalline silica appeared in *x*-ray diffraction patterns of the 0.5 material, the lime/silica ratio of 0.5 was taken as the reyerite ratio. This ratio corresponds to the one found by Mackay and Taylor (1954).

Reactions at lower temperatures indicate that CSHI is the first phase which is formed in a short time. An increase in reaction time leads to the formation of gyrolite, which is converted to reyerite after prolonged hydrothermal treatment. The rate of this transformation is dependent upon temperature and time, though high pressure and low solid-to-liquid ratio are minor accelerators. It is possible to stop this conversion, and the result will be a random mixed-layered material intermediate between reyerite and gyrolite. The transformation of gyrolite to reyerite takes about four months at 220° C. Gyrolite does not form below 145° C. The experiments further suggest that gyrolite is a metastable phase, while reyerite is actually stable above 145° C. This is the reason why gyrolite rarely occurs as a pure phase in nature.

Since gyrolite is metastable and is often converted partially to reyerite, it is impossible to determine its chemical composition by hydrothermal equilibrium studies. *X*-ray diffraction data may aid in a detection of mixed-layering, but only if interlayered phases are predominant. It has been observed that frequently gyrolite-reyerite mixed-layered phases contain only small amounts of one component, which does not alter the *x*-ray powder patterns appreciably. A good example is the natural mineral "truscottite" (reyerite) from Greenland which was investigated by single crystal *x*-ray diffraction methods. Non-integral basal reflections were observed which clearly indicate that this reyerite contains a small amount of gyrolite in interlayered positions. It is suspected that synthetic gyrolite would show similar interlayering features, if single crystals of appropriate size could be grown.

It was observed that the rate of conversion of gyrolite to reyerite is mainly dependent on the temperature. This is the reason why "purest" gyrolite should appear close to its lower stability limit (at about 145° C.). At this temperature, however, all reactions are very slow, so that the experimentation time has to be increased if a complete reaction of the raw materials is expected. Such an increase of reaction time will also enhance the formation of reyerite from metastable gyrolite, and therefore prevent the formation of pure gyrolite.

Another possibility to form gyrolite was briefly investigated. A sample

of synthetic reyerite was reacted at 200° C. (saturated steam pressures) for two weeks. It was assumed that reyerite would convert into gyrolite if gyrolite were a stable phase at that temperature, but no change in crystal structure was noted.

All these experiments demonstrate that it is impossible to determine the C/S ratio in synthetic gyrolite. The results further show that this molar ratio can vary between 0.5 and 0.67. At a ratio of 0.67 xonotlite appears together with gyrolite. Definite information can only be given for the reyerite ratio which is 0.5.

DISCUSSION OF THE GYROLITE-REYERITE RELATIONSHIP

X-ray and electron diffraction data

Hydrothermal experiments have shown that pure reyerite can easily be synthesized under saturated steam conditions. A synthesis of pure gyrolite was found to be impossible because this phase is metastable and converts to reyerite. This phase transformation passes through stages intermediate between the two end-members, which can be observed with great ease if the reaction is interrupted before reaching equilibrium. These intermediate phases are characterized by diffraction peaks which appear in non-integral positions along the (000 l) diffraction nodes. Since selected area electron diffraction studies demonstrate that the intensity and sharpness of the ($hki0$) diffraction spots do not change in the course of this conversion, it has to be assumed that the phase transition consists of a contraction of the lattice. This observation is confirmed by the consistent sharpness of the (2020) and (4150) peaks in x -ray powder patterns. The intermediate phases resulting from a partial shrinkage of the gyrolite lattice are, therefore, one-dimensional disorder structures. The fact that the ($hki0$) reflections of natural or synthetic gyrolite and reyerite have the same relative intensities and spacing (Fig. 4) leads to the conclusion that both mineral species are composed of layers which have exactly the same structure and composition. The same conclusion is reached if the intensities of the basal reflections are compared. Mackay and Taylor (1954) already noted that the basal reflections of gyrolite and reyerite appear strong and weak in identical bands at similar $\sin \theta/\lambda$ values, although the indices of corresponding intensities do not coincide. Such an intensity distribution is obtained only if both minerals are composed of essentially the same basic structural layers and differ but in the manner of stacking of such layers. The reyerite lattice represents then the tightest stacking of these structural layers ($c = 18.7 \text{ \AA}$), while gyrolite is composed of the same structural units, which are loosely stacked ($c = 22.1 \text{ \AA}$). Since the variations in intensity of the basal reflections of

both gyrolite and reyerite, plotted against $\sin \theta/\lambda$ values form a smooth curve, which is similar to the form-factor function curve for montmorillonite-organic liquid complexes (Bradley, 1953), it has to be assumed the interlayer space in gyrolite is filled with material of low scattering power, such as water molecules.

Single crystal studies of reyerite, which were presented by Mackay and Taylor (1953) strongly suggested trigonal symmetry for this mineral. Other specimens investigated by the same authors seemed to be hexagonal. Our electron diffraction studies revealed that all specimens had hexagonal Laue symmetry. The conflicting evidence can be explained, if it is assumed that the basic layers, of which both minerals are composed, actually have trigonal symmetry. Perfect stacking of these structural layers leads to a trigonal arrangement (reyerite), which sometimes may appear hexagonal if one basic layer is rotated against the other. In the case of gyrolite the structural layers are separated from each other probably by a layer of water molecules and may be rotated against each other by 60° . This rotation produces a hexagonal Laue symmetry.

Intermediate phases which have been observed are also composed of such structural layers. In their case the stacking arrangement corresponds partially to reyerite, which means several layers are perfectly stacked, and partially to gyrolite where layers are loosely arranged and have a wider c -spacing. Due to the imperfect stacking of the gyrolitic component these mixed-layer crystals appear to have hexagonal Laue symmetry, although their c -parameter may correspond nearly to reyerite.

Chemical composition of gyrolite and reyerite

Diffraction data have shown that both minerals are composed of the same basic structural layers, which must have the same chemical composition. Hydrothermal experimentation suggests that reyerite has a C/S ratio of 0.5. Dehydration studies reveal that only little water is lost below 600° C. (about 1%), which appears to be adsorbed molecular water. Between 600° and 800° C. a weight loss of about 4% is registered, which corresponds to the expulsion of hydroxyl water. The chemical composition of reyerite is therefore $\text{CaO} \cdot 2\text{SiO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, giving the formula $\text{Ca}_2[\text{Si}_4\text{O}_9(\text{OH})_2]$. Six molecules are present in the unit cells. The calculated density of 2.46 compares favorably with the observed density of 2.48. This composition corresponds to that proposed by Mackay and Taylor (1954); it is, however, in disagreement with the formula suggested by Strunz and Mischeelson (1958) who assume a C/S ratio of 0.75.

The chemical composition of gyrolite has undergone several revisions since the mineral was first described. Mackay and Taylor (1953) sug-

gested a C/S ratio of 0.67, while Strunz and Mischeelson (1958) propose a ratio of 0.75. The present investigation demonstrates that the exact C/S ratio cannot be deduced from hydrothermal experimentation. It can only be shown that the ratio has to be lower than 0.67. Additional information as to the chemical composition can be obtained from *x*-ray diffraction and dehydration data. Diffraction data clearly indicate that gyrolite is composed of the same basic layers which also occur in reyerite. These structural units, which are tightly superposed to form the reyerite lattice, have a C/S ratio of 0.5. If gyrolite had a C/S ratio higher than 0.5, that is, higher than these layers, the additional calcium would have to be located in the interstices between two adjoining reyerite-type sheets. Dehydration data show that about two-thirds of the total water content of gyrolite is lost below 200° C. The water loss does not affect the crystal structure indicating that the water is loosely bound interlayer water. Therefore, calcium ions, which could be present between layers, must be in exchange positions similar to ions between montmorillonite layers. The ion-exchange capacity of gyrolite is, however, on the order of 0.1 meq. per 100 grams. This value is much too low to account for an appreciable calcium content between the reyerite-type sheets. Since reyerite shows only a small water loss below 200° C., it cannot contain loosely bound interlayer water. Infrared spectrographs of the two phases confirm the observation that gyrolite contains water molecules which are not found in reyerite. The hypothesis that calcium may appear as a calcium hydroxide sheet between the basic layers cannot be maintained in the face of adverse evidence. The reasoning presented leads to the conclusion that gyrolite must have the same C/S ratio as reyerite. Consequently the chemical composition of gyrolite is $\text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The calculated density based on the hexagonal unit cell ($c = 22.1 \text{ \AA}$) which contains 12 molecules, is 2.35. This value is somewhat lower than the observed density of 2.39. It has been shown that gyrolite easily converts to reyerite at high temperatures and moderate pressures.

The formula of gyrolite is therefore $\text{Ca}_2[\text{Si}_4\text{O}_9(\text{OH})_2] \cdot 3\text{H}_2\text{O}$.

Dehydration of gyrolite and reyerite

The chemical formulae of gyrolite and reyerite clearly reflect the close relationship which exists between both phases. Actually they suggest that gyrolite could be a water expanded reyerite. The dehydration characteristics of the two minerals seem to support this view because they differ only in respect to their water loss at low temperatures (below 200° C.). A heat treatment of gyrolite up to about 400° C. will only remove interlayer water, which can be replaced by exposure of the material to the atmosphere. The gyrolite lattice, however, is not contracted

if the interlayer water is driven off. Yet both minerals show the same loss of hydroxyl water between 600° and 800° C., which indicates similarity of both structures. After heating to 825° C. gyrolite is converted to wollastonite (β -CaSiO₃) and amorphous silica. Reyerite is transformed to pseudowollastonite (α -CaSiO₃) and silica at 835° C. These observations on synthetic phases are in contradiction with the results obtained by using natural minerals (Mackay and Taylor, 1953).

The fact that gyrolite and reyerite are not converted to the same high-temperature phases, although both minerals seem to have similar lattices and composition, has been used as argument in favor of a different chemical structure for the two minerals. It will be shown that such a conclusion is not necessarily warranted and that the interpretation of these differences which result from the thermal treatment will also explain other contradictory evidence.

It has been demonstrated that gyrolite and reyerite are composed of the same basic structural units. In reyerite these basic layers, which probably have trigonal symmetry, are stacked in such a way that interstices are at a minimum. The structure of this reyerite type layer arrangement corresponds closely to the structural building plan of pseudowollastonite (α -CaSiO₃). Jeffrey and Heller (1953) have pointed out that pseudowollastonite has a triclinic unit cell which departs only slightly from a hexagonal symmetry ($a=6.85$ Å, $c=19.65$ Å). During the transformation of reyerite to pseudowollastonite the c -axis remains the same while the $(21\bar{3}0)$ direction of gyrolite (3.18 Å) coincides with the $(11\bar{2}0)$ direction (3.40 Å) of pseudowollastonite. This similarity of their structures favors a transformation of reyerite to pseudowollastonite, although the latter phase is stable only above 1125° C. (Muan and Osborn, 1952). In gyrolite the structural layers are separated by molecular water and show distinct rotational disorder. The bonds between these basic units must be weakened due to this enlargement of the interstices. Hence at 800° C. the gyrolite structure gives way to an amorphous material, from which wollastonite crystallizes, because it is the stable phase at this temperature. This reasoning shows clearly that the presence of different high temperature phases, which appear after a heat treatment of synthetic gyrolite and reyerite, can be explained on the basis of stacking differences of the same layers.

Strunz and Mischeelson (1958) suggested that gyrolite is a water-expanded reyerite. This hypothesis is indicated by chemical composition, x -ray and electron diffraction, infrared spectroscopy and in part by dehydration characteristics. It is only partially correct, however, because the heat treatment of gyrolite at 200° to 400° C., which removes the interlayer water, does not reduce the c -parameter to 18.7 Å. This sig-

nifies that gyrolite cannot be converted to reyerite by dehydration at atmospheric pressures. Therefore it has to be assumed that the interlayer water is not essential for the wider separation of the reyerite-type layers in gyrolite. It was suggested earlier that these structural layers may have trigonal symmetry. If successive layers are perfectly matched, the resulting crystal structure will be trigonal and will have a short c -parameter, (reyerite). An angular displacement of 60° of the successive layers will create hexagonal symmetry. Since this angular displacement is connected with a lattice expansion of about 3.4 \AA it must be assumed that the basic layers are undulating. Therefore the misalignment is responsible for the expansion of the structure. The interstices resulting from this misfit of undulating sheets are filled with molecular water which can be easily removed without changing the basic structure.

The actual structure of this reyerite-type layer has not been determined. Mackay and Taylor (1953) already noted that the a -parameter is much too large for a kaolinite-type or mica-type structure. Mamedov and Belov (1958) suggest that reyerite is composed of a silicate network, which consists of octagonal and pentagonal rings, and a closely packed layer of calcium octahedra. The silica tetrahedra of the network, which represents a condensation of wollastonite chains, are pointing upwards and downwards. This alternating position of the tetrahedral vertices gives the sheet an undulating effect. The symmetry of such a layer arrangement is not trigonal, however. Strunz and Micheelson (1958) propose that zeophyllite is a $\text{Ca}(\text{F}, \text{OH})_2$ -expanded reyerite. Such an interpretation requires a C/S ratio of 0.75 for reyerite, which cannot be confirmed.

CONCLUSIONS

The present investigation has shown that hydrothermal experiments may be used to determine the chemical composition of hydrated calcium silicates. The reaction in the system $\text{CaSiO}_3\text{-SiO}_2\text{-H}_2\text{O}$ revealed that reyerite has a CaO/SiO_2 ratio of 0.5. This composition agrees with the analytical results presented by Mackay and Taylor (1954), but differs from the formula given by Strunz and Micheelson (1958). At temperatures below 250°C . the reaction between lime and silica at saturated steam pressures as well as at supersaturated steam conditions is extremely sluggish, so that equilibrium is only attained after several months. Therefore it is nearly impossible to obtain pure low temperature phases (gyrolite, tobermorite). Several attempts to produce pure gyrolite were not successful, because gyrolite converted to reyerite before the raw materials were completely reacted. During the transformation of gyrolite to reyerite intermediate phases are detected, which are mixed-

layer minerals. Due to this conversion and due to the slow rate of reaction between lime and silica at low temperatures, it is impossible to determine the exact chemical composition of gyrolite on the basis of hydrothermal experimentation.

It had been demonstrated by Mackay and Taylor (1953) and by Strunz and Micheelson (1958) that gyrolite and reyerite are structurally related. Due to the fact that the basal reflections of both minerals follow the same form-factor function curve, it has to be assumed that the basic layers are the same for both mineral phases. The expansion of the lattice in gyrolite ($c = 22.1 \text{ \AA}$) compared to reyerite ($c = 18.7 \text{ \AA}$) may be due to interlayer water. Although gyrolite loses about two-thirds of its water below 200° C. , the lattice does not contract to the reyerite spacing. During this dehydration the relative intensities of the basal reflections do not change. Selected area diffraction patterns of gyrolite and reyerite show that the ($hki0$) reflections have the same intensities in both minerals. These observations support the hypothesis that both minerals are composed of the same unit layers, that they have the same chemical composition in respect to lime and silica. The individual layers have probably trigonal symmetry. Reyrite represents a close stacking of these basic layers, so that the trigonal symmetry is maintained and a small c -parameter is observed. If the basic layers are rotated 60° , a hexagonal symmetry of gyrolite is obtained. Due to the improper fit of the layers the lattice is irreversibly expanded and molecular water penetrates between the layers.

The idealized formula for reyerite therefore is $\text{Ca}_2[\text{Si}_4\text{O}_9(\text{OH})_2]$. The structure is trigonal ($a = 9.7 \text{ \AA}$, $c = 18.7 \text{ \AA}$). Gyrolite has the same composition except for molecular water: $\text{Ca}_2[\text{Si}_4\text{O}_9(\text{OH})_2] \cdot 3\text{H}_2\text{O}$. This structure is hexagonal having the same a -parameter.

The upper stability limit of reyerite at saturated steam pressures is about 300° C. At this temperature reyerite is slowly transformed into xonotlite and α -cristobalite according to the formula:



The appearance of wollastonite below 425° C. is in agreement with the findings of Buckner, Roy and Roy (1960).

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