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Structure and Polytypism in Synchysite and Parisite
from Mont St. Hilaire, Quebec

by

KOK KEONG CHEANG, B. Sc. (Hons.)

A thesis submitted to the Faculty of
Graduate Studies and Research in
partial fulfilment of the requirements
for the degree of Master of Science.

Carleton University

Ottawa, Ontario

April, 1977

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The undersigned hereby recommend to the Faculty of
Graduate Studies acceptance of this thesis, submitted by
Kok Keong Cheang, B. Sc.(Hons), in partial fulfilment of
the requirements for the degree of Master of Science.

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Chairman, Department of Geology

Supervisor

ABSTRACT

Analysis of synchysite from Mont St. Hilaire gave $(\text{La}_{0.25}\text{Ce}_{0.53}\text{Pr}_{0.04}\text{Nd}_{0.13}\text{Sm}_{0.01}\text{Y}_{0.02})\text{Ca}_{1.04}\text{F}_{0.97}\text{Cl}_{1.99}\text{O}_6$. The mineral is optically uniaxial with $\omega=1.648-1.650$, $\epsilon=1.740-1.744$; weakly pleochroic with ω light-yellow and ϵ yellow. Density=3.90 (meas.) and 3.908 g/cm^3 (calc.). It has a fair {001} cleavage and is readily soluble in dilute HCl. Analysis of parisite from the same locality gave $(\text{La}_{0.36}\text{Ce}_{1.00}\text{Pr}_{0.10}\text{Nd}_{0.40}\text{Sm}_{0.03}\text{Gd}_{0.03}\text{Y}_{0.07})\text{Ca}_{1.02}\text{F}_2\text{Cl}_3\text{O}_9$. The mineral is uniaxial $\omega=1.670-1.673$, $\epsilon=1.768-1.772$; weakly pleochroic with ω colourless and ϵ yellow. Density= 4.301 g/cm^3 (calc.). It has a fair {001} cleavage and is not attacked by concentrated HNO_3 .

TGA of synchysite in air (to 1000°C) shows two stages of weight loss (decarbonation), 19.5% between $220-650^\circ\text{C}$ and 7.5% between $650-870^\circ\text{C}$. F was essentially not liberated.

Synchysite exists in two trigonal polytypes with space group $P3_1$. The 12T polytype has $a=7.126$ and $c=55.08\text{\AA}$ whereas the 24T polytype has $a=7.126$ and $c=110.2\text{\AA}$. Parisite also exists in two trigonal polytypes with space group $P3_1$. The 18T polytype has $a=7.143\text{\AA}$, $c=84.33\text{\AA}$ and the 72T polytype has $a=7.143$ and $c=337.3\text{\AA}$. Both synchysite and parisite show three distinct pseudo-periods along c . Synchysite and parisite have similar, but distinguishable X-ray powder diffraction patterns, but polytypes of each mineral cannot be distinguished from each other by X-ray powder diffraction patterns.

The basic structural block of synchysite is essentially similar to that of bastnaesite but synchysite contains alternate CeF- and Ca- layers. The pseudo-periods arise because of the large degree of

freedom of the carbonate groups in choosing one of two possible sites and one of two orientations in each site. Polytypism in synchysite is a result of different ways of stacking identical sequences of carbonate groups in different orientations and in different sites.

The structure of parisite is derivable by stacking alternately, the synchysite slabs with the bastnaesite slabs in 1:1 ratio. Pseudo-periods and polytypism arise in the same manner as in synchysite.

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Dr. P. Mainwaring (Carleton University) and Dr. T.T. Chen (Mines Branch, Ottawa) performed the electron-microprobe analyses. J.L. Bouvier of the Geological Survey of Canada, provided the fluorine analyses.

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Introduction

Parisite ($\text{CaCe}_2(\text{CO}_3)_3\text{F}_2$ or $2\text{CeFCO}_3 \cdot \text{CaCO}_3$) was first discovered by J.J. Paris in 1835 at the emerald mines, Muso Valley, Colombia, where it occurred in veinlets in folded carbonaceous shales. Since then, parisite has been reported from a number of localities including Italy, U.S.A., U.S.S.R., Malawi and Canada. Synchysite ($\text{CaCe}(\text{CO}_3)_2$ For $\text{CeFCO}_3 \cdot \text{CaCO}_3$), first discovered by Flink in 1901 in pegmatitic veins at Narssarssuk, Greenland, has been reported from the Swiss Alps, Norway, Italy, Mongolia, U.S.A., and Canada. The name "synchysite" was derived from Greek roots meaning "mistake of identity" in allusion to the initial mistake in identifying this mineral for parisite.

The earlier literature on synchysite and parisite was largely concerned with whether or not synchysite was identical to parisite. In Nordenskiöld's treatise (1894), and in Flink's (1898) first report, the mineral was simply referred to as parisite. In Flink's second treatise (1901), he concluded that synchysite and parisite must be different minerals based on differences in their chemical compositions, cleavage properties, specific gravities (3.902 for synchysite, 4.364 for parisite), refractive indices and crystal forms (rhombohedral for synchysite, hexagonal for parisite).

However, in their detailed studies on parisite from Quincy, Massachusetts, U.S.A., Palache and Warren (1911) found that the

physical properties of synchysite given by Flink were essentially consistent with the properties of parisite they studied. They suspected that the synchysite of Flink might well be impure or partially altered parisite which would account for the difference in chemical composition and density. Consequently, Quersigh (1912), remeasured the refractive indices and redetermined the CaO content of synchysite from Greenland, using relatively fresh material. Quersigh's new data were more consistent with those for parisite than for synchysite, and were in strong support of the views of Palache and Warren.

Oftedal (1931a), by means of X-ray diffraction technique, showed that the distinct pseudo-cells for the two minerals were different, $a' = 4.09\text{\AA}$, and $c' = 18.20\text{\AA}$ for synchysite, and $a' = 4.094\text{\AA}$, and $c' = 27.93\text{\AA}$ for parisite. However, he did not specify the space groups of these minerals.

Finally, detailed crystallographical investigations by Donnay and Donnay (1953) clearly established the existence of synchysite as a member of a family of rare-earth fluocarbonates which included parisite, bastnaesite (CeFCO_3) and roentgenite ($\text{CaCe}_3(\text{CO}_3)_5\text{F}_3$ or $3\text{CeFCO}_3 \cdot 2\text{CaCO}_3$). They observed that a large proportion of the crystals studied were syntactic intergrowths of two minerals in this family. Thus, the earlier confusion may now be accounted for. The refractive indices of synchysite reported by Flink were probably measured from the parisite overgrowth on synchysite, and the synchysite analysed by Quersigh was probably mainly parisite.

According to Donnay and Donnay (1953), synchysite was either orthorhombic, or monoclinic with $\beta = 90^\circ$, and parisite, rhombohedral with space group R3. However, the space group of synchysite was not given. Both minerals displayed prominent, pseudo-hexagonal symmetry with several pseudo-periods along the c-axis, designated as c''' , c'' and c' . The dimensions of the true cell were, $a = 7.107\text{\AA}$, $c = 54.72\text{\AA}$ for synchysite and $a = 7.17\text{\AA}$ and $c = 84.11\text{\AA}$ for parisite.

The structures of minerals in this family were qualitatively described by Donnay and Donnay (1953) as based on stacking, in various proportions, of four different layers parallel to the basal plane. These layers are:

- 1) Ce, F layer
- 2) Ca layer
- 3) CO_3 layer between two Ce, F layers
- 4) CO_3 layer between a Ca layer and a Ce, F layer.

Recently, using electron microscopy and a multiple beam direct lattice imaging technique, Landuyt and Amelinckx (1975) confirmed qualitatively the nature of the layered structure of minerals in this family. In addition, they discovered two rhombohedral polytypes of parisite which differed only in the c-repeat distances (42Å and 84Å).

Preliminary X-ray studies of single crystals of synchysite

and parisite from Mont St. Hilaire revealed the existence of two new polytypes of synchysite and two new polytypes of parisite. The descriptions and structural interpretation of these polytypes form the bulk of this thesis.

Geological Occurrences

Synchysite

Narssarssuk, Greenland:

At the type locality, Narssarssuk, Greenland (Flink, 1901), synchysite was found in abundance in pegmatitic veins and segregations in syenite as small crystals 1-2 mm in length and about 0.5 mm wide. Lateral faces on these crystals are usually badly developed, but their bases are commonly glossy and shining. The colour is ash-grey to brown due to alterations. Synchysite occurs frequently with earlier-formed neptunite, epididymite, aegirine, and orthoclase, and also with albite, elpidite, fluorite, cordylite and polyolithionite all of which crystallized later than, or contemporaneously with synchysite.

Swiss Alps:

Parker et al. (1939) described the occurrence of synchysite in hydrothermal Alpine veins from the Val Nalps, whereas Iitaka and Stalder (1961) reported a rare synchysite-bastnaesite combination from the Grimsel granite at Oberaar. Minerals commonly associated with synchysite from the Swiss Alps included scheelite, columbite, wulfenite, monazite, xenotime, calcite, siderite, ankerite, apatite, fluorite, ilmenite, haematite, rutile, anatase, brookite, quartz, muscovite and sphene.

Norway:

Saebøe and Neumann (1961) documented the first Norwegian occurrence of synchysite from the Konsberg mine, while Raade (1969), reported an occurrence of white and red synchysite crystals from a Permian granite near the Nidre Eiker Church, Norway. At the latter locality, the associated sphene crystals were often altered to a mixture of synchysite, anatase, brookite, quartz and muscovite. The association synchysite- anatase, was considered important in elucidating the origin of synchysite.

Italy:

Emiliani and Gandolfi (1965) noted turbid, brownish-red synchysite occurring in the Predazzo granite in Italy. The mineral was described as "sometimes biaxial with a 2V of less than 10° and is yttrium-bearing". Synchysite here occurs with datolite, gadolinite, hellandite, ancylite and uraninite.

Mongolia:

Lozhinski (1971), documented a synchysite occurrence with francolite and calcite in the Havers' canals of dinosaur ribs from the Nemegt Valley in Mongolia. This occurrence is significant because the tendency of rare earth elements to concentrate in association with phosphorous and fluorine is clearly manifested, particularly in sedimentary rocks, in the fossilized debris of bone tissues.

Dover, New Jersey, U.S.A.:

Y-bearing synchysite (doverite) has been documented from

Dover, New Jersey (Smith et al., 1955). The ~~doverite~~ aggregates are confined to the coarser-grained and pegmatitic phases rather than with the host, albite-oligoclase granite. The mineral here is extremely fine-grained and occurs as irregular aggregates mixed with xenotime, haematite, apatite, bastnaesite, rutile, sphene, and quartz.

Canada:

Chao et al. (1967), identified the first Canadian occurrence of synchysite at Mont St. Hilaire, Quebec (described later) whereas Cerny and Bristol (1972) also reported synchysite from the Precambrian pegmatites in Manitoba. The associated mineral assemblages include bastnaesite, allanite, monazite, microcline, jamesonite, yttrotantalite, thorite and uranophane.

Parisite:

Muso, Colombia:

Parisite was first discovered in 1835 by J.J. Paris, owner of the emerald mines, Muso Valley, Colombia, where it occurred with pyrite, marcasite, cerian dolomite, albite, calcite, quartz, gypsum, and emerald, in veinlets and pockets of intensely folded, carbonaceous shale beds.

Italy:

Tacconi (1905) reported on the occurrence of parisite in veinlets in the riebeckite-granite at Montorfano, N. Italy.

There, parisite forms thin, hexagonal crystals generally embedded in a chlorite mass which is encrusted with stilbite and chabazite and associated with fluorite, pyrite and quartz.

Quincy, Massachusetts, U.S.A.:

Parisite occurs as small, 1-3 mm long, slender grains, in the riebeckite-aegerite granite at Quincy, Massachusetts (Palache and Warren, 1911), where it is associated with astrophyllite, microcline and aegirine crystals. They are most abundant in wide open spaces and pockets in the pegmatite pipes, but are also found as grains in massive rock.

U.S.S.R.:

Nefedov (1941) identified an yttroparisite found as small inclusions within fluorite in pegmatites of the Adun-Cholun district, Transbaikalia, U.S.S.R. The pegmatite veins form steep, pipe-like stockwork within granites. The main mineral assemblages include quartz, potash feldspar, albite, muscovite, black tourmaline, monazite, xenotime, apatite, calcite, scheelite, rutile, brookite and struverite.

Malawi:

According to Garson (1965), parisite occurred with cordylite, astrophyllite, monazite, synchysite, bastnaesite, calcite, ankerite, and strontianite, in apatite-rich carbonatites in Malawi. Bastnaesite and parisite are reported as small flakes, seldom exceeding 1 mm across, and are concentrated in cavities and druses.

Canada:

Mandarino and Tovell (1963), identified a pink to red parisite, found replacing long (up to 20 mm) bastnaesite, from the syenite pegmatites near Marathon, Canada. Parisite has recently been found at Mont St. Hilaire (Chao, personal communication), as tabular (0.3 x 1 x 1 mm) as well as long (2 x 2 x 3 mm) prismatic crystals displaying prominent, oscillatory growth.

Occurrence at Mont St. Hilaire, Quebec

The synchysite and parisite specimens used in this study were found in vugs and cavities at the Desourdy Quarry, located on the north-northeast slope of Mont St. Hilaire (Fig. 1).

Mont St. Hilaire, a plug-like, igneous, intrusive complex, is located about 32 km east of Montreal, Quebec. It is one of the nine Monteregian Hills which extend for about 120 km on an east-west curved trend, from the Oka complex on the west to Mont Brome on the east.

Mont St. Hilaire comprises two main intrusions: an earlier gabbroic rock, chiefly essexite (2), forms about sixty-five per cent of the western portion, whereas a porphyritic, nepheline-sodalite (5) complements the eastern half. The surrounding plain is underlain by shales (1) with thin, interbedded limestone layers. An igneous breccia zone (4), consisting of variable amounts of hornfels, marbles and essexite fragments as inclusions (3), encloses the syenite mass. The syenite body is frequently cut by numerous pegmatitic veins and camptonite dykes (Gold, 1963).

FIG. 1 GEOLOGICAL MAP OF MONT ST. HILAIRE.

(AFTER D. P. GOLD - 1962)

Numerous rare minerals, found only in a few similar occurrences such as the Kola Peninsula, U.S.S.R., Landesundfiord, Norway and the Narsarsuk-Kangerdluarsuk area in Greenland, have been reported to occur in the veins, vugs and inclusions in the nepheline-syenite body at Mont St. Hilaire (Chao et al., 1967). In particular, synchysite is found associated with bastnaesite, doubly-terminated siderite, calcite, albite, rutile, biotite and pyrite in carbonate vugs. In another occurrence, brownish-grey synchysite crystals associated with thomsonite are found on a large (6cm x 6cm) analcite crystal. Parisite is relatively rare at Mont St. Hilaire, and occurs with aegirine, microcline, albite, calcite, biotite, ancylite, transparent pectolite and sphene in silicate vugs. In one instance, tiny, curved, pinkish ancylite crystals are found growing on parisite.

Chemical Composition

Introduction

To date, only a few chemical analyses of synchysite and parisite are available in the literature. For those that are available, Donnay and Donnay (1953), questioned the reliability because of their frequent observation of syntaxitic intergrowth of several mineral species, on apparent single crystals of minerals in this group. They were of the opinion that it would be impractical to check a large number of crystals by single crystal X-ray diffraction method in order to obtain sufficient pure material for chemical or spectroscopic analyses. In this study, the problem of intergrowth was resolved by using the electron-microprobe to analyse synchysite and parisite crystal fragments (0.1 mm in diameter) the purity of which were previously checked by X-ray using a Gandolfi camera.

Experimental

The analyses for synchysite, P-1 - P-5 (Table 1), and for parisite, (Table 2), were performed by P. Mainwaring on a Cambridge MK5 electron-microprobe at an accelerating voltage of 15kv and a specimen current of 50 nanoamperes, whereas samples T-1 - T-5 for synchysite (Table 1), were analysed by T.T. Chen on a Materials Analysis Company (MAC) electron-microprobe at 20kv and a specimen current of 35 nanoamperes.

A preliminary qualitative scan was first made to survey

Table 1. Electron Microprobe Analyses of Synchysite from Mont St. Hilaire (wt %)

	P-1	P-2	P-3	P-4	P-5	T-1	T-2	T-3	T-4	T-5	Average
CaO	18.1	17.9	18.0	18.2	18.5	18.2	17.3	17.2	17.7	17.5	17.9
La ₂ O ₃	12.0	13.0	12.2	11.6	11.4	14.2	12.5	12.5	13.4	13.1	12.6
Ce ₂ O ₃	27.5	28.3	27.7	27.5	27.4	26.4	24.7	26.5	26.0	25.9	26.8
Pr ₂ O ₃	2.0	1.9	2.1	2.2	2.2	1.8	1.9	2.0	2.1	2.0	2.0
Nd ₂ O ₃	6.3	6.1	6.1	6.4	6.5	7.0	7.5	7.1	7.2	7.2	6.7
Sm ₂ O ₃	0.6	0.8	0.6	0.7	0.6	0.6	0.8	0.5	0.7	0.6	0.6
Y ₂ O ₃	0.6	0.6	0.6	0.7	0.4	0.6	0.5	0.7	0.6	0.6	0.6
*CO ₂	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0
*F	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
Total	99.8	101.3	100.0	100.0	99.7	101.5	97.9	99.2	100.4	99.6	99.9
O=F	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Corr. Total	97.4	98.9	97.6	97.6	97.3	99.1	95.5	96.8	98.0	97.2	97.5

*O₂ determined by TGA to 1000°C.

*F determined by pH measurements.

P-1 to P-5 Analyst P. Mainwaring

T-1 to T-5 Analyst T.T. Chen

Table 2. Electron Microprobe Analyses * of Parisite from
Mont St. Hilaire (wt %).

	P-6	P-7	P-8
CaO	10.8	10.6	10.3
La ₂ O ₃	19.8	10.8	14.3
Ce ₂ O ₃	28.8	30.5	32.6
Pr ₂ O ₃	2.0	2.9	2.8
Nd ₂ O ₃	6.8	12.6	8.2
Sm ₂ O ₃	0.7	0.8	0.7
Gd ₂ O ₃	0.7	0.9	0.8
Y ₂ O ₃	0.7	1.5	0.5
**CO ₂	24.5	24.5	24.1
**F	7.0	7.0	6.9
Total	101.8	102.1	101.2
O=F	2.9	2.9	2.9
Corr. Total	98.9	99.2	98.3

Number of Ions on the Basis of 90

Ca	1.04	1.02	1.01
La	0.66	0.36	0.48
Ce	0.95	1.00	1.09
Pr	0.07	0.10	0.09
Nd	0.22	0.40	0.27
Sm	0.02	0.03	0.02
Gd	0.02	0.03	0.02
Y	0.03	0.07	0.02

*Analyst P. Mainwaring

**CO₂ and F calculated from stoichiometry

the elements present for the selection of standards. The standards chosen were the rare earth-bearing synthetic glasses, REE1 (for Gd), REE2 (Nd, Sm), REE3 (La, Pr, Y), and synthetic CeO_2 (Ce) and a synthetic diopsidic augite (Ca). Because of the strong cratering effect on synchysite and parisite under the electron beam, the specimens were translated at a rate of $10 \mu\text{m}/\text{minute}$ during the counting process. Eight to twelve 10-second counts were collected for each element. The intensities of SmLa_1 and GdLa_1 were corrected for CeLa_2 and CeY_1 interferences using the $\text{CeLa}_2/\text{CeLa}_1$ and $\text{CeY}_1/\text{CeLa}_1$ intensity ratios obtained from the CeO_2 standard. The X-ray intensity data of each element were then computer-corrected for generation (atomic number), absorption and fluorescence effects, using an updated version of the program Emodr 7 by Rucklidge and Gasparri (1969).

The CO_2 content of synchysite was obtained from thermogravimetric analysis but that of parisite was not determined due to the small amount of material available and it was assumed to be stoichiometric. The F content of synchysite was measured with an ion-analyser by J.L. Bouvier, Geological Survey of Canada. The amount of F in parisite was not determined because parisite could not be brought into solution even when attacked with concentrate nitric acid. The accuracy in F determination was estimated at about $\pm 10\%$ of the amount present.

Discussion

It can be noticed from Tables 1 and 2, that the corrected total weight percent of synchysite and parisite analyses are respectively short of one hundred percent. This is attributed to the strong cratering effect of synchysite and parisite, when subjected to bombardment under the electron beam, resulting in a reduction of the total intensity counts of each element and hence, the final weight percentages. Furthermore, small amounts of other rare earth elements which may be present, but not within the detectability limit of the microprobe, may also have contributed to the lower values in the final total weights. This is in agreement with the observation that the atomic proportions of the total rare earth elements in both synchysite (0.98) and parisite (1.98; average of samples P-6, P-7 and P-8), are slightly less than 1 and 2 respectively.

The analyses of synchysite from Mont St. Hilaire (Table 1) show that the mineral is Ce-selective, essentially constant in composition and conforms closely to the ideal formula, $\text{CaCeF}(\text{CO}_3)_2$, Ce here being taken to include other members of the rare earth group and Y. The structural formula of synchysite, calculated from the averaged analysis on the basis of six oxygen atoms per formula, is $(\text{La}_{0.25}\text{Ce}_{0.53}\text{Pr}_{0.04}\text{Nd}_{0.13}\text{Sm}_{0.01}\text{Y}_{0.02})\text{Ca}_{1.04}\text{F}_{0.97}\text{C}_{1.99}\text{O}_6$. With this formula, assuming $Z=18$, and based on the refined cell parameters (see Table 1), the calculated density of synchysite is 3.908 g/cm^3 which agrees very well with the measured value of 3.90 g/cm^3 for synchysite from Mont St. Hilaire.

The only available chemical analyses for synchysite from other localities are on the material from Narssarssuk, Greenland, provided by Nordenskiöld and others (in Boggild, 1953) as shown in Table 3, where they are compared with the analysis of synchysite from Mont St. Hilaire. As shown by analyses 2 and 3, synchysite from Greenland typically contains minor amounts of Na and K in substitution of Ca. The relatively low values of CaO, CO₂ and F and relatively high value of Fe₂O₃ in analysis 2 are probably due to impurities in the sample analysed. The substantial amount of H₂O in analysis 4 is presumably in substitution for F and CO₃ groups. The number of ions in the formula of each synchysite analysis was recalculated on the basis of 6 O atoms as shown in Table 3. Sample 4, however, was calculated on the basis of 5 cationic charges.

Parasite from Mont St. Hilaire (Table 2) is also Ce-selective, and conforms closely to the ideal formula, 2CeFCO₃·CaCO₃, but the compositions of the individual rare earth elements Ce, La and Nd vary from sample to sample (Table 2) albeit the total rare earth elements is relatively constant for all samples. Assuming stoichiometric amounts of F and CO₂, the analysis of parasite (using sample P-7 as typical), based on nine oxygen atoms per formula, was recalculated to

Table 3. Comparison of Chemical Analyses of Synchysite from
Mont St. Hilaire, Quebec and Synchysite from
Narsarsuk, Greenland. (wt %)

	1	2	3	4
CaO	17.9	12.2	17.13	16.63
Na ₂ O	n.d.	1.5	0.19	-
K ₂ O	n.d.	0.7	0.12	-
Fe ₂ O ₃	n.d.	2.2	-	0.11
La ₂ O ₃	21.9	52.1	22.88	28.67
Ce ₂ O ₃	26.8		28.14	21.98
Y ₂ O ₃	0.6	2.5	1.23	1.18
Al ₂ O ₃	n.d.	0.7	-	-
CO ₂	27.0	23.0	26.54	25.99
F	5.7	5.1	5.82	5.04
H ₂ O	n.d.		-	2.10
Total	99.9	100.0	102.05	101.70
O=F	2.4	-	2.45	2.12
Corr. Total	97.5	100.0	99.60	99.58
Density (g/cm ³)	3.908	-	3.902	3.900

Number of Ions on the Basis of 6 O

Ca	1.0	0.75	0.99	0.94
Na	n.d.	0.17	0.02	-
K	n.d.	0.05	0.01	-
Fe ³⁺	n.d.	0.10	-	-
La	0.4	1.10	0.45	0.57
Ce	0.5	1.2	0.56	0.43
Y	0.0		0.04	0.03
Al	n.d.	0.05	-	-
C	2.0	1.81	1.96	1.89
F	1.0	0.93	1.00	0.85
OH	n.d.	-	-	0.32
H ₂ O	n.d.	-	-	0.21

1. Mont St. Hilaire, Quebec (This study).

2. Narsarsuk, Greenland (Nordenskiöld, 1894).

3. " (Flink, 1898).

4. " (Flink, 1901).

n.d. = not detected

La₂O₃ includes Pr₂O₃, Nd₂O₃, Sm₂O₃

The density of parisite, calculated from its structural formula, is 4.301 g/cm^3 and is essentially within the range of measured values reported elsewhere (Tables 4 and 6).

Chemical analyses for parisite from various localities are also shown in Table 4, for comparison with the typical (P-7) St. Hilaire result. Generally, the parisite analyses from the above localities (Table 4) are in fairly good agreement with those from Mont St. Hilaire with the exception of analysis 5 (Table 4), which is relatively low in CO_2 and F contents, and high in total rare earth contents. For each parisite analysis the number of ions was also calculated on the basis of 90 atoms (Table 4).

Table 4. Comparison of Chemical Analyses of Parisite from
Mont St. Hilaire, Quebec and Parisite from other localities (wt. %)

	1 (P-7)	2	3	4	5
CaO	10.6	10.44	10.70	11.40	10.10
Na ₂ O	n.d.	-	0.20	0.30	-
K ₂ O	n.d.	-	0.10	0.20	-
Fe ₂ O ₃	n.d.	-	0.25	0.32	-
La ₂ O ₃	29.5	30.33	29.24	27.31	18.00
Ce ₂ O ₃	30.5	30.56	30.67	30.94	44.21
*CO ₂	24.5	24.58	24.22	24.16	23.48
*F	7.0	7.07	6.82	6.56	5.55
H ₂ O	n.d.	-	0.10	tr	-
Gangue	n.d.	-	-	1.02	-
Total	102.1	102.98	102.80	102.21	101.34
O=F	2.9	2.98	2.87	2.76	2.34
Corr. Total	99.2	100.00	99.93	99.45	99.00
Density (g/cm ³)	4.301	-	4.302	4.320	4.358
	(Calc.)				

Number of Ions on the Basis of 9.0

Ca	1.0	1.00	1.03	1.09	0.97
Na	n.d.	-	0.04	0.05	-
K	n.d.	-	0.01	0.02	-
Fe	n.d.	-	0.02	0.02	-
La	1.0	1.00	0.98	0.90	0.60
Ce	1.0	2.0	1.00	1.01	1.45
C	3 (calc)	2.00	2.96	2.95	2.87
F	2 (calc)	2.00	1.93	1.85	1.57

- 1 Mont St. Hilaire, Quebec (This study).
- 2 Locality unknown (Palache et al., 1951).
- 3 Muso, Colombia (Warren, 1899).
- 4 Quincy, Massachusetts (Damour and Deville, 1910).
- 5 Muso, Colombia (from Palache and Warren, 1911).

tr = trace

n.d. = not detected

La₂O₃ includes Y₂O₃, Pr₂O₃, Nd₂O₃, Sm₂O₃

*CO₂ and F calculated

Thermal Studies

A Fisher Scientific 100 Thermogravimetric (TGA) system was used to study the thermal behaviour of, and to analyse the volatile components in synchysite. The samples used were cleaned by hand-picking under a binocular microscope and then finely ground. The purity of samples was checked by the X-ray powder diffraction method to ensure the absence of a significant amount of parisite which has been found frequently intergrown with synchysite from other localities. Runs were made both in air, and in vacuum, at a heating rate of 10°C per minute, using samples of approximately 12 mg. The maximum temperature attained was about 1000°C .

In air, synchysite undergoes two stages of weight loss (Fig. 2a) at temperatures between $220\text{--}650^{\circ}\text{C}$ (19.5%), and between $650\text{--}870^{\circ}\text{C}$ (7.5%). The total weight loss of 27.0% in air, is comparable with the amount of CO_2 , 27.6%, calculated from the ideal formula. At this stage, it was felt necessary to analyse the heated synchysite end-product for F, in order to check whether F was liberated with the CO_2 . The F content in the heated synchysite product, was determined with an ion-analyser to be 7.2% corresponding to 5.3% in the original material, and is in good agreement with the F content (5.7%) found in the unheated synchysite. Hence, it was concluded that the total weight loss in the TGA run must be solely due to decarbonation.

The total weight loss in vacuum was 25.7%, the smaller weight loss being attributed to the incomplete decarbonation

Fig 2b Differential Thermal Analysis Curve of Y-synchysite, Kirgizia (Semenov, 1959)

of synchysite. This was confirmed as the quenched end-product effervesced slightly in dilute, hydrochloric acid whereas the heated product, quenched in air, did not. Synchysite did not undergo complete decarbonation when heated in vacuum probably because insufficient time was permitted for the reaction to proceed to completion even though the temperature attained was at 1000°C . The lack of sufficiently pure material prevented a further TGA run in vacuum.

The quenched product of the TGA run in air showed no sign of melting at 1000°C and gave an X-ray powder diffraction pattern containing some relatively broad lines attributable to that of a mixture of $(\text{Ca, R.E.})\text{F}_2$, La_2O_3 and CaO . The superimposition of some of the lines in the powder patterns of individual compounds is thought to have contributed to the broadening of some of these lines. A sample of synchysite, quenched from 590°C in air on the TGA run, also gave a similar powder diffraction pattern, albeit the lines were slightly more diffused, suggesting that collapse of the synchysite structure started at the completion of the first stage of decarbonation. The products are the same as those of the material quenched from 1000°C .

The end-product of the TGA run, quenched in vacuum, showed no sign of melting, and gave an X-ray powder pattern corresponding to that of a calcium, rare earth fluoride $(\text{Ca, R.E.})\text{F}_2$. pH-measurements of the fluoride activity in the synchysite end-product, heated and quenched in vacuum, corresponded to 5.5% of F in the unheated synchysite, thus confirming that F was not

liberated at least up to 1000°C. This is probably because F combined with some Ca and R.E. to form $(Ca, R.E.)F_2$ which was stable at that temperature.

The two stages of weight loss in synchysite, both in air and in vacuum, can be correlated with the results of the differential thermal analysis (Fig. 2b) of yttrian-synchysite from Kirgizia, which showed a prominent endothermal inflection at 500°C and a minor peak around 600°C (Semenov, 1959). The lower temperatures at which these peaks occur are probably due to a slower heating rate in his DTA run, the overall effect of which, is to shift the peak positions towards the lower temperature end of the graph.

Physical Properties

Generally, synchysite and parisite occur as hexagonal, tabular crystals ranging in size from 0.5 to 1.00 mm in diameter with an average thickness of 0.5 mm. However, one larger (2x2x3 mm) parisite crystal, distinctly prismatic in habit, showed prominent oscillatory growth resulting in a pagoda-shaped appearance. Both synchysite and parisite are yellowish-brown with vitreous to resinous lustre and yellowish-white streaks. Both minerals have one set of fair {001} cleavage and hardness of 4-4.5 on the cleavage surface. The crystals of both minerals are opaque, but thin splinters are transparent. Synchysite dissolves readily in dilute hydrochloric acid at room temperature whereas parisite is not attacked even by concentrate nitric acid.

Optically, both synchysite and parisite are uniaxial positive, but may be locally anomalously biaxial with a small 2V of $0-8^{\circ}$ in synchysite and $0-7^{\circ}$ in parisite. 2V was estimated from crushed crystal fragments in conventional immersion mounts under the polarising microscope and were accurately determined to within $\pm 0.5^{\circ}$ on the spindle stage. Since both synchysite and parisite in this study were found to be trigonal, the biaxial characteristics observed in some of them may be attributed to structural strain, probably induced during mechanical crushing. Incidentally, synchysite with 2V less than 10° has been reported from the Predazzo Granite in Italy (Emiliani and Gandolfi, 1965).

Both synchysite and parisite are weakly pleochroic, with ω = light-yellow, ϵ = dark-yellow and hence, both these minerals exhibit absorption with $\epsilon > \omega$.

The refractive indices of synchysite and parisite from Mont St. Hilaire were measured at room temperature using a spindle stage and crystals previously oriented by X-ray method. Sodium vapour lamp was used as an illuminator. All refractive index liquids used were checked by using a refractometer.

Since the refractive indices α and β for grains displaying biaxial characteristics have essentially the same value, they are designated as ω . The refractive indices of synchysite are ω = 1.648-1.650 and ϵ = 1.740-1.744 whereas parisite has ω = 1.670-1.673 and ϵ = 1.768-1.772. Their birefringences of 0.092 (synchysite) and 0.098 (parisite) are comparatively high. Parisite has larger refractive indices than synchysite and hence, may be distinguished from it by this property.

The density of synchysite was measured with a Berman balance, at room temperature, on approximately 24 mg of material, and the mean of twenty determinations was taken. The density of parisite was not determined due to lack of material. The densities were also calculated using the formula:

$$D_x = \frac{Z \cdot M \cdot 1.6602}{V}$$

where D_x = density (g/cm^3)

V = cell volume ($\text{\AA}^3$)

M = formula weight (atomic weight units)

Z = number of formulae/unit cell.

The properties of synchysite and parisite from Mont St. Hilaire are summarized in Table 5.

The refractive indices of these two minerals from Mont St. Hilaire are well within the range of those reported for synchysite and parisite from other localities (Table 6). It is to be noted that the refractive indices of synchysite reported by Flink (1901) and Quersigh (1912) (Table 6) correspond to those of parisite instead, and the refractive indices for parisite from Muso, Colombia (Boggild, 1953) are much too low.

The density of synchysite crystals from Mont St. Hilaire was determined to be $3.90 \pm 0.05 \text{ g/cm}^3$, which is in excellent agreement with the calculated value of 3.908 g/cm^3 , and is well within the range of $3.90\text{--}3.94 \text{ g/cm}^3$ reported for synchysite from other localities (Table 6). The calculated density of parisite from Mont St. Hilaire, 4.301 g/cm^3 , is comparable with the observed values $4.30\text{--}4.40 \text{ g/cm}^3$ for parisite from other localities (Table 6). The low density (4.039 g/cm^3) of parisite from Switzerland is probably measured on specimens intergrown with synchysite.

Table 5: Properties of Synchysite and Parisite from
Mont St. Hilaire

Properties	Synchysite	Parisite
Size	0.5-1.0 mm diameter; 0.2-1.0 mm thick	0.5-2.0 mm wide; 0.1-3.0 mm thick
Form	hexagonal, tabular	hexagonal, tabular; sometimes prismatic
Colour	yellowish-brown	light-yellow to dark yellowish-brown
Lustre	vitreous, greasy	vitreous, resinous
Streak	light yellowish-white	faint yellowish-white
Cleavage	fair on (001)	fair to good on (001)
Reaction with acid	effervesces in cold, dilute hydrochloric acid	not attacked even by concentrate nitric acid
Density (g/cm^3)	3.90 ± 0.05 (meas.) 3.908 (calc.)	- 4.301 (calculated)
Refractive Index	$\omega=1.648-1.650 \pm 0.002$ $\epsilon=1.740-1.744 \pm 0.002$	$\omega=1.670-1.673 \pm 0.002$ $\epsilon=1.768-1.772 \pm 0.002$
Birefringence	0.092	0.098
Orientation	$X=a^*$, $Y=a$	$X=a^*$, $Y=a$
Optic Sign	Uniaxial+ve, locally anom. biaxial with $2V=$ $0-8^\circ$	Uniaxial +ve, locally anom. biaxial with $2V=0-7^\circ$
Pleochroism	weak, ω =light yellow ϵ =dark yellow	weak, ω =colourless ϵ =yellow
Absorption	$\epsilon > \omega$	$\epsilon > \omega$
Extinction	parallel to c-axis	parallel to c-axis

Table 6. Comparison of Refractive Indices and Densities of Synchysite and Parisite from Mont St. Hilaire and from other localities.

Locality	Synchysite		Parisite	
	Density (g/cm ³)	ω ϵ	Locality	Density (g/cm ³) ω ϵ
Narssarsuk, Greenland (Flink, 1901)	3.902	1.6742 1.7701 (Na)	Muso, Colombia, (Boggild, 1953)	4.358 1.569 1.670
Greenland (Quersigh, 1912 in Palache et al., 1951)	-	1.6730 1.7690	Quincy, Massachusetts, U.S.A. (Palache and Warren, 1911)	- 1.676 1.757
Switzerland, Parker et al. (1939)	3.940	1.649 1.74	Muso, Colombia (Palache et al., 1951)	- 1.6717 1.7712 (Na)
Transvaal, S. Africa (Sohnge, 1944 in Palache et al. 1951)	3.900	1.644 1.744	Muso, Colombia (Vrba in Boggild, 1953)	4.364 - -
Narssarsuk, Greenland (Donnay and Donnay, 1953) (calc. from ionic refractivities).....	4.15 4.05 3.99	1.650 1.745 $\pm 0.002 \pm 0.002$ 1.641 1.744	Greenland (Donnay and Donnay, 1953)	4.29 (calc.) $\pm 0.002 \pm 0.002$
Swiss Alps (Itaka & Stalder, 1961).	-	1.649 1.750	(calc. from ionic refractivities)	1.667 1.768
S. Malawi (Garson, 1965)	-	1.645 1.748	Switzerland (Graeser, 1965)	- 4.039
Mongolia (Lozinskii, 1971)	-	1.64	S. Malawi (Garson, 1965)	- 1.672 1.771
Mont St. Hilaire (This study)	3.90 $\pm$ 0.05 (meas.) 3.908 (calc.)	1.648- 1.650 1.740- 1.744 $\pm 0.002 \pm 0.002$ (Na) (Na)	Eastern Sayan (Somina et al., 1972)	4.37 1.672 1.760
			Unknown (Vlasov, 1966)	4.32 4.40 (calc.)
			Marathon, Canada (Man- darino & Tovell, 1963)	- 1.676 1.770
			Mont St. Hilaire (This study)	4.301 (calc.) 1.670- 1.673 1.768- $\pm 0.002 \pm 0.002$ (Na) (Na)

X-Ray Crystallography

Preparation and Orientation of the Single Crystals

The crystals of synchysite and parisite were crushed in a mortar and fragments, about $0.1 \times 0.2 \times 0.2$ mm in size, displaying at least partial cleavage planes or crystal faces, were selected, and mounted onto the tips of lead-free glass capillaries. Prior to X-ray studies, the crystal fragments of synchysite and parisite were checked for optical homogeneity on a spindle stage under the polarising microscope, to eliminate twinned crystals or polycrystals. After this preliminary screening of more than a hundred and thirty crystal fragments, only 25 fragments of synchysite and 20 fragments of parisite were found suitable for single crystal X-ray studies. Using the cleavage traces as a guide, each optically homogeneous fragment was adjusted so that a crystallographic axis was approximately perpendicular to the rotation axis of the goniometer head which was then mounted on the precession camera for the final alignment with the X-ray beam. Precession and Weissenberg photographs were taken with filtered $\text{MoK}\alpha$ ($\lambda = 0.7107\text{\AA}$) and $\text{CuK}\alpha$ ($\lambda = 1.5418\text{\AA}$) radiations. Because of the presence of very weak superlattice reflections which are important in the determination of space group symmetry, long exposures from 120 to 180 hours were used in some cases.

Pseudo-Periods and Cell Dimensions

Synchysite

For most crystals of synchysite from Mont St. Hilaire, three pseudo-periods along c^* are present which are identical to those found by Donnay and Donnay (1953) for synchysite from other localities. The pseudo-periods are best seen on 0-level a^* -precession photographs (Figs. 3 and 4) where the most intense layer lines (reciprocal lattice nets perpendicular to c^*) mark the pseudo-period c''' . Another well-marked pseudo-period c'' with $c''=2c'''$ is indicated by the medium-strong layer lines half-way between the most intense ones. The third pseudo-period c' ($c'=4c'''$) is marked by the layer lines of medium intensity half-way between the c'' layer lines and is more difficult to recognize. However, for a few synchysite grains, the a^* -precession photographs show an additional, but much fainter pseudo-period c_1 (Fig. 4) with $c_1=8c'''$, which has not yet been observed in synchysite from other localities. As the two varieties of synchysite are identical in other crystallographical aspects, differing only in the repeat distances, they must be considered two polytypes of synchysite and are designated as synchysite - 12T and synchysite - 24T, using notations of Ramsdell (1947). The former is the more common type and the latter is apparently rare.

The true c -repeats can only be obtained from long exposure upper level a^* - or a -precession photographs (Figs. 5, 6 and 7) which show that for both polytypes the two equally-spaced weak

Fig. 3. 0-level a^* -precession photograph of synchysite - 12T, showing the pseudo-periods c''' , c'' and c' without the extra superlattice reflection along the a^*c^* -net. ($\mu = 30^\circ$; Zr filtered $M\alpha$ radiation).

Fig. 4. 0-level a^* -precession photograph of synchysite - 24T showing the extra superlattice reflections c_1 , along the a^*c^* -net ($\mu = 30^\circ$; Zr filtered $\text{MoK}\alpha$ radiation).

Fig. 5. 2nd-level a^* -precession photograph of synchysite - 12T showing the extremely faint reflections (also observed in synchysite - 24T) which eliminated the mirror planes along the $a^* c^*$ - net as well as perpendicular to the c -axis. ($\mu = 30^\circ$; Zr filtered $\text{MoK}\alpha$ radiation).

Fig. 6. 0-level a-precession photograph of synchysite - 12T showing the extremely faint reflections which eliminated the mirror planes along the ac^* net as well as perpendicular to c . The true a is obtained from the faint row lines one-third the distance between the intense ones. ($\mu = 30^\circ$; Zr filtered $MoK\alpha$ radiation).

Fig. 7. 0-level a-precession photograph of synchysite - 24T showing the extremely faint reflections which eliminated the mirror planes along the ac^* - net as well as perpendicular to c . The true a is indicated by the faint row lines one-third the distance between the intense row lines ($\mu = 30^\circ$; Zr filtered $MoK\alpha$ radiation).

reflections occur within the c' pseudo-period along the row lines parallel to c^* . Thus, the true c for the 12T polytypes is $3 \times 4c'''$ or $12c'''$ and the true c for the 24T polytypes is $2 \times 3 \times 4c'''$ or $24c'''$.

Parisite

Similar to synchysite, parisite crystals from Mont St. Hilaire also display three pseudo-periods along c^* (Figs. 8 and 9) which are identical to those found by Donnay and Donnay (1953) for parisite from other localities. The c''' pseudo-period is the most pronounced and is also the basic pseudo-period. The other two pseudo-periods are less pronounced and are designated as c'' and c' with $c'' = 3c'''$ and $c' = 6c'''$. In addition to the three pseudo-periods in what might be called the "normal type" of parisite, some crystals studied showed a few extra weaker reflections suggesting two more pseudo-periods (Fig. 9). These extra reflections are here designated as c_1 and c_2 with $c_1 = 12c'''$ and $c_2 = 24c'''$. Because these extra reflections cannot be explained by twinning or by syntaxial intergrowth with another member within the bastnaesite-synchysite-parisite family, the second type of parisite crystals that display c_1 and c_2 pseudo-periods must be considered as a polytype of the "normal type" of parisite. The former is therefore designated as parisite - 72T and the latter, parisite - 18T according to Ramsdell's notation.

The true c -repeat of parisite - 18T and 72T are determined to be $3 \times 6c'''$ or $18c'''$ and $2 \times 2 \times 3 \times 6c'''$ or $72c'''$ respectively, as the upper layer a^* - and a -precession photographs (Figs. 10 and 11) revealed two additional equally-spaced weak spots

Fig. 8. 0-level a^* -precession photograph of parisite - 18T showing the pseudo-periods c''' , c'' and c' without the extra superlattice reflection along the a^*c^* - net. ($\mu=30^\circ$; Zr filtered $\text{MoK}\alpha$ radiation).

Fig. 9. 0-level a^* -precession photograph of parisite - 72T showing the pseudo-periods c''' , c'' , c' and the two extra superlattice reflections c_1 and c_2 (indicated by arrow heads) along the a^*c^* - net. ($\mu = 30^\circ$; Ni filtered $\text{CuK}\alpha$ radiation).

Fig. 10. 2nd-level a^* -precession photograph of parisite - 18T showing the extremely faint reflections (also observed in parisite - 72T) which eliminated the mirror planes along the $a^* c^*$ plane as well as perpendicular to the c -axis. ($\mu = 30^\circ$; Zr filtered $\text{MoK}\alpha$ radiation).

Fig. 11. 0-level a-precession photograph of parisite - 18T showing the extremely faint reflections (also observed in parisite - 72T) which eliminated the mirror planes along the ac^* -net as well as perpendicular to c . The true a is obtained from the faint row lines one-third the distance between the intense ones. ($\mu = 30^\circ$; Zr filtered $MoK\alpha$ radiation).

within the c' pseudo-period.

A pseudo-period is also observed along the a^* - direction for both polytypes of synchysite and of parisite from Mont St. Hilaire. This is consistent with the results found by Donnay and Donnay (1953) who reported a pseudo-period a' approximately $4.1\text{\AA}$ in synchysite and parisite from Greenland with the true a at 30° from a' and $a = a'\sqrt{3}$. But for the materials from Mont St. Hilaire, there are very faint row lines on long-exposure upper level a^* - axis precession photographs, suggesting that the true period may be tripled in both polytypes of synchysite and of parisite.

The preliminary parameters of the $a c'$ pseudo-cells of synchysite and parisite were measured from the precession photographs. These parameters were further refined by a least-square method (Hounslow and Chao, modified version, 1976) using powder diffraction data. The refined values are summarized in Table 7.

Space Group Symmetry

Synchysite

Both synchysite - 12T and 24T display prominent six-fold symmetries along the c -crystallographic directions of their ac' pseudo-cells as shown by precession photographs of the more intense reciprocal lattice layers (Fig. 12) as well as by the c -axis cone-axis photographs (Fig. 13). The Laue symmetry of the ac' pseudo-cell for both synchysite polytypes is $6/mmm$. However,

Table 7: Data for Synchysite and Parisite

Cell parameters (Å)	Synchysite (CeFeCO ₃ .CaCO ₃)			Parisite (2CeFeCO ₃ .CaCO ₃)		
	12T	24T	2	18T	3	4
a'	4.114	4.114	4.103	4.124	4.124	4.143
a = $\sqrt{3}a'$	7.126	7.126	7.107	7.143	7.143	7.176
c'	4.590	4.590	4.560	4.685	4.685	4.673
c''	2x4.590	2x4.590	2x4.560	3x4.685	3x4.685	3x4.673
c'	4x4.590	4x4.590	4x4.560	6x4.685	6x4.685	6x4.673
c ₁	-	8x4.590	-	-	12x4.685	-
c ₂	-	-	-	-	24x4.685	-
c	12x4.590	24x4.590	12x4.560	18x4.685	72x4.685	18x4.673
c/a	7.73	15.46	7.70	11.81	47.22	11.72
Space Group	P3 ₁	P3 ₁	Orthorhombic or monoclinic	P3 ₁	P3 ₁	R3
Volume of ac cell V(Å ³)	201.9x12	201.9x24	199.5x12	207.0x18	207.0x72	208.7x18
Molecular weight M.W.	316.85	316.85	319.23	536.29	536.29	538.37
Formula units per cell, Z	18	36	18	18	72	18
Density (g/cm ³)						
Dcalc.	3.908	3.908	3.99	4.301	4.301	4.29
Dobs.	3.903	3.903	4.05-4.15	-	-	4.05-4.41

1,3 - Mont St. Hilaire, Quebec (This study); All lengths expressed in Å units and known to ± 0.3%

2,4 - Narssarsuk, Greenland (Donnay and Donnay, 1953).

Fig. 12. 0-level precession photograph of synchysite - 12T (also synchysite - 24T) showing the 6-fold symmetry of the ac' pseudo-cell along the c -crystallographic direction. ($\mu = 30^\circ$; Ni filtered $CuK\alpha$ radiation).

Fig. 13. c^* cone-axis precession photograph of synchysite - 12T (also synchysite - 24T) showing the 6-fold symmetry of the ac' pseudo-cell. The darkest, innermost ring is the 0-level reciprocal lattice. ($\mu = 20^\circ$; Zr filtered $\text{MoK}\alpha$ radiation).

it is more difficult to determine the space group symmetry of the true cells because the superlattice reflections are too weak to be recorded clearly and the reciprocal lattice layers of the true cells are too closely spaced to allow complete isolation of a particular layer. Long exposure (up to 180 hours) a^* and a -axes precession photographs (Figs. 5, 6 and 7) brought out the faint reflections, which are sufficient to eliminate the presence of mirror planes of any kind but are too few in number to establish extinction rules and diffraction symmetry unequivocally. The lack of mirror planes of any kind in the synchysite diffraction patterns rules out all space groups in the hexagonal system, the Laue symmetry groups of which are either $6/m$ or $6/mmm$. As orthorhombic and monoclinic crystals yield mmm and $2/m$ Laue groups respectively, the lack of mirror planes also eliminates all space groups in the orthorhombic and monoclinic systems which Donnay and Donnay (1953) proposed for synchysite. It follows that the only space groups which are consistent with the X-ray diffraction data for synchysite are those in the trigonal system that yield Laue symmetry $\bar{3}$, namely $P\bar{3}$, $P\bar{3}_1$, $P\bar{3}_2$, $P\bar{3}$, $R\bar{3}$ and $R\bar{3}$.

A simple test for pyroelectricity on synchysite using liquid nitrogen method yielded negative results. Thus, the absence of a centre of symmetry can neither be established nor denied. Bastnaesite is very strongly piezoelectric (Wooster, 1931) establishing the absence of a centre of symmetry in this mineral. The structural resemblance of synchysite and parisite

to bastnaesite rules out centrosymmetric space groups for synchysite and parisite (Donnay and Donnay, 1953) and only $P3$, $P3_1$, $P3_2$ and $R3$ need further consideration. Despite the fact that the true lattice reflections of synchysite - 12T and 24T are too weak and too few to establish systematic extinction rules, the indices of those weak reflections that are present clearly violates the rule $-h+k+l = 3n$ for rhombohedral lattices. Thus, the space group $R3$ can be eliminated with confidence for both 12T and 24T polytypes. On long-exposure a^* - axis precession photographs, (Figs. 3 and 4) of both 12T and 24T polytypes the $00l$ reflections observed obey the rule $l=3n$ and are consistent with the extinction requirement for space groups $P3_1$ and $P3_2$, but not for space group $P3$. However, it is possible that some $00l$ reflections that do not satisfy the condition $l=3n$ are too weak to be recorded. Therefore, space group $P3$ cannot be totally disregarded. It is therefore concluded that the space group symmetry for synchysite - 12T and - 24T is most likely $P3_1$ or $P3_2$.

Parisite

The precession photographs of parisite - 18T and - 72T exhibit almost identical properties as those of synchysite,

- namely:
- 1) The ac' pseudo-cell displays ideal $6/mmm$ symmetry (Figs. 14 and 15)
 - 2) The weak superlattice reflections of the hkl type indicate the absence of mirror planes of any kind (Figs. 10 and 11)

Fig. 14. 0-level precession photograph of parisite - 18T (also parisite - 72T) showing the 6-fold symmetry of the ac' pseudo-cell along the c -crystallographic axis. ($\mu = 30^\circ$; Ni filtered $CuK\alpha$ radiation).

Fig. 15. c^* cone-axis precession photograph of parisite - 18T (also parisite - 72T) showing the 6-fold symmetry of the ac' pseudo-cell. The darkest, inner-ring is the 0-level reciprocal lattice. ($\mu = 20^\circ$; Zr filtered $\text{MoK}\alpha$ radiation)

- 3) The liquid nitrogen test for pyroelectricity confirmed the negative results reported by Oftedal (1931a, p.456).

The line of reasoning used for the space group determination for synchysite is also applicable to parisite. Thus, the most likely space group for both parisite polytypes is $P3_1$ or $P3_2$.

At this juncture, it is appropriate to point out that the rhombohedral synchysite ($c=12c'''$) and the two rhombohedral parisite polytypes (with $c=9c'''$ and $c=18c'''$) reported by Landuyt and Amelinckx (1975) may be designated as synchysite - 12R and parisite - 9R and - 18R respectively. Hence, to date, the known polytypes of synchysite and parisite are:

synchysite	parisite
12T	9R
12R	18R
24T	18T
	72T

X-ray Powder Diffraction Pattern

Although powder diffraction data for synchysite from a number of localities are available in the literature, reliable data for parisite are scarce. The powder diffraction patterns given for parisite in the literature are very similar to those of synchysite so that it may be difficult to distinguish the two minerals using the existing data. Besides, the frequent occurrence of syntactic intergrowth of minerals in this family casts some doubt on the purity of samples used.

Experimental

To avoid interference from other minerals in syntactic intergrowths with synchysite and parisite, crystal fragments of these minerals were checked with the Gandolfi camera for purity prior to the preparation of the powder diffraction films. The powder diffraction patterns (Tables 8 and 9) were taken with a 114.6mm diameter Debye-Scherrer camera and 0.3 mm collimator system using CuK_α ($\lambda=1.5418\text{\AA}$) radiation and Ni filter. The patterns were measured with a Kirem coincidence scale. The measured 2θ values were corrected for film shrinkage and camera diameter errors by using metallic Si as an internal standard. The powder patterns were indexed on the basis of the hexagonal ac' cell, using the single crystal photographs as a guide.

Discussion

Generally speaking, there are strong similarities in the overall

Table 8: X-Ray Powder Diffraction Data of Synchysize

hkl ac' cell	1/I ₀	1 d _{obs}	d _{calc}	1/I ₀	2 d _{obs}	1/I ₀	3 d _{obs}	1/I ₀	4 d _{obs}	1/I ₀	5 d _{obs}
002	80	9.17	9.180	60	9.1	100	9.1	ms	9.1	m	9.1
004	40	4.58	4.590	50	4.53	60	4.55	m	4.55	m	4.53
110	100	3.567	3.563	100	3.55	100	3.56	s	3.53	s	3.52
111	5	3.499	3.498	-	-	5	3.49	-	3.45	-	-
112	20	3.324	3.322	40	3.32	60	3.31	wb	3.30	vww	3.32
-	-	-	-	-	-	-	-	-	-	vw	3.13
006	10	3.061	3.060	30	3.07	20	3.07	wb	3.05	vw	3.03
-	-	-	-	-	-	20	3.04	-	-	-	-
-	-	-	-	-	-	-	-	-	-	vw	2.99
-	-	-	-	-	-	-	-	-	-	vww	2.85
114	100	2.812	2.815	100	2.80	100	2.81	s	2.80	s	2.78
116	5	2.323	2.322	20	2.30	20	2.31	vw	2.30	w	2.27
008	5	2.292	2.295	-	-	20	2.28	wb	2.28	vw	2.20
300	50	2.059	2.057	50	2.06	80	2.05	ms	2.04	ms	2.035
302	5	2.006	2.007	20	2.01	20	2.002	vww	1.995	vw	1.980
118	40	1.929	1.930	50	1.934	60	1.918	ms	1.916	m	1.908
304	40	1.878	1.877	40	1.873	80	1.870	m	1.863	m	1.861
-	-	-	-	-	-	5	1.821	vwb	1.824	-	-
220	10	1.783	1.782	10	1.777	20	1.781	m	1.772	w	1.768
222	3	1.750	1.749	10	1.749	20	1.749	w	1.727	vw	1.740
311	3	1.705	1.704	10	1.704	20	1.704	w	1.689	-	-
224	20	1.662	1.661	30	1.661	60	1.658	w	1.647	m	1.645
308	10	1.532	1.532	30	1.528	-	-	w	1.512	mw	1.519
1112	10	1.406	1.406	30	1.401	-	-	wb	1.395	mw	1.389
414	10	1.292	1.292	10	1.345	-	-	-	-	m	1.276

plus 19 lines
to 0.802 Å

1) Mont St. Hilaire, Quebec (This study); 114.6mm camera, CuK α radiation ($\lambda = 1.5418$ Å), Si internal standard, visual intensities

2) Predazzo Granite, Italy (Emiliani and Gandolfi, 1965); 57.65mm camera, CuK α radiation (1.542 Å), visual intensities. Indices in the original publication were based on an orthorhombic cell and may be derived from the indices adopted using the transformation matrix $\begin{matrix} 2/3 & 1/3 & 0 \\ 0 & 0 & 10 \\ 0 & 0 & 1/2 \end{matrix}$.

3) Quincy, Massachusetts, U.S.A. (Smith et al., 1960); 114.6mm camera, CuK α radiation ($\lambda = 1.5418$ Å); haematite lines removed. Transformation matrix to original cell as in 2.

4) Doverite (synchysite-Y), Dover, New Jersey (Smith et al., 1960); 114.6mm camera, CuK α radiation, ($\lambda = 1.5418$ Å); lines from xenotime, haematite, quartz and bastnaesite removed.

5) Synchysite-Nd, Kangasala, Finland (Vorma et al., 1966).

s = strong m = medium w = weak v = very b = broad

Table 9: X-Ray Powder Diffraction Data of Parisite

hkl ac' cell	I/I ₀	¹ d _{obs}	d _{calc}	I/I ₀	² d _{obs}	I/I ₀	³ d _{obs}
002	40	14.03	14.054				
004	20	7.02	7.027				
006	40	4.68	4.685				
110	100	3.565	3.572	70	3.55	70	3.55
112	10	3.455	3.461				
113	5	3.332	3.337				
114	20	3.188	3.184				
115	10	3.013	3.015				
116	100	2.838	2.840	100	2.83	90	2.86
210	15	2.338	2.338				
213	5	2.280	2.269				
1110	10	2.204	2.208				
301	80	2.060	2.057	100	2.04	80	2.04
218	40	1.951	1.946				
305	60	1.938	1.936	70	1.94	40	1.942
306	50	1.882	1.887	100	1.87		
308	20	1.777	1.778	70	1.77	20	1.772
224	5	1.732	1.731				
3010	40	1.663	1.663				
2112	50	1.658	1.655	100	1.65	60	1.655
0018	20	1.561	1.562				
3012	20	1.543	1.548	70	1.53	30	1.547
3111	5	1.425	1.424				
321	10	1.417	1.417	50	1.40		
3113	10	1.345	1.344	70	1.33	30	1.342
416	30	1.297	1.297	100	1.28	100	1.288
						30	1.160
						30	1.145
				Plus 6 lines to 1.05 Å			

1) Mont St. Hilaire (This study); 114.6mm camera; CuK α radiation ($\lambda = 1.5418 \text{ \AA}$); Si internal standard, visual intensities.

2) Muso, Colombia (Ofstedal, 1931a); in powder data file card 2-1257 ; 57.65mm camera, CuK α radiation ($\lambda = 1.539 \text{ \AA}$), visual intensities.

3) Ochsenfeld, Binnatal, Switzerland (Graeser, 1965).

powder patterns between synchysite and parisite. The similarity is especially noticeable with respect to the more intense lines which reflect the similarities in the crystal structure and the geometry of the ac''' cell of the two minerals. The differences in the weaker lines with respect to the number of lines, d -values and intensities are accountable by the difference in the c' and c'' pseudo-periods in synchysite and parisite. The powder diffraction patterns of the minerals may be easily distinguished by using the low θ reflections. Synchysite is characterized by an intense line at $9.1\text{\AA}$ whereas parisite is characterized by two moderately intense lines at $7.0\text{\AA}$ and $14.0\text{\AA}$. However, polytypes of each mineral cannot be distinguished from each other on the basis of powder diffraction patterns because the c_1 and c_2 type of reflections characteristic of the polytypes are all too weak to be recorded on the powder patterns.

It may be seen from Table 8 that the d -values in the pattern of synchysite from Mont St. Hilaire are similar to those of synchysite from Quincy, Massachusetts but are consistently larger than those for synchysite from other localities. The differences are attributable to compositional variations; synchysites from Mont St. Hilaire and Quincy are (Ce,La)-rich; those from Predazzo, Italy and New Jersey, U.S.A. are Y-rich; and that from Kangasala, Finland is Nd-rich. In pattern 4 (Table 8), the lines 3.13 and $2.85\text{\AA}$ which are absent in other patterns are probably due to gadolinite that is known to occur in close association with synchysite (Vorma et al., 1966). The line at $2.99\text{\AA}$ may be due

to allanite. The extra broad and faint $1.82\text{\AA}$ line present only in the powder patterns from Quincy and Dover, New Jersey, are probably due to haematite.

The powder pattern for parisite from Muso, Colombia and from Ochsenfeld, Binnatal, Switzerland contain only the strong lines as compared with the pattern of parisite from Mont St. Hilaire (Table 9). The absence of the weaker lines may be due to the design of the camera and/or very short exposures. Mandarino and Tovell (1963) listed the strongest lines of a pinkish-red parisite from Marathon, Canada as: $3.58(10)$, $2.850(10)$, $2.066(9)$, $4.71(8)$, $1.964(8)$, $1.891(8)$ and $1.671(7)$.

Structural Models Proposed for Synchysite and Parisite

Owing to the similarities in chemical composition, and the geometry of the pseudo-cells, and the frequent occurrence of syntaxic overgrowth among the minerals of this family, it has long been recognized that their structures are closely related (Oftedal, 1931a, Donnay and Donnay, 1953). However, there has been no detailed structural analysis of any member in the family using modern techniques probably for several reasons. Single crystals suitable for structural determination are difficult to obtain. The complicated pseudo-periods result in large true cells enclosing large numbers of independent atoms. It is now generally accepted that the end-member structures are those of a basic bastnaesite CeFCO_3 slab (B) and a basic synchysite slab (S) that contains a CeF-layer and a Ca-layer. The structure of other members in this family are composed of bastnaesite and synchysite slabs in various ratios, for example, parisite may be represented by BS with the ratio B:S = 1:1 and roentgenite by BS_2 with the ratio B:S = 1:2. Theoretically, structures with other B:S ratios are also possible and indeed, three new members recently discovered (Landuyt and Amelinckx, 1975) proved to have BS_4 , B_3S_4 and B_3S_2 compositions.

A structural model for bastnaesite was first proposed by Oftedal (1931a), and was significantly modified later by Donnay and Donnay (1953). Although the structure has not been refined and confirmed by modern crystallographic methods, it is nevertheless consistent with respect to X-ray diffraction data, symmetry,

spatial relationship, principle of electrostatic charge balance, and optical properties of the mineral. In the following paragraphs, the writer will endeavour to propose a structural model for synchysite and for parisite, in the light of the bastnaesite model of Donnay and Donnay (1953).

The Structure of Bastnaesite

Bastnaesite is hexagonal, $P\bar{6}2c$, with $a=7.162$, $c=9.787\text{\AA}$. The cell contains $6(\text{CeFCO}_3)$. The equipoint positions and coordinates (in order of x, y, z) of the atoms in bastnaesite determined by Donnay and Donnay (1953) are as follows:

F_1	2(a)	0,	0,	0
F_2	4(f)	1/3,	2/3,	0
Ce	6(g)	0.333,	0,	0
C	6(h)	0.245,	0.333,	1/4
O_1	12(i)	0.333,	0.333,	0.138
O_2	6(h)	0.067,	0.333,	1/4

The structure contains CeF layers at $z=0$ and $1/2$ (Fig. 16a) with the CO_3 group situated half-way between two CeF layers. Ce is coordinated with three F atoms (Fig. 16b) at $2.39\text{\AA}$, two O_2 atoms at $2.49\text{\AA}$ and six O_1 atoms at $2.74\text{\AA}$. Each F has 3 Ce neighbours with a triangular arrangement. The plane of the CO_3 group is vertical, parallel to the ac plane and that accounts for the large positive birefringence of the mineral. The height of the CO_3 group determines the value of $c/2$ so that $c/2$ is equal to the O_1-O_2 distance plus the O_1-O_1 distance or $4.89\text{\AA}$.

Fig. 16 The structure of bastnaesite (after Donnay and Donnay, 1953) showing (a) the Ce-F layer at levels $z=0$ and $z=1/2$, with carbonate groups at $z=1/4$ and $3/4$, and (b) a vertical section by plane $y=1/3$.

The Structure of Synchysite

Donnay and Donnay (1953), suggested that the structure of synchysite consists of CeF-layers and Ca-layers stacked alternately along the c-axis. The distance between a CeF-layer and the adjacent Ca-layer is $4.56\text{\AA}$, corresponding to the pseudo-period c'' . The basic repeat from one CeF-layer to the next is thus equal to c'' or $2c'''$ or $9.12\text{\AA}$. The CO_3 groups lie between a CeF-layer and a Ca-layer. The plane of the CO_3 group must be nearly vertical (parallel to the c-axis) as in bastnaesite in order to account for the large positive birefringence ($\epsilon - \omega = 0.092$). However, as the height of the CO_3 group is $4.89\text{\AA}$ and is considerably larger than that of a slab composed of a CeF-layer and a Ca-layer, Donnay and Donnay (1953) concluded that the plane of the CO_3 group must be tilted. They calculated the amount of tilt to be approximately equal to $\sin^{-1}(4.56/4.89)$ and erroneously gave the value of 11° whereas the true value is about 21° . Because of the uncertainty in space group symmetry, no atomic positions were proposed for the CO_3 groups.

In the construction of a structure model for synchysite from Mont St. Hilaire, the positions of the heavy Ce and Ca cations suggested by Donnay and Donnay (1953) are retained as shown in Figures 17, 18 and 19. The main problem is to fit the CO_3 group in the space group $P3_1$ within the framework of the bastnaesite structure. If one is to accept the assumption that the plane of the CO_3 group is tilted by about 21° , the birefringence of the crystal would be expected to decrease significantly. To a first

Fig. 17: (001) projection of the structure of synchysite - 12T within one c'' pseudo-period between $z=0$ and 0.083 showing the Ce-F layer at level $z=0$ with F_1 in site (b) and the two possible orientations of the carbonate group at height $z=0.043$ in site (a). Ca atoms at $z=0.083$ overlap with Ce in the projection.

Fig. 18: (001) projection of the structure of synchysite - 12T' within the ac''' pseudo-period between $z=0.167$ and 0.25 showing the Ce-F layer at level $z=0.167$ with F_2 in site (a) and the two possible orientations of the carbonate group at level $z=0.210$ in site (b).

Fig. 19: Schematic section of a portion of the crystal structure of Synchysite - 12T along plane $x=1/3$ showing the stacking sequences of the CeF and Ca layers and the positions of the CO₃ groups.

approximation, the contributions to the birefringence from Ce^{+3} , Ca^{+2} and F^{-1} ions can be ignored as the ionic refractivities R_ω and R_ϵ , according to Donnay and Donnay (1953), are negligibly small, $R_\epsilon - R_\omega$ for Ce^{+3} , Ca^{+2} and F^{-1} being 0.04, 0.00 and 0.00 respectively. The birefringence of the crystal may be considered wholly due to the CO_3 group for which $R_\omega = 9.58$, $R_\epsilon = 11.32$ and $R_\epsilon - R_\omega = 1.74$. Assuming elliptic variation of refractivity with vibration directions, the quantity $R_\epsilon - R_\omega$ for the CO_3 group tilted by 21° , is calculated to be 1.28, corresponding to a decrease of approximately 26% whereas the actual observed birefringence for synchysite is only a few percent less than that for bastnaesite. Thus, one is forced to the conclusion that tilting of the CO_3 group in the synchysite structure is not acceptable. This conclusion is also supported by considerations of the spatial relationships. Any significant amount of tilt of the plane of the CO_3 group would shorten the packing distance of O-F and force the F atoms to move out of the CeF plane. In addition, the oxygen atoms would also interfere with the Ca atoms resulting in unreasonable interatomic distances. Therefore, in fitting the CO_3 group within the framework of the bastnaesite structure, the basic assumption adapted is that the plane of the CO_3 group must be vertical or very nearly vertical.

The fact that the space group $P3_1$ to which synchysite belongs, is a subgroup of $P6_2c$ with all symmetry operators suppressed except 3_1 , provides a much greater degree of freedom for fitting the CO_3 group. For instance, for a CeF layer at height z , with

the symmetry restrictions removed, the F atoms may either assume sites (a) at (0,0), (1/3,2/3) and (2/3,1/3) as shown in Fig. 17, or sites (b) at (1/3,1/3), (0,2/3) and (2/3,0) (Fig. 18) without altering the overall configurations. Similarly, the CO₃ groups immediately above and below the CeF layer may either occupy sites (b) or (a). In addition, in each site at (a) or (b), the CO₃ group may further choose between two orientations (Figs. 17 and 18). These different orientations are from here on referred to as 1 and 2 in (a)-sites, 3 and 4 in (b)-sites. Thus, by alternating F atoms in sites (a) and (b) in adjacent CeF layers as in the present structure model of synchysite, it is made possible for the CO₃ group to assume a vertical orientation as predicted from the observed birefringence in synchysite. The only adjustment needed is a rotation of the CO₃ group within its own plane by approximately 4.7° about the centre of the oxygen atom (O₁, O₆, O₇ and O₁₂, Fig. 19) that is in touch with three fluorine atoms. The rotation of the CO₃ group is in a direction away from the Ca atoms and towards the Ce atoms to avoid a slightly too short approach between the oxygen and Ca atoms.

As the CO₃ groups have two degrees of freedom in each of the (a)-sites (orientations 1 and 2) and the (b)-sites (orientations 3 and 4), the four independent CO₃ layers within an asymmetric cell of synchysite - 12T may give a total of 2⁴ or 16 possible stacking sequences. However, some stacking sequence pairs are related by an inversion operation such as 1342 and 2431 or 1341 and 1431 and therefore must be considered identical and one of each pair must be eliminated. Other sequences such as 1331, 1441,

2332 and 2442 produce structures with horizontal mirror planes and therefore, are not possible sequences for synchysite. Thus, of the sixteen sequences, there are only six different, but equally acceptable sequences, namely: 1332, 1342, 1432, 1442, 1341 and 2432. In this thesis, the sequence of 1342 is chosen arbitrarily to represent the structure of synchysite - 12T (Fig. 19).

The proposed atomic parameters for synchysite - 12T are given in Table 10. The parameters for C and O atoms were calculated on the assumption that they form a rigid equilateral triangle with O-O distance of $2.19\text{\AA}$ (Donnay and Donnay, 1953) and C-O distance of $1.264\text{\AA}$. The shortest O-O approach between oxygen atoms from two different CO_3 groups was assumed to be $2.70\text{\AA}$.

The structure of synchysite - 24T may be derived from the structure of synchysite - 12T by stacking successively any two different stacking sequences such as 1342 and 1332 which would produce the extra c_1 type superlattice reflections and cause the doubling of the c-axis. The rhombohedral 12R polytype may also be derived from the 12T polytype by displacing the successive stacking sequences by $1/3$ along the a-axis. The relationship of the three polytypes are schematically shown in Fig. 20.

Furthermore, if two adjacent cells on the same level start with different packing sequences, superlattice reflections along the a^* -directions would occur resulting in multiplying of the a-axis. Superlattice reflections of this nature, have indeed, been observed on photographs of some synchysite crystals.

Table 10: Predicted Atomic Parameters for Synchysite - 12T

Atom	x	y	z	Atom	x	y	z
Ce 1	0.333	0	0	01	0.333	0.333	0.024
2	0.333	0	0.167	2		0.308	0.064
3	0	0.333	0	3		0.308	0.064
4	0	0.333	0.167	4		0.692	0.103
5	0.667	0.667	0	5		0.944	0.125
6	0.667	0.667	0.167	6		0.667	0.142
				7	0.333		0.191
Ca 1	0.333	0	0.083	8	0.611	0.667	0.209
2	0.333	0	0.25	9	0.359		0.231
3	0	0.333	0.083	10	0.308	0.333	0.269
4	0	0.333	0.25	11	0.056		0.291
5	0.667	0.667	0.083	12	0.333		0.309
6	0.667	0.667	0.25	13	0.667	0	0.024
				14	0.944	0.277	0.042
F 1	0.333	0.667	0	15	0.692	0.025	0.064
2	0.333	0.333	0.167	16	0.308	0.641	0.103
3	0	0	0	17	0.056	0.389	0.125
4	0	0.667	0.167	18	0.333	0.667	0.142
5	0.667	0.333	0	19	0.333	0.667	0.191
6	0.667	0	0.167	20		0.944	0.209
				21		0.692	0.231
C 1	0.333	0.232(4)	0.043	22	0.667	0.975	0.269
2	0.333	0.768	0.124	23		0.723	0.291
3	0.435	0.667	0.210	24		0	0.309
4	0.232	0.333	0.290	25	0	0.667	0.024
5	0.768	0.101	0.043	26	0.723		0.042
6	0.232	0.565	0.124	27	0.975		0.064
7	0.333	0.768	0.210	28	0.359		0.103
8	0.667	0.899	0.290	29	0.611		0.125
9	0.899	0.667	0.043	30	0.333		0.142
10	0.435	0.667	0.124	31	0.333	0.667	0.191
11	0.245	0.565	0.210	32	0.056	0.389	0.209
12	0.101	0.768	0.290	33	0.308	0.641	0.231
				34	0.025	0.692	0.269
				35	0.277	0.944	0.291
				36	0	0.667	0.309

Legend:

 Ce-F layers

 Ca layers

1, 2, 3, 4 positions of carbonate groups

Fig.20 Schematic representations of stacking sequences in synchysite: (a) -12T (1342), (b) -12R (1342) and (c) -24T (13421332). The numerals 1 and 2 represent the two possible orientations in the (a)-sites, and 3 and 4, the two possible orientations in the (b)-sites.

Interatomic Distances and Valence Summation in Synchysite - 12T

In the proposed structure of synchysite - 12T, the Ce atoms are strongly bonded to three F atoms at 2.38 Å and two O atoms at 2.35 Å forming a distorted trigonal bipyramid. In addition, they are weakly bonded to six oxygen atoms at a larger distance of 2.73 Å. The Ca atoms are surrounded by eight oxygen atoms, two at 2.35 Å, three at 2.45 Å and three at 2.45 Å forming a slightly distorted rhombohedron. The different orientations of the CO₃ groups do not change the interatomic distances nor the coordination configurations. A listing of the interatomic distances within the c''' pseudo-period is given in Table 11. The interatomic distances within the rest of the true ac cell are identical to those within the c''' pseudo-period as the structure is built up by repeating the c''' slab with different CO₃ orientations. The fact that all the bond lengths fall well within the range of values found in other compounds (Table 11) serves as a support of the proposed model.

A further check on the validity of the proposed model is provided by the valence summation using the method of Donnay and Allmann (1970). The method is, in fact, a modification of the Pauling second rule which deals with local and overall electrostatic charge balance in ionic compounds. The distribution of bond valences or bond strengths of Pauling are weighted by the interatomic distance according to the following equations.

$$(1) \text{ For } L \leq \bar{L}, v = v_i (\bar{L}/L)^p ;$$

$$(2) \text{ For } \bar{L} \leq L \leq L_{\max}, v = v_i (L_{\max} - L / L_{\max} - \bar{L}) ,$$

Table 11: Estimated Bond Lengths (Å) and Bond Valences (v.u.) in Synchysite

Anion \ Cation	XI _{Ca1}	XI _{Ca2}	VIII _{Ca1}	VIII _{Ca2}	III _{C1}	III _{C2}	III _{C3}	III _{C4}	ΣC ^v
IX _{F1}	2.72				1.27				1.0
VI _{O1}	0.21 x3				1.33				1.96
	2.35		2.29		1.27				
II _{O2}	0.43		0.28		1.33				2.04
			2.43		1.27				
VI _{O3}			0.24 x3		1.33				2.05
			2.43			1.27			
VI _{O4}			0.24 x3			1.33			2.05
		2.35	2.29			1.27			
II _{O5}		0.43	0.28			1.33			2.04
		2.72				1.27			
VI _{O6}		0.21 x3				1.33			1.96
		2.72					1.27		
VI _{O7}		0.21 x3					1.33		1.96
		2.35		2.29			1.27		
II _{O8}		0.43		0.28			1.33		2.04
				2.43			1.27		
VI _{O9}				0.24 x3			1.33		2.05
				2.43				1.27	
VI _{O10}				0.24 x3				1.33	2.05
	2.35			2.29				1.27	
II _{O11}	0.43			0.28				1.33	2.04
	2.72							1.27	
VI _{O12}	0.21 x3							1.33	1.96
Average Bond Length, $\bar{l}$	2.63*	2.63*	2.40	2.40	1.27	1.27	1.27	1.27	
ΣA ^v	2.12	2.12	2.0	2.0	4.0	4.0	4.0	4.0	

L_{max} (Ce) = 3.17L_{max} (Ca) = 3.25Ca₁-O₂ = 2.18-2.82Ca₁-O₂ = 2.29-2.82

} (International Tables for X-ray Crystallography, V.III, p.260-262)

ΣA^v = valences of bonds emanating from cationΣC^v = valences of bonds reaching anion* The ideal valence sum (ΣA^v) for Ce is two, the valence of Ce less the valence of F - all Ce-F bond lengths equal 2.38 Å.

Roman numerals denote coordination number.

where $\bar{L}$ is the mean bond length of the cation polyhedron found in the structure under consideration; $L_{\max}$ is the largest cation-anion distance that will still be considered a bond; v_i is the ideal bond valence (formal cationic charge divided by coordination number). p is found to be equal to $\bar{L}/(L_{\max}-\bar{L})$ by imposing the condition that the two curve segments have equal slope at their common point ($L=\bar{L}$, $v=v_i$).

The calculation of valence summation was performed using a computer program (Chao, 1971). As the fluorine atoms are bonded to Ce only, it was assumed that each fluorine atom has the ideal bond valence of 1, 1/3 from each of the three Ce neighbours. Each Ce atom emanates $3 \times 1/3$ of its valences of bonds to its three F neighbours. Thus, in the valence summation calculations, only two of three valences of each Ce atom were distributed among the other oxygen atoms. The $L_{\max}$ for Ce-O bonds was assumed to be 3.17 Å instead of the value of 3.02 Å proposed by Donnay and Allmann (1970) to take care of the difference due to larger coordination number. The results are tabulated together with the interatomic distances in Table 11. The sums of valences of bonds reaching the oxygen atoms ($\sum C^V$) are in good agreement with the expected value of 2 with maximum deviations of 3%. Thus, the proposed structure model for synchysite - 12T satisfies the second rule of Pauling.

The Structure of Parisite

The proposed structure of parisite is essentially a modification of the structure proposed by Donnay and Donnay (1953) in which the bastnaesite slabs and synchysite slabs are stacked alternately in the ratio of 1:1. The direct prove of this stacking arrangement is provided by the observations made recently by Landuyt and Amelinckx (1975) using the method of direct lattice resolution in transmission electron microscopy. The stacking arrangement is also supported by the fact that the weighted average height of the synchysite slab and bastnaesite slab $[1/3(2 \times 4.590 + 4.890) = 4.690 \text{ \AA}]$ is in very good agreement with the observed pseudo-period c''' ($4.685 \text{ \AA}$) in parisite. The modification involved is primarily in the positions and orientations of the carbonate groups in the synchysite and bastnaesite slabs.

Parisite-18T from Mont St. Hilaire belongs to the space group $P3_1$ and contains 18 formula units of $2\text{CeFCO}_3 \cdot \text{CaCO}_3$ per cell. Thus, within an asymmetric cell, there are two successions of synchysite-bastnaesite slabs. Due to the degeneration of symmetry, the carbonate group in the bastnaesite slabs, similar to those in synchysite, may assume orientations 1 and 2 in (a)-sites and orientations 3 and 4 in the (b)-sites. Consequently, the number of possible ways of stacking becomes 128. However, not all of the 128 ways of stacking produce distinct structures. For example, the stacking sequence 133422 with the origin at the base of one synchysite slab, is identical to the sequence 422133 with the origin shifted to the base of the next synchysite slab. The sequences 243312 and 312243 are related to the first two sequences respectively by an inversion,

equivalent to an exchange of the positive end and the negative end of the c-axis. By eliminations of this kind, the total number of different ways of stacking is reduced to 32. Among these 32 ways, 8 ways of stacking, such as 123311, 143411, 134312, produce horizontal mirror planes and are therefore, not permissible. This further reduces the number of permissible ways of stacking to 24, a listing of which is presented in Table 12. All of the 24 stacking arrangements are crystal-chemically, equally sound and acceptable.

No reference can be made without accurate measurements of the extremely weak superlattice reflections. The stacking sequence 133422 has been arbitrarily selected to represent the structure of parisite-18T. The atomic parameters calculated on the basis of the adapted stacking sequence are given in Table 13. The proposed structure of parisite-18T is illustrated in Fig. 21.

The validity of the proposed structure is supported by the facts that all interatomic distances (Table 14) are well within the range of values found in other compounds and it obeys closely Pauling's second rule as shown by valence summation calculations (Table 14).

Other polytypes of parisite may be derived from the 18T structure. The structure of the 72T polytype may be obtained by stacking successively, four different stacking sequences of the 18T polytype such as 133422, 134411, 143322 and 143421 which would produce a superlattice with $c=4 \times 84.33 \text{ \AA}$. The 9R polytype discovered by Landuyt and Amelinckx (1975) may be derived from the 18T polytype by repeating only one-half of an 18T stacking sequence (such as 133 of 133422) and by displacing the successive half-sequences $1/3$ along the a-axes.

Table 12: The 24 Permissible Stacking Sequences in Parisite - 18T

2	2	1	1	2	1	1	2
2	1	1	2	2	2	1	1
4	4	4	4	3	3	4	4
3	3	3	3	3	3	4	4
3	3	3	3	3	3	3	3
1	1	1	1	1	1	1	1

2	1	2	1	2	1	2	1
2	2	2	2	2	2	2	2
4	4	4	4	3	3	3	3
4	4	4	4	3	3	4	4
3	3	4	4	4	4	4	4
1	1	1	1	1	1	1	1

2	1	2	1	2	1	2	1
2	2	2	2	2	2	2	2
4	4	3	3	4	4	4	4
3	3	4	4	3	3	4	4
4	4	3	3	3	3	3	3
1	1	1	1	2	2	2	2

1,2 refers to positions of CO₃ groups in (a)-sites,
 3,4 refers to positions of CO₃ groups in (b)-sites.

Commentation

Table 13: Predicted Atomic Parameters for Parisite - 18T

Atom	x	y	z	Atom	x	y	z
Ce 1	0.333	0	0	0 1	0.333	0.333	0.016
2			0.109	2		0.056	0.027(5)
3			0.167	3		0.308	0.042
4			0.276	4		0.685	0.067
5	0	0.333	0	5	0.333	0.944	0.081(6)
6			0.109	6		0.667	0.093
7			0.167	7		0.667	0.125
8			0.276	8		0.933	0.138
9	0.667	0.667	0	9	0.333	0.667	0.151
10			0.109	10		0.611	0.183
11			0.167	11		0.352	0.194
12			0.276	12		0.308	0.209
Ca 1	0.333	0	0.055	13	0.308	0.333	0.234
2	0.333	0	0.221	14	0.056		0.248
3	0	0.333	0.055	15	0.333		0.260
4	0	0.333	0.221	16	0.333		0.292
5	0.667	0.667	0.055	17	0.067	0.333	0.305
6	0.667	0.667	0.221	18	0.333		0.317
F 1	0.333	0.667	0	19	0.667	0	0.016
2		0.333	0.109	20	0.944	0.277	0.027(5)
3		0.333	0.167	21	0.692	0.025	0.042
4		0.667	0.276	22	0.315	0.648	0.067
5	0	0	0	23	0.056	0.389	0.081(6)
6		0.667	0.109	24	0.333	0.667	0.093
7		0.667	0.167	25	0.333	0.667	0.125
8		0	0.276	26	0.067	0.400	0.138
9	0.667	0.333	0	27	0.333	0.667	0.151
10		0	0.109	28	0.333	0.667	0.183
11		0	0.167	29		0.944	0.194
12		0.333	0.276	30		0.692	0.209
C 1	0.333	0.232	0.028	31		0.975	0.234
2		0.767	0.081	32	0.667	0.723	0.248
3		0.755	0.138	33	0	0	0.260
4		0.435	0.195	34	0	0	0.292
5	0.232	0.333	0.248	35	0	0.734	0.305
6	0.245	0.333	0.304	36		0	0.317
7	0.768	0.101	0.028	37		0	0.016
8	0.233	0.565	0.081	38		0.723	0.027(5)
9	0.245	0.577	0.137	39	0.975	0.667	0.042
10	0.333	0.768	0.195	40	0.352		0.067
11	0.667	0.899	0.248	41	0.611		0.081(6)
12	0.667	0.912	0.304	42	0.333		0.093
13	0.899	0.667	0.028	43	0.333	0.600	0.125
14	0.435		0.081	44	0.333		0.138
15	0.423		0.137	45	0.333		0.151
16	0.232		0.195	46	0.333	0.667	0.183
17	0.101	0.768	0.248	47	0.056	0.389	0.194
18	0.088	0.755	0.304	48	0.308	0.648	0.209
				49	0.025	0.692	0.234
				50	0.277	0.944	0.248
				51	0	0.667	0.260
				52	0	0.667	0.292
				53	0.266	0.933	0.305
				54	0	0.667	0.317

Fig. 21: Schematic Section of a portion of the crystal structure of Parisite - 18T along plane $x=1/3$ showing the stacking sequences of the CeF and Ce layers and the positions of the CO₃ groups.

Table 14: Estimated Bond Lengths (Å) and Bond Valences (v.u.) in Perovskite

Anion \ Cation	XI _{Ca1}	XI _{Ca2}	XI _{Ca3}	XI _{Ca4}	VIII _{Ca1}	VIII _{Ca2}	III _{C1}	III _{C2}	III _{C3}	III _{C4}	III _{C5}	III _{C6}	ΣCV
IX _F													1.0
	2.73						1.26						1.96
VI _{O1}	0.21 x3						1.33						
	2.35				2.35		1.26						2.05
II _{O2}	0.44				0.28		1.33						
					2.45		1.26						2.05
VI _{O3}					0.24 x3		1.33						
					2.45			1.26					2.05
VI _{O4}					0.24 x3			1.33					
	2.35				2.35		1.26						2.08
II _{O5}	0.47				0.28		1.33						
	2.73						1.26						1.96
VI _{O6}	0.21 x3							1.33					
	2.73							1.26					1.96
VI _{O7}	0.21 x3							1.33					
	2.48	2.48						1.26					2.03
II _{O8}	0.35	0.35						1.33					
		2.72						1.26					1.99
VI _{O9}		0.22 x3						1.33					
		2.73							1.26				
VI _{O10}		0.21 x3							1.33				1.96
		2.35				2.35			1.26				
II _{O11}		0.46				0.28			1.33				2.07
						2.46			1.26				
VI _{O12}						0.24 x3			1.33				2.05
						2.45				1.26			
VI _{O13}						0.24 x3				1.33			2.05
					2.35	2.35				1.26			
II _{O14}					0.47	0.28				1.33			2.08
					2.73					1.26			
VI _{O15}					0.21 x3					1.33			1.96
					2.73					1.26			
VI _{O16}					0.21 x3					1.33			1.96
	2.35				2.48					1.26			
II _{O17}	0.44				0.36					1.33			2.12
	2.73									1.26			
VI _{O18}	0.21 x3									1.33			1.96
Average Bond Length, Å	2.44	2.65	2.65	2.65	2.43	2.43	1.26	1.26	1.26	1.26	1.26	1.26	
ΣAV	2.14	3.00	2.10	2.00	2.00	2.00	4.0	4.0	4.0	4.0	4.0	4.0	

$\text{Lmax(Ca)} = 3.17$ $\text{Ca-O} = 2.18-2.82$
 $\text{Lmax(Ca)} = 3.05$ $\text{Ca-O} = 2.29-2.82$ [International Tables for X-ray Crystallography, V.III, p.260-262]
 ΣAV = valence of bonds emanating from cation
 ΣCV = valence of bonds reaching anion
 The total valence sum (ΣAV) for Ca is 9.08, the valence of Ca less the valence of F — all Ca-F bond lengths equal 2.35 Å.
 Roman numerals denote coordination number.

The 18R polytype may be produced simply by displacing successive full 18T stacking sequences $1/3$ along the a-axes. The stacking relationships of these polytypes to the 18T polytype are shown schematically in Fig. 22.

Legend

— Ce-F layers

--- Ca layers

1,2,3,4 orientations of carbonate groups

Fig.22 Schematic representations of stacking sequences in parisite. (a) -18T (133422) (b) -72T (133422134411143322143421; 1/3 of total sequence) (c) -9R (133) (d) -18R (133422). The numerals 1 and 2 represent the possible orientations in the (a)-sites, and 3 and 4, the two possible orientations in the (b)-sites.

Concluding Remarks

The proposed structural models for the trigonal synchysite and parisite from Mont St. Hilaire are consistent with observed X-ray and optical data and are crystal-chemically sound. The valence sums are in complete agreement with the second rule of Pauling and the interatomic distances are well within the range of distances found in other compounds.

The degeneration of symmetry in the bastnaesite structure provides the degree of freedom for the carbonate groups in choosing one out of two permissible orientations in each of two possible structural sites. The different orientations of the carbonate groups in successive slabs within the otherwise identical framework of heavy cations are responsible for the various pseudo-periods observed in synchysite and parisite.

The different ways of stacking identical sequences of carbonate groups in different orientations and in different sites are the fundamental mechanism for polytypism in both synchysite and parisite.

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