A study of the minerals sturtite and pimelite

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A STUDY OF THE MINERALS
STURTITE and PIMELITE

by

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ABSTRACT

This thesis comprises a mineralogical study of two minerals:

(a) Sturtite

(b) Pimelite

Both minerals were supplied from the collections of the Department of Geological Sciences of Durham University.

Although they have already been described by several authors there are still some doubts and major contradictions between them. The present study is an attempt to clarify those problems. These two minerals were also in the Joint Committee on Powder Diffraction Standards (JCPDS) 1977 list of minerals for which powder diffraction data was required.

The present study consists of mainly X-ray Diffraction Techniques and Thermal Techniques (Differential Thermal Analysis and Thermogravimetric Analysis). Also during the study Electron Microscope Techniques were used and Electron Microprobe Analysis obtained for both minerals.

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X-RAY DIFFRACTION STUDIES

1. Powder Photograph Studies

The powder photographs were taken using a 114.59 mm Philips Debye-Scherrer camera. The method used was the Straumanis film mounting technique as described by Azaroff and Buerger (1958). The specimens were prepared in the following manner:

The specimen was first ground with an agate pestle and mortar and then mounted around a glass fibre (held in a brass holder) using flexible collodion as the mounting adhesive. The brass holder was mounted in a camera and then centered, by means of an alignment device, and the specimen X-rayed.

During the experiments the following instruments were used:

Philips PW 1130 3kV generator-diffractometer using iron filtered Co radiation at 50kV-30mA.

Philips PW 1010 1 kV generator-diffractometer using vanadium filtered Cr radiation at 30kV-10mA.

Philips PW 1320-1310 2kV generator-diffractometer using nickel filtered Cu radiation at 45kV-25mA.

The instrumental conditions used can be seen in Table 1.

Three different tubes Cr, Cu and Co were used in order to minimise the problems of fluorescence in the sample. Pimelite contains large quantities of nickel and the values of mass absorption coefficient for Cr, Co and Cu radiations are 142.3, 72.5 and 48.3 (McKinley et al., 1966). respectively showing that for pimelite copper radiation is the best, but for sturtite, which contains large amounts of iron and manganese, chromium radiation was required.

X-ray diffraction line measurements were carried out using a Hilger and Watts film measuring scale fitted with a vernier device capable of reading the lines to 0.05 mm.

A computer programme (DPOW) was used to obtain the d-spacings, this was based on Cohen's least squares method which was originally written by M. George (1969), and later modified by Allan Hall, of this department (Akinci, 1971). The d-spacings obtained from this programme have been corrected for film shrinkage, however, in certain samples no back reflection data was obtained, therefore, in this case the programme was modified by introducing theoretical data into the calculations.

Two crystallographic computer programmes were also used. They were GENSTRUK and COHEN (Marples & Shaw, 1966), but unfortunately they proved unsuccessful.

2. Powder Diffractometer Studies

As well as powder photography, powder diffractometer studies were undertaken on the same instruments.

The methods followed were those described by Klug and Alexander (1962) and Taylor (1971) in which the sample was cavity-mounted and in which the powdered sample was mounted on a glass slide using acetone as the mounting medium.

The specimens were then subjected to X-ray analysis in a Philips high angle PW 1050/25 goniometer attached to all three machines and the preliminary runs taken to obtain the optimum conditions of scan speed, pulse height analysis and slit widths. These settings are shown in Table 1.

X-ray diffraction 2θ scans were made between the range 3° to 100° and the diffraction peaks obtained were converted to d-spacings by means of conversion tables. The sample Pimelite was also X-rayed under special conditions, e.g. glycolation, and an accurate measurement made of the 060 reflection, to determine the dioctahedral or trioctahedral nature of the crystal structure.

TABLE 1

Instrumental Conditions for X-ray Powder Photograph and Diffraction Studies

Radiation	Cr, Co, Cu K-Alpha	Radiation	Co K-Alpha
Collimator	Fine, Clay Collimator	Slits	2°, 0.2°, 2°
Camera	114.59 mm, Philips	Rate of Scan	1° 2θ/min
Exposure time	Varied 5-72 hrs	Counter	Sealed proportional and pulse height analysis
Film	Ilford, Ind. G-Fast	Mount Type	Smear and cavity
Film Mounting	Straumanis Technique	Operation	Ratemeter
		Time Constant	4
		Multiplication Factor	2×10^2 cps

B - ELECTRON MICROPROBE ANALYSIS

ELECTRON MICROPROBE ANALYSIS

Due to the variety of chemical formulae for pimelite, it was decided to analyse both samples on the electron microprobe to determine their exact compositions.

A Cambridge Scientific Instruments Geoscan, with a take-off angle of 75° was employed during the experiment. X-ray excitation was achieved by a beam of 15KeV electrons, normal to the surface, and focused to a minimum spot size about one micron in diameter. Fixed time counting was used throughout the analysis. A beam current of about 62.5 μA yielded an effective specimen current of approximately 0.04 μA.

Specimens were prepared as polished samples and coated with carbon under the same conditions as the standards.

Analytical runs were begun by counting on each of seven standards. Three peak and two background readings were taken before and after counting on the unknowns. Standard readings were repeated after every eight or nine peak and background readings on the unknown, to check the extent of drift, and provide a basis for its correction.

Details of the operating conditions used are shown in Table 2.

Corrections:

Low counts were first corrected for a 4 micro-seconds dead time and drift, with the aid of the on-line Varian 620-100 computer, by the program "TIM-3" written by Dr. A. Peckett. This is an assemblerversion of the Fortran IV TIM 1 of Duncomb and Jones (1970). The program corrects for mass absorption, secondary fluorescence and the atomic number effect (stopping power and electron back-scatter) in the manner described by Sweatman and Long (1969) for K, L and M lines.

TABLE 2

Operating Conditions and Standards used for Electron Microprobe Analysis

Element	Line	Analysing Crystal	Counter	2θ (Peak)	2θ (Background)	Standard
Si	$K\alpha_1$	KAP	Flow	$31^\circ 02'$	$-1^\circ +1^\circ 30'$	Wollastonite
Al	"	"	"	$36^\circ 32'$	± 2	Al_2O_3
Mg	"	"	"	$43^\circ 42'$	-2	MgO
Mn	"	LiF	"	$62^\circ 48'$	+2	Mn Metal
Ca	"	"	"	$113^\circ 02'$	-2	Wollastonite
Ni	"	"	"	$48^\circ 34'$	+2	Ni Metal
Fe	"	"	"	$57^\circ 20'$	+2	Fe Metal

C - DIFFERENTIAL THERMAL ANALYSIS (DTA)

DIFFERENTIAL THERMAL ANALYSIS (DTA)

DTA has proved especially useful in the determination of the clay minerals, because clay minerals are not easily identified by classical methods due to their fine grain size and similarity in chemical composition.

The method used was that described by Mackenzie (1957).

The specimen under examination was heated up at a uniform rate of 10°C/min. side-by-side with a sample of pure dry alumina powder (which is thermally inert) in matching platinum crucibles. Any differences in temperature between the two, caused by reactions in the specimen, are recorded on a chart recorder as either an endothermic peak or an exothermic peak depending on whether heat is either absorbed or evolved.

During the experiments a Stanton Equipment Standata 5-50" model in conjunction with a West Controller were employed.

D - THERMOGRAVIMETRIC ANALYSIS

THERMOGRAVIMETRIC ANALYSIS (TGA)

Powdered samples of both sturtite and pimelite were submitted to TGA studies using a Stanton-Automatic Direct Reading - Thermobalance.

In this technique the loss of weight of the sample is measured as the sample is gradually heated up at a constant rate.

Due to the disagreements between analysis and formulae given in the literature, and also the low analysis totals obtained from Electron Microprobe studies, an attempt was made, using the TGA, to obtain water loss and dehydration curves for both minerals.

To obtain the water loss the following formula was used:

$$\frac{\text{Scale loss (in milligrams)}}{\text{Weight of sample}} \times 100 = \%\ \text{Water}$$

I. STURTITE

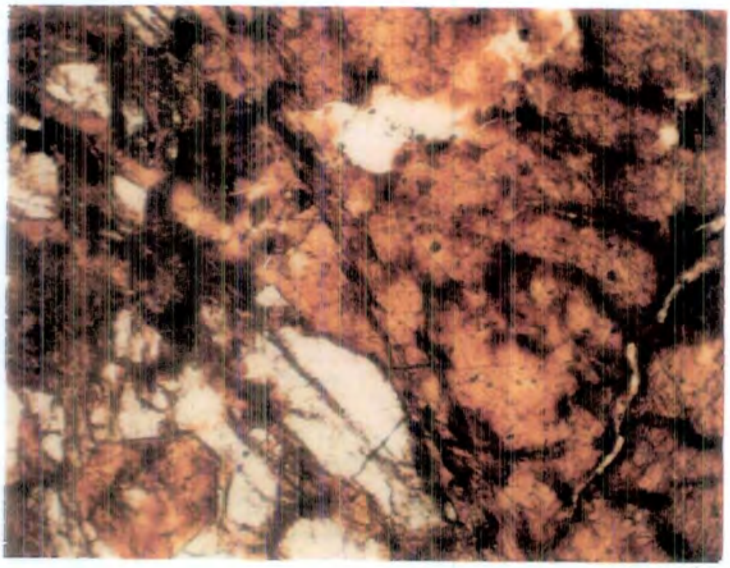

Plate 1. A photomicrograph of Sturtite (reddish-brown). Carbonate minerals in light-coloured areas. X nicols, transmitted light, 100x.

STURTITE

Sample No: 6624 Broken Hill, NSW,
Australia

This name was given in honour of the explorer Captain Charles Sturt who was the first white man to have visited Broken Hill on the 22nd October 1844.

The mineral was first described by Hodge-Smith (1930) who concluded that it was an amorphous mineral; unfortunately this is the only information available.

a. Physical Characters

Sturtite is a very brittle and friable mineral, easily broken up by the fingers. The hardness is slightly over 3; the colour is jet black and the streak is yellowish-brown.

b. Microscopic Observation

It appears under the microscope to be colourless to pale brown and has the appearance of an isotropic substance (Plate 1). Very slight anisotropy and bireflectance, together with reddish internal reflections may be attributed to impurities or alteration (iron hydroxides). Under both reflected and transmitted light microscopic examination reveals discrete grains of sturtite of pseudohexagonal outline.

The reflectivity of the mineral is very low and may be approximately 7%.

The examined sections show that galena, sphalerite and some chalcopyrite droplets together with major amounts of carbonate (calcite) minerals are associated with sturtite. Some quartz, probably replaces the minerals along the cracks.

Both sturtite and associated minerals are deformed in the same manner, they are partially cracked and stressed. This possibly indicates that deformation took place after the formation of the associated minerals and the sturtite. Subsequently ironhydroxides (goethite) replaced sturtite starting from the cracks or pseudograin boundaries which are thought to be prior to alteration or deformation (metamorphism?).

According to Hodge-Smith (1930) quartz, spessartite and rhodochrosite are also associated minerals. But the specimen examined showed no trace of these minerals.

c. Chemistry

Hodge-Smith (1930) gives the formula:

$Fe_2O_3.6(Mn,Ca,Mg)O.8SiO_2.23H_2O$

His chemical analysis of sturtite is shown below, together with the analysis obtained in the present study.

	A wt.%	B wt.%
SiO_2 (Free)	0.79	
SiO_2 (Combined)	32.35	36.41
Fe_2O_3	10.22	13.53
Al_2O_3	0.44	-
MnO	25.18	20.52
CaO	2.19	2.81
MgO	0.65	0.98
H_2O	28.16	13.00
Total	99.98	87.25

A - Hodge-Smith; B - present study.

The water loss obtained from TGA gives 13 H_2O % (see fig.1) which is insufficient to take Electron Microprobe Analysis to 100 percent. The total weight percent of sturtite obtained from the microprobe was 74.25% and the addition of 13 percent H_2O only increased the total weight percent to 87.25%.

d. X-ray Study of Sturtite

During the study several X-ray powder photographs and diffraction charts were taken on carefully picked specimens using varying exposure times and conditions.

As a result, it was found that Hodge-Smith's (1930) conclusion was correct, since some specimens gave no diffraction lines and all the lines found in other specimens could be accounted for as impurities.

The amorphous nature was later confirmed by using the Electron Microscope (JEM 120 Transmission El.Mic) which gave no diffraction pattern. However, it was observed during the electron microscope experiment that diffraction patterns were produced after some time, presumably due to the heating effect of the electron beam and water loss under vacuum conditions causing crystallisation. A number of different patterns were obtained from the sturtite ~~pimelite~~ at these elevated temperatures, but unfortunately none of them corresponded with any minerals from the JCPDS index (1977).

d-spacings obtained from hand specimen material containing sturtite:

2θ (Degrees)	d (Å)	Rel.Int.	Corresponding Impurities
39.226	3.41	40	Galena
42.997	3.12	20	Sphalerite
44.994	2.99	100	Tetrahedrite
45.618	2.96	30	Galena?
55.306	2.47	5	Calcite
60.949	2.26	10	Calcite
66.393	2.09	60	Galena
67.067	2.07	10	Tetrahedrite
73.284	1.92	10	Calcite
74.832	1.88	10	Calcite
76.330	1.85	20	Tetrahedrite
79.776	1.78	20	Galena
84.046	1.71	5	Galena
119.525	1.32	5	Galena

Radiation = CrKα 28/10
Exp. Time = 72 hrs
Coll. = Fine

After the above X-ray data of compound sturtite was taken, an attempt was made to obtain X-ray data from individual materials. The following results were obtained from the individual specimens which were carefully picked under the microscope.

X-ray data from area of high metallic lustre;

2θ	d(Å)	Rel.Int
26.025	3.42	80
30.025	2.97	100
43.125	2.09	50
51.125	1.78	40
53.425	1.71	20
62.55	1.48	10
69.85	1.34	5
71.00	1.32	5
78.95	1.21	5
84.875	1.14	5

All these lines correspond with Galena.

Conditions
Rad = CuKα
Exp. Time = 10 hrs
Coll = Fine
Rating = 40/20

The sample from an area of dull or resinous lustre gives a pattern which fits calcite and sphalerite.

2θ	d(Å)		
32.20	3.13	100	Sphalerite
34.35	3.03	5	Calcite
42.00	2.49	5	"
46.00	2.29	5	"
50.60	2.09	5	"
55.45	1.92	25	"
56.90	1.88	5	"
65.975	1.64	5	"

Radiation = Co K 45/25
Exp.Time = 16 hrs
Coll. = Fine

Specimen from the brownish area (under the microscope) gives the following d-spacings.

2θ	d(Å)	Rel.Int	
29.775	3.00	100	Tetrahedrite
36.325	2.47	5	Calcite
39.80	2.26	10	"
43.65	2.07	10	Tetrahedrite
48.10	1.89	20	Calcite
49.10	1.85	20	Tetrahedrite
57.95	1.59	30	"
61.327	1.51	20	"

e. T.G.A. Analysis of Sturtite

The total water loss obtained from thermogravimetric analysis gave 13% water (Fig.1). The first water loss occurs between the temperatures of 50°-250°C (10.5%) and second loss occurs between the temperatures of 250-450°C.

f. Conclusions

Carefully hand picked sturtite gave no X-ray or electron diffraction pattern and is therefore amorphous. The chemical composition of the material studied compares closely with that for the original sturtite except in the water content. The amount required to bring the total on the present microprobe analysis to 100% would give a water figure closely similar to the original analysis.

The maximum temperature attained in the T.G.A. analysis was 500°C and it is known that some minerals can retain water to much higher temperatures. Unfortunately the significance of this fact was realised when no further time was available for experimental work.

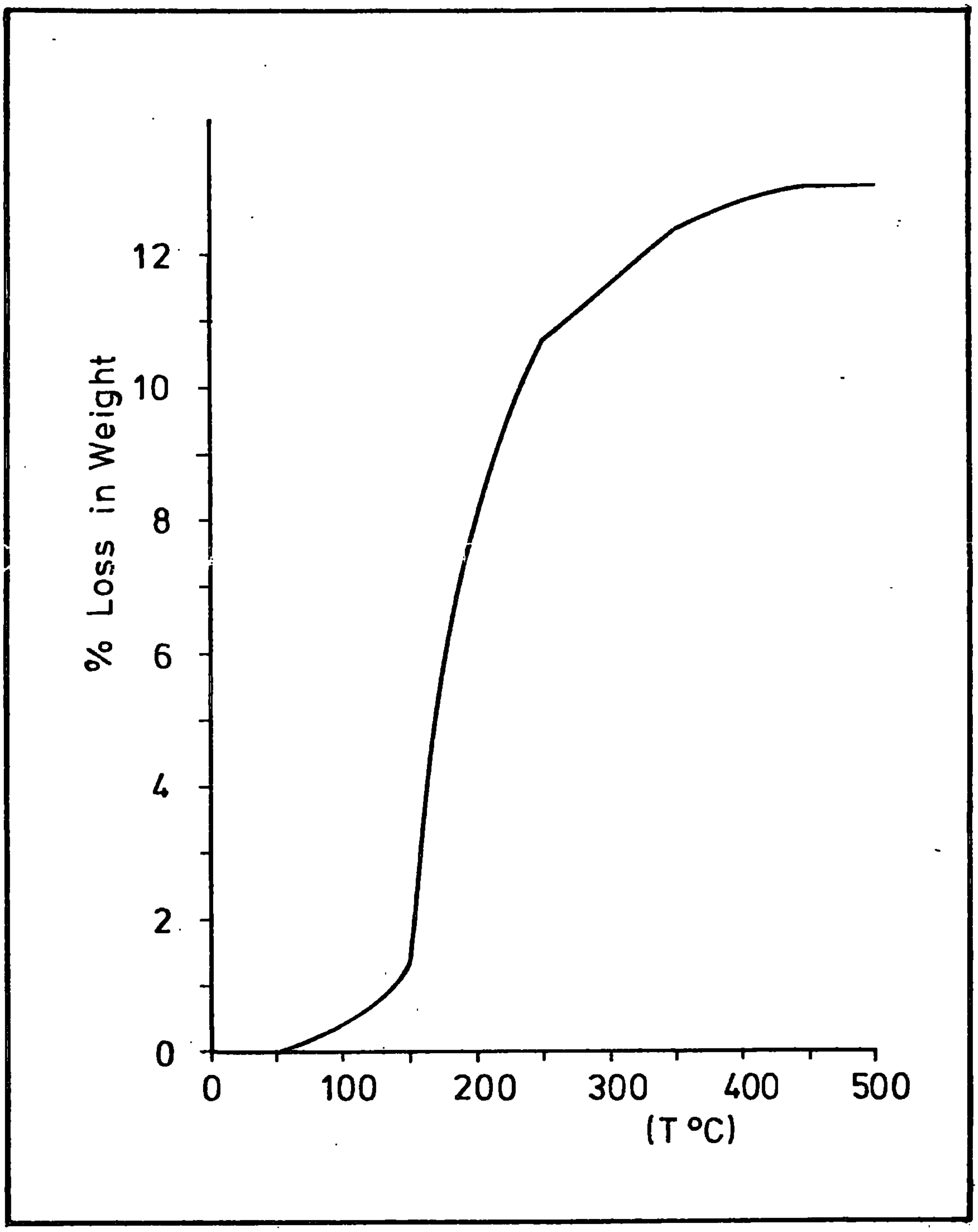

Figure 1. Dehydration Curve for Sturtite

II. PIMELITE

PIMELITE

a. Literature Survey

This mineral was first described by Professor Martin H. Klaproth in 1788 as "Gruner Chrysopraserde" (Faust, 1966), one of the members of the "hydrous nickel-magnesium silicates".

According to Dana (1920, 6th Edn.) the name pimelite comes from the Greek, fatness. Dana states that pimelite minerals consist of two members; hard pimelite (presumably the pimelite itself in the present study) and pimelite Schmidt (Alipite) which are very similar to each other in many respects. The only distinction between the two appears to be the fact that alipite adheres to the tongue and hard pimelite does not. Specimen 9032, in the present study strongly adheres to the tongue which suggests that this may well be alipite rather than hard pimelite. However, no other reference to alipite in literature has been found.

Dana also states that pimelite is a massive mineral, apple green in colour and has a greenish-white streak. The hardness is 2.5 and it has a greasy feel.

Dana gives the following analysis for both pimelites:

	Hard Pimelite	Pimelite Schmidt (Alipite)
SiO_2	35.80	54.63
Al_2O_3	23.04	0.30
Fe_2O_3	2.69	(FeO) 1.13
NiO	2.78	32.66
MgO	14.66	5.89
CaO	-	0.16
H_2O	21.03	5.23
Total	100.00	100.00

Cailliere (1935) indicates that pimelite appears to be a very altered serpentine mineral. Thermal analysis gave both loss of free water and also a peak about 550°-750°C. X-ray analysis gives the following d-spacings:

8.16
6.92
4.37
3.58
2.48
2.00
1.67
1.55
1.30

These values are entirely different from the ones obtained for pimelite in the present study and previous researches. Therefore, it seems that this material was not pimelite.

Spangenberg (1938) gives the formula for pimelite as follows:

$3(Ni,Mg)O.4SiO_2.H_2O+XH_2O$

and says no essential alumina or ferric iron is present in pimelite (Faust, 1966). It contains much zeolitic water and shows lattice shrinkage like montmorillonite; the layer spacing falls on dehydration from 12.8Å to 9.6Å, when X = 0.3 and the X-ray diffraction pattern is then exactly similar to that of talc.

Strunz (1949) suggests that pimelite shows the characteristics of a nickel-saponite.

Voorthuijsen and Franzen (1951) concluded that they had synthesized pimelite and gave to their preparation the formula (per unit-cell): $Ni_6Si_8O_{20}(OH)_4$

This formula is an idealized one, showing no layer charge. It seems likely, as in the case of Strese and Hofmann's Mg-montmorillonite, that there are some gaps in the octahedral layers giving rise to a negative charge.

The d-spacings obtained from their work are shown below

d (Å)		
4.21	8	Br
4.13		
2.425	10	Br
1.691	3	Br
1.513	8	Sh
1.307	5	Br
1.288	2	Br
1.136	2	Br
1.069	2	Br
1.008	2	Br
0.893	2	Br
0.846	1	Br
0.823	2	Br

Slansky (1955) suggests the following formula for pimelite (from Kremze):

$$(Ni,Mg)_3 \left[(OH)_8(Si_4O_{10})\right] .nH_2O$$

He states that pimelite from Kremze shows three colour varieties:

A. Almost white, very light-green

B. Light-green, a little more intensively coloured than A

C. Darker-green

All the varieties form a compact aggregate, non-transparent, but are somewhat translucent at the edges. Hardness 2-3.

The pimelite occurs most frequently in veins (often in a network of veins) running irregularly in the weathered serpentine, less abundantly as filling between a network of veins of SiO_2 and as crusts on weathered material. Some samples indicate the origin of the pimelite from colloidal solutions - the cavities in the veins are reniformly delimited, the veins are zoned by the different varieties (Slansky, 1955).

According to Slansky, under the microscope pimelite appears mostly as an anisotropic aggregate without any marked structure, more rarely as veinlets with a fibrous structure, or as more or less perfect spherulites. He also gives the following table for refractive indices of pimelite.

Pimelite	nNa	α'Na	γ'Na
Variety A	1,570±0.002		
Variety B	1,589±1.598		
Variety C		1,563±1.368	1,566 to 1,571

The following qualitative Spectral Analysis of pimelite for the essential elements, are in accord with the present study (Table 3).

TABLE 3

Results of qualitative spectral analysis of pimelite (Data for pimelite A, B, C, after Slansky, 1955)

Pimelite	Mg	Ni	Si	Mn	Fe	Ca	Al	Ba	Co	Cu	Ti	Cr	Zn	Na	Ag	Sr	K
Variety A	X	X	X	+	-	+	-	-	-	-	-	-	-	-	-	-	?
Variety B	X	X	X	+	-	+	-		?	-	-	-					
Variety C	X	X	X	+	-	+	-	-	-	-	-	-	-		-	-	?
Present Study	X	X	X	-	-	+						-					-

X = essential

\+ = subordinate to small

\- = trace amount

X-ray data of pimelite (after Slansky, 1955) compared with pimelite from Zabkowice. CuKα 30/20.

Pimelite Kremze Variety A		Pimelite Křemže Variety B		Pimelite Křemže Variety C		Pimelite Zabkowice (Polsko)	
10.0	ss	9.9	ss	10.0	ss	9.9	ss
4.49	ss	4.67	s	4.50	ss	4.54	ss
		4.30	ss				
3.22	s	3.31	s	3.25	s	3.21	s
		3.14	s				
2.56	ssB	2.53	ssB	2.56	ssB	2.56	ssB
2.29	ww	2.28	ww	2.27	ww	2.27	ww
1.73	w	1.73	w	1.73	w	1.73	w
1.52	ss	1.52	ss	1.53	ss	1.54	ss
1.37	ww						
1.31	m	1.32	m	1.32	m	1.32	m
1.26	ww	1.27	ww				
0.99	w	1.00	w	1.00	w	1.00	w
0.89	w	0.88	w	0.89	w	0.87	w

Although there are minor differences, it can be seen from the above data that the varieties are identical.

Slansky (1955) also states that pimelite does not belong to the smectite group. His evidence for this is the fact that smectites have their first basal reflection at about 15Å, whereas the first basal reflection of pimelite is about 10Å. However this does not take into account that there is the possibility of either 1, 2 or 3 layers of water in the interstitial position (layers).

According to Slansky (1955) the course of the differential thermal curves of the pimelite is characterized by two endothermic peaks, the first between 50-200°C and the second between 750-900°C. It is probable that the first reaction represents the escape of the free water and the second one represents the escape of the constitutional water (see fig.2).

Mempton and Roy (1955) give the stability limit of pimelite as 335°C. At this point pimelite gave Ni-Talc as a decomposition product.

Warshaw and Roy (1961) indicate that pimelite is a trioctahedral smectite due to the 2:1 layering and show an idealised formula of:

$$Ni_{3-x}Al_xSi_{4-y}Al_yO_{10}(OH)_2$$

Ostrowicki (1965) has pointed out that pimelite represents the richest crystalline phase of the weathering zone of serpentinites from Szklary. It forms veins which vary in thickness from tenths of a millimetre to several centimetres. Vein forms often assume a nest-like shape. Pimelite occurs in large amounts in the green and more rarely in the red weathering products of the deposit.

He concludes that pimelite is related to the talc group because of its physical andoptical properties and structure. He also suggests that the position of pimelite within specific mineral groups needs to be revised.

Ostrowicki indicates that the nickel content of pimelite ranges from 17.34 to 31.81 weight percent.

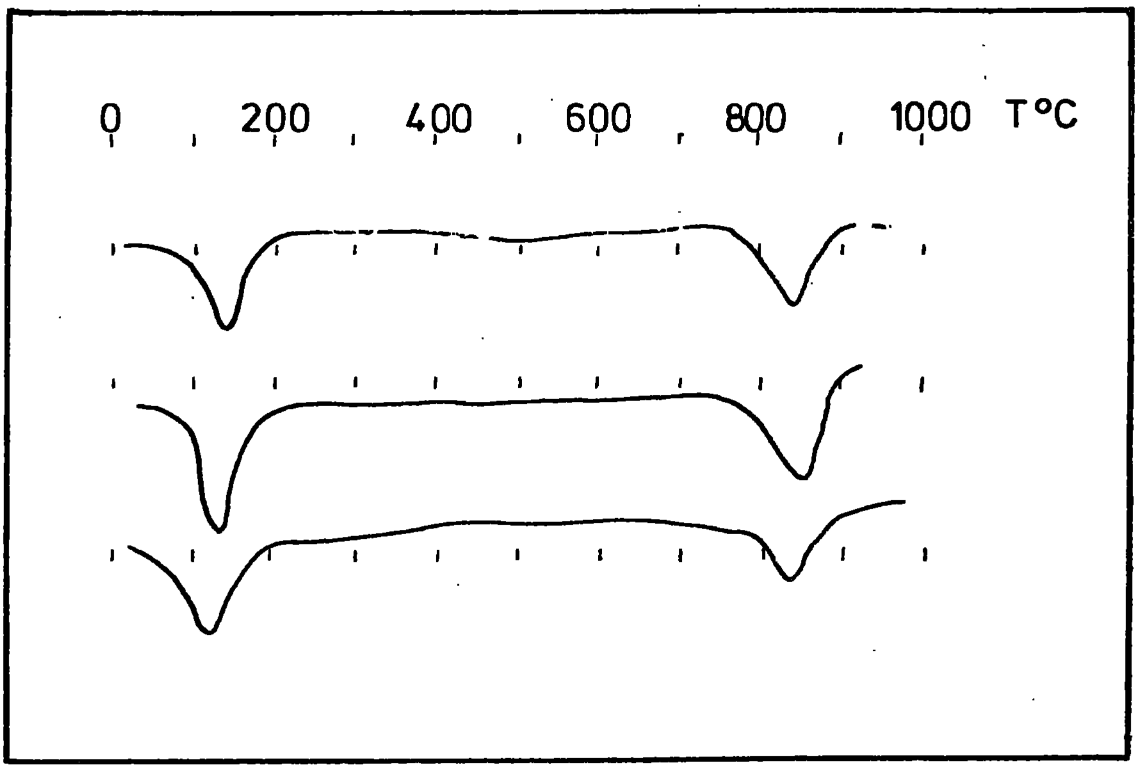

Figure 2. DTA Curves for Pimelite (From Slansky, 1955).

His analysis is shown below:

SiO_2	50.74
Al_2O_3	0.13
Fe_2O_3	0.04
NiO	31.81
MgO	7.36
CaO	0.07
MnO	0.02
Na_2O	0.06
K_2O	0.07
H_2O+	6.60
H_2O-	2.98
Total	99.88

Ostrowicki also gives differential thermal analysis results almost the same as Slansky (1955) (fig.3).

The following analysis was given by Faust (1966) during a study of the hydrous nickel-magnesium silicates:

SiO_2	47.20
Al_2O_3	0.22
Fe_2O_3	0.20
NiO	27.66
MgO	11.42
CaO	0.16
H_2O+	9.38
H_2O	3.64
Total	99.88

He suggests from his X-ray powder diffraction studies that pimelite is a member of the smectite group of minerals.

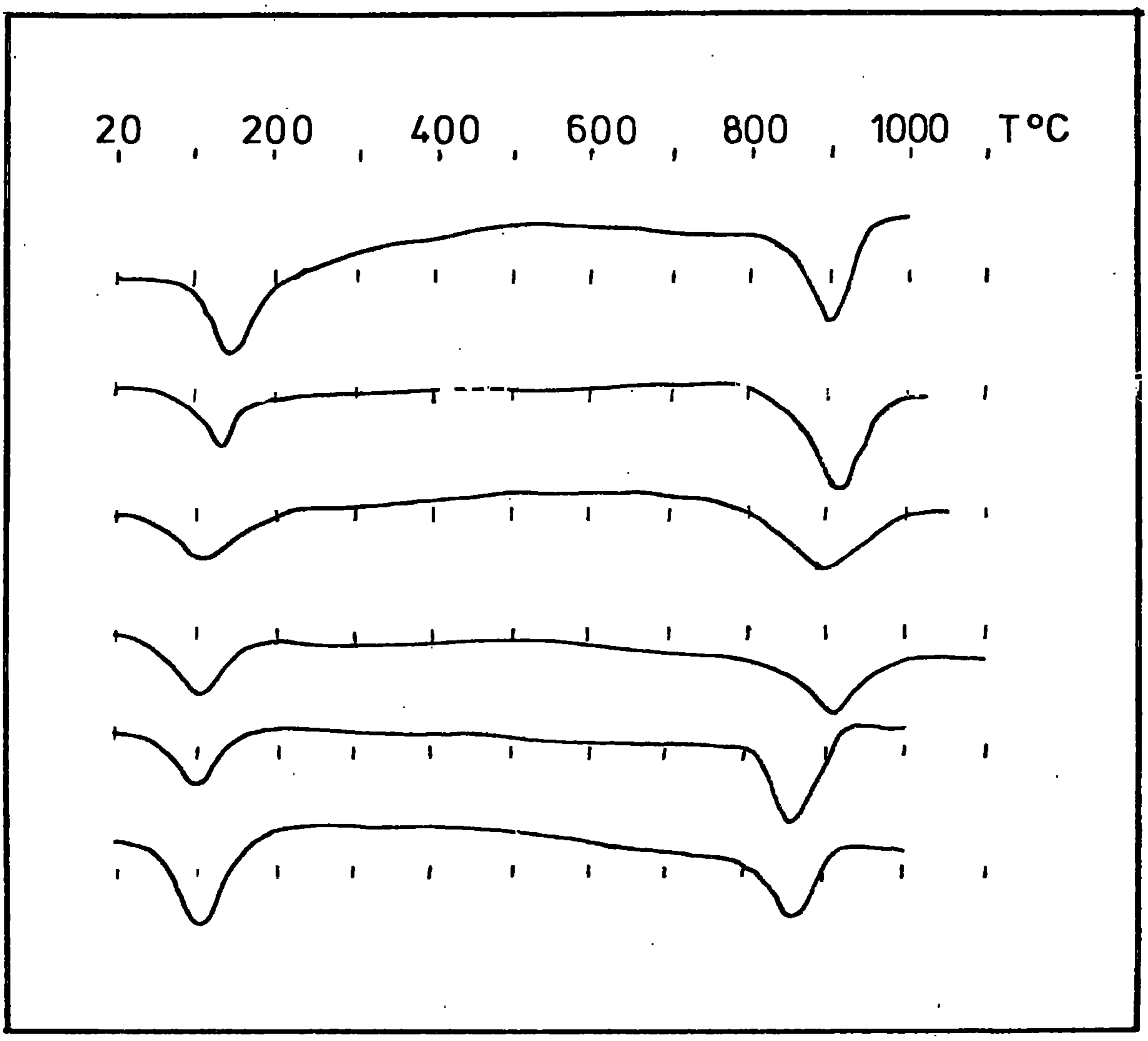

Figure 3. DTA Curves for Pimelite (From Ostrowicki, 1965).

Thorez (1975) gives the following d-spacings for pimelite

4.21	8B
4.13	
2.425	10B
1.691	3B
1.513	8B

and states that pimelite belongs to the Ni-saponite group, but does not discuss the problem.

PIMELITE IN THE PRESENT STUDY

b. Microscopic Observations: (Specimen No.9032 Silesia)

Microscopic determination of the mineral shows that it is very fine to cryptocrystalline in grain size.

The colour is always very light green. Some quartz grains(?) may be present in fine grained aggregates.

Under plane polarized light, it appears to be faintly pleochroic, while crossed-polars examination shows its medium to high birefringence (may be upper second, third order).

Beyond the presence of tiny quartz grains the mineral is fairly pure. Many irregular polishing scratches indicate that pimelite is quite a soft mineral which is in agreement with Dana's numerical data (hardness 2.5).

Result of Electron Microprobe Analysis:

During the probe analysis the following results were obtained:

SiO_2	41.50	
Al_2O_3	-	
FeO	0.02	
NiO	30.78	
MgO	8.09	
CaO	0.10	
H_2O	11.00	(Obtained from TGA)
Total	91.49	

According to the above result pimelite should contain 19.51% H_2O but the water loss obtained from the thermogravimetric analysis (fig.6) makes the total weight 91.49% which still indicates the presence of other oxides. Unfortunately it has not been possible to check these results within the available time.

The variation between the analysis given by Dana (1970), Ostrowicki (1965), Faust (1966) and the present study suggests that materials named pimelite by various authors are members of a solid solution series from a nickel rich end member to a magnesium end member.

c. Atomic Formula of Pimelite

According to the suggestions of various authors, pimelite may have the same structure as either (a) talc, (b) serpentine or (c) the smectite group. The corresponding atomic formulae would then be close to

(a) $Mg_3Si_4O_{10}(OH)_2$
(b) $Mg_6Si_4O_{10}(OH)_8$
(c) $\underset{\substack{\downarrow \\ M^{+}_{2x}}}{Mg_{3-x}}Si_4O_{10}(OH)_2.nH_2O$

Some of the available analyses were therefore recalculated on a water free basis to 11 oxygens for (a) and (c) and 14 oxygens for (b).

The Dana analysis for alipite, which corresponds closely in nickel content with that found in the present study, in each case gave Si values appreciably higher than 4, suggesting that the material may have been contaminated with SiO_2 (Table 4).

His analysis for hard pimelite (Table 5) contains much more Al_2O_3 and less NiO than in all other analyses. Compared with the normal range of compositions for talc, silica is low, alumina and water too high. For (b) the water content is low and also the number of octahedrally coordinated cations (Table 5).

For (c) however, the formula is reasonable:

$$(Mg_{1.72}Ni_{0.17}Fe^{III}_{0.16}Al_{0.97})_{3.02}(Si_{2.83}Al_{1.17})_4O_{10}(OH)_2.1.76H_2O$$

and corresponds with the formula for saponite given by Warshaw and Roy (1961) p.1468, table 3: $Mg_{3-x}Al_xSi_{4-y}Al_yO_{10}(OH)_2$. It does not correspond with the formula which they give for pimelite - $Ni_{3-x}Al_xSi_{4-y}Al_yO_{10}(OH)_2$ - in that the nickel content is so low.

The analyses of Faust (1966) (Table 6) and the present study (Table 7) also give poor agreement for (a) and (b) but can be fitted reasonably to (c) if allowance is made for vacancies in the tetrahedral positions as indicated in the formula for stevensite given by Warshaw and Roy (loc.cit.) - $Mg_{3-x}\square_xSi_{4-y}\square_yO_{10}(OH)_2$. The absence of alumina in this formula distinguishes stevensite from all other trioctahedral smectites with the exception of hectorite, which is lithium bearing.

The formula can be written:

TABLE 4

Recalculated chemical analysis of Alipite (Dana 6th Edn., p.678)

	Wt.%	Mol.Wt.	Mol.Prop	O's	Cats.	Cats 110's	Cats 140's
SiO_2	54.63	60	9105	18210	9105	4.38*	5.67*
Al_2O_3	0.30	102	29	87	58	.03	.04
NiO	32.66	74.7	4372	4372	4372	2.10	2.67
FeO	1.13	72	156	156	156	.08	.10
MgO	5.89	40.3	1461	1461	1461	0.70	.89
CaO	0.16	56	29	29	29	.01	.02
H_2O	5.23	18	2905		5810	2.79	3.56
	100.00			2.2854			

F1 11/2.2854 = 4.8131
F2 14/2.2854 = 6.1258

*Both Si too high, but 11 oxygens nearest
?Probably contamination with SiO_2

TABLE 5

Recalculated chemical analysis of Hard Pimelite (Dana 6th Edn., p.677)

	Wt.%	Mol.Wt	Mol.Prop	O's	Cats.	Cats. 11O's	Cats. 14O's
SiO_2	35.80	60	5967	11934	5967	2.83	3.59
Al_2O_3	23.04	102	2258	6774	4516	2.14	2.72
Fe_2O_3	2.69	160	168	504	336	.16	.20
NiO	2.78	74.7	372	372	372	.17	.22
MgO	14.66	40.3	3638	3638	3638	1.72	2.19
CaO	-						
H_2O	21.03	18	11683		11683	5,53	7.04
Total	100.00			2.3222			

F1 11/2.3222 = 4.7368
F2 14/2.3222 = 6.0287

F1 $(Si_{2.83}Al_{1.17})_4O_{10}(OH)_2(Mg_{1.72}Ni_{0.17}Fe^{III}_{0.16}Al_{0.97})_{3.02}\cdot 1.76H_2O$

F2 $(Si_{3.59}Al_{0.41})_4O_{10}\quad(Mg_{2.19}Ni_{0.22}Fe^{III}_{0.20}Al_{2.31})_{4.92}$

TABLE 6

Recalculated Chemical Analysis of Pimelite
(based on Faust (1966) Chemical Analysis)

	Wt.%	Mol.Wt.	Mol.Prop	O's	Cats.	Cats. 11O's	Cats. 14O's
SiO_2	47.20	60	7867	15734	7867	3.86	4.91
Al_2O_3	0.22	102	22	66	44	0.02	0.02
Fe_2O_3	0.20	160	13	39	26	0.01	0.02
NiO	27.66	75	3688	3688	3688	1.81	2.31
MgO	11.42	40.3	2834	2834	2834	1.39	1.77
CaO	0.16	56	29	29	29	0.01	0.02
H_2O+	9.38	18	5211	-	10422	5.12	6.52
H_2O-	3.64						
Total	99.88			2·2390			

Fi 11/2.239 = 4.9129
F2 14/2.239 = 6.2528

F1 (11 oxygens) $(SiAlFe^{3+})_{3.89}(Ni_{1.81}Mg_{1.39})_{3.2}(OH)_2 1.56H_2O$

(a) Si low, Mg, Ni high, too much H_2O
(b) Si too high for Si_4O_{10}, total Ni and Mg too low

F2 (14 oxygens) $Ni_{1.81}Mg_{1.19})_3(Si_{3.86}Al_{0.02}\square_{0.12})_4O_{10}(OH)_2 1.56H_2O$ ≈ Stevensite

TABLE 7

Recalculated Chemical Analysis of Pimelite

	Wt.%	Mol.Wt	Mol.Prop.	Oxygens	Cations	Cations 11 oxygens
SiO_2	41.50	60	6916	13832	6916	3.81
Al_2O_3	-					
FeO	0.02	72	2	2	2	-
NiO	30.78	75	4104	4104	4104	2.26
MgO	8.09	40.3	2007	2007	2007	1.11
CaO	0.10	56	1	1	1	
H_2O	11.00	18	6111	-	12222	6.74
Total	91.49			1.9946		

$11/1.9946 = 5.5149$

$$(Ni_{2.26}\underset{\begin{subarray}{c}\downarrow\\ Mg_{0.37}\end{subarray}}{Mg}{}_{0.74})_3(Si_{3.81}\square_{0.19})_4O_{10}(OH)_2 2.37H_2O$$

Faust $(\mathrm{Ni}_{1.81}\underset{\substack{\downarrow\\ \mathrm{Mg}_{0.20}\mathrm{Fe}^{3+}_{0.02}}}{\mathrm{Mg}}{}_{1.19})_3(\mathrm{Si}_{3.86}\mathrm{Al}_{0.02}\,\square_{0.12})_4\mathrm{O}_{10}(\mathrm{OH})_2\cdot 1.56\mathrm{H}_2\mathrm{O}$

Present Study $(\mathrm{Ni}_{2.26}\underset{\substack{\downarrow\\ \mathrm{Mg}_{0.37}}}{\mathrm{Mg}}{}_{0.84})_3(\mathrm{Si}_{3.81}\,\square_{0.19})_4\mathrm{O}_{10}(\mathrm{OH})_2\cdot 2.37\mathrm{H}_2\mathrm{O}$

Both analyses show a similar deficiency in silicon which will give a layer charge that is apparently compensated by interlayer cations as indicated. The presence of vacancies in the octahedral layer indicated by the Warshaw and Roy formula is not supported by these analyses. The pimelite of the present study has a somewhat higher nickel content than that of Faust, but both are apparently nickel-rich varieties of the trioctahedral smectite stevensite.

Confirmation of this possibility required the examination of X-ray diffraction data.

d. X-ray study of pimelite in present work

The following results were obtained from the X-ray powder photographs;

2θ Degrees	d(Å)	Rel.Int(Visual Estimate)
8.825	10.00	80 (Broad)
19.50	4.55	50 (line at head of diffuse band)
27.55	3.23	20 (Broad)
33.90	2.64	40 (Head of diffuse band)
39.60	2.27	20
53.175	1.72	10
60.775	1.52	100
71.825	1.31	5

The diffraction lines were difficult to measure accurately due to their broad nature and the values shown above are the average values obtained from the measurements of a number of films. Also due to the crystallization of the specimen, no back reflections were obtained. The only distinct line produced was the 1.52Å (060) reflection indicating the trioctahedral nature of pimelite (Warshaw and Roy, 1961).

The d-spacings obtained from the X-ray diffractometer shown below;

d(Å)	Rel.Int
9.97-10.27	100
4.54- 4.56	40
3.23- 3.24	20
2.62- 2.64	40
1.52-	80

After soaking overnight in ethylene glycol the following results were obtained:

d(Å)	Rel.Int
15.09	100
4.56	40
3.34	20
2.64-2.68	40
1.52	80

The first recorded reflection expands up to 15.09Å but changes in the other reflections were negligible. The 1.52Å line remained constant (Plate 2). The fact that the first recorded peak expands from 10Å up to 15Å suggests a smectite type structure with interlayer water molecules being replaced by ethylene glycol molecules.

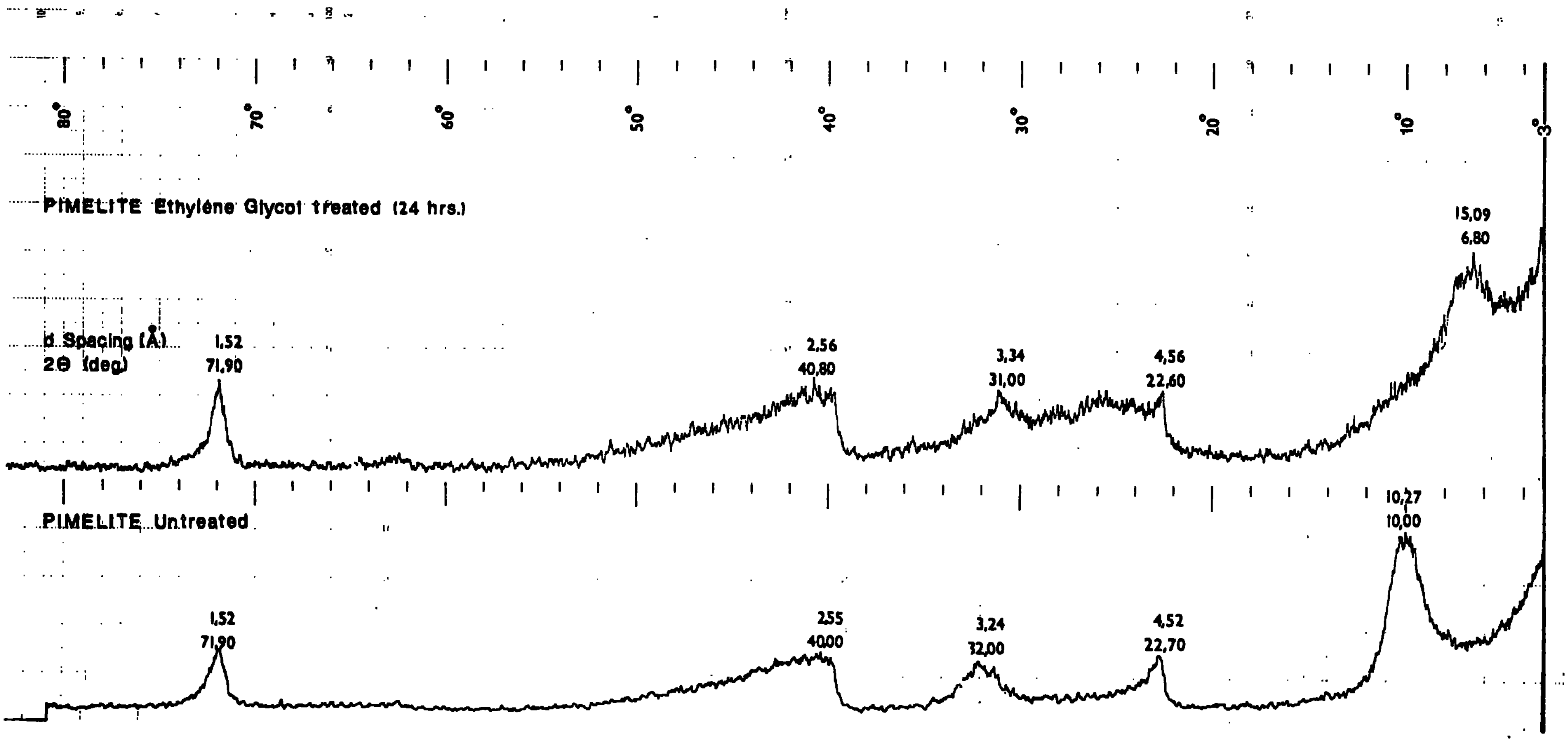

Plate 2. Untreated and Ethylene glycol treated (24 hrs) X.R.D. charts for pimelite.

As well as smear mounts, cavity mounts of the pimelite sample were run and the results obtained are shown below.

d(Å)	Rel.Int.
10.27	100
4.56	50
3.22	20
2.59	50
1.52	80
1.31	5(negligible)

There are indications from the films obtained using copper radiation of a diffraction maximum at approximately 15Å although this peak was rather uncertain and difficult to measure as it was barely clear of the hole in the film (Plate 3).

e. DTA Analysis of Pimelite

During the differential thermal analysis the pimelite was first heated in air flow which gave two endothermic and one exothermic peak (fig.4). The first endothermic peak occurs when the temperature is between 50° and 200°C indicating the escape of free water as Slansky (1955) stated. The second endothermic peak occurs between the temperature of 800°-1000° (if the sample firmly packed, fig.4/c). This peak also confirms the conclusion of Slansky (1955) in fig.2 and Ostrowicki (1965) in fig.3 which indicates the escape of the combined water at the same temperature.

Apart from these two peaks, between the temperature of 300°-500° and sometimes 200°-500° (this difference is

Plate 3. X-ray film of Pimelite

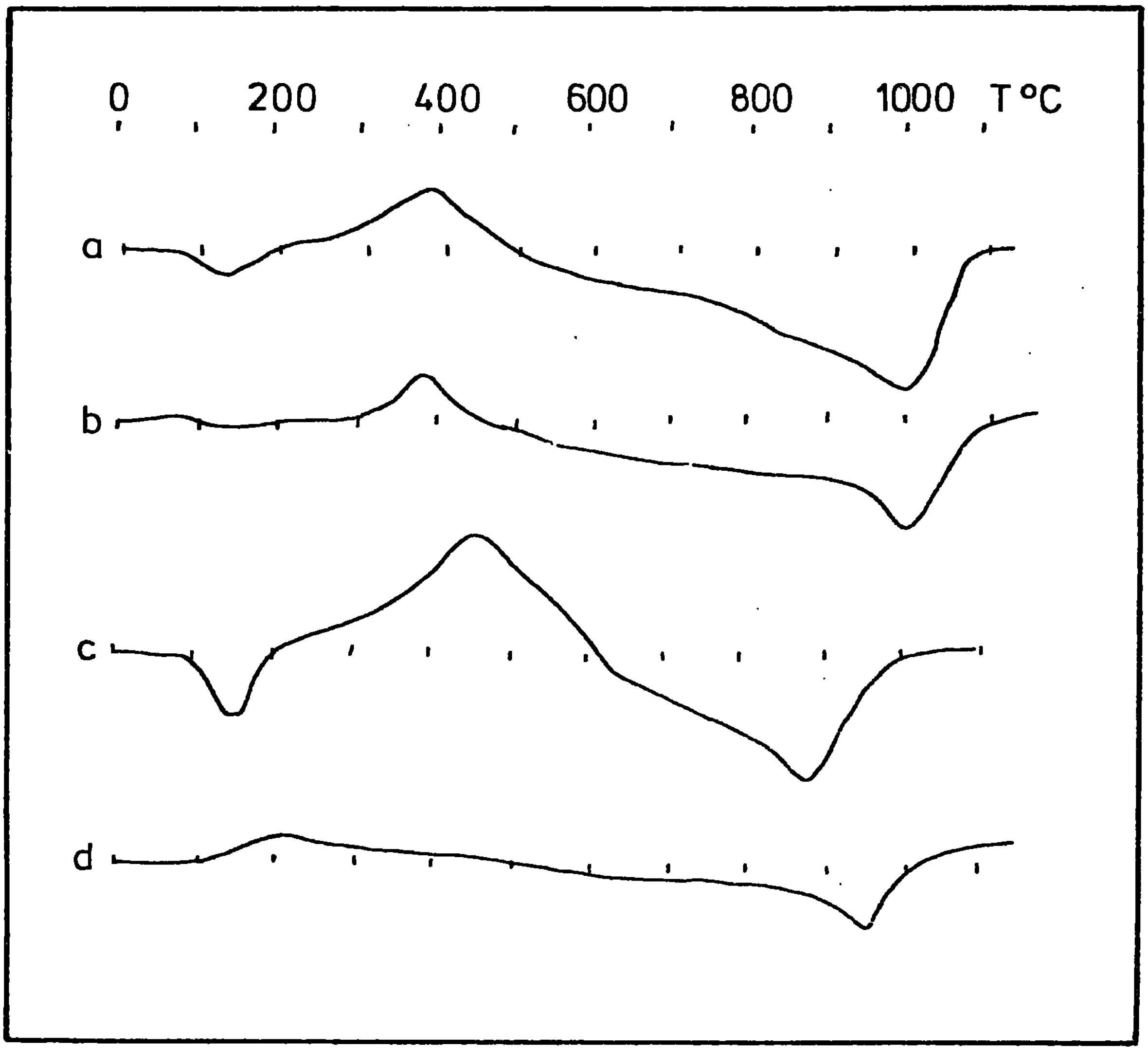

Figure 4. DTA Curves for Pimelite

a,b running in air flow
c " " " " (specimen firmly packed)
d running in nitrogen flow

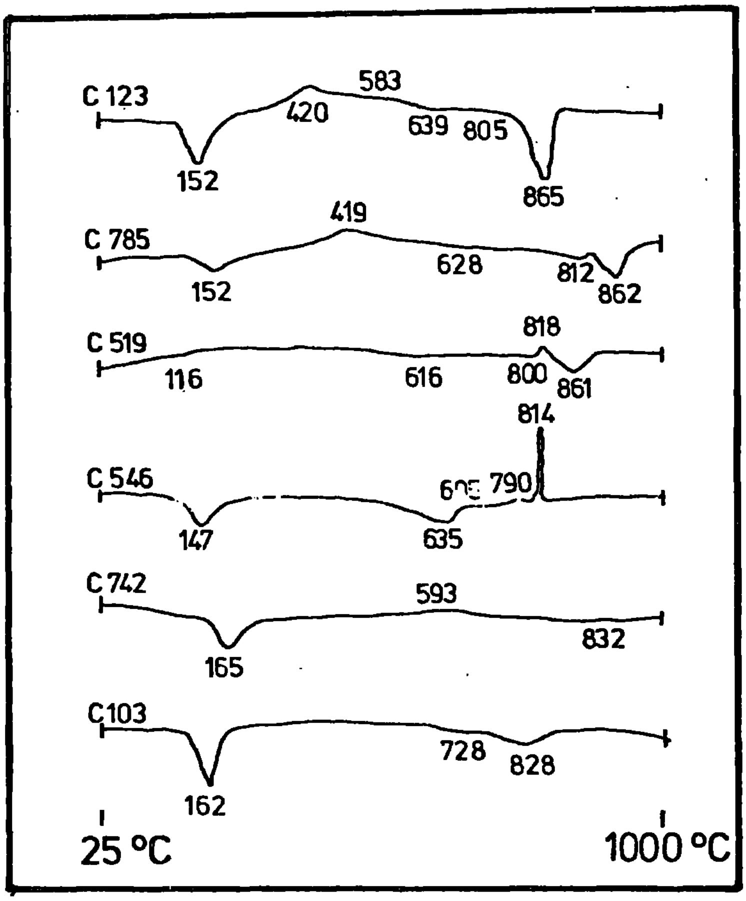

Figure 5. DTA Curves for Stevensite (From Faust <u>et al</u>., 1959).
C-123, Stevensite No.4, Paterson, New Jersey;
C-785, Synthetic stevensite, Bowen & Tuttle preparation T-2-37.
C-519, Stevensite No.5 with serpentine, Mine Creek, North Carolina, USA.
C-546, Ghassoulite, Morocco, C-742; and Hectorite, Hector, California, C-103.

most probably related to the firmness of packing and the amount of material) an exothermic peak occurs. This peak has not been recorded in the literature.

An attempt was made to investigate the presence of any organic material, in case its presence might be having an effect on the results in air flow. Consequently during the DTA in a nitrogen flow the exothermic peak decreased substantially and the first endothermic peak almost vanished, whereas the second endothermic peak remained constant (fig.4/d).

After this section had been written, the curves for stevensite shown in figure 5 were discovered in the paper by Faust, Hathaway and Millot 1959. The first of these curves (C-123) is closely similar to figure 4a obtained in this study.

f. TGA analysis of pimelite

The average of three thermogravimetric analyses of pimelite gave about 11% water loss (see fig.7) (Dehydration curve of pimelite done by Slansky 1955 also can be seen in fig.6).

The total analysis of pimelite from the electron microprobe together with the H_2O obtained from TGA still shows a low value suggesting perhaps the presence of other oxides. No CO_2 was observed by wet chemistry using the method suggested by Groves (1951).

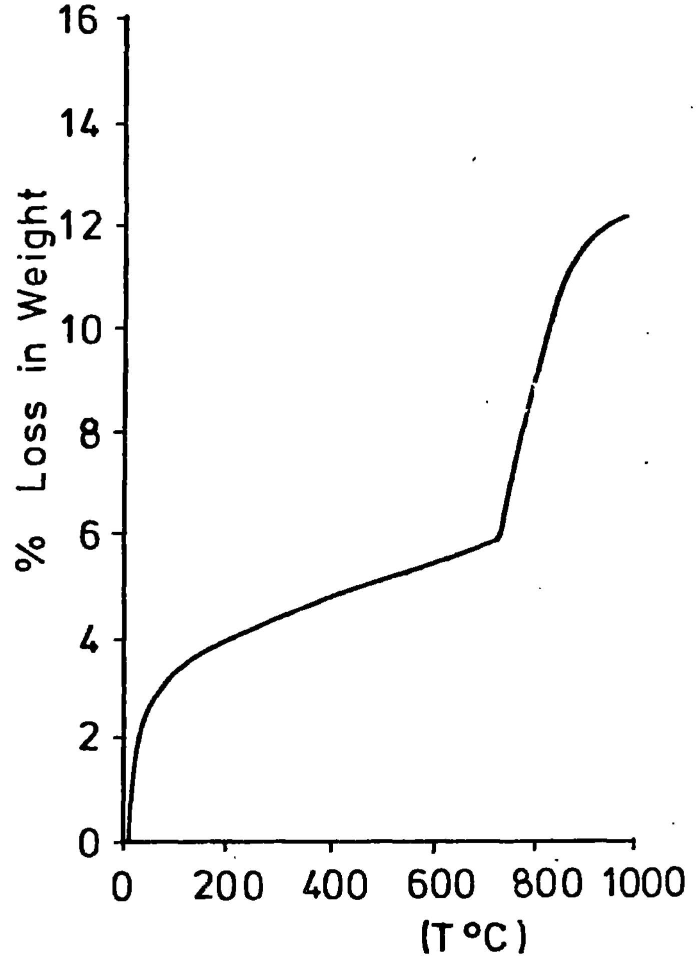

Figure 6. Dehydration Curve for Pimelite
(From Slansky, 1955).

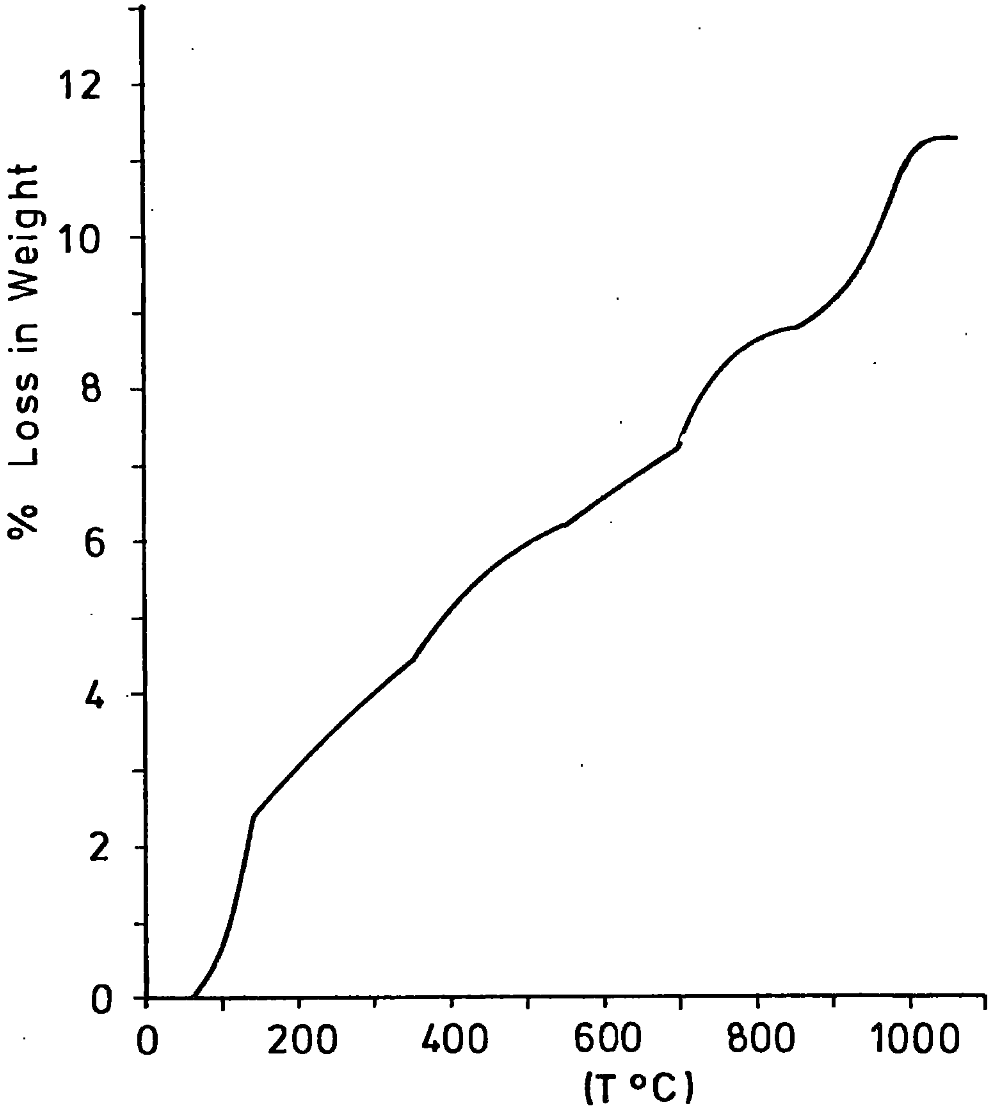

Figure 7. Dehydration Curve for Pimelite

The total analysis obtained, together with several analyses from the literature are shown for pimelite on pages 33-36.

g. Conclusions

From the swelling properties of the pimelite examined and recalculation of the chemical analysis, it is concluded that it is a smectite mineral related to stevensite. D.T.A. results correspond with those for stevensite given by Faust (fig.5) and pimelite is apparently a nickel stevensite. The mineral of this study is equivalent to 75% of the pure nickel end member with 25% of the pure magnesium end member and interlayer magnesium. The Faust (1961) analysis is less rich in nickel.

Having reached these conclusions, a paper by Brindley and Maksimovic(1974) was brought to the author's attention. Their conclusions differ from those given above, suggesting that pimelite is talc-like and can only be caused to swell partially and with difficulty by soaking in ethylene glycol for about 1 month (note added in proof p.227). This was not found in the present investigation - overnight soaking was sufficient.

Thus it is not thought necessary to modify the above conclusions, except to agree with Brindley and Maksimovic (1974) that further work on a wider range of pimelite specimens would be justified.

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