Gonnardite and disordered natrolite-group minerals: their distinction and relations with mesolite, natrolite and thomsonite

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Abstract

This paper presents a literature survey of compositions of the fibrous zeolites mesolite, natrolite, thomsonite and their derivatives such as pseudomesolite, high-Na mesolite, tetranatrolite, paranatrolite, ranite, and gonnardite, and evaluates them in the light of new electron probe analyses and X-ray powder data for gonnardites and associated minerals from Aci Castello, Gignat, Hills Port, Kladno, and Lamo. The analyses are plotted on the basis of bivalent *vs.* trivalent cations per 80 oxygen cell and a new chemical classification is tentatively proposed. It is concluded that ranite is definitely not synonymous with gonnardite and until species status is confirmed it is useful to retain this term as a Ca- and Al-rich disordered variety of natrolite. It is further concluded that natrolite and tetranatrolite contain up to 2 Ca, ranite 2–4 Ca, gonnardite 4–6 Ca and thomsonite 6–8 Ca atoms with corresponding limits on the Al atoms. Compositions are governed by NaSi = CaAl and to some extent by Na_2 = Ca type replacements and the Al-content generally varies sympathetically with Ca-content. The plot reveals that most high-Na mesolites are ranites, a number of gonnardites are ranites and one or two are tetranatrolites. The compositional field of gonnardite crosses that of mesolite (and pseudomesolite), but these minerals can be easily distinguished optically and by their powder patterns. The unit cell volumes increase in the order tetranatrolite, ranite, gonnardite and paranatrolite, therefore if the $\underline{10}40$ (or $\underline{14}60$) line can be identified in the powder patterns one can distinguish between these minerals. New infrared spectra of gonnardite, ranite and tetranatrolite are compared with each other and with published spectra, and differences are noted. DSC results for gonnardite and ranite are compared and appear to be diagnostic.

KEYWORDS: zeolite, gonnardite, natrolite, ranite, mesolite thomsonite

Introduction

GONNARDITE has had an unfortunate history since its discovery (Lacroix, 1896) and its species status is uncertain today. The structural study of gonnardite in the space group *Pbmn* by Amirov *et al.* (1972) does not change the picture as no chemical, optical or powder data are given. Their structure differs from that of the thomsonite structure by Alberti *et al.* (1981) in its choice of origin and assumes complete Si/Al disorder. Mazzi *et al.* (1986) give a structure for gonnardite in the space group previously attributed to tetranatrolite but their material is more akin to ranite in composition than either to tetranatrolite of Chen and Chao (1980) or to gonnardite of Hey (1932*a*). Most identifications of gonnardite as recently reviewed by Gottardi and Galli (1985) are based on either the optical properties which are not defined, or on powder diffraction patterns which cannot be distinguished with certainty from those of tetranatrolite, paranatrolite and ranite. The mineral seldom occurs alone; it is associated with thomsonite or ranite or tetranatrolite—therefore the purity of material used for analyses is uncertain. One has to agree with this extract from Gottardi and Galli (1985): 'On the whole, the problem of the gonnardite symmetry and structure is still open. The only sample which seems to be rather pure is from Kloch, Styria; the formula given in the title page is an informed guess only'. Of the three alleged gonnardite analyses by electron microprobe one is on probable tetranatrolite (Anal. 19, Table 1), the other is on a mixture of tetranatrolite and gonnardite (Anal. 27, Table 1) and the third is on ranite (Anal. 23a, Table 1). There

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is no reliable standard infrared spectrum of gonnardite; therefore all identification based on IR methods are suspect. For a proper understanding of the gonnardite problem, a literature survey of the fibrous zeolites was carried out. The references other than those marked [MA 4-319] etc. were consulted in original. New electron probe, optical, X-ray, infrared and differential scanning calorimetry (DSC) data are presented and both the new and old data are evaluated for possible distinctive criteria.

Experimental methods

Electron probe analyses of the minerals were performed for the author at Chicago University, Modena University, the Smithsonian Institution and Queen's University of Belfast. Optical examination was carried out by the author on either the probe mounts or on carefully selected powdered samples by oil immersion to check the elongation sign and relative refractive index. Water (and CO_2) determination on two samples was made at the BM(NH) on a Perkin Elmer-240 elemental analyser.

X-ray examination was made with Cu-$K\alpha$ radiation, either by powder photography, camera dia. 114.59 mm, or by powder diffractomy. Rotation and Weissenberg photographs were also made of some samples, all of which showed streaks rather than sharp spots. Approximate cell dimensions derived from the single crystal photographs were used to index the powder patterns and refined constants were derived from the accurately indexed powder lines. Indexing was facilitated by comparison of powder and rotation patterns taken on Debye-Scherrer or Weissenberg cameras.

Infrared spectra were obtained at the Queen's University on the Perkin Elmer-598 I.R. Spectrophotometer using KBr disks containing approximately 1 mg sample, abscissa expansion = ×1, medium slit = 3 cm^{-1}, scan time 12 min. Differential scanning calorimetry results were obtained on a Stanton Redcroft DSC 700 model using 10.9 mg samples at the Lambeg Industrial Research Association (LIRA), Lisburn. The conditions were: start (25), final (600), rate (20), gas (air).

For plotting analytical results, B (largely Ca) and T (largely Al atoms) were chosen as the two axes following Hey (1932*a*, p. 67) and not the ratios $B/(B + M)$ and Si/(Si + Al) which are extensively used in modern literature but are difficult to deal with. Selected analyses in most cases had the balance error E less than ±13%, where $E = 100 \times \{T - (2B + M)\}/(2B + M)$, all atoms based on an 80 oxygen anhydrous cell, B, M and T stand for bivalent, monovalent and trivalent cations respectively.

Experimental data

Literature chemical data are in part listed in Table 1 and shown in full in Fig. 1(*a–d*). To obtain new data, Northern Ireland gonnardite, thomsonite, mesolite and natrolite and gonnardites from Italy, France, Norway, Austria and Hawaii were used in this study. Paranatrolite was detected by its X-ray powder lines in the patterns of tetranatrolite from Hills Port and Aci Castello. The letter I preceding the investigated specimens stands for BELUM:I and signifies an Ulster Museum, Belfast, specimen.

Hills Port gonnardite. Gonnardite occurs at Hills Port, Island Magee, County Antrim, in the Tertiary basalt as previously noted by Thompson (1970). Other associated zeolites are either chabazite or heulandite or both. Natrolite, tetranatrolite, paranatrolite, thomsonite and other zeolites occur throughout the district. The gonnardite forms spherules, up to 3 cm in length. They show compositional and colour zonation. The colour varies between various shades of salmon red and white. Mineralogically the gonnardite spherules are composed largely of gonnardite with minor amounts of thomsonite and tetranatrolite. The gonnardite has negative elongation and shows extensive zonation from core to rim (Fig. 1*e*) and is selectively enriched in Sr, Mg and K. Averaged electron probe analyses of the Hills Port zeolite spherules are listed in Tables 2 and 3.

A Hills Port gonnardite spherule heated to 800 °C for one hour lost 15.7% weight. It changed to positive elongation and became almost isotropic, refractive index around 1.55. The X-ray powder patterns of the unheated and heated material are given in Tables 4 and 5.

Gignat gonnardite. Compared with the Hills Port gonnardite the Gignat gonnardite shows a limited zonation Fig. 1*e*. Averaged electron probe analyses of the Gignat gonnardite are shown in Fig. 1*b* and are listed in Table 2. The Gignat specimen used for this study showed optical variations with Ca–Al-rich areas showing negative elongation and Na–Si-rich areas either positive or positive and negative elongation which reflects upon the compositions of the various parts of the spherules as shown in Fig. 1*e*. The powder pattern of the Gignat gonnardite is listed in Table 4.

Lamo ranite. Ranite from the type locality of Lamo has negative elongation; it becomes positive during examination as the grains warm up with the heat from the microscope lamp and becomes negative again upon cooling. Its composition by electron probe analysis is given in Table 2 and its X-ray powder pattern is given in Table 4. An electron probe analysis of the associated tetranatrolite showing a positive elongation is given in Table 2.

Table 1. Recalculated literature analyses of the fibrous zeolites

No.	T	B	M	E%	Locality and Reference
Natrolite					
1	15.93	0.07	15.67	+1	Bound Brook,New Jersey, Dunn (1976)
2	16.10	0.10	16.23	+2	Ice River, Canada, Grice & Gault (1981)
3	16.36	0.40	15.04	+3	Gulac's Hill, Hungary, Alberti et al. (1983)
4	16.04	0.19	16.13	-3	Kola, Kuzmankov (1950)
5	16.15	-	16.35	-1	Moravia, Cerny and Povondra (1966)
6	15.58	0.25	15.73	-4	Moravia, Cerny and Povondra (1966)
7	16.62	0.69	14.80	+3	Hawaii, Iijima and Harada (1969)
8	16.24	0.58	15.12	0	Japan, Harada and Nakao (1969)
9	15.97	0.83	15.01	-4	Japan, Harada and Nakao (1969)
10	15.25	0.05	16.04	-7	Quebec, Chen and Chao (1980)
11	16.09	0.64	13.72	+7	Badkhyz, U.S.S.R., Raevskii and Brovko (1980)
12	15.79	0.27	15.74	-3	Mori, Venetia, Cavinato (1926)
13	17.45	0.16	14.85	+15	Yani, Japan, Matsubara et al. (1979)
14	17.97	2.91	11.95	+1	Bohemia, Cermakova et al. (1962)
Tetranatrolite					
15	14.63	0.16	15.28	-6	Karnasurt Mts., U.S.S.R., Guseva et al. (1975)
16	15.36	0.36	14.28	+2	Greenland, Andersen et al (1969)
17	15.60	0.82	14.74	-5	Quebec, Chen and Chao (1980)
18	16.90	1.28	13.62	+5	Gulac's Hill, Hungary Alberti et al. (1982)
Gonnardite and ranite					
19	17.28	1.44	14.60	-1	Hawaii (probe), Iijima and Harada (1969)
20	17.80	2.28	13.12	+1	Do (wet chemical)
21	17.24	3.00	11.48	-1	Maze, Japan, Harada et al. (1967)
22	17.84	2.60	11.88	+4	Saga, Japan, Ueno et al. (1982)
23	19.96	2.88	11.84	+13	Brevig, Norway, Paijkull (1874)
23a	18.44	3.00	12.86	-2	Norway (probe), Mazzi et al. (1986)
24	15.56	7.58	4.28	-20	India, Ramasamy (1981)
25	17.50	5.86	6.86	-6	Gignat, France, Pisani (Gonnard, 1871)
26	17.16	5.36	7.56	-6	Gignat, mix. with thomsonite, Hey (1932a)
27	16.88	4.06	7.94	+5	Hungary, Alberti et al. (1982)
Mesolite and pseudomesolite					
28	16.10	5.39	4.69	+4	Carlton Peak, Minnesota, Winchell (1900)
29	15.31	5.31	6.08	-9	Mt. Peloritani, Sicily, Stella-Starrabba (1947)
30	15.64	6.12	4.18	-5	Tezuka, Japan, Harada et al. (1968)
31	17.03	6.23	5.34	-4	Oshima, Japan, Harada et al. (1968)
32	17.04	4.21	9.93	-7	Waniguchi, Japan, Harada et al. (1968)
33	16.01	6.25	9.56	-28	Waniguchi, Japan, Harada et al. (1968)
34	16.30	6.27	4.17	-3	Iceland, Cavinato (1926)
Thomsonite					
35	17.18	3.45	10.70	-3	New Zealand, Benson (1942)
36	20.19	8.48	4.23	-7	Yani, Japan, Matsubara et al. (1979)
37	19.32	7.56	4.82	-3	Tyamir, U.S.S.R., Efimov et al. (1966)
38	19.60	7.94	4.41	-3	Tyamir, U.S.S.R., Efimov et al. (1966)
39	18.01	5.33	5.88	+9	Iragawa, Japan, Harada et al. (1969)
40	18.56	5.51	7.28	+1	Maze, Japan, Harada et al. (1967)
41	20.52	7.46	5.03	+3	Sextant Rapids, Canada, Walker (1932)
42	19.27	7.05	4.88	+2	Table Mtn., Colorado, Henderson and Glass (1933)
43	19.11	5.66	6.29	+8	Island Magee, Co. Antrim, Tomkeieff (1934)
44	19.57	8.36	4.08	-6	Crimea, Shkabara (1940)
45	19.29	8.02	4.13	-4	California, Alberti et al. (1981)

Kladno high-Na mesolite. Kladno material of Antonin (1942) was found optically to show partly negative and partly positive elongation, but the entire sample became negative when immersed in water. Powder and fibre rotation patterns (not given) of this high-Na mesolite are identical to those of Lamo ranite.

Kloch zeolites. Gonnardite is observed in the Kloch specimens in minor amounts but the majority of Kloch material is either tetranatrolite or ranite or a mixture of tetranatrolite and ranite (see definitions below). The Kloch tetranatrolite has positive elongation and it is fluorescent under both long- and short-wave UV light. Its electron probe analysis (Table 2) gives less Ca and Al than the material analysed by Meixner *et al.* (1956, Anal. A).

Another Kloch zeolite with similar behaviour to ranite in having negative elongation which becomes (reversibly) positive on gentle heating is probably ranite. Its X-ray pattern is identical to that of the associated tetranatrolite except for larger cell dimensions as evident from the powder patterns of the mixtures containing both the minerals.

Zeolites from Italy. The Aci Castello material described by Meixner *et al.* (1956, Anal. C) is probably a gonnardite as seen from their optical and chemical data, but material from the same locality examined by this author has positive elongation and chemically matches (Table 2) the definition (below) of a tetranatrolite. Its powder pattern (Table 4) indicates that it contains a minor amount of paranatrolite.

Hawaii gonnardite. The gonnardite from Oahu, Hawaii, previously described by Hay and Iijima (1968) and Iijima and Harada (1969) shows optically that the material is a mixture of positively

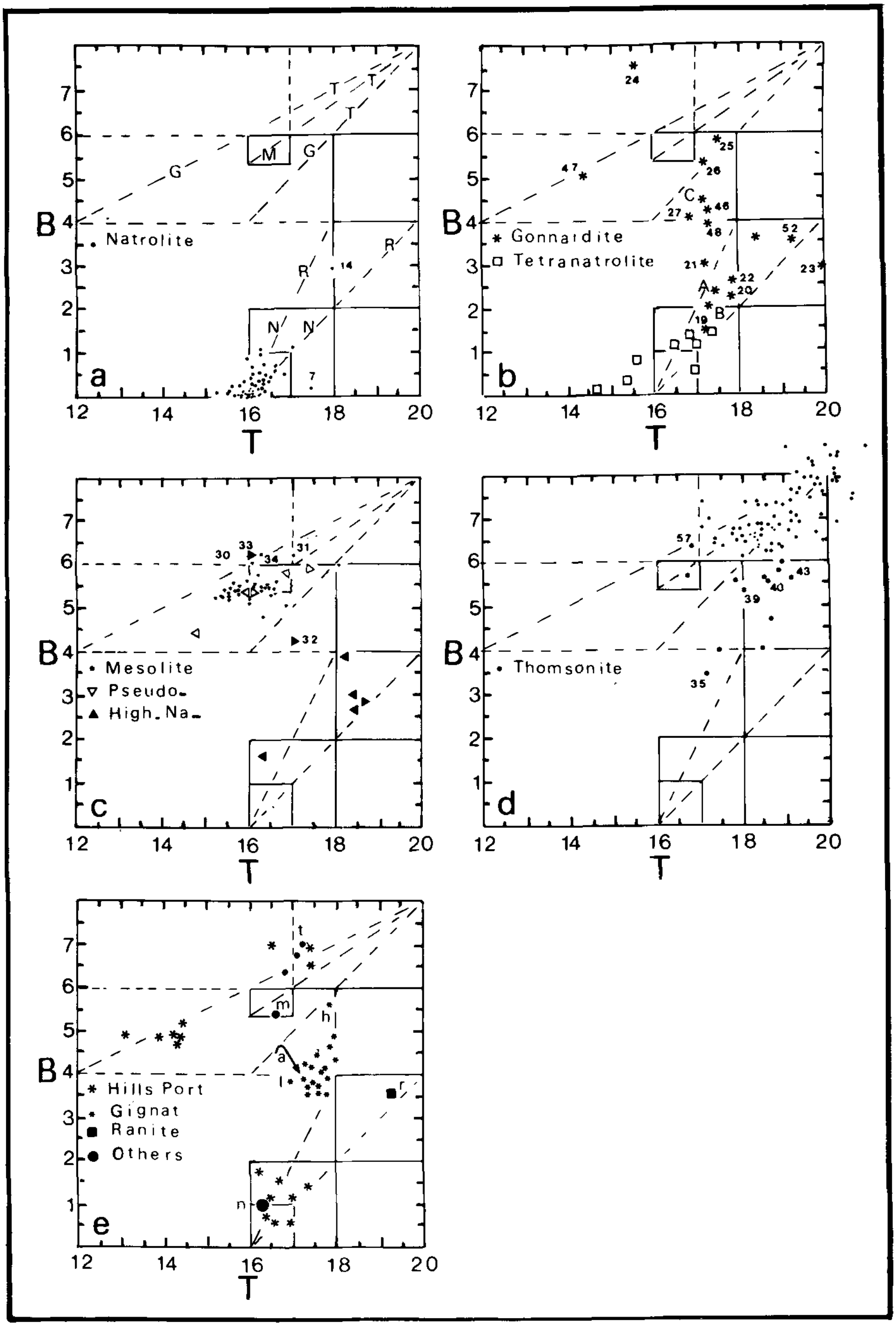

FIG. 1 (*a–d*). Literature analyses in Table 1 and others (see text), and (*e*), new analyses (Tables 2 and 3) of the natrolite and thomsonite group zeolites plotted to reveal their relative compositional fields in terms of bivalent (*B*) and trivalent (*T*) cations per 80 oxygen anhydrous cell. The letters G, M, N, R, T respectively mark the trend lines of gonnardite, mesolite, natrolite (and tetranatrolite), ranite and thomsonite. The numbers in Fig. 1 (*a–d*) refer to analyses listed in Tables 1–3, the letters r, m, n, t refer to analyses of ranite, mesolite, natrolite and thomsonite, and the letters a, h and l respectively refer to average of several data points, high-Ca point and low-Ca point for the Gignat gonnardite.

Table 2. Electron probe analyses of gonnardites, tetranatrolites and ranites

	46	47	48	49	50	51	52	54
SiO_2	41.79	47.66	43.45	43.09	47.68	43.3	39.36	44.48
Al_2O_3	26.79	22.78	27.91	27.36	27.94	26.9	30.73	27.23
Fe_2O_3	0.00	0.00	0.00	0.02	0.00	0.0	0.33	0.24
MgO	0.00	0.32	0.00	0.00	0.00	0.0	0.00	0.00
CaO	7.21	7.38	6.95	2.45	2.14	2.0	6.34	0.98
SrO	0.00	1.77	0.00	0.00	0.00	0.0	0.04	0.11
BaO	0.00	0.09	0.00	0.04	0.00	0.0	0.02	0.00
Na_2O	7.75	3.61	8.69	12.60	13.50	13.5	11.94	14.61
K_2O	0.11	1.61	0.00	0.02	0.03	0.0	0.04	0.23
[H_2O]	[16.35]	[14.78]	13.0	[14.42]	[8.71]	[14.3]	11.2	[12.14]
Total	100.00	100.00	100.00	100.00	100.00	100.0	100.00	100.00
Cations on the basis of 80 oxygens								
Si	22.87	25.50	22.85	23.06	23.82	23.19	20.73	23.30
Al	17.28	14.36	17.30	17.32	16.46	16.98	19.09	16.81
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.13	0.10
Mg	0.00	0.26	0.00	0.00	0.00	0.00	0.00	0.00
Ca	4.23	4.22	3.92	1.42	1.16	1.15	3.58	0.55
Sr	0.00	0.54	0.00	0.00	0.00	0.00	0.01	0.03
Ba	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Na	8.22	3.74	8.86	13.08	13.06	14.02	12.19	14.84
K	0.08	1.10	0.00	0.02	0.02	0.00	0.03	0.15
[H_2O]	[29.86]	[26.31]	22.80	[26.02]	[14.70]	[25.54]	19.68	[21.20]
E%	+3.18	-3.75	+3.59	+8.65	+6.88	+4.04	-0.93	-4.10
Sign	-	-	-	+	+	+	-	+

46. Gonnardite, type locality at Gignat, France, Adair analyst, (I9472).
47. Gonnardite from inner parts of spherules, Hills Port, Antrim, Average of seven analyses, SrO range 0.83–3.44%, Vezzalini analyst, (I4371).
48. Gonnardite, type locality at Gignat, France, normalized to 13.0% H_2O, Dunn analyst, water by Din, (I9472).
49. Tetranatrolite-paranatrolite mixture, Aci Castello, Sicily, Vezzalini analyst, (I9213) off BM 1958–698.
50. Tetranatrolite-paranatrolite mixture, outer extremity of gonnardite spherules, Hills Port, Co. Antrim, Vezzalini analyst, (I4371).
51. Kloch tetranatrolite, Dunn analyst, (I9183).
52. Ranite, Lamo, normalized to 11.2% H_2O, Vezzalini analyst, Water by Easton, (I9477).
54. Tetranatrolite associated with Lamo ranite, Vezzalini analyst, (I9477).

and negatively elongated zeolites. X-ray powder patterns (not given) indicate the material is probably a mixture of two phases, tetranatrolite and ranite. The comparative unit cell data for the various zeolites are compiled in Table 6.

Infrared spectra and DSC data. The infrared spectra of the Hills Port gonnardite, Gignat gonnardite, Lamo ranite and Kloch tetranatrolite are given in Fig. 2. The DSC scans of the Hills Port gonnardite and Lamo ranite are given in Fig. 3.

County Antrim thomsonite, mesolite and natrolite. Electron probe analyses of the other relevant Co. Antrim zeolites, thomsonite, mesolite and natrolite are given in Table 3.

Discussion

The B–T plot of the fibrous zeolite analyses

The gonnardite, tetranatrolite and ranite analyses of this study (Table 2) are plotted in Fig. 1*e* together with analyses of the ordered zeolites, natrolite, mesolite and thomsonite (Table 3). They show a broad range of compositions; for example Ca ranges between 0.5 atoms to 7 atoms and Al from 13 atoms to 19.5 atoms covering the entire range of compositional fields of natrolite, mesolite and thomsonite. Some parts of the Hills Port gonnardite spherule plot in the natrolite–tetranatrolite field, some in or near the

Table 3. Electron probe analyses of some Co. Antrim zeolites

	55	56	57	58	59
SiO_2	43.29	42.02	43.98	43.43	46.62
Al_2O_3	27.36	27.07	27.20	25.99	27.09
Fe_2O_3	0.04	-	-	-	-
MgO	0.04	0.24	0.68	0.15	0.36
CaO	11.78	11.76	10.36	9.02	1.35
BaO	0.07	-	-	-	-
Na_2O	3.24	3.17	4.22	5.41	14.28
K2O	0.01	0.00	0.07	0.00	0.07
$[H_2O]$	[14.17]	[15.74]	[13.48]	[16.00]	[10.23]
	100.00	100.00	100.00	100.00	100.00
Cations on the basis of 80 oxygens					
Si	22.96	22.73	23.10	23.53	23.75
Al	17.10	17.25	16.83	16.59	16.27
Fe	0.02	-	-	-	-
Mg	0.04	0.18	0.53	0.12	0.27
Ca	6.70	6.82	5.83	5.24	0.73
Ba	0.02	-	-	-	-
Na	3.34	3.33	4.30	5.41	14.12
K	0.00	0.00	0.05	0.00	0.05
$[H_2O]$	[25.07]	[28.40]	[23.62]	[28.91]	[17.42]
E%	1.54	-0.46	-1.41	2.85	0.93

55- Hills Port thomsonite in the gonnardite spherules, Vezzalini analyst, average of 4 spots, (I4371).

56- Hills Port thomsonite in the gonnardite spherules, Price analyst, (F65).

57- Hills Port thomsonite in the gonnardite spherules, Price analyst, (I9040).

58- Dunseverick mesolite, average of 4 different analyses, Price analyst, (I9041).

59- Magheramourne orange-coloured natrolite, Price analyst, (I9042).

thomsonite field and some near or beyond the mesolite field. Fortunately the gonnardite composition is recognized because it is selectively enriched in K, Mg, Sr compared with the parts which consitute thomsonite or tetranatrolite. The Gignat gonnardite spherule shows a different zonation trend, the extent of which is much lower than that of the Hills Port gonnardite. For example the Gignat gonnardite compositions are limited between about 3.5 and 6 Ca atoms and between 17 and 18 Al atoms, whereas those of the Hills Port gonnardite are limited between 4 and 6.5 Ca and between 13 and 17 Al atoms. The unusual zonation of the Hills Port gonnardite spherules and its difference from the zonation of the Gignat gonnardite spherules raises two questions: (*a*) where do the gonnardite compositions begin and where do they end in relation to the compositional fields of thomsonite, mesolite, pseudomesolite, ranite, tetranatrolite and natrolite, and (*b*) which parent mineral does gonnardite belong to and what is its precise definition?

In order to reconcile the above differences and to answer these questions, the averaged analyses of this study were plotted with the following literature analyses to 1987: natrolite (Fig. 1*a*); gonnardite (including ranite) and tetranatrolite (Fig. 1*b*); mesolite, pseudomesolite and high-Na mesolite (Fig. 1*c*) and thomsonite (Fig. 1*d*), either listed in Table 1, or taken from Alberti *et al.* (1982, 1983), Foster (1965), Hey (1932*a*,*b*, 1933), Mazzi *et al.* (1986), Meixner *et al.* (1956), Nawaz *et al.* (1985) and Wise and Tschernich (1978). The letters T, G, M, N and R mark the trend lines as defined in Fig. 1. The trend lines are of the type CaAl = NaSi ± Ca = Na_2.

Chemical classification

Natrolite. Figure 1*a* shows that most of the natrolite analyses are clustered around the ideal composition $[Na_2Al_2Si_3O_{10} \cdot 2H_2O]$ i.e. Al = 16 and Ca = 0. A few others occur along the trend lines marked N and R and all except two are within the field of Al = 16–17 and Ca = 0–1.

There is an element of uncertainty about the exceptional analyses numbered 7 and 14; the former has 15% balance error, whereas the latter is reportedly on material whose optical properties given by Cermakova *et al.* (1962) match those of ideal natrolite.

Gonnardite, tetranatrolite and ranite. Figure 1*b* shows the plot of all new and published analyses of material that has been called gonnardite, ranite and tetranatrolite. These analyses plot along G, N and R lines (see Fig. 1*a*); the latter two show replacement of the type NaSi = CaAl and NaSi = CaAl + Ca = Na_2. It is clear that all analyses except two (Nos. 19, 24) plot between Ca = 2 and Ca = 6 atoms. Number 24 can be ignored because of its −20% balance error and number 19 because of identity uncertainty as below. Numbers 19 and 20 (with higher Ca and Al) are on material from the same veinlet but the fact that the elongation is either positive or positive and negative (Iijima and Harada, 1969; p. 190) suggests that what the authors call a 'thomsonite' may be two minerals, a tetranatrolite and a ranite. For the rest of the analyses there is a noticeable gap in compositions at about Ca = 3.5. The replacement lines are absent between natrolite and mesolite compositions, the compositions below 3.5 Ca are along natrolite trend lines (N, R) and those above are along thomsonite trend lines (T, G), and the ranite compositions are along the N and R trend lines.

Thus the plot provides a strong basis for a chemical subdivision of the field as below. The tetranatrolite and natrolite clearly plot below the 2 Ca mark and below the 18 Al boundary.

Gonnardites and ranite, trending along the N and R lines, with Ca less than 4 and Al between 17 and 20 atoms, described in the literature and found in this study to have negative elongation or positive and negative elongation (due to reversible dehydration), constitute a distinct chemical entity and the old name ranite could still be used for this group. The Vevja Quarry gonnardite (Mazzi *et al.*, 1986; Anal. 23a, Table 1) comes into this category; the sample used for their structure determination has unfilled water-sites and positive elongation (Gottardi, priv. comm.). One of the authors of the above paper (Larsen, 1987, priv. comm.) has indicated that the water content of this gonnardite is variable dependent upon relative humidity of the storage environment, as reflected in their two *a* values of 13.21 and 13.27 Å, although it is not known whether or not the high-water sample has the negative elongation of ranite. The suggestion of Mazzi *et al.* (1986) that tetranatrolite and gonnardite are identical is similar to the suggestion of Mason (1957) that ranite and gonnardite are identical, and one that is not borne out by this study.

The name gonnardite in its strictest sense should be restricted to those gonnardites with Al less than 18 and Ca = 4–6 and which have the optical properties and compositions as defined by Hey (1932*a*) for type gonnardite, i.e. negative elongation and composition closer to that of thomsonite and mesolite than to natrolite. These gonnardites plot along the extended thomsonite trend lines, T and G, and accord with the TEM study of thomsonite–gonnardite domains by Rinaldi (1982). It is quite possible that some gonnardites have domains of ranite and vice versa, so that the plotted compositions depart from the trend lines G and R. The optical variation shown by the Gignat gonnardite of this study may be caused in this way, and its Na-rich composition (Fig. 1*e*) relative to previous studies (Hey, 1932*a*; Reeuwijk, 1972; Gonnard, 1871) can be also explained similarly.

Mesolite, pseudomesolite and high-Na mesolite. Pseudomesolite and mesolite are identical (Nawaz *et al.*, 1985), and their compositions plot very close to the ideal composition of Ca 5.33 and Al 16. Most plot along the trend line M indicating replacements of the type CaAl + NaSi ± Ca = Na_2. It is noteworthy that the M line lies between the two gonnardite trend lines. The high-Na mesolites appear to be unrelated to mesolite. One of the seven analyses (No. 33) has −28% error and has to be disregarded; the other with less than 2Ca atoms is most certainly of tetranatrolite which has been found at this locality in this study, and a third (No. 32) is probably of gonnardite. The other four including the two from Kladno, Bohemia, plot in the ranite field and presumably all four are ranites.

Thomsonite. The thomsonite analyses are either clustered about the ideal point of 8Ca, 20Al or plot along the three trend lines T which can be defined as CaAl = NaSi ± Ca = Na_2. Almost all analyses have Al 17 or more; therefore it is a convenient boundary between thomsonite on the one hand and gonnardite and mesolite on the other. There are about twelve analyses that plot below the 6Ca mark but only six constitute a serious departure as they lie in or near the mesolite, gonnardite or ranite fields. One of these (Ca 4, Al 18.5) is on Salesl material by the late Dr Hey (1932*a*) who provided the remainder of his analysed sample to the auther for an optical examination. This showed the material to be both positively and positively and negatively elongated similar to ranite. It would be interesting to know what the others turn out to be.

Table 4. X-ray powder patterns of gonnardite, ranite and tetranatrolite*

	Gonnardite				Ranite		Tetranatrolite	
	(1)		(2)		(3)		(4)	
hkl	d	I	d	I	d	I	d	I
200	6.642	80	6.682	60	6.622	60	6.568	70
101	5.898	90	5.910	80	5.898	90	5.910	90
220	4.698	80	4.718	60	4.685	60	4.642	40
211	4.409	90	4.424	80	4.409	80	4.405	80
310	4.199	20	4.234	20	4.175	20	4.148	30
301	3.678	10	3.703	5	-		-	
400	3.324	10	3.300	2	3.305	2	-	
321	3.219	70	3.226	60	3.211	80	3.189	70
112	3.110	40	3.111	40	3.114	60	3.117	40
420,202	2.954	50	2.954	40	2.961	70	2.947	70
411	2.897	100	2.902	100	2.897	100	2.868	100
510,312	2.599	40	2.606	30	2.598	50	2.585	30
431	2.466	50	2.478	40	2.464	50	2.441	30
440,402	2.350	5	2.360	5	2.342}	20	2.330}	15
521	2.311	5	2.323	5	}		}	
332,530	2.271	20	2.276	20	2.272	20	2.260	10
600,422	2.212	50	2.218	40	2.208	50	2.194	30
620	2.105	5	2.104	2			-	
213,611	2.063	20	2.067	20	2.068	10	2.065	10
541,303	1.972	10	1.972	15	1.975	15	1.969	10
631,323	1.884	20	1.891	20	1.892	20	1.887	15
640,602	1.845	10	1.849	10	1.840	5	1.813}	30
701,413	1.817	30	1.816	30	1.815	25	}	
641,622	1.771	10	1.775	5	1.772	5	-	
730,721	1.749	20	1.758	20	1.744	10	1.723	10
503,632	1.694	10	1.696	10	1.696	5	1.691	5
651,800	1.648}	30	1.651}	30	1.651	10	1.656	5
523	}		}		1.634}	10	1.631	10
712	1.634	20	}		}		1.618	10
820,741	1.604	20	1.610	10	1.601	5	1.585	5

* Cu-K alpha radiation, estimated intensity, camera dia. 114.59mm

1 - Hills Port gonnardite, I8620, with associated thomsonite and tetranatrolite.

2 - Gignat gonnardite, I9472.

3 - Lamo ranite, A.M.N.H. Spec. 13238.

4 - Aci Castello tetranatrolite, I9213 off BM1958-698, with associated paranatrolite.

X-ray data

The X-ray powder patterns of gonnardite, tetranatrolite and ranite (Table 4) are almost identical, except for minor relative intensity differences of certain line pairs. Accurate measurement is needed to distinguish the patterns at high *d*-spacing but at lower *d*-spacings the unit cell volume differences are noticeable and indexing is more complicated. The patterns and indexing (Table 4) are very similar to those of the gonnardite of Mazzi *et al.* (1986) and to the tetranatrolite and paranatrolite (Chen and Chao, 1980; Chao, 1980).

The unit cell dimensions of these minerals are a function of the degree of disorder, the relative Ca and Al contents, the water content, and the parent structure type, whether the natrolite-type or thomsonite-type. The Si and Al disorder reduces $b-a$ to zero and the symmetry from orthorhombic to tetragonal. The Al tetrahedra are larger than the Si tetrahedra and Ca atoms have higher coordination than Na atoms, hence Ca- and Al-rich zeolites have more water and larger cell volumes; for example a thomsonite-type zeolite such as a gonnardite would have a higher unit cell volume than a natrolite-type zeolite such as a tetranatrolite. Ranite with intermediate composition has a lower cell volume and paranatrolite with a large excess of water has a higher cell volume than that of gonnardite. Consequently, qualitative distinction is possible by means of X-ray powder patterns provided the $\underline{1}040$ line ($\underline{1}460$ in the case of paranatrolite), a fairly strong one in this region, can be identified and accurately measured (Table 6). The paranatrolite line occurs at about 1.252, gonnardite line between 1.230 and 1.240, ranite line above 1.223 Å and tetranatrolite line below it.

Thermal data

Heat treatment. The thermal product of the Hills Port gonnardite tentatively identified by X-ray powder diffraction as hexagonal anorthite and nepheline (Table 5) is somewhat different from that of the Gignat gonnardite identified by Reeuwijk (1972) as high-temperature plagioclase and nepheline. These differences are not unexpected, as the two gonnardites differ in composition and probably neither was a pure specimen in the form used.

Table 5. Powder pattern of the heated Hills Port gonnardite.

d	I	d	I
7.56	14	2.276	11
4.45	56	2.127	28
3.821	100	2.036	14
3.746	84	2.023	14
3.493	14	1.870	28
3.351	31	1.796	14
3.280	26	1.774	17
3.209	11	1.764	9
2.863	80	1.590	17
2.564	84	1.585	14

Diffractometer pattern using Cu K alpha radiation, Si standard, specimen I4371 heated to 800°C for 1 hour.

Infrared spectrum. Infrared spectra of gonnardite are given by Pongiluppi (1975), Ramasamy (1981), Alberti *et al.* (1983), and Ueno *et al.* (1982), but none of these is satisfactory for one reason or another. For example, Alberti *et al.* (1983) give an infrared spectrum of tetranatrolite which is identical to the standard infrared spectrum of the type material by Chen and Chao (1980) and to their gonnardite spectrum, thereby implying that the gonnardite spectrum is identical to the tetranatrolite spectrum. In the absence of a standard infrared spectrum of gonnardite the one given in Fig. 2*b* of this study is reluctantly accepted as a standard. The Lamo ranite spectrum of Fig. 2*c* is accepted as a standard for ranite. In general the minima of tetranatrolite are sharper and less broad than either gonnardite or ranite. Its transmittance at 792 cm^{-1} is the largest of all the other absorption minima of tetranatrolite. In contrast to this the transmittance maxima of gonnardite and ranite occur at *c.* 2600 cm^{-1}. The ranite peak corresponding to the 792 cm^{-1} tetranatrolite minimum is shifted towards lower frequency at 780 cm^{-1}, and for gonnardite towards higher frequency at 800 cm^{-1}. The 2150 cm^{-1} absorption peak of tetranatrolite is somewhat taller than the corresponding peaks of gonnardite and ranite. The 465 cm^{-1} transmittance peak of tetranatrolite is fairly sharp and quite strong, gonnardite has only a weak broad minimum whereas ranite has a somewhat less sharp, less tall and broader peak. The 1625 cm^{-1} absorption peak of tetranatrolite is somewhat less intense than that of gonnardite (1640 cm^{-1}) but it is of about the same intensity as the peak of ranite (1620 cm^{-1}). The infrared spectrum of the Kloch zeolite (Fig. 2*d*) is very similar to the spectra of Canadian tetranatrolite (Chen and Chao, 1980) and of Hungarian tetranatrolite (Alberti *et al.*, 1983) except for the additional absorption peak at 2920 cm^{-1}. This peak is absent from the ranite and gonnardite spectra. It could be due to better resolution of the spectrum or (less likely) to an unknown impurity. The infrared spectrum of the Hills Port gonnardite (Fig. 2*a*) is identical to the spectrum of the type gonnardite except for the additional minor transmittance hump at about 550 cm^{-1}.

DSC scans. No differential scanning calorimetry scans of relevant zeolites were available to compare with the DSC scans of Fig. 3; therefore comparisons are made with the DTA data of tetranatrolite (Andersen *et al.*, 1969), and of natrolite, mesolite, scolecite, thomsonite, gonnardite and edingtonite (Van Reeuwijk, 1972; Gottardi and Galli, 1985). The DSC scan of the Lamo ranite with major absorption peaks at 125, 410 and 500 °C is unique. It has minor peaks at about 250° and a step at around 75 °C. Its DTA data bear slight resemblance to those of mesolite, scolecite and edingtonite but not to those of natrolite and tetranatrolite, both with a single absorption peak respectively at 350 ± 20 °C and 309 °C. The DSC scan of the Hills Port gonnardite is distinct from that of the Lamo ranite. It has a single major peak at 385 °C with a shoulder at 395 °C, two minor broad peaks at 125° and 315 °C and one very minor sharp peak at about 340 °C. Its resemblance with the DTA of thomsonite and gonnardite of Van Reeuwijk (1972) and with thomsonite of Gottardi and Galli (1985) is unmistakable; hence the conclusion that its structure is a derivative of thomsonite. It is noticed that the DTA of the gonnardite of Gottardi and Galli (1985) contains a single major absorption peak at a slightly lower temperature than the single absorption peak of their natrolite. This situation is similar to the DTA data of Andersen *et al.* (1970) which show that the single tetranatrolite absorption peak occurs at a lower temperature than the single natrolite absorption peak.

Conclusions

Natrolite compositions are restricted to between 16–17 Al atoms and between 0–1 Ca atoms. Tetranatrolites which like natrolite have positive elongation plot between 14–18 Al and 0–2 Ca mark whereas ranite or gonnardite, except

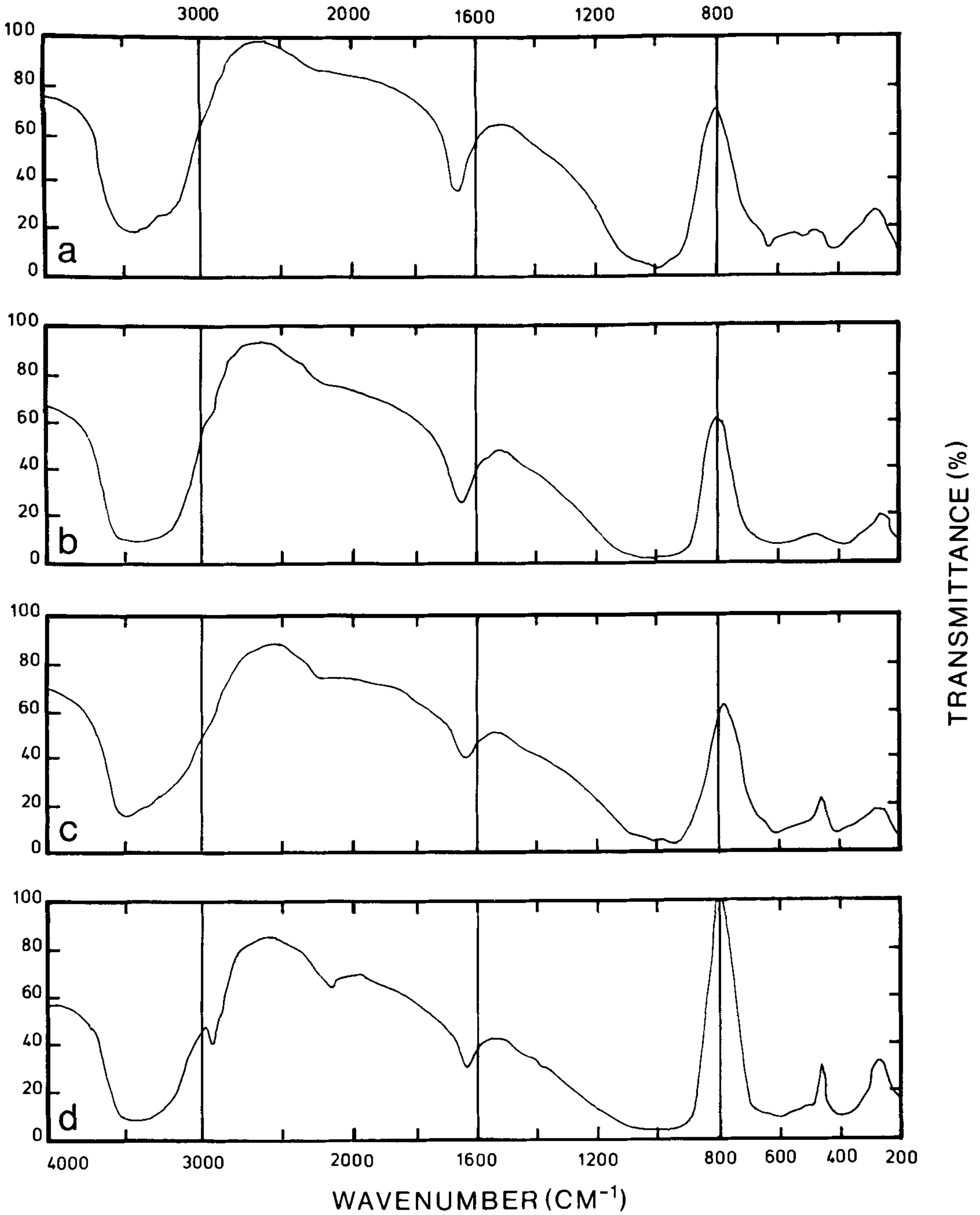

FIG. 2. Infrared spectra of zeolites; (*a*) Hills Port gonnardite, (*b*) Gignat gonnardite, (*c*) Lamo ranite, (*d*) Kloch tetranatrolite.

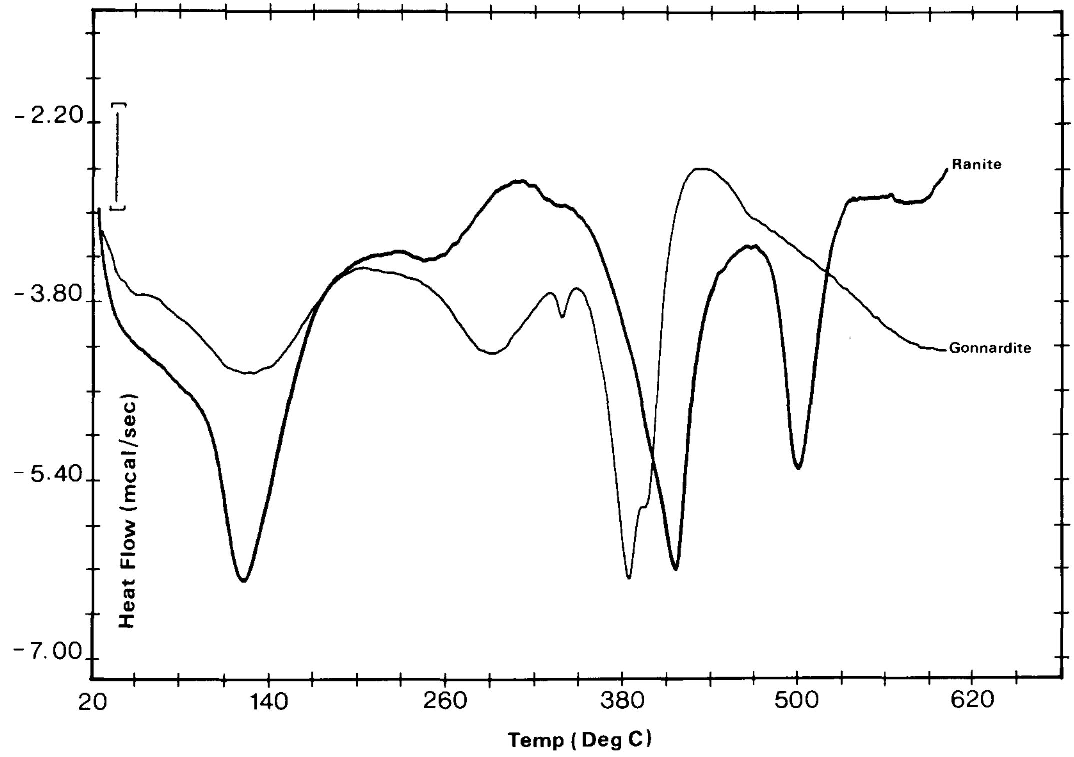

FIG. 3. Differential scanning calorimetry (DSC) data for Hills Port gonnardite and Lamo ranite.

for two dubious exceptions, plot above the 2 Ca mark and below the 6 Ca mark. This presents a valid argument to suggest that natrolite and tetranatrolites contain less than 2 Ca atoms and less than 18 Al atoms whereas ranite and gonnardite contain between 2 and 6 Ca atoms.

Gonnardite appears to be on the thomsonite trend lines, whereas ranite appears to be on natrolite trend lines; therefore, in spite of the possible co-crystallization of gonnardite and ranite, there is a compositional gap at about 3.5 Ca atoms. Compositions above about 4 Ca atoms are traditionally considered to be those of gonnardite which is always negatively elongated and it is suggested that these compositions alone should be accepted as constituting gonnardite. The maximum Al of gonnardite is about 18 atoms but the minimum may be as low as 13. Compositions lying between 2–4 Ca atoms and between 17 and 20 Al atoms, and trending along the R lines (extension of N lines) have either negative elongation or negative and positive elongation (due to reversible partial dehydration) as of ranite and it is suggested that this group be given the name ranite. A number of high-Na mesolites are ranites with two possible exceptions, one being a tetranatrolite and the other a gonnardite. Unit cell dimensions and volumes increase in the order: tetranatrolite, ranite, gonnardite and paranatrolite. The accurate indexing and measurement of *d*-spacings in powder patterns of $\underline{1}0\underline{4}0$ (or $\underline{1}4\underline{6}0$ of paranatrolite) can be used to identify these minerals. The compositions and powder patterns of thomsonite, mesolite and natrolite are quite distinct from the compositions and powder patterns of the four minerals referred to above.

Infrared spectra suggest and DSC scans confirm that gonnardite is distinct from ranite and from tetranatrolite; the latter two are related to natrolite while the former is derived from thomsonite.

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Table 6. Approximate cell dimensions and the position of 1040 line (Å).

Mineral	Locality	a	b	c	1040*
Gonnardite	Hills Port	13.29	13.29	6.59	1.230
	Gignat	13.33	13.33	6.59	1.240
	Kloch	13.32	13.32	6.62	1.236
Ranite	Bohemia	13.18	13.18	6.62	[1.224]
	Lamo	13.25	13.25	6.60	1.226
Tetranatrolite	Aci Castello	13.13	13.13	6.62	1.218
	Hills Port	13.10	13.10	6.63	1.220
	Kloch	13.16	13.16	6.60	1.223
	Oahu	[13.10]	[13.10]	-	1.220
Paranatrolite	Hills Port	19.03	19.03	6.59	1.252
	Aci Castello	19.07	19.07	6.58	1.252
	Canada	19.10	19.10	6.58	[1.254]

* For paranatrolite it is 1460 line. Values in square brackets are calculated.

determined by Mr. V. K. Din and A. J. Easton at the British Museum (Nat. Hist.). Bongt Lindquist, Frantisek Cech and J. A. Ferraiolo provided specimens for comparative study. Dr Jack Preston allowed the use of his X-ray diffraction facility, and Drs Michael Harriot and G. Svehla prepared the infrared spectra at the Queen's University, Belfast. Messrs L. B. Archibald and J. Bingham of LIRA are thanked for the DSC scans.

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