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BULLETIN NO. 114

FERRI-SEPIOLITE IN HYDROTHERMAL CALCITE-QUARTZ-CHALCEDONY VEINS ON NÛGSSUAQ IN WEST GREENLAND

BY

K. BINZER AND S. KARUP-MØLLER

WITH 3 FIGURES AND 3 TABLES IN THE TEXT,
AND 1 PLATE

KØBENHAVN
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Abstract

Ferri-sepiolite has been found in low temperature fracture veins in volcanic rocks. The veins are composed of an early calcite-quartz generation and a late generation of calcite, quartz, chalcedony and minor amounts of ferri-sepiolite. The late generation developed simultaneously with deformation of the early minerals. Fluid inclusion studies on the associated calcite give a temperature of formation of the early generation of 65°–80° C. Secondary inclusions in calcite which may have formed simultaneously with the late generation homogenize at temperatures between 40° and 50° C. The mineral veins probably formed from circulating meteoric waters. Optical and other physical properties of the ferri-sepiolite together with X-ray crystallographic and chemical data of the mineral are compared with the similar properties of ferri-sepiolite from East Greenland.

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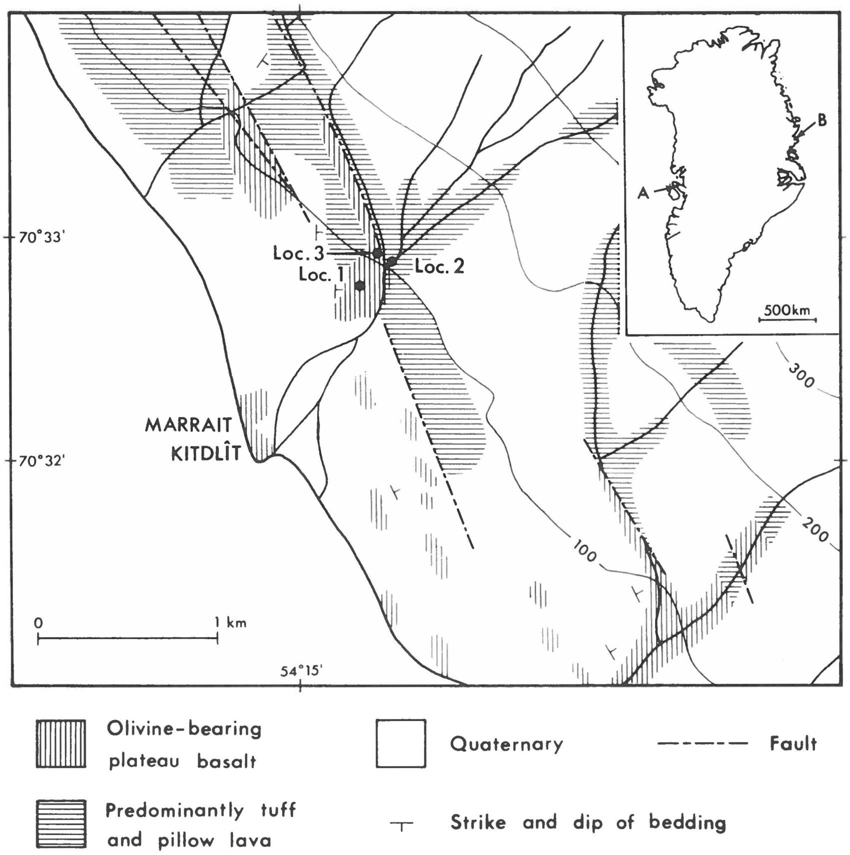

Fig. 1. Geological map of the area around Marrait kitdlît on Nûgssuaq in West Greenland (after K. Binzer, S. Skytte and K. Strand Petersen). The erratic ferri-sepiolite bearing block was found by K. Binzer at locality 1. The ferri-sepiolite veins were discovered by A. Rosenkrantz and A. K. Pedersen at localities 2 and 3 respectively. On the small index figure the Marrait kitdlît locality is located at A. The East Greenland ferri-sepiolite locality at Steensbys Bjerg is located at B.

Introduction

Ferri-sepiolite, first discovered in East Greenland north-east of Steensbys Bjerg (Mt. Steensbye) on Hold with Hope, has recently been found in the vicinity of Marrait kitdlît on Nûgssuaq in West Greenland (fig. 1). The East Greenland variety was found by Dr. E. NIELSEN in 1946 and later described by BØGGILD (1951), who gave it the name gunnbjarnite. From X-ray crystallography, STRUNZ (1958) classified the mineral as an iron-bearing sepiolite belonging to the palygorskite group of minerals and termed it ferri-sepiolite, a name now generally accepted.

According to BØGGILD (1951) ferri-sepiolite from East Greenland occurs closely associated with calcite and rarely enclosed in abundant chalcedony and quartz. The minerals form 0.5 to 3.0 cm thick, irregular veinlets occurring randomly in a three metres wide, basaltic dyke cutting Triassic and Cretaceous sediments.

Ferri-sepiolite from Nûgssuaq in West Greenland was found in 1969 by one of the authors (K.B.) in an erratic block at location 1 fig. 1, characterized essentially by chalcedony covered by a few millimetres thick layer of a brown, micaceous to fibrous mineral, which was later identified as ferri-sepiolite. It was then realized that Professor A. ROSENKRANTZ in 1968 had collected ferri-sepiolite from fracture veins at location 2. During the summer of 1972 still another locality with similar material was discovered by A. K. PEDERSEN at location 3. Several specimens were collected from this locality.

Host rocks for the mineral veins are mafic volcanics belonging to the West Greenland basaltic province.

Stratigraphical position of the mineral veins

Ferri-sepiolite and its associated minerals occur along irregular fracture veins in volcanic rocks of the West Greenland basaltic province consisting of several kilometres of plateau basalts.

The ferri-sepiolite at locality 2 (figs 1 and 2) occurs in thin, fine-grained, picritic lavas. These lavas lie below a fossiliferous conglomerate with basalt pebbles referred to the Upper Danian (ROSENKRANTZ, 1971). The irregular fractures are composed of ferri-sepiolite, calcite and

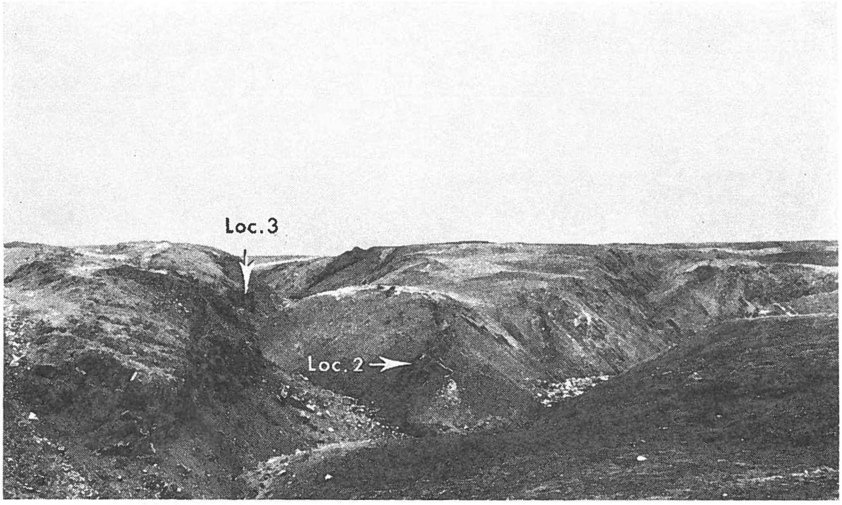

Fig. 2. Photograph of the area around localities 2 and 3 viewed from the south-south-east. The calcareous conglomerate deposited on the picritic lavas stands out distinctly above the arrow marking locality 2 and forms the crest of the ridge extending towards the north-north-west. A. ROSENKRANTZ photograph 2 August 1968.

chalcedony. Quartz may be present but has not been identified in the few specimens collected here.

At locality 3, vertical, irregular veins with a width of up to 10 cm were found in fine-grained, aphanitic basalt mapped by the Geological Survey of Greenland as 'aphyric basalt'. These rocks occur about 100 m stratigraphically above the fossiliferous conglomerate. The mineral veins closely resemble those found at locality 2. However, quartz is present in addition to ferri-sepiolite, calcite and chalcedony.

Hydrothermal mineral veins composed essentially of xonotlite, pectolite and natrolite from the Marrait kitdlît area (fig. 1) have been described by KARUP-MØLLER (1969). The relationships between these veins and those with ferri-sepiolite remain unknown.

Mineral description of ferri-sepiolite

Physical properties

The physical properties of ferri-sepiolite from East and West Greenland are summarized in table 1.

The mineral ranges in shape from fibres (plate 1 b) to elongated micaceous flakes (plate 1 a). The fibre direction of ferri-sepiolite is parallel to the *a* crystallographic axis. Individual fibres easily split along this direction due to perfect cleavage parallel to (001) and good cleavage

Table 1. *Physical and optical properties of ferri-sepiolite.*

	West Greenland	East Greenland (Bøggild, 1951)
Crystal system	Orthorhombic	Orthorhombic
Sign	Negative	Negative
n_α	< 1.54	< 1.54
n_β	1.553 ± 0.002	1.554 (1.540–1.571)
n_γ	1.574 ± 0.002	1.579 (1.561–1.593)
2V	82–85°	*c.* 60°
Cleavage	(001) perfect (010) good	(001) perfect (010) good
Colour	Brown	Brown
Pleochroism	β: yellow γ: brown	

parallel to (010). The termination of the individual flakes is round to irregular. Due to the perfect (001) cleavage the refractive indices n_β and n_γ could easily be determined on powdered material. The value n_α is judged to be lower than 1.54 from comparison in thin section with the refractive indices of associated quartz and chalcedony. The refractive indices of ferri-sepiolite from both East and West Greenland vary within narrow limits. According to Caillère & Hénin (1961), the mean refractive index of normal sepiolite is 1.50, whereas that of xylotile, a ferri-sepiolite with 16.76 to 21.70 per cent Fe_2O_3, is 1.58. Thus, an increase in the iron content of the mineral is accompanied by an increase in its refractive indices.

X-ray crystallography

X-ray diffractometer diagrams on ferri-sepiolite from both West and East Greenland are reproduced as fig. 3 and show that the East Greenland variety is more poorly crystallized than that from Nûgssuaq as the peaks are less marked and not so sharp.

X-ray diffractometer data on the West Greenland variety are listed in table 2 and compared with the X-ray diffractometer data on sepiolite from Little Cottenwood in Utah. The d_{hkl} value of each ferri-sepiolite line is slightly lower than that of the corresponding sepiolite line. The intensity of some of the lines, e.g. no. 19 are strikingly different. The cell dimensions of the Nûgssuaq ferri-sepiolite were determined as a = 5.21 Å, b = 26.73 Å and c = 13.50 Å. The Refbase III program of E. Leonardsen was used for the calculations.

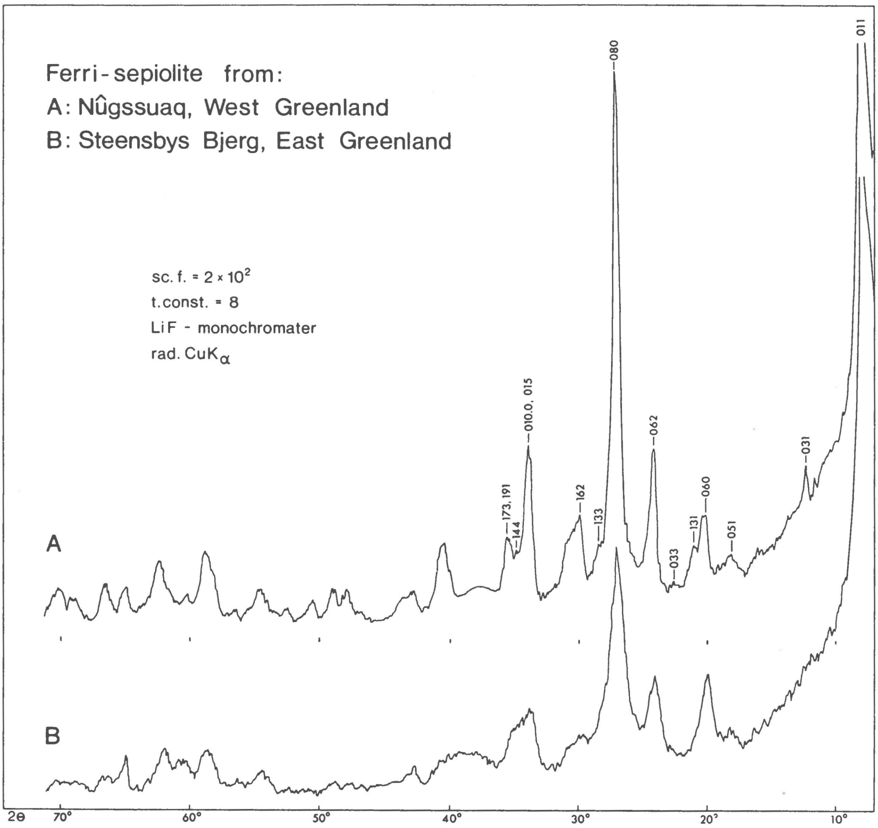

Fig. 3. X-ray diffractometer diagrams of ferri-sepiolite.

Table 2. *X-ray diffractometer data on ferri-sepiolite and sepiolite.*

	Ferri-sepiolite Nûgssuaq, West Greenland GGU no. 158332			Sepiolite Little Cottenwood, Utah, U.S.A. Measured values from ASTM card 13–595 (Brindley, 1959)			
	I	d_{hkl} (meas.)	d_{hkl} (calc.)	*I*	d_{hkl} (meas.)	d_{hkl} (calc.)	Indices
1	100	11.88	12.00	100	12.1	12.07	011
2	4	7.375	7.424	10	7.47	7.49	031
3				6	6.73	6.75	040, 002
4	2	4.961	4.967	8	5.01	5.01	051
5	10	4.457	4.455	25	4.498	4.500	060
6	4	4.266	4.266	40	4.306	4.305	131
7	2	3.977	3.999	8	4.022	4.024	033

(continued)

Table 3. *Chemical analyses of ferri-sepiolite.*

	Ferri-sepiolite Nûgssuaq, West Greenland					Ferri-sepiolite Steensbys Bjerg, East Greenland			
	Wt. $^0/_0$	Cation Quot.	Unit cell content*			Wt. $^0/_0$	Cation Quot.	Unit cell content*	
SiO_2	47.51	0.791	Si	10.48	SiO_2	43.15	0.718	Si	9.76
TiO_2	0.06	0.001	Ti	0.04		–	–	–	–
Al_2O_3	2.35	0.046	Al	0.62	Al_2O_3	3.29	0.064	Al	0.86
Fe_2O_3	9.98	0.125	Fe^{+3}	1.66	Fe_2O_3	14.57	0.182	Fe^{+3}	2.46
FeO	1.18	0.016	Fe^{+2}	0.22	FeO	1.06	0.015	Fe^{+2}	0.20
MnO	0.35	0.005	Mn	0.06	MnO	0.13	0.002	Mn	0.02
MgO	15.17	0.376	Mg	4.98	MgO	12.98	0.322	Mg	4.38
CaO	1.40	0.025	Ca	0.34	CaO	3.66	0.065	Ca	0.88
Na_2O	0.18	0.006	Na	0.08		–	–	–	–
K_2O	0.07	0.002	K	0.02		–	–	–	–
H_2O	19.20		H_2O	10.36	H_2O	19.36		H_2O	10.82
OH			OH	4.00	OH			OH	4.00
	97.45					98.20			

Analyst: A. SIMONSEN & H. HANSEN Analyst: H. A. NIELSEN

* Calculations based on ideal anion content of unit cell ($O^{--} = 30$, $OH^{-} = 4$).

Chemistry

Chemical analyses of ferri-sepiolite from both East and West Greenland are listed in table 3. The following formulae based on structure determination by BRAUNER & PREISINGER (1958) were obtained.

Ferri-sepiolite from West Greenland:

$(Fe^{+3}_{0.38}Fe^{+2}_{0.11}Mg_{2.49}Ca_{0.17}Mn_{0.03}Ti_{0.02}K_{0.01}Na_{0.04})\ [(OH_2)_2\ (OH)_2Si_{5.24}Al_{0.31}Fe_{0.45}0_{15}]\cdot 3.17\ H_2O$

Ferri-sepiolite from East Greenland:

$(Fe^{+3}_{0.54}Fe^{+2}_{0.10}Mg_{2.19}Ca_{0.44}Mn_{0.01})\ [(OH_2)_2(OH)_2Si_{4.88}Al_{0.43}Fe_{0.69}0_{15}]\cdot 3.41\ H_2O$

Mineral relationships

The following description is based almost exclusively upon fifteen mineral specimens collected by A. K. PEDERSEN at locality 3. They are all numbered GGU 158332.

The mineral veins appear to have developed during two stages of crystallization at low temperatures (see p. 12). During the first of these calcite and minor amounts of quartz were precipitated. Subsequently, deformation took place and calcite, quartz, chalcedony and ferri-sepiolite formed.

Table 2 (continued).

	Ferri-sepiolite Nûgssuaq, West Greenland			Sepiolite Little Cottonwood, Utah, U.S.A. (Measured values from ASTM card 13–595)			
	I	d_{hkl} (meas.)	d_{hkl} (calc.)	I	d_{hkl} (meas.)	d_{hkl} (calc.)	Indices
8	15	3.717	3.712	30	3.750	3.744	062
9				12	3.533	3.535	142
10	60	3.341	3.342	30	3.366	3.375	080
11	4	3.173	3.173	35	3.196	3.196	133
12	10	3.002	3.024	12	3.050	3.051	162
13				4	2,932	2.929 2.928	091 073
14				8	2.825	2.825	114, 172
15				4	2.771	2.779	124
16	15	2.670	2.673 2.672	20	2.691	2.700 2.680	0100 015
17	2	2.607	2.600	30	2.618	2.618	144
18					2.586	2.586 2.582	035 220
19	4	2.550	2.537 2.534	55	2.560	2.559	173 191
20				6	2.479	2.482	231
21				25	2.449	2.451	202, 240
22				16	2.406	2.402	
23	6	2.241		30	2.263	2.263	
24				4	2.260	2.202	
25	2	2.119		8	2.125		
26	2	2.067		20	2.069		
27	4	1.918		4	2.033		
28				4	1.957		
29				2	1.921		
30	4	1.871		8	1.881		
31	4	1.812		2	1.818		
32	2	1.751		6	1.760		
33				10	1.700		
34				4	1.637		
35	6	1.581		10	1.592		
36	2	1.542		16	1.550		
37				16	1.518		
38	6	1.495		8	1.502		
39	4	1.440		4	1.468		
40	4	1.412					
41	2	1.367					
42	4	1.345					

The first formed material is characterized by a structureless aggregate of medium to coarse-grained calcite enclosing minor amounts of idiomorphic to partly idiomorphic quartz. The quartz always contains numerous growth lines and rarely exceeds 0.5 cm in size. Cavities in the vein material up to at least 1 cm are bounded by crystal faces of both calcite and quartz.

The late precipitated minerals formed simultaneously with deformation and dissolution of early calcite and quartz. Pronounced shear zones were the result of this deformation. They occur mainly along the margin of the vein material, parallel to the basalt contact, but they also cut across the veins. The sheared vein material is characterized by irregular layers of calcite alternating with layers of quartz and chalcedony. These layers rarely exceed 1 mm in thickness. Part of the calcite present is crushed, unreplaced early calcite. However, the major portion was precipitated during the period of deformation presumably from mobilized early calcite. The quartz-chalcedony layers are composed of granular quartz grading into areas or aggregates of spherulitic chalcedony. Cracks in adjacent early calcite and spaces between grains of this mineral are filled sometimes with quartz, sometimes with spherulitic chalcedony. Early and late quartz often lie in contact with each other and cannot be sharply distinguished, which suggests that crystallization of the two overlapped.

Chalcedony has sometimes crystallized upon corroded quartz crystals (plate 1 c). Idiomorphic quartz crystals against calcite have often recrystallized as chalcedony along their margins presumably when solutions penetrated along the quartz-calcite contact. Primary calcite in contact with late quartz-chalcedony material (but not elsewhere) often contains isolated, perfectly circular chalcedony spherules (plate 1 d). Sometimes the central areas of these consist of a quartz crystal in which fine growth lines mark the hexagonal prism.

Ferri-sepiolite first crystallized when deformation of early calcite and quartz took place. It hardly forms 5 % of the mode and occurs in thin fractures cutting the primary calcite. Fibres or flakes of the mineral may sweep around spherules enclosed in calcite (plate 1 d). The major portion of the mineral is associated with small lensoid-shaped calcite grains or aggregates of these up to 1 cm in length and less than 2 mm in diameter. These aggregates of grains lie parallel to each other and they are wrapped in shiny, dark brown coloured ferri-sepiolite, sometimes shaped as thin micaceous flakes (plate 1 a) rarely as fibres. Some specimens are composed exclusively of this material, while in others it lies in irregular contact with early calcite and quartz. In one such specimen calcite—ferri-sepiolite intergrowth was found to grade into pronounced ferri-sepiolite rich shear zone material. These relationships suggest that all ferri-sepiolite crystallized as deformation took place.

Some of the specimens are characterized by the presence of stalactitic chalcedony precipitated in cavities which presumably developed when shearing of the vein material occurred. On the surface stalactitic aggregates appear to be composed of parallel orientated, thin columns each consisting of chalcedony spherules. Ferri-sepiolite lies in this material with its fibre direction parallel to the stalactitic direction. In one specimen from locality 2, such enclosed ferri-sepiolite material formed a twisted layer resembling petrified wood. It was one centimetre in thickness, several centimetres in width and extended in the chalcedony material through the whole 15 cm length of the specimen. Isolated chalcedony rods or groups of these, each up to one millimetre in diameter and 2 cm or more in length occur isolated in the ferri-sepiolite layer. These rods closely resemble the elongated calcite aggregates associated with ferri-sepiolite forming the specimen shown on plate 1 a from locality 3.

The *P-T* conditions of mineral vein formation

The maximum thickness of the West Greenland volcanics on Nûgssuaq is estimated to be around four kilometres. The volcanics around localities 2 and 3 are situated in the lower middle portion of this sequence. The formation of the vein minerals presumably took place in open fractures from circulating meteoric waters. The pressure of formation therefore is considered to have been equal to the hydrostatic pressure and could therefore hardly have exceeded 300 bars.

The temperature of formation of the mineral veins is based on the study of gas-liquid inclusions in the early precipitated calcite. The investigations were carried out by J. Rose-Hansen, who provided the following information.

The calcite contains primary and secondary fluid inclusions. The primary inclusions occur in clusters distributed at random. Most of the inclusions are spherical or ellipsoidal in shape while a few are semifaceted. They generally are too small for heating runs, with a diameter rarely exceeding 10 μm. Only few have a maximum diameter of 20 μm. The secondary inclusions, generally present parallel to cleavage directions of the calcite, are predominantly elongated and tabular. The ratio between the long and the short direction of these is more than five to one. Necking down of former larger inclusions is not uncommon. Generally the inclusions are less than 5 μm in the longer direction, and thus poorly suited for heating runs.

At room temperature all the inclusions form two phase liquid-gas. Heating and cooling runs were made on 1.0–1.5 mm thick, polished plates on a modified Leitz heating-cooling stage. The temperature was measured with a Pt-resistance sensor combined with a chromelalumel thermocouple in contact with the sample. The thermocouple was calibrated against the freezing point and boiling point of water and in the run against the melting point of benzil placed in a capillary ampoule in contact with the specimen. Heating rate was about two degrees a minute.

All the inclusions homogenized in the liquid phase. Filling temperature for the primary inclusions was 60–70° C and for the secondary inclusions around 40° C. The pressure of formation is assumed to have been not greater than 300 bars, which gives an upwards temperature correction of maximum 10° C.

The freezing temperature of the inclusions was found to be minus 10 °C determined as the melting point of inclusions cooled to minus 40° C.

No daughter minerals were detected on cooling. The freezing temperature corresponds to an equivalent NaCl content of 14 per cent.

The study of the gas-liquid inclusions therefore shows that the early calcite and associated quartz crystallized at a minimum temperature somewhere between 65 and 80° C. The secondary inclusions may have formed during the deformation period when ferri-sepiolite and associated late quartz, chalcedony and calcite developed. If this assumption is correct, then the homogenization temperature of the secondary inclusions implies that the ferri-sepiolite crystallized at temperatures of between 40 and 50° C, depending on the pressure of formation.

Discussion

Although sepiolite is a relatively common mineral, ferri-sepiolite appears to be rather rare, known only from a few places. A number of published analyses of sepiolite have been listed by DOETLER (1914) and by MIGEON (1936). These analyses show that sepiolite may contain up to 3.6 $^0/_0$ Fe_2O_3, 2.5 $^0/_0$ FeO, 2.5 $^0/_0$ Al_2O_3, 2.5 $^0/_0$ MnO and 1.5 $^0/_0$ CaO. A high content of one of these elements is not necessarily correlated with either particularly low or high contents of any one of the others. An unusual nickel-rich variety with 9.78 $^0/_0$ NiO has been described by CAILLÈRE (1936) and an aluminous variety with 7.05 $^0/_0$ Al_2O_3 by ROGERS *et al.* (1956).

Sepiolite from Theben with 18.4 $^0/_0$ FeO has been published by KOBELL (1843). Xylotile, also known under the name 'Bergleder', and now considered a ferri-sepiolite, is known from a few localities as described by CAILLÈRE (1936). This author has published four analyses of the mineral from Madagascar with Fe_2O_3 contents ranging from 16.76 to 21.70 $^0/_0$ while that of FeO varied between only 0.20 and 1.50 $^0/_0$ (CAILLÈRE & HÉNIN, 1961). Less than half a per cent of each of the following elements were also present: aluminum, manganese and calcium.

Analyses of sepiolite with values of Fe_2O_3 between about 3.5 and 10 $^0/_0$ apparently have not been published. This may imply that such sepiolite varieties cannot crystallize. If this is the case then a true gap exists in the solid solution series between normal sepiolite with less than

3.5 % Fe_2O_3 and ferri-sepiolite with contents of more than 10 % Fe_2O_3. If this can be proved, either experimentally or by structural investigations, then the so-called ferri-sepiolite should be considered a distinct mineral species.

According to HATHAWAY & SACHS (1965) sepiolite is known in the following geological environments:

1. As a primary mineral in both recent and old lacustrine and deep sea environments.
2. In dolomite and marble deposit, either as a primary mineral or of diagenetic origin.
3. Associated with serpentine from altered ultramafic rocks.
4. Precipitated from hydrothermal solutions or formed as the result of hydrothermal activity.

No sharp distinction exists between 1 and 2 and between 3 and 4. The mineral is well-known from recent lacustrine and deep sea environments (HARDIE & EUGSTER, 1970; HATHAWAY & SACHS, 1965). The stability range of sepiolite at 25°C and at a pressure of one atmosphere has been investigated by WOLLAST *et al.* (1968), who found that the mineral under certain conditions is easily precipitated from sea water.

Only a few examples of sepiolite developed from hydrothermal activity are given in the literature. In most cases the mineral developed during hydrothermal alteration processes. EHLMANN *et al.* (1962) have described sepiolite as a hydrothermal mineral from a number of widely distributed occurrences in Utah and Nevada. They consider the mineral in association with quartz and opal to have crystallized from low temperature hydrothermal solutions during the last stage of sulphide mineral deposition in carbonate beds. Fissure veins with sepiolite in limestone at the Stansvik iron mine in Finland is considered to have crystallized directly from hydrothermal solutions (AUROLA, 1957).

The present investigation has shown that ferri-sepiolite from Nûgssuaq crystallized from low temperature aqueous solutions along calcite-quartz-chalcedony veins in volcanic rocks but only during periods of deformation. The temperature of crystallization is assumed to range between 40 and 50°C and the pressure of formation to be lower than 300 bars. The origin of the solutions remains uncertain. Most probably they were circulating meteoric waters the chemical components of which were dissolved from the volcanic rocks they penetrated.

Xonotlite, pectolite and natrolite-bearing fracture veins from the Marrait kitdlît area occur in similar rock types as the ferri-sepiolite bearing fracture veins and are considered to have crystallized from hydrothermal solutions of magmatic origin at temperatures close to 300°C at a water pressure of 300 bars or less (KARUP-MØLLER, 1969).

Unfortunately, the relationships between these vein types and the ferri-sepiolite-bearing veins are unknown. The mineralogy of the ferri-sepiolite bearing veins is entirely different from that of the veins with xonotlite, pectolite and natrolite. The only mineral in common is calcite, present in very small amounts in the latter vein type. Thus in respect to temperatures of formation, origin of mineral solutions and mineralogical composition, the ferri-sepiolite veins are strikingly different from those with xonotlite, pectolite and natrolite.

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S. Karup-Møller
Institut for Petrologi
Øster Voldgade 5–7
1350 København K
Denmark

K. Binzer
Danmarks geologiske Undersøgelse
Thoravej 31
2400 København NV

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Færdig fra trykkeriet den 26. november 1974.

PLATE

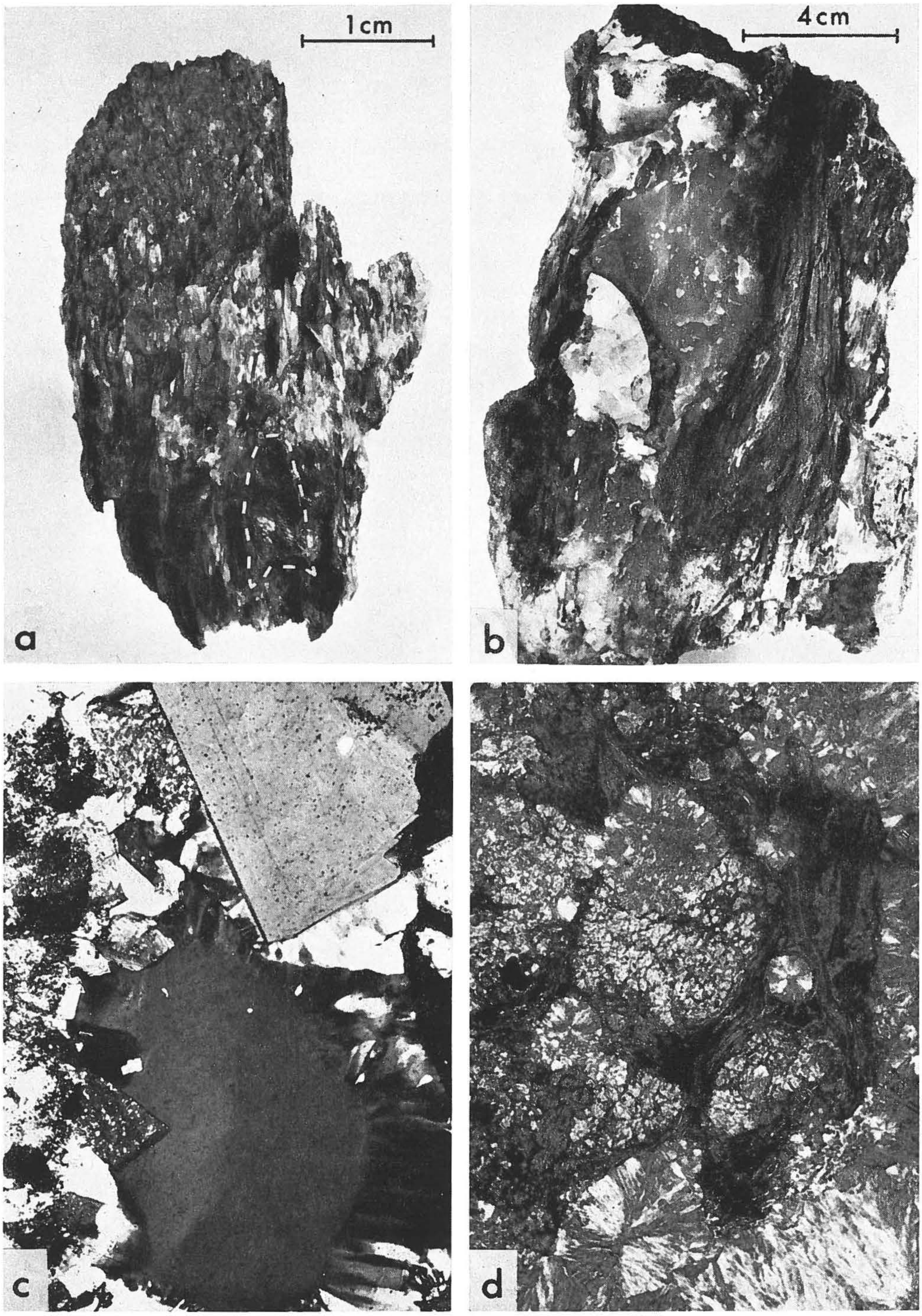
Plate 1

Plate 1 a. Specimen of numerous, small elongated and parallel-arranged calcite grains or aggregates of these wrapped in micaceous, dark brown coloured iron-sepiolite flakes. One particularly large flake is outlined. (Specimen from loc. 3, fig. 1).

Plate 1 b. Specimen of massive chalcedony with a twisted layer of fibrous, dark brown coloured ferri-sepiolite resembling petrified wood. The white area in the centre left is an aggregate of calcite crystals which has crystallized upon the ckalcedony material. (Specimen collected by A. Rosenkrantz at loc. 2, fig. 1).

Plate 1 c. Two early quartz crystals in fine-grained aggregate of late calcite and chalcedony. Fine growth lines are present in the crystal in the upper portion of the photograph. The crystal in the lower part of the photograph has been corroded and chalcedony has crystallized upon the corroded section of the crystal. (× 95. Crossed nicols. Thin section of specimen from loc. 3, fig. 1).

Plate 1 d. Ferri-sepiolite sweeping around spherulitic chalcedony grains. The grainy material, predominantly at bottom right, is calcite. (× 25. Crossed nicols. Thin section of erratic block at loc. 1, fig. 1).


1 cm
a
4 cm
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