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THE GENESIS OF BELGIAN AND DUTCH FLINTS AND CHERTS

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ABSTRACT

Different analyses were carried out on several Dutch and Belgian flints and cherts.

As a result of the observations conclusions are drawn about the properties of flint and chert and a theory on the formation of flint and silicification of limestones through a calcium silicate intermediary is presented.

Calculations on the physico-chemical aspects of this theory are presented. These calculations turned out to accord with several field observations.

INTRODUCTION

Although an excellent paper was given by Millot (1960) on the subject, the authors were still puzzled by silica, silex and silicifications. Millot's work succeeded in bringing together the significant field observations and theoretical considerations available at that time. He did away with tales about colloidal silica and the flocculation of silica due to a change in pH or to the concentration of other ions in the natural waters. He discussed the notion of H_4SiO_4 in true solution in natural waters stressing the fact that its concentration hardly ever reaches saturation.

Still a number of questions remain. These questions are for a large part due to the slow diffusion of physicochemical data obtained by our colleagues in the chemistry and physics departments into our own files. Other questions could simply not be solved because at that time the necessary thermodynamical data about the substances that take part in the various reactions we wanted to study were not available. Therefore, this paper is more or less a continuation of the paper of Millot (1960) applying new data and methods not previously used or only recently available.

Much of this work, however, corroborates speculations or assumptions of earlier investigators.

Confusion still seems to exist about the names in use for aggregates of fine grained silica such as flint or chert. The book by Frondel (1962) settles the disputes on this subject but some confusion still may be present due to terminology. The substances to be discussed in this paper are without exception chalcedony, but we feel the need to use two different terms for rather different types of chalcedony as follows:

Flint, a dense fine-grained form of silica which is very tough and breaks with a conchoidal fracture and cutting edges, of various colours (Howell, ed., 1957).

Chert, cryptocrystalline varieties of silica regardless of colour, composed mainly of petrographically microscopic chalcedony and/or quartz particles whose outlines range from easily resolvable to nonresolvable with a binocular microscope at magnifications ordinarily used. Particles rarely exceed 0.5 mm in diameter (Ireland et al., 1947).

The samples termed flint in this paper generally occur in the soft porous chalk of the southern province of The Netherlands and the adjacent parts of Belgium, generally belonging to Upper Cretaceous

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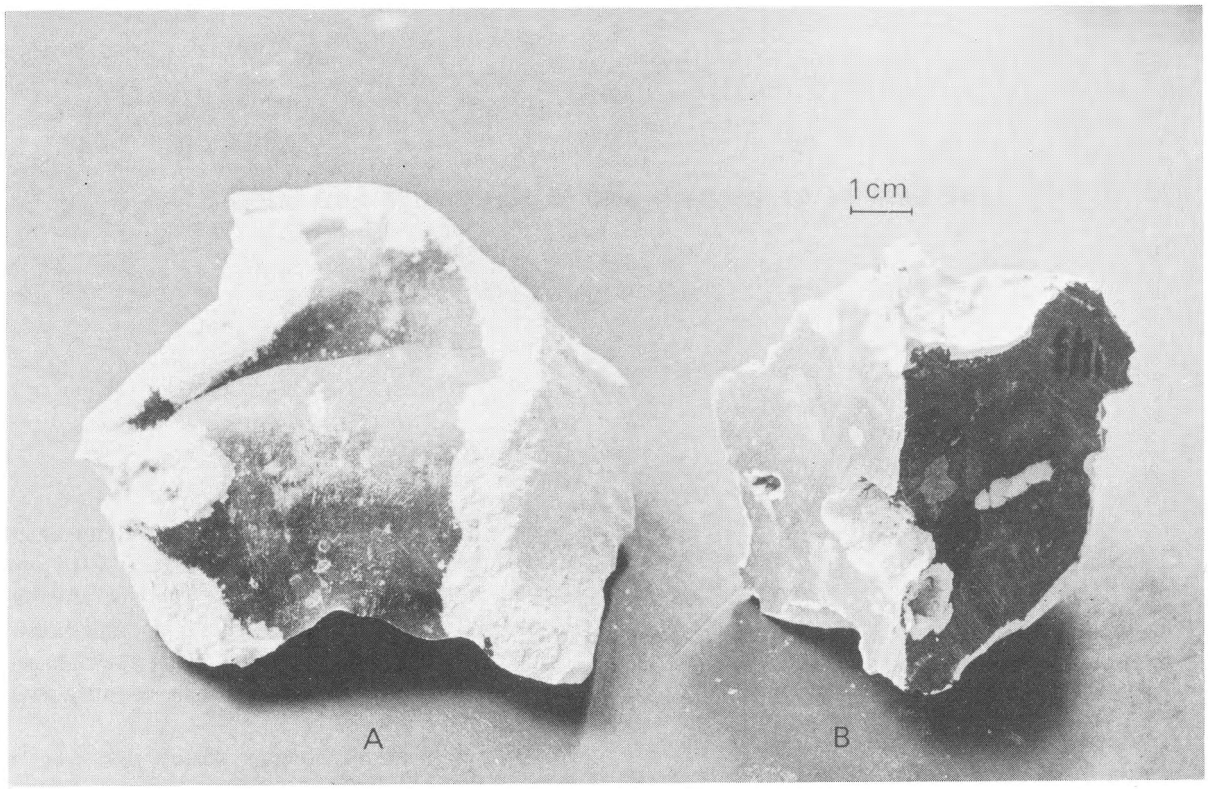

Fig. 1
Flint samples 129 (left) and 143 (right, cut).

formations. The samples termed chert occur in dense limestones of Carboniferous age in the eastern part of Belgium. These cherts are cryptocrystalline silica aggregates with rectangular intersecting fracture planes.

MATERIAL

The following samples were chosen for investigation:

Flints:

6a rolled flint, basal conglomerate Diestian (Miocene), Bolderberg, Belgium.
119 rolled flint, kiezeloolite formation, Pliocene, Brunssum, The Netherlands.
120 ibid.
127 silicified oolite, ibid.
129 bedded flint, horizon VII, Upper Senonian, Gulpen chalk, ENCI-quarry, Maestricht, The Netherlands; black, fig. 1a. This sample was

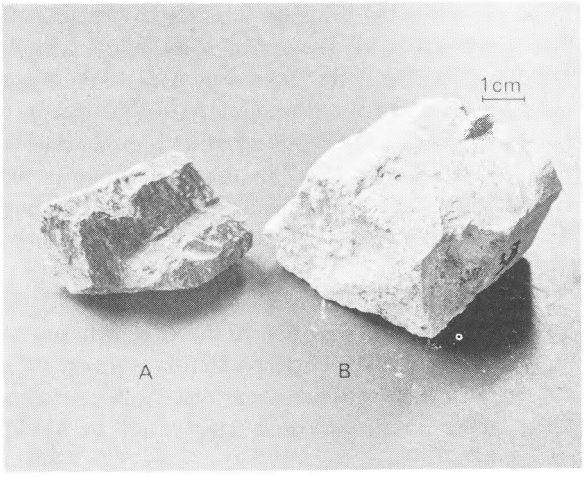

Fig. 2
Chert samples 25 (left) and 38b.

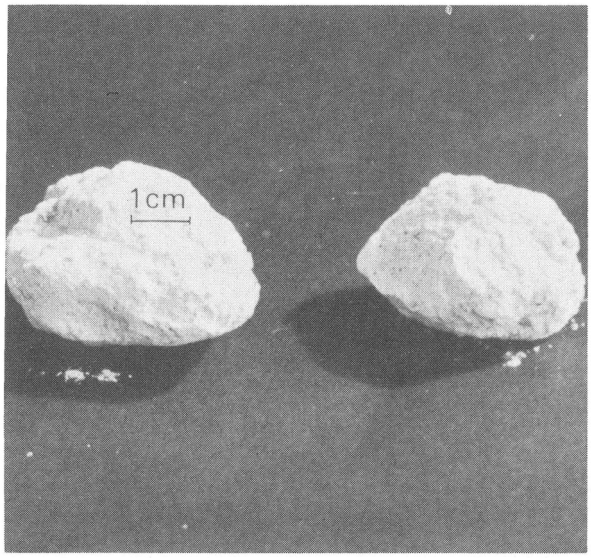

Fig. 3
Silicified chalk sample 110.

taken from the collection of the Laboratory of Soil Science.

143 bedded flint, horizon IV-w, Upper Senonian, Gulpen chalk, Jeker valley, Belgium, black. fig. 1b.

145 bedded flint, horizon VI-w; ibid; black and gray.

147 bedded flint, horizon VII-I; ibid; light gray.

148 bedded flint, horizon VII-14; ibid, black.

152 bedded flint, horizon VIII-2½, Upper Senonian, Maestricht chalk, Bemelen, The Netherlands, dark gray.

159 bedded flint, cover quarry Hallembaye, Belgium, grayish brown. The numbers 143 – 159 were sampled by the authors.
Horizon classification after Excursion Guides of the International Symposion on Flint, Maestricht, 1969.

Cherts: (all cherts belong to superficial silicifications)

25 black silicified Tournaisian (Carboniferous) limestone, bituminous, Sprimont, Belgium, fig. 2a.

33a ibid, fossiliferous, Florzé, Belgium.

38a ibid, white, very porous, Bois de Comblain, Belgium.

38b ibid, gray, fig. 2b.

53 white, porous, Ouhar, Belgium.

Silicified chalk:

110 superficial silicification, Platte Bosch, South Limburg, The Netherlands, white, powdery, porous, light material, fig. 3.

133 bedded silicification, Maestricht chalk, Juliana quarry, Bemelen, The Netherlands; hard, fine grained, light yellow silicification.

Idiomorphic pedogenic quartz crystals:

62 from a clay sample of Tournaisian weathering clay, Buresse, Belgium, fig. 4.

Silicified fossils:

63 silicified coral (Caninia), Tournaisian limestone, Buresse, Belgium.

122 silicified coral (Caninia), Tournaisian limestone, Ouhar, Belgium.

123 silicified crinoid, ibid, Ouffet, Belgium.

124 ibid, Sprimont, Belgium.

126 partly silicified Belemnite, Gulpen chalk, Epen, The Netherlands.

Quartz concretion:

125 Quartz concretion from carboniferous weathering clay, Ouhar, Belgium, fig. 5.

PROCEDURES

X-ray diffraction pattern and thermal analyses were made of all the samples. They were investigated with the polarising microscope and with a scanning electron microscope. Chemical analyses were made using X-ray spectroscopy.

X-ray diffraction

X-ray diffraction patterns obtained with a quadruple Guinier de Wolff camera and Co/K_α radiation show the flints to contain quartz, some calcite and sometimes mica whereas the chert samples show quartz and mica but no calcite. The patterns sometimes show harmonic reflections of quartz of the type discussed by Goodyear and Duffin (1957). Other silica phases were hardly seen. In the patterns of samples 110 and 129 lines of low tridymite are visible.

In order to determine the presence of preferred

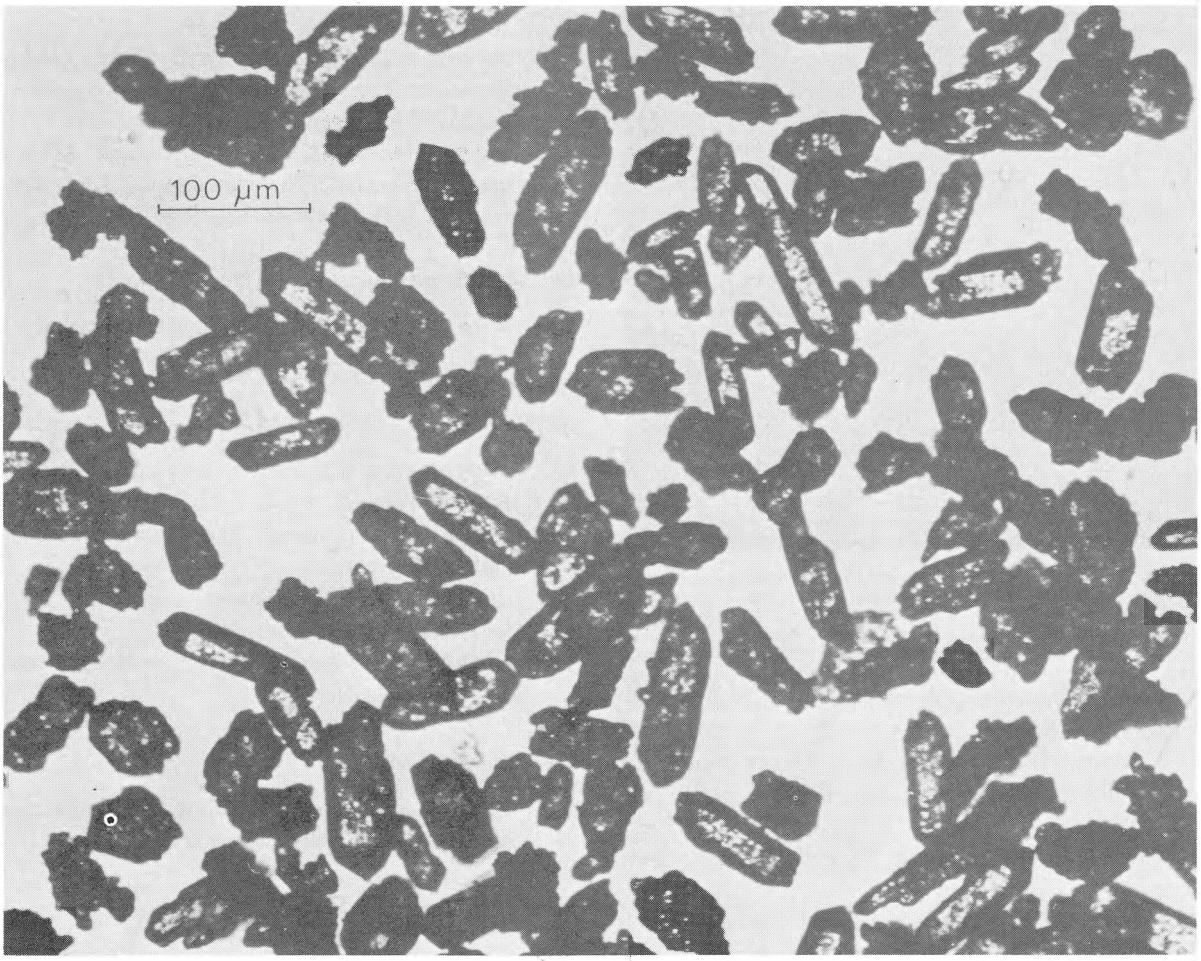

Fig. 4
Idiomorphic quartz crystals from a Tournaisian weathering clay. Sample 62.

orientation of the quartz crystals in the sample they were cut into slabs and mounted in the diffractometer. Not one of the slabs showed such a preferred orientation, although some reflections are less intense than the standard quartz pattern provided by the ASTM index (Card no. 5-0490). This discrepancy is not correlated with the direction of the cutting plane as far as could be established. Apart from the occurrence of additional minerals a difference between flint or chert could not be established with the reported X-ray methods.

One sample (no. 25) was investigated with a Guinier-Lenné camera. This instrument allows the continuous recording of the entire diffraction pattern while the sample is subjected to linear heating rate. The alpha-beta transition of the quartz is clearly visible on the diffractrogram (fig. 8) although a DTA trace at

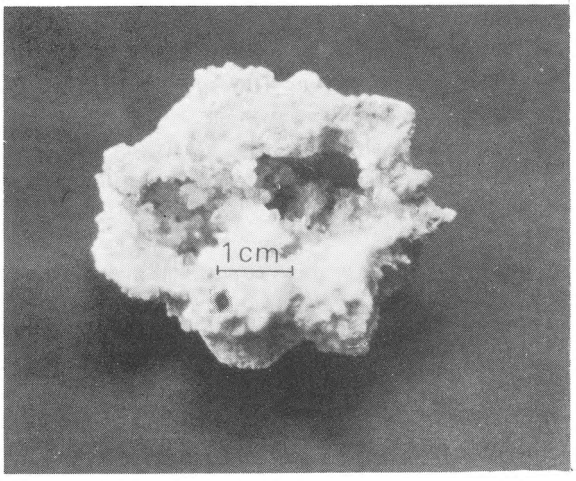

Fig. 5
Quartz concretion sample 125.

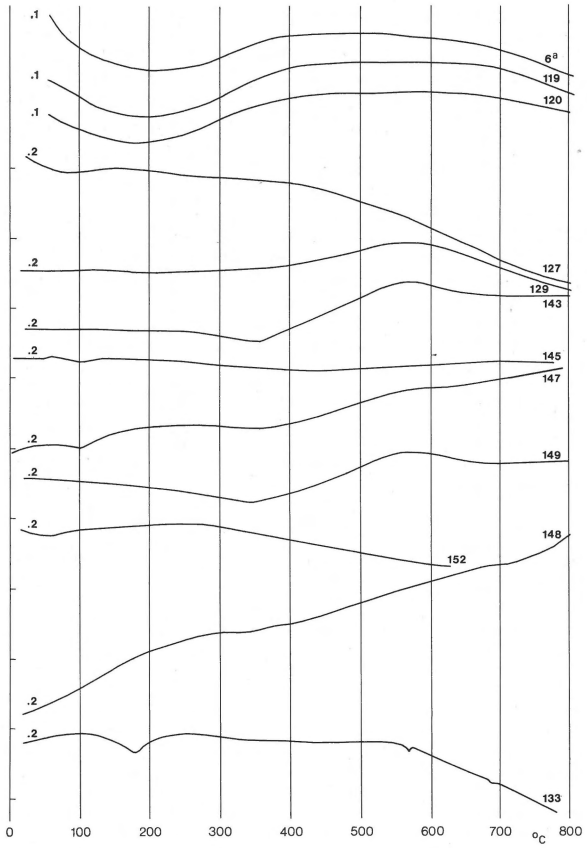

Fig. 6
D.T.A. traces of flint samples. Heating rate 10°C/min.. N_2 atmosphere. Sensitivity given with the samples.

10° C/min. at a sensitivity of .2° C/inch does not show this transition. Comparison with a comparable X-ray pattern of well-crystallized pegmatite quartz showed that the alpha-beta transition of this chert sample is much slower, i.e. it takes more time for the reaction to complete at the specifications of the analysis (film movement 5 mm/h; temperature increasing linearly 1.24° C/min., chromel/alumel thermocouples, CuK_α radiation).

Differential thermal analysis

Fig. 6 and 7 show the DTA traces of the samples investigated. The sensitivity is listed with each trace, the samples were heated in a N_2 atmosphere at 10° C/min. Fig. 6 shows the flint patterns, fig. 7 those of cherts and other samples reported earlier. The shape of a DTA trace is a function of quite a number of variables such as sample shape, heating rate, sensitivity of the amplifier etc. In our case these variables were kept as constant as possible with the exception of the sensitivity which had to be enlarged in some cases in order to record very small deflections from the base line. The apparatus used is a DuPont – 900 with a 850° C cell, using chromel/alumel thermocouples and microtubes of fused quartz as sample holders, and Al_2O_3 as a reference. Although it is possible to make the alpha-beta transition visible in a few cases by increasing the heating rate, the samples are marked by the absence of the characteristic peak at 573° C. Comparison with sample 125 (fig. 7) of waterclear euhedral quartz crystals of about 2 to 8 mm, shows the difference. A $\alpha - \beta$ quartz transition is also visible in samples 133 and 62. The large endothermal deviation from the baseline between the beginning of the pattern and approximately 400° C is another striking feature of a number of samples. Comparison with sample 110 (fig. 7), a badly crystal-

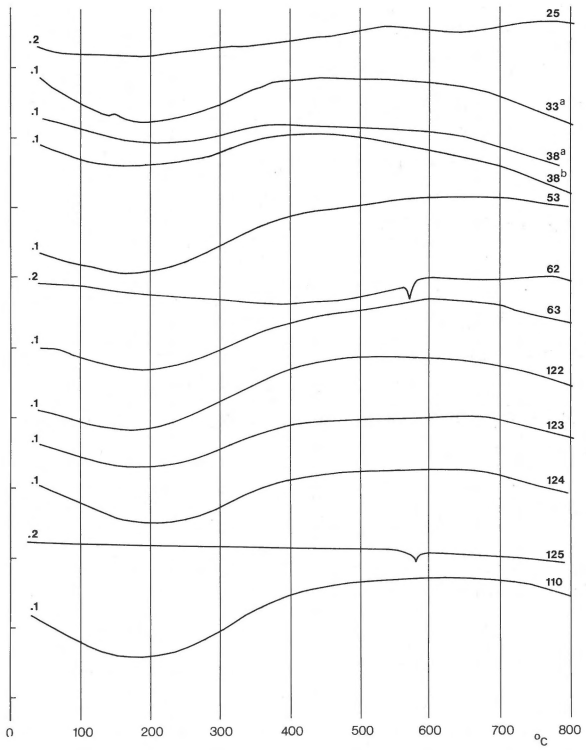

Fig. 7
D.T.A. traces of cherts and other silicifications. Heating rate 10°C/min.N_2 atmosphere. Sensitivity given with the samples.

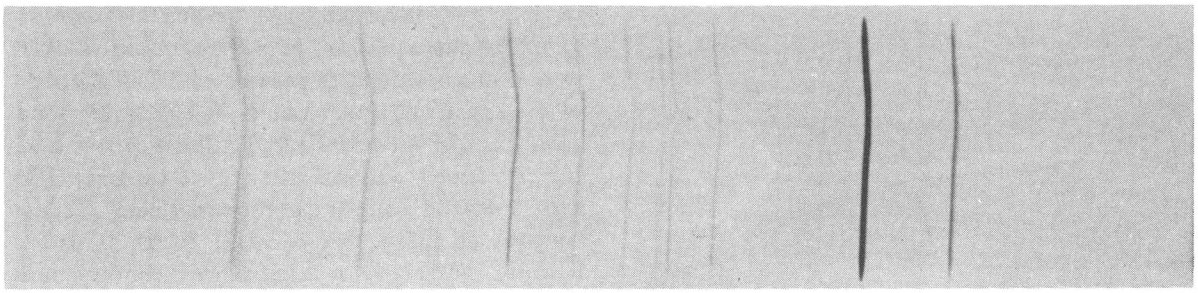

Fig. 8
Guinier-Lenné photograph of the alpha-beta quartz transition in chert sample 25. Cu K-alpha radiation.

lized low tridymite suggests that these samples contain tridymite-like phases. Sample 129, however, which holds some tridymite according to X-ray analysis does not show this depression. The trace of sample 133 shows an endothermic reaction between 110° and 200° C ascribed to tridymite.

The patterns of the flint samples (fig. 6) point to larger differences among the samples than the patterns of cherts (fig. 7). Regrouping on the basis of pattern type brings the samples 6a, 119 and 120 together with the cherts. These samples represent flint pebbles that were exposed to atmospheric conditions for a long time while the other flint samples were freshly taken from the calcareous rocks. The chert samples have been formed during the Tertiary (probably Miocene) period and were assumedly exposed to atmospheric conditions since that time. Observation indicates that long exposure to atmospheric conditions brings about a change in the flint samples that is macroscopically visible through a change of colour. Perhaps this is the reason for the differences described above.

DTA traces made in an atmosphere of air under the same circumstances as those in N_2 show for chert samples a rise before 400° C that is very pronounced in sample 25 and is ascribed to the oxidation of organic material present in the sample.

Thermo gravimetrical analysis

The weight loss curves of the samples are shown in figures 9 and 10. These traces were also made in a N_2 atmosphere. The sample was kept as close to 50 mg as possible, the heating rate is again 10° C/min., the apparatus used is a 950 DuPont Thermobalance. The maximum weight loss was observed in sample 152, appr. 7%. Other samples lose less than 4% weight. The flint samples (fig. 9) show again the differences between the specimens exposed to atmospheric conditions, 6a, 119, 120 and 127. Sample 129 in the collection of our institute, was exposed to comparable conditions. They show an increased weight loss only after 400° C. The other flint samples show in addition a marked weight loss between room temperature and 100° C.

The cherts and silicified fossils (fig. 10) show an increase of weight loss at 600° – 700° C, no weight

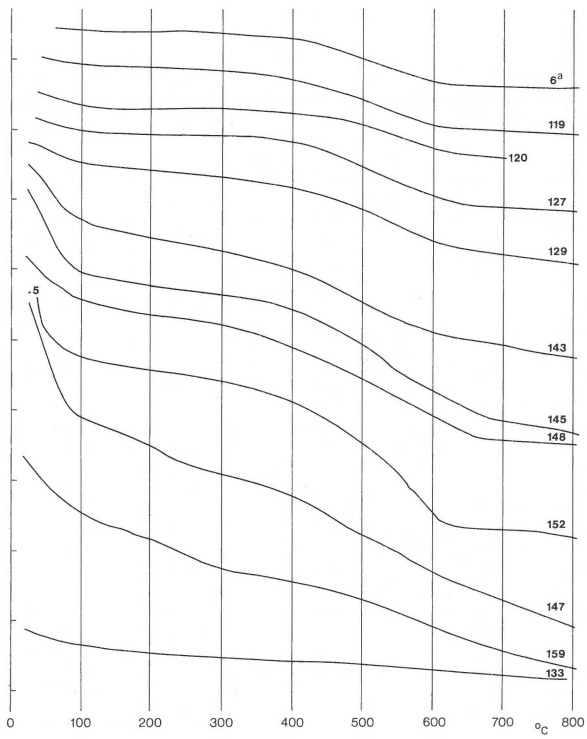

Fig. 9
T.G.A. traces of flints. Heating rate 10°C/min.N_2 atmosphere. Sensitivity .2 mg/inch.

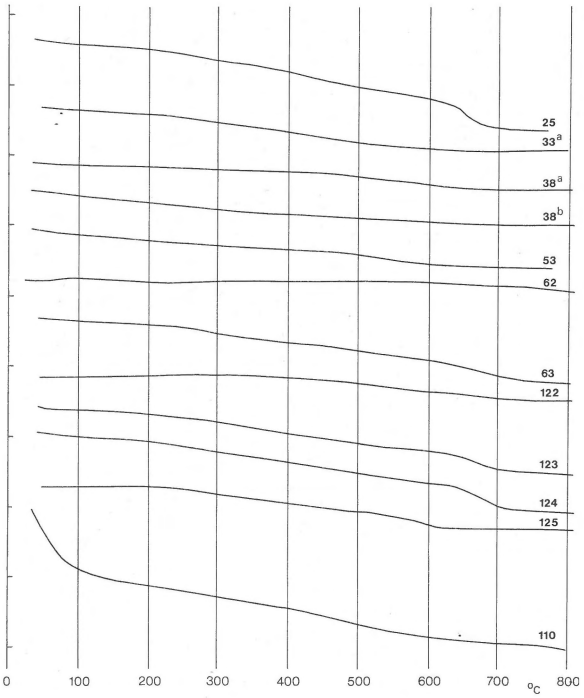

Fig. 10
T.G.A. traces of chert samples and other silicifications. Heating rate 10°C/min.N_2 atmosphere. Sensitivity .2 mg/inch.

loss at all or a slight continuous loss of weight over the whole temperature range.

Sample 110 (fig. 10), a superficial silicification, shows a marked weight loss between room temperature and 100° C.

It can be concluded from these analyses that the exposure to atmospheric influences changes the composition of flints considerably. They lose a large amount of water, a loss that takes time, as witnessed by the fact that powders stored over P_2O_5 for about 2 months still show these conspicuous differences.

Description of thin sections

A number of samples were not suitable for thin sectioning. The others will be described in the groups used in the earlier descriptions. Four thin sections of flints have been studied (no. 6, 119, 127 and 129). The pebbles 6 and 119 show a rim rich in pigment and dark vermicular patterns that proved to be cavities filled with air under magnifications of 1000 x. The silica phase is cryptocrystalline of low birefringence with some fields of coarser grain. Sand grains of quartz are enclosed here and there. No. 6 shows patches of smaller granular structure with some tiny crystals with idiomorphic outlines, other patches have a botroidal habit. Without crossed polarizers fragments of fossils are visible, marked by pigmented outlines or clear material. The lighter coloured rim of the pebble (no. 6) shows brownish patterns that may be explained by infiltration of humuslike material. With crossed polarizers such features are hardly visible. The granular pattern intersects the faint outlines of original impurities. Pebbel 119 is cracked and healed. The cracks are filled with a clearer silica substance of smaller granular pattern. Two such systems can be observed. The youngest shows the smallest granules and is clearer than the older. Again fossil traces are marked by pigment patterns or as pigment free patches of a finer granular pattern.

Sample 127 is a silicified oolite. The growth pattern of the spherical particles is seen as concentric rings of variable slightly yellow pigmentation. With crossed polarizers the material of the silicified spheres is much like that of the flint pebbles described earlier. Some smaller spheres show a radiating pattern of cryptocrystalline quartz, the radiating rays cross the circular boundary of the spherical particle. The pores between the spheres are filled with equant quartz grains of much larger size (.1 to .3 mm) without strain effects, lacking the well known wavy extinction seen in quartzites. The slightly yellow pigmentation marking the spheres and the concentric rings is not related to the granular or radiating pattern of the quartz. Tiny calcite fragments (in the order of 1 micron) are concentrated within the zones of yellow pigment.

Sample 129 is a flint fragment with some zones and rims of the original calcareous rock. The granular structure of the silica is much like that of the other flint samples. The fossil remains are also marked by clear patches of smaller granular structure. The cavities of the fossils within the calcareous material are either empty or filled with silica of a granular or a radiating pattern. The most interesting part, however, is the interface between the flint and the calcareous material. The calcite is of small grainsize, and a light brownish pigmentation. The flint still preserves some but not all of the pigment. The silicification front seems to push part of this pigment into the porous calcareous rock creating a zone of pigment concentration of some millimetres. The replacement of calcite by silica follows a whimsical pattern crossing through

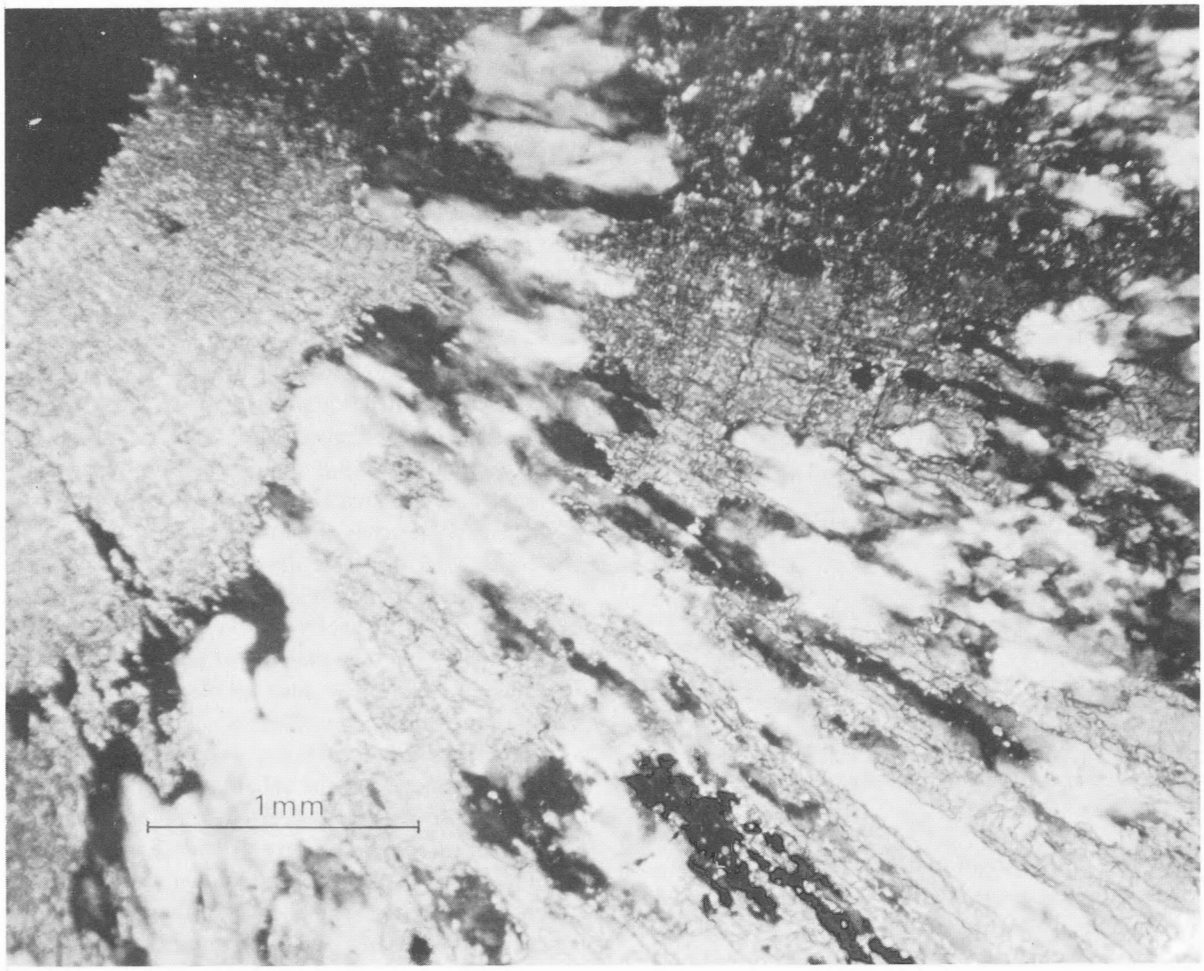

Fig. 11
Thin section of belemnite sample 126. Radiating quartz fibres are clearly visible. X-pol.

a shell here, following its outlines in another place, eating away some calcite crystals here and sparing some elsewhere. With a magnification of 650 x a phase of high refringence but low birefringence is visible between the silica and the calcite. The refringence is smaller than that of calcite but higher than that of silica. This phase, which never exceeds 2 to 10 micron and has a granular structure of either very small crystals or crystal aggregates, leads us to the assumption that silicification may take place through an intermediate phase, possibly a calcium silicate. In a later part this assumption is the basis of a physicochemical approach to the silicification process.

After this detailed discussion of flint samples it is easier to describe the features of the cherts. The silica in the cherts 25, 33a, 38 a & b and 53 exhibit the same granular structure as in the flints. The amount of pigment is larger and varies. Traces of fossils stand out through pigment free silica of different granular size or radiating sheaves of the same material. Some samples show traces of calcite; others hold rectangular impressions partially filled by quartz at the site of pyrite crystals. The sections of silicified fossils such as belemnites or corals again show some of the aspects of the replacement of calcite by silica. Conspicuous spiculae of silica in belemnites that are extremely thin (0.1 mm) have been isolated and mounted in an X-ray camera. The resulting pattern betrayed subparallel orientation of quartz crystals and small domain size. The corresponding optical pattern is shown in fig. 11.

Fig. 12
Scanning electron photograph of sample 120. Magnification 9000x. T.F.D.L. Wageningen.

Scanning electron microscopy

Scanning electron microscopy was carried out with the help of Miss Pfäutsch of the Department of Medical Physics of the University of Münster (Germany) and that of Mr. S. Henstra of the Service Institute for Applied Mechanics and Technical Physics, Wageningen, The Netherlands. Samples 6, 25, 33a, 38a, 53, 63, 110, 120, 122, 123, 124, 126, 129, 133, 143, 145, 147, 148, 152 and 159 have been investigated.

The samples of the flint group show without ex-

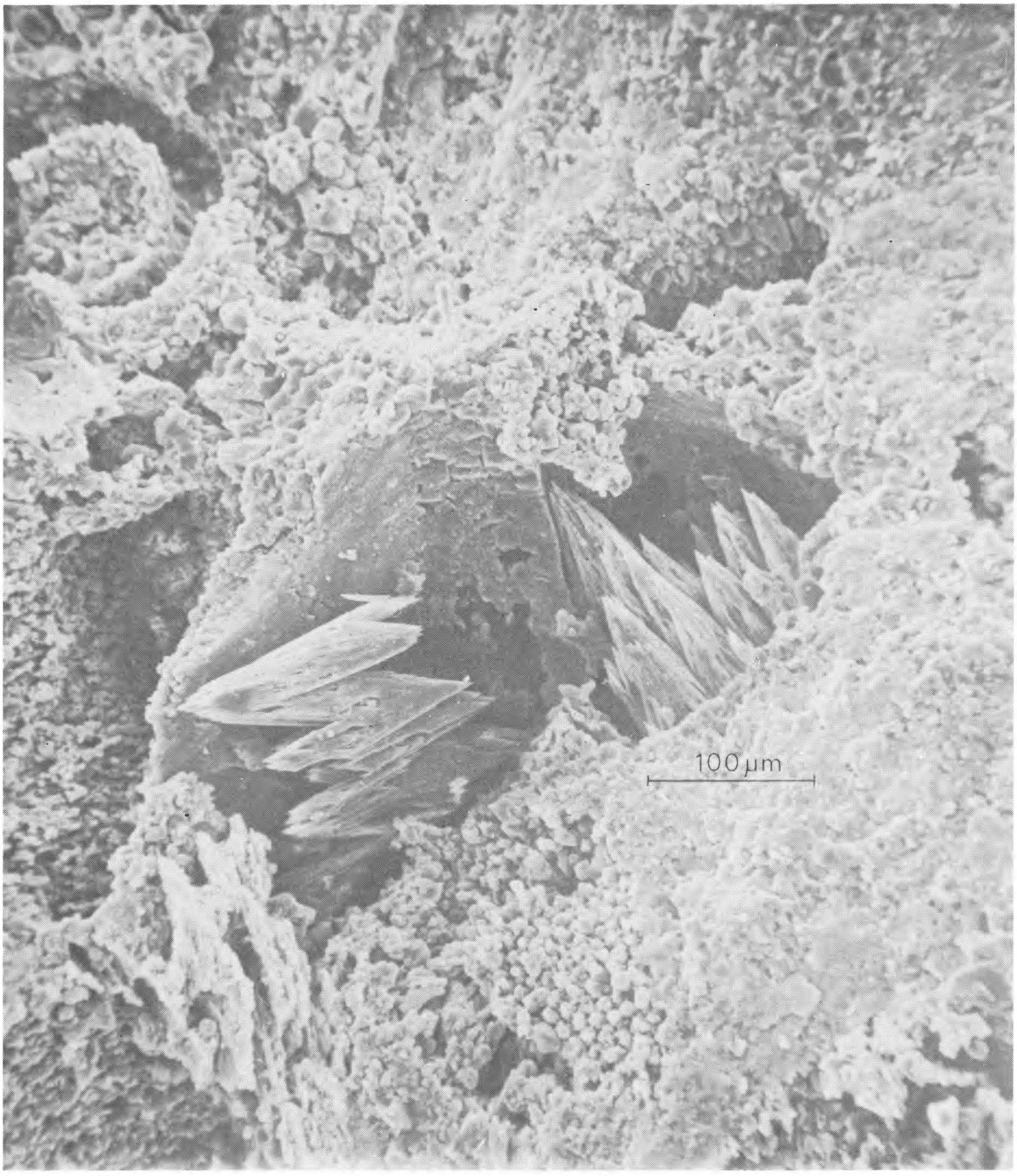

Fig. 13
Scanning electron photograph of sample 133, showing tridymite pseudomorphs of calcite. Magnification 260x. Münster.

ception a remarkably dense structure, even at magnifications up to 9000 x (fig. 12 no. 120). At that magnification the outlines of a few calcium carbonate crystals may be visible. Obviously density is increasing towards the centre of the flints.

In flint 152 silicification has not been completed

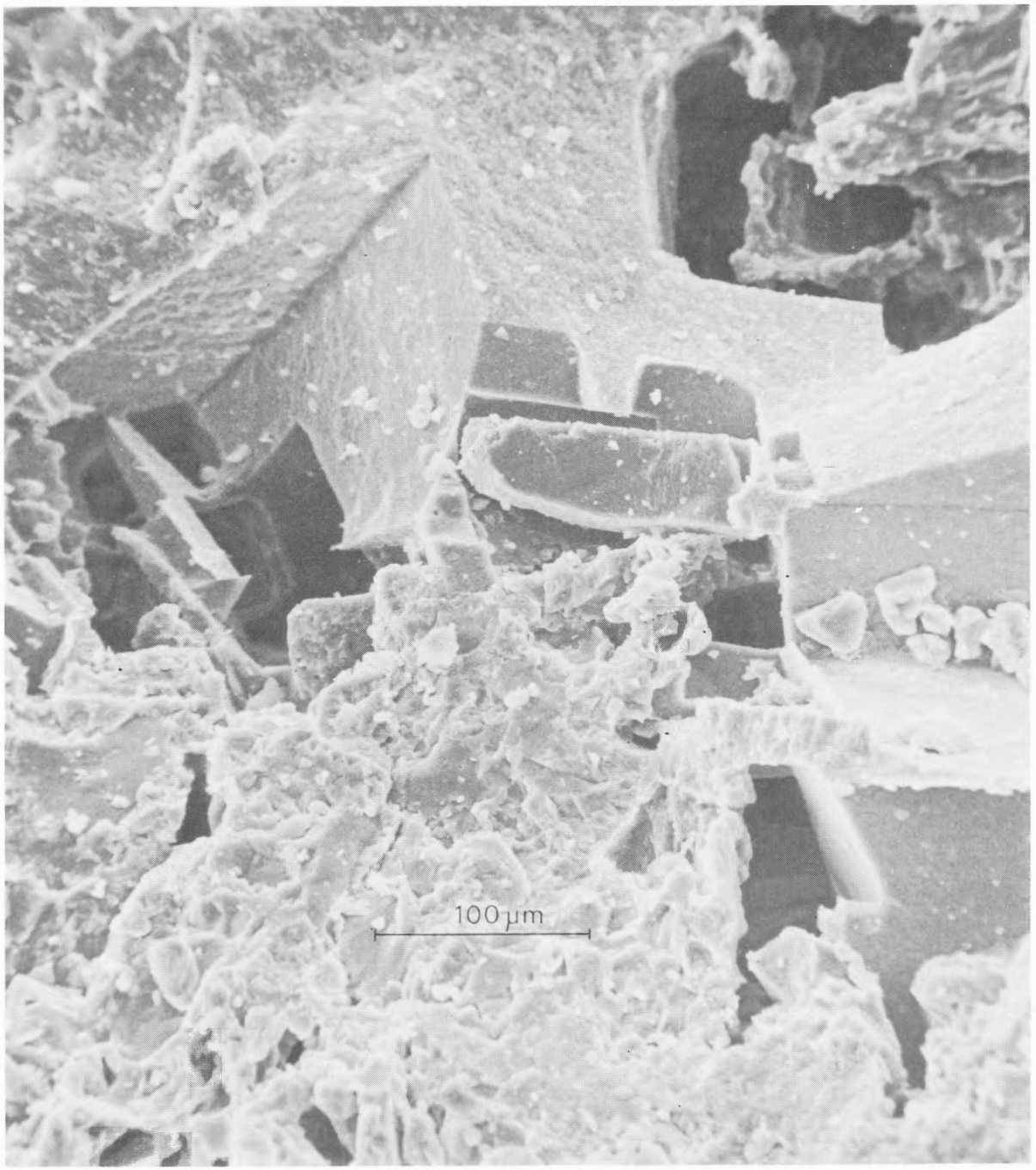

Fig. 14
Scanning electron photograph of sample 63, showing cubic pyrite holes. Magnification 330x. Münster.

and several domains of calcite crystals are visible even by low magnifications. Silicified bryozoa are sometimes found. On ridges of the fracture planes the outlines of very small quartz crystals may be discovered. Sample 133, silicified chalk, shows a less dense structure. Domains of calcite-shaped crystal groups

Fig. 15
Scanning electron photograph of sample 63, showing leafy structure. Magnification 750x. Münster.

are frequently found (fig. 13) but as the X-ray analysis did show tridymite but no calcite, these crystals are expected to be tridymite pseudomorphs of calcite.

The samples of the chert group are generally more porous than that of the flint group and show more

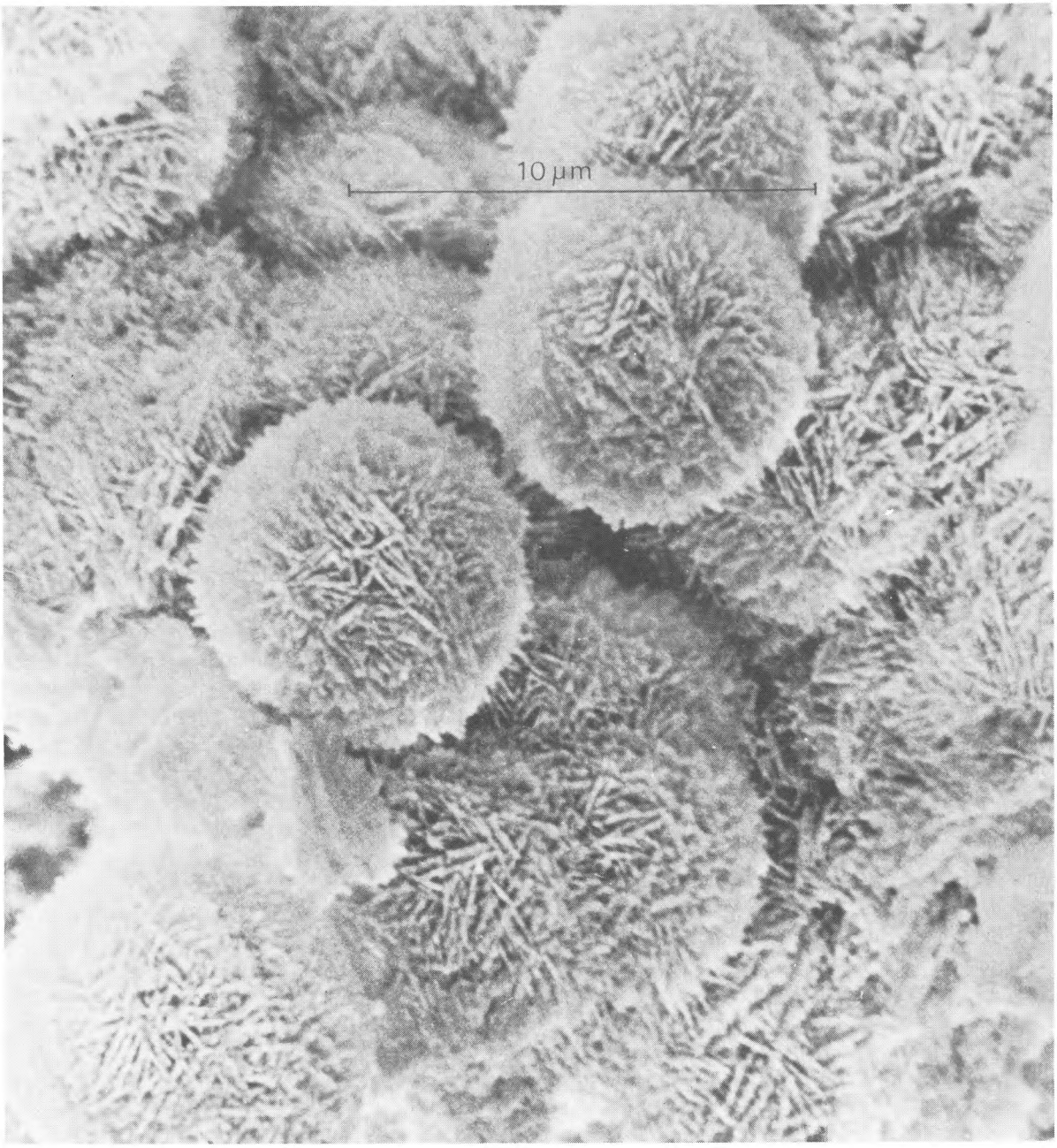

Fig. 16
Scanning electron photograph of sample 110, showing botryoidal structures with a crystalline surface. Magnification 7200x. T.F.D.L. Wageningen.

diversity.

Cubic holes that are due to pyrite crystals that occurred in the original limestone are frequently seen (fig. 14, no. 63).

Well shaped small quartz crystals are abundant in voids and a somewhat leafy structure may be observed (fig. 15). In silicified fossils larger quartz agglomerations are frequent.

Sample 110 showed a botryoidal structure, consisting of agglomerates on the surface of which small

platy crystals have developed (fig. 16). These structures are thought to be amorphous silica that has crystallized towards the above mentioned "badly crystalline" tridymite.

X-ray spectroscopy

X-ray spectroscopy was carried out on 20 flint and chert samples. Most variable were the Ca-, Si- and Fe-contents. In most of the samples traces of A1, S, K and Ti occurred.

Regarding the small amount of samples no clear differences between flint and chert or between various flint layers were distinguishable.

A possible mechanism of silicification

It was observed by R e n a r d (1878) that the structure of silicified limestones preserves that of the original rock before the silicification. Moreover, the structure of fossils, the distribution of organic matter and comparable features seem to be preserved by the process. In such cases we have to exclude the removal of carbonates and a subsequent filling of the empty holes and voids by a gel-like material of silica. In other cases such a process will certainly take place as witnessed by the many chalcedony pipes and void fillings in vesicular volcanics.

For the type of silicification preserving structures of the original rock as well as of fossils the only possible mechanism seems to be a shifting of the interface between the carbonate and the silica phase until all the carbonate is removed and replaced by silica. Such a shifting interface might be visualized as an extremely thin film with carbonate on one side and silica on the other. In the film we have to assume the formation of phases of silica and calcium ions and water. Transport of ions has to be possible in this film, because in the end calcium and CO_2 have to be removed and SiO_2 deposited.

Besides the morphological and dynamic aspects of this form of silicification, the physicochemical side has to be considered. The morphology of the process suggests a set of reactions involving a first step consisting of the transformation of calcite into a calcium silicate with the removal of CO_2 and a second step concerning the transformation of this calcium silicate into one of the phases of SiO_2 with the removal of calcium ions. The intermediate calcium silicate enables the particle by particle replacement and the preservation of structures and such a feature as the distribution of organic matter. Moreover, it is known from numerous investigations of the various cement systems, that quite a few calcium silicates are stable at low temperatures and pressures or tend to be formed metastably under such circumstances (S p e a k m a n 1968, S t e i n 1968). The occurrence of a calcium silicate, probably tobermorite, has been observed in carbonate rich sediments of the Jordan valley which also hold other authigenic minerals (W i e r s m a, 1970). O v c h a r e n k o (1969) reports the formation of tobermorite at the interaction of clay minerals and calcium hydroxide.

The replacement of silica by calcite has been reported also. This process, less widespread than silicification, also seems to take place at low temperatures and pressures. Therefore, a possible set of reactions has to provide a solution for both silicifications and calcification.

Once it is assumed that an intermediate calcium silicate takes part in the process, we may regard such phases as one of the tobermorites, okenite, gyrolite, xonotlite, riversideite, plombierite, foshagite, hillebrandite or others as suitable possibilities. Phases without H_2O in their framework seem less probable but not impossible (S t e i n 1968). Still we had to use betawollastonite in the calculations because its formula is well known and thus its free energy of formation is rather reliable. Because of their problematical formulae (especially tobermorites) we refrained from using the others as far as free energy values are available. The values for tobermorites nevertheless are reported in table 1, together with the other free energy values we used in our equations.

The first equation describes the reaction between H_4SiO_4, calcite and beta-wollastonite:

$$2\,CaCO_3\,(s) + H_4SiO_4 + 2H^+ = \\ = CaSiO_3(s) + Ca^{2+} + 2\,CO_2(g) + 3\,H_2O \qquad (1)$$

The free energy change of this reaction is:

$$-370.2 - 132.18 - 188.52 - 170.1 + 539.4 + \\ + 312.65 + 0 = -9.0$$

From this equilibrium constant is found:

$$\log K = +9.0/1.364 = 6.7$$

For the equilibrium circumstances we may write, assuming that activity coefficients are close to unity:

$$\log [Ca^{2+}] + 2 \log P_{CO_2} + 2\,pH - \log [H_4SiO_4] = 6.7 \quad (2)$$

The equation (2) shows that this reaction depends on four variables. In order to find the influence of pH and the activities of calcium and H_4SiO_4 on the stability field of $CaSiO_3$ we can draw equilibrium diagrams for a constant pressure of CO_2 such as the ones in fig. 17, 18. $CaSiO_3$ is seen to be stable within the volumes ABCDEFGH(IJ).

The second reaction concerns the removal of the calcium silicate and the formation of quartz, chalcedony, dense aggregates of cryptocrystalline quartz and low trydimite or even aggregates of cryptocrystalline quartz and amorphous material:

$$CaSiO_3(s) + 2H^+ = Ca^{2+} + SiO_2(s) + H_2O \quad (3)$$

The free energy change of this reaction is:

$$-132.2 - 204.6 - 56.7 + 370.2 + 0 = -23.3 \text{ Kcal.}$$
(in case of quartz)

$$-132.2 - 202.98 - 56.7 + 370.2 + 0 = -21.68 \text{ Kcal.}$$
(in case of amorphous SiO_2)

In this work we prefer to use values for silica phases that correspond with the free energy of formation of H_4SiO_4, reported by Reesmann and Keller, because this value has been determined by dissolving silica in water. From this is found:

$\log K = 23.3/1.364 = +17.1$ (in case of quartz)

$\log K = 9.6/1.364 = +15.9$
(in case of amorphous silica)

For the equilibrium circumstances we may write, assuming that activity coefficients are close to unity:

TABLE 1

Standard free energies of formation of the components used in this paper

(kCal/Mol)

Component	Formula	ΔF_f°	Source
beta-wollastonite	$\frac{1}{2}CaSiO$	−370.2	1
9 Å tobermorite	$\frac{1}{2}Ca_{10}[Si_{12}O_{31}](OH)_6.3\,H_2O$	−2140.9	2
11 Å tobermorite	$\frac{1}{2}Ca_{10}[Si_{12}O_{31}](OH)_6.8\,H_2O$	−2287.4	2
14 Å tobermorite	$\frac{1}{2}Ca_{10}[Si_{12}O_{31}](OH)_6.18H_2O$	−2573.2	2
	H_2O (l)	−56.7	3
	CO_2 (g)	−94.26	3
	Ca^{2+}	−132.2	3
calcite	$CaCO_3$ (s)	−269.7	3
dolomite	$CaMg(CO_3)_2$ (s)	−518.7	4
silicic acid	H_4SiO_4	−312.7	5
quartz	SiO_2 (s)	−204.6	6
amorphous silica	SiO_2 (s)	−202.98	7
	H^+	0	convention

1 : Robie (1959)
2 : Mtschedlow-Petrossian and Babuschkin (1959)
3 : Rossini et al. (1952)
4 : Robi (1959)
5 : Reesmann and Keller (1968)
6 : Kelley and King (1961)
7 : Wagman et al. (1968)

$$\log [Ca^{2+}] + 2pH = 17.1 \quad \text{(in case of quartz)} \qquad (4)$$

$$\log [Ca^{2+}] + 2pH = 15.9 \quad \text{(in case of amorphous silica)} \qquad (5)$$

Similar reactions can be envisaged for the other calcium silicate phases mentioned earlier. With the available free energy of formation values however, it turns out that the first reaction equation results in a positive free energy change of the reaction slight though it is. This implies that tobermorite may not be a stable phase at the standard circumstances of 1 at. at the reference temperature of 25° C. The composition of the tobermorite used for the determination of the reported free energy of formation values is not precisely known and if we may assume that the stochiometrical formula did not fit this composition too well, a slight change in these values may lead to different theoretical conclusions.

This reasoning leads to other considerations about the use of the earlier approach. It is well known that and the P_{CO_2} that determines whether silicification or calcification will take place:

$$\log [Ca^{2+}] + 2 \log P_{CO_2} + 2pH - \log [H_4SiO_4] = 6.7 \qquad (2)$$

$$\log [Ca^{2+}] + \log P_{CO_2} + 2pH = 10. \qquad (6)$$

$$\log P_{CO_2} \qquad \log [H_4SiO_4] = -3.3 \qquad (7)$$

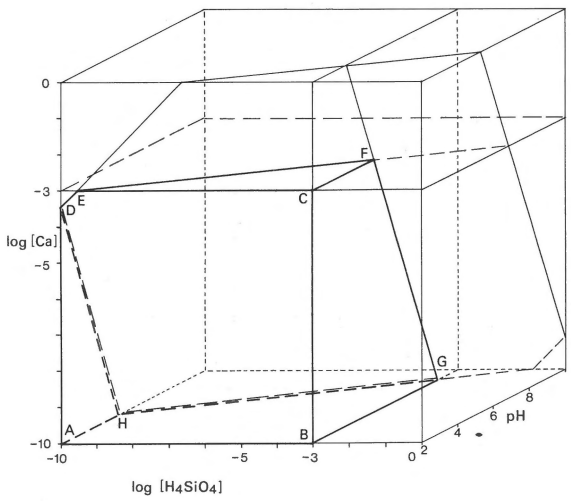

Fig. 17
Stability range of $CaSiO_3$ for log P_{CO_2} = –2. Equation (1).

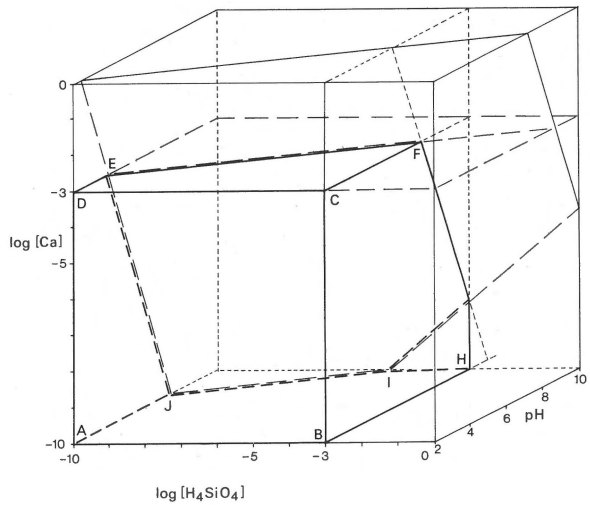

Fig. 18
Stability range of $CaSiO_3$ for log P_{CO_2} = –4. Equation (1).

small changes in the free energy of formation values of the compounds that are used in certain reactions may upset such neat conclusions about the formation of certain substances. For instance, if the earlier value for H_4SiO_4 had to be used (300.5 Kcal/mol., S i e v e r 1957) even reaction (1) should have shown a small but positive value. With the value –312.65 Kcal./mol. reported recently by Reesmann and Keller such a reaction shows beta wollastonite to be stable, the same holds for –318.6 reported by W a g m a n et al (1968).

The silicification scheme, presented above, has implications that accord with several features known from the field.

- The formation of cristobalite (G i g o u t, c.s., 1969) and tridymite instead of quartz or amorphous silica has frequently been reported and a few of the samples under discussion contain low-tridymite or phases akin to it. From W a g m a n et al. (1968) it can be seen that the alpha phases of cristobalite and tridymite have free energy of formation values in between the limits set by quartz (204.75 Kcal./mol.) and amorphous silica (–202.98 Kcal./mol.). It is easily understood that both cristobalite and tridymite fit very well into the reaction scheme presented above.
- Selective replacement of Ca in Ca/Mg limestones by silica is reported by Chilingar (1956). This is

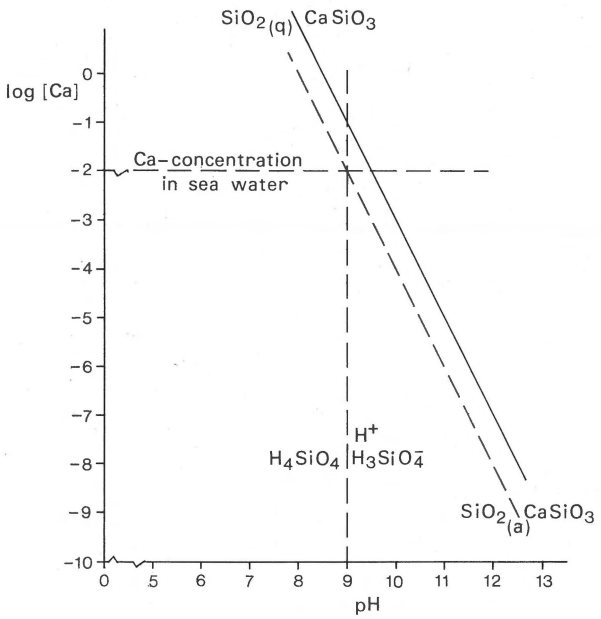

Fig. 19
Stability of $CaSiO_3$ versus quartz or amorphous SiO_2. Equation (3).

easily understood when dolomite is used instead of calcite in reaction equation (1).

– It is frequently found that fossils in limestones are silicified. This was also found by Vishnyakow, who concludes that coarse crystalline calcite is selectively replaced by quartz. Impurities of the limestone may affect the equilibrium.

Silicification under terrestrial circumstances is strongly related to eluviation and will generally occur in subsoils where silica is accumulated and cations such as Ca and Mg are removed, which favours the reactions (1) and (3).

Under sea floor conditions we also have to consider other equilibria. Diffusion does occur but no eluviation. Electrolyte concentrations are high and activity coefficients are much lower than unity. This should be kept in mind for the following considerations.

In the case of seawater in contact with calcareous bottom sediments we may expect the activity of Ca^{2+} in the liquid to be in equilibrium with crystalline $CaCO_3$.

From: $CaCO_3 + 2H^+ = Ca^{2+} + CO_2 + H_2O$ follows the equation:

$$\log [Ca^{2+}] + \log P_{CO_2} + 2pH = +10 \qquad (6)$$

From a combination of equation (2) and (6) we may find a relationship between the activity of H_4SiO_4 Assuming a maximum value for log $[H_4SiO_4]$ of -3, the critical value for log P_{CO_2} is -6.3. If this value is larger we will expect calcification, provided the pH is large enough for the formation of a calcium silicate. If the value of pH is too small or the pressure of CO_2 is larger, calcium carbonate will be formed at the expense of silica. In fig. 19, the relationship between the activity of Ca^{2+} and the pH for the formation of $CaSiO_3$ is shown for quartz and amorphous silica, derived from equation 3:

$$CaSiO_3 + 2H^+ \leftrightarrows H_2O + Ca^{2+} + SiO_2 \qquad (3)$$

leading to:

$$\log [Ca^{2+}] + 2pH = 15.9 \text{ (amorphous silica) or } 17.1 \text{ (quartz)}$$

The figure also shows the calcium activity in seawater and the boundary between dissociated H_4SiO_4 and H_4SiO_4. From this figure it follows that the phases under discussion are more or less in equilibrium under the conditions at the ocean floor and that slight changes in pH, in the local concentration of Ca^{2+} or slight changes in temperature (the diagram is valid for 25° C) determine whether or not chert is formed in calcareous sediments at the ocean floor. The diagram also pertains to circumstances that may occur in soils or in sediments directly below these soils.

DISCUSSION

The morphology and the position of silicification horizons or curtains in the earth's crust are rather variable. Millot (1960) reports a number of characteristic silicifications in carbonate free environment supposing that the original quartz grains function as surfaces for further crystallization. Where silicification occurs in an environment with carbonates we may discern two different cases.

(1) The silicification is rather superficial and connected with soil formation in weathering material of carbonate rocks. In this case the silica can be derived from this weathering residue together with the sediments deposited by local rivers. Clay minerals akin to muscovite and illite produce no silica during transformation into kaolinite (Slager & Van Schuylenborgh, 1970) but the liberation of Al^{3+}

through this weathering and the subsequent removal by eluviation causes the liberation of H_4SiO_4. This silica charged water meets the limestone underneath and may create silicification according to the process described.

(2) Silicification may also be related to sedimentary structures or sedimentary processes. Bedded flints in limestones are correlated with zones of biological activity (burrow-holes or concentration of fossils) or with a change of grain size or other sediment features. Chilingar (1956) assumes a relation between flint layers and depth of the basin. Investigations of Harder (Harder, 1965; Harder and Menschel, 1967; Harder and Flehmig, 1970) point to the possibility of sedimentation of silicarich hydroxyde gels that especially may reach high concentrations when detrital sedimentation is impeded. Harder (1965) showed that quartz may easily form from the above silica-rich hydroxyde gels.

Repeated occurrence of flint zones indicates oscillation of sedimentary circumstances. Limburg flint depostis are related with grain size, corroborating this assumption (Felder, 1960; Vishnyakov, 1953). Defretin (1958) assumes a relationship between flint formation and biological activity through a change of P_{CO_2} and pH. The presence of silica skeletons is related to flint formation and depends on environment also. Silica skeletons have a very high solubility, almost as high as amorphous silica.

Once crystalline silica has been formed, a gradient in the solution will speed the crystallization of more silica and the removal of this compound from the immediate surroundings. Chilingar (1956) reports a low silica content of limestones in the vicinity of chert or flint. The outer rims and covers of chert or flint are often incompletely silicified and concentric features often are characteristic of flints and cherts. Both phenomena can be explained by assuming a gradient of silica set up by the flint occurrence and diffusion of silica through the porous medium of the rock.

CONCLUSIONS

A. *On the properties*

1. The difference between flint and chert in the sense defined at the beginning of this report is only a matter of grainsize, porosity, and dehydration features.
2. Other silica phases than quartz seem to be restricted to porous calcareous bedrocks.
3. Flint holds a certain amount of water that is removed gradually during the exposure to atmospheric conditions. The removal of water is slow and not reversible. Cherts as defined in this paper do not show this removal.

B. *On the genesis*

1. An intermediate calcium silicate is assumed to play an important role in the type of silicifica- alteration of limestones. The calcium silicate should be identical with or akin to the hydrated calcium silicates that play an important role in the hardening of cement.
   The observations of the presence of tobermorite, one in limestone and one in an experiment with calcium hydroxide and clay minerals corroborate this assumption. Observations in a thin section of a flint show the presence of an unidentified phase at the contact of silica and calcite.
2. The mechanism of silicification as described in this paper may provide for the explanation of the formation of flint beds in calcareous sea-bottom sediments.
3. The mechanism proposed does not contradict the field observations that are known to the authors.
4. The origin of the silica in superficial silicifications under terrestrial circumstances is ascribed to weathering processes. The silica in the bedded flints originate from redistribution of silica present in the original limestone. The original form of these silica is not yet known.

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