

ALLOPHANE AND ITS INITIAL CRYSTALLIZATION PRODUCTS AS CONCRETIONS IN THE SOUTH LIMBURG CHALK

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ABSTRACT

Silicon-alumina concretions with about equal amounts of both components and ranging in crystallinity between allophane and initial crystallization toward halloysite or gibbsite were found in and on Upper Cretaceous limestones. These concretions were probably the result of accumulation of Late Tertiary and Early Pleistocene weathering products, accumulated by stagnation of percolating waters. Crystallization might have been inhibited by the electrolyte concentrations in the limestone pore waters. Pure allophane material was much like the allophane originally described in 1816.

INTRODUCTION

About two years ago, amorphous, soft, white concretions of unknown origin were found by the third author, while

studying the exposure of Maastrichtian and Danian calcarenites in the Curfs quarry near Geulhem, Southern Limburg, The Netherlands (Fig. 1).

These concretions originated from seemingly undisturbed limestone deposits and occurred in horizontal lenses that varied considerably in length (several decimetres up to several metres) and width (several centimetres up to several decimetres).

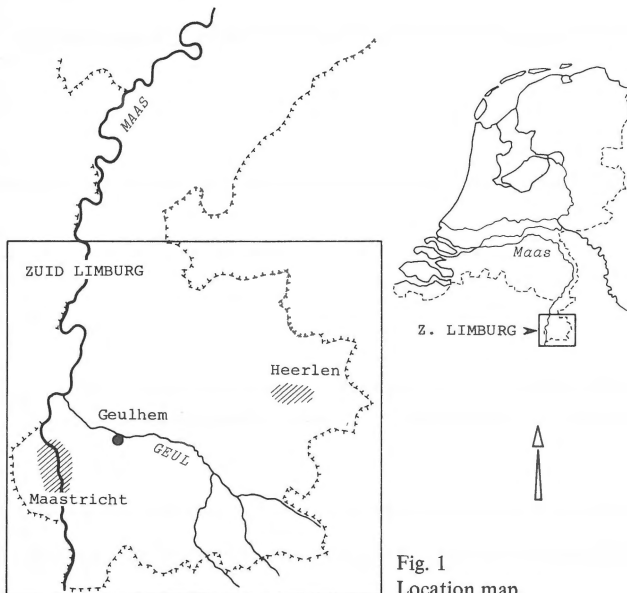


Fig. 1
Location map.

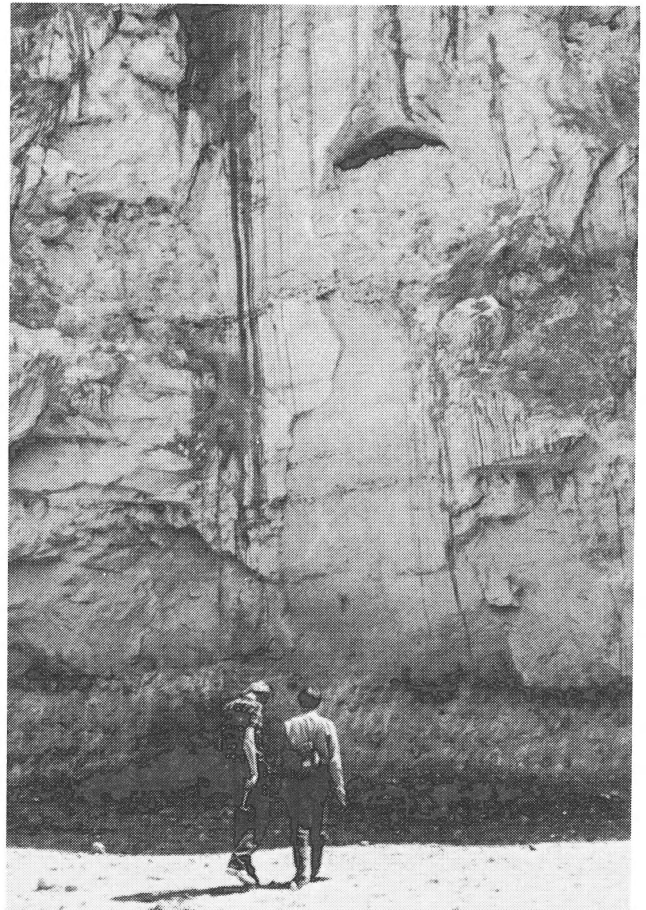


Fig. 2
A horizontal karst gallery with a vein of material of type 1. (Curfs quarry, Maastrichtian)

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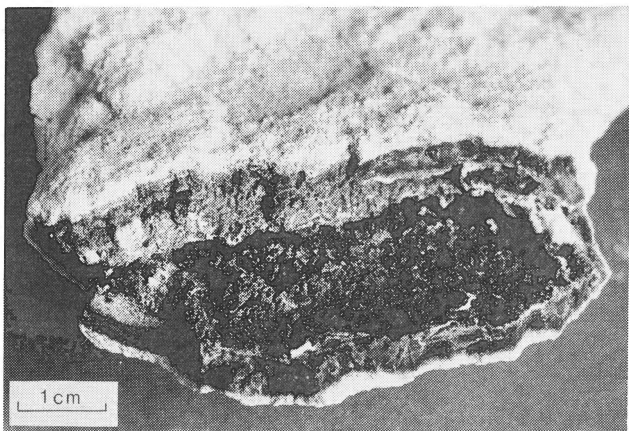


Fig. 3
Concretion type 2

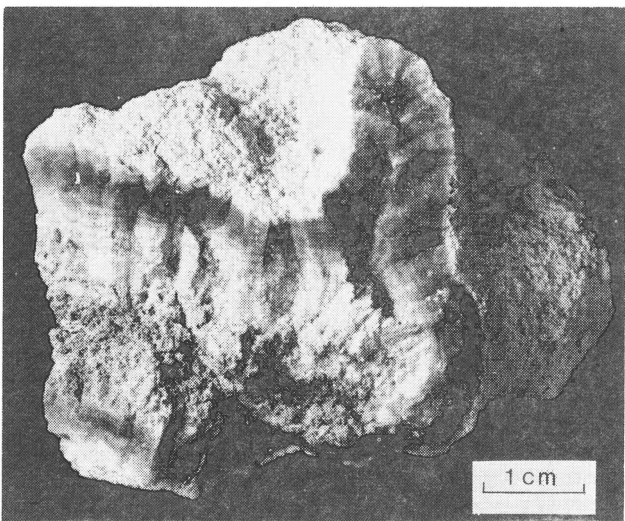


Fig. 4
Concretion type 3, cross section.

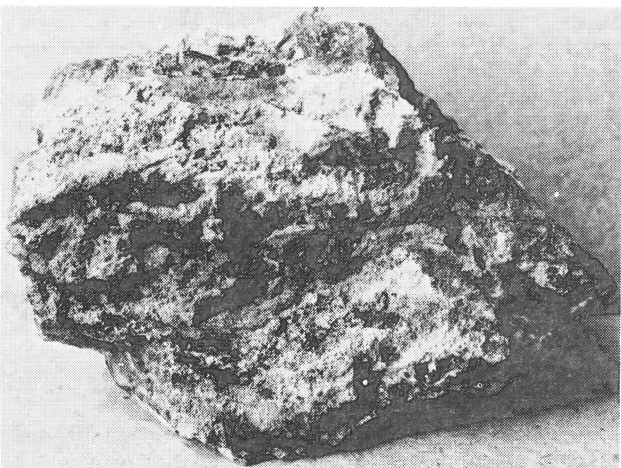


Fig. 5.
Concretion type 5. Width is about 20 cms.

More detailed study by the authors led to the discovery of several types of concretions:

Type 1: Soft, white concretions. These concretions slake in water, forming a gel-like substance, and shrink upon drying. They occur as more or less horizontal lenses in caves completely or nearly completely filled with limestone debris (Fig. 2). Such caves occur both in Maastrichtian and Danian calcarenites. Occasionally, lenses of this type of concretions are found in undisturbed limestones.

Type 2: Concretions that occur along vertical fracture planes in the limestone. These concretions consist of black or brown radially built outer walls, and are either hollow or filled with crystalline, white material or soft, unoriented material. They occur in the Danian limestones (Fig. 3).

Type 3: Concretions that occur in more or less horizontal planes in the limestone. These concretions are irregularly shaped, and very soft. They consist of radially built yellow or yellowish brown outer parts, surrounding soft, white material. These concretions occur in the Danian limestone (Fig. 4).

Type 4: This type of concretion consists of hollow pipes with crystals on the inner walls. The outer part of these concretions is formed by soft, porous material of chalky habit, free of CaCO_3 ; the inner part consists of brittle, yellowish material, similar to the radial parts of the concretions of Type 2. Type 4 was not found in situ.

Type 5: Along the walls of the dolinas in the top of the Danian limestone accumulations of varying aspect occur. These are mostly one to several decimetres thick; they show white, brown and black zoning and are soft in white and black parts but somewhat brittle in glassy brown parts. (Fig. 5). These accumulations occur between the limestone and infillings of Tertiary sand.

The relative position of these concretions is illustrated in Fig. 6.

PROCEDURES

In the investigation of the material, X-ray diffraction has been carried out with a quadruple Guinier-de Wolff camera and with a diffractometer, using iron-filtered Co-K alpha radiation. For DTA a DuPont 900 apparatus with an 850°C cell was used; TGA was carried out with a DuPont 950 thermobalance in combination with a DuPont 990 unit. Thermogravimetry was carried out in N_2 atmosphere. Scanning electron microscopy was carried out with a JEOL equipment, chemical analysis with X-ray fluorescence.

From sample 74-20, 10 separate analyses were made. In this sample, the Cation Exchange Capacity was determined, and the pH of the sample in 1M NaF was determined.

SAMPLES

The following samples were chosen for further investigation:

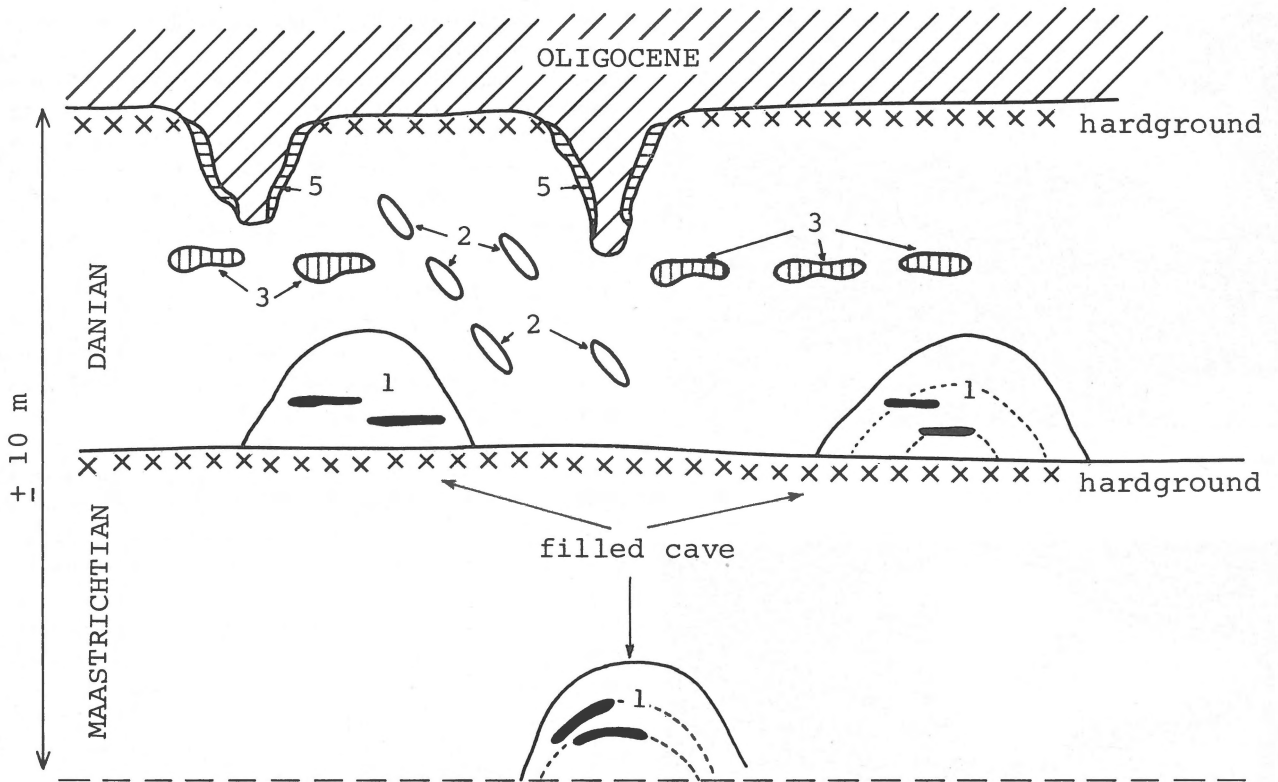


Fig. 6
Schematic cross section of a face of the Curfs quarry, showing the horizontal karst galleries and the various concretions.

- 74-20 a/b: Two samples of concretion type 1.
 74-21 : Concretion type 3, outer part
 -22 : Concretion type 3, yellow, radial part
 -23 : Concretion type 3, white, granular infilling
 -24 : Concretion type 3, brown, radial part
 -25 : Concretion type 3, soft, white infilling
 -27 : Concretion type 2, brown, massive outer part
 -28 : Concretion type 2, white, soft infilling
 -29 : Concretion type 2, white, glassy infilling
 -30 : Concretion type 4, outer part
 -31 : Concretion type 5, white, powdery
 -32 : Concretion type 5, light brown, powdery
 -33 : Concretion type 5, dark brown, glassy
 -34 : Concretion type 5, black, powdery
 -35 : Concretion type 3, hard, massive core. (grey)

X-RAY DIFFRACTION

Most of the samples contained some imperfectly crystalline gibbsite and/or halloysite (hydrated); in some samples quartz and calcite were detected. Results are given in Table 1.

The concretion of type 4 showed an increase in gibbsite and a decrease in halloysite towards the centre.

TABLE 1.

X-ray diffraction analysis (+) indicates halloysite not detected in Guinier photographs, but visible in diffractometer traces of unoriented powder.

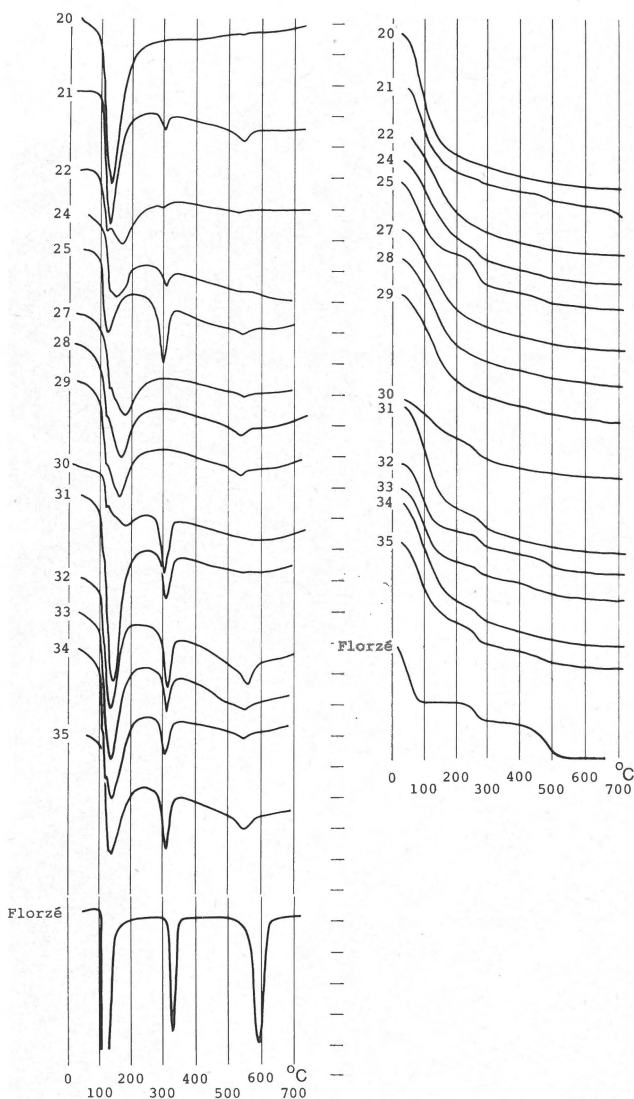
Sample	20	21	22	23	24	25	27	28	29	30	31	32	33	34	35
Gibbsite	-	-	-	-	-	-	-	-	++	++	++	++	++	++	++
Halloysite	-	++	(+)	++	(+)	++	-	+	+	-	+	++	+	(+)	++
Quartz	-	+	-	-	+	--	--	+	--	++	+	+	+	+	+
Calcite	-	++	-	-	-	-	+	+	+	+	-	-	-	-	+

Only sample 20, of concretion type 1 was found to be completely amorphous.

THERMAL ANALYSIS

The results of DTA and TGA are given in Fig. 7.
 DTA. The differential thermal analysis of the samples shows one to three characteristic peaks:

1. an endothermic peak with a maximum between 120 and 170°C, frequently consisting of two or more steps.
2. an endothermic peak with a maximum between 300 and 310°C, absent or weak in some samples.
3. an endothermic peak with a maximum between 530 and 570°C, absent or weak in some samples.



TGA traces show that these endothermic reactions are associated with loss of water. TGA traces show four trajectories of increased dehydration:

1. between starting temperature and 150°C
2. between 250 and 300°C
3. between 450 and 500°C
4. above 650°C (due to the decarbonation of calcite)

The discrepancy between these temperature trajectories and those of the DTA endothermic reactions are due to the fact that samples for DTA are kept in narrow tubes, so that dehydration is somewhat impeded.

For comparison, the traces of a mixture of halloysite and gibbsite from Florzé (B u r m a n & v a n d e r P l a s, 1968) are given at the bottom of Fig. 7. It appears that the trajectories of weight loss of the Curfs concretions compare well with those of well crystalline gibbsite and halloysite. The samples in the present investigation show rather long trajectories of dehydration. This may be due to the low grade of crystallinity, which induces a gradual transition between adsorbed water and more strongly bound water. The various steps in the first dehydration, as illustrated by the DTA traces may well be due to the same phenomenon.

When taking the dehydration at about 300°C as an indication for the presence of gibbsite, and the dehydration at about 500°C as one for the presence of halloysite, it is obvious, that halloysite is more easily detected with X-ray diffraction than is gibbsite. Gibbsite is obviously easier detected in DTA or TGA.

Fig. 7

DTA and TGA traces of air-dry samples.

For DTA: about 10 mgs each sample; vertical scale 2eC/unit

For TGA: 25.0 mgs each sample (sample 30: 18.5 mgs). Vertical scale: 2 mgs/unit.

TABLE 2.
Chemical analyses (samples dried at 105°C)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	CO ₂	H ₂ O
74-20 a	44.5	31.5	<0.1	<0.1	0.2	4.9	<0.1	<0.1	<0.1	1.5	<0.1	17.3
20 b	45.1	31.9	<0.1	<0.1	0.1	4.2	<0.1	<0.1	<0.1	1.5	<0.1	17.2
20*	44.8	31.7	<0.1	<0.1	<0.1	4.5	<0.1	<0.1	<0.1	1.5	<0.1	17.5
21	38.4	28.9	0.8	<0.1	0.2	9.1	<0.1	<0.1	<0.1	0.5	5.8	13.6
22	40.3	36.3	0.2	<0.1	0.1	3.2	<0.1	<0.1	<0.1	0.2	1.1	16.8
23	25.4	45.9	1.0	<0.1	0.2	1.4	<0.1	<0.1	<0.1	0.2	<0.5	23.7
24	38.3	36.5	0.6	<0.1	0.2	2.9	<0.1	<0.1	<0.1	0.3	<0.5	18.5
25	17.6	50.2	1.8	<0.1	0.2	1.2	<0.1	<0.1	<0.1	0.3	<0.5	26.7
27	41.6	33.5	2.1	<0.1	0.2	3.1	<0.1	0.1	<0.1	0.2	<0.5	16.9
28	37.4	35.1	0.3	<0.1	0.2	5.3	<0.1	0.1	<0.1	0.1	<0.5	19.8
29	39.5	37.2	0.1	<0.1	0.2	3.7	<0.1	<0.1	<0.1	0.1	1.8	16.2
30	38.4	35.6	1.0	<0.1	0.3	2.3	0.1	0.1	<0.1	0.2	<0.5	19.8
31	34.2	40.2	0.7	0.3	0.2	2.7	<0.1	<0.1	<0.1	<0.1	<0.5	19.5
32	38.0	30.8	11.6	<0.1	0.4	1.7	<0.1	0.1	<0.1	<0.1	<0.5	15.6
33	38.4	27.0	15.1	<0.1	0.4	2.0	0.1	0.1	<0.1	0.1	<0.5	14.7
34	36.4	37.4	0.5	0.8	0.2	3.0	<0.1	<0.1	<0.1	<0.1	<0.5	19.5
35	36.3	38.4	0.7	<0.1	0.2	2.5	<0.1	<0.1	<0.1	0.3	<0.5	18.8

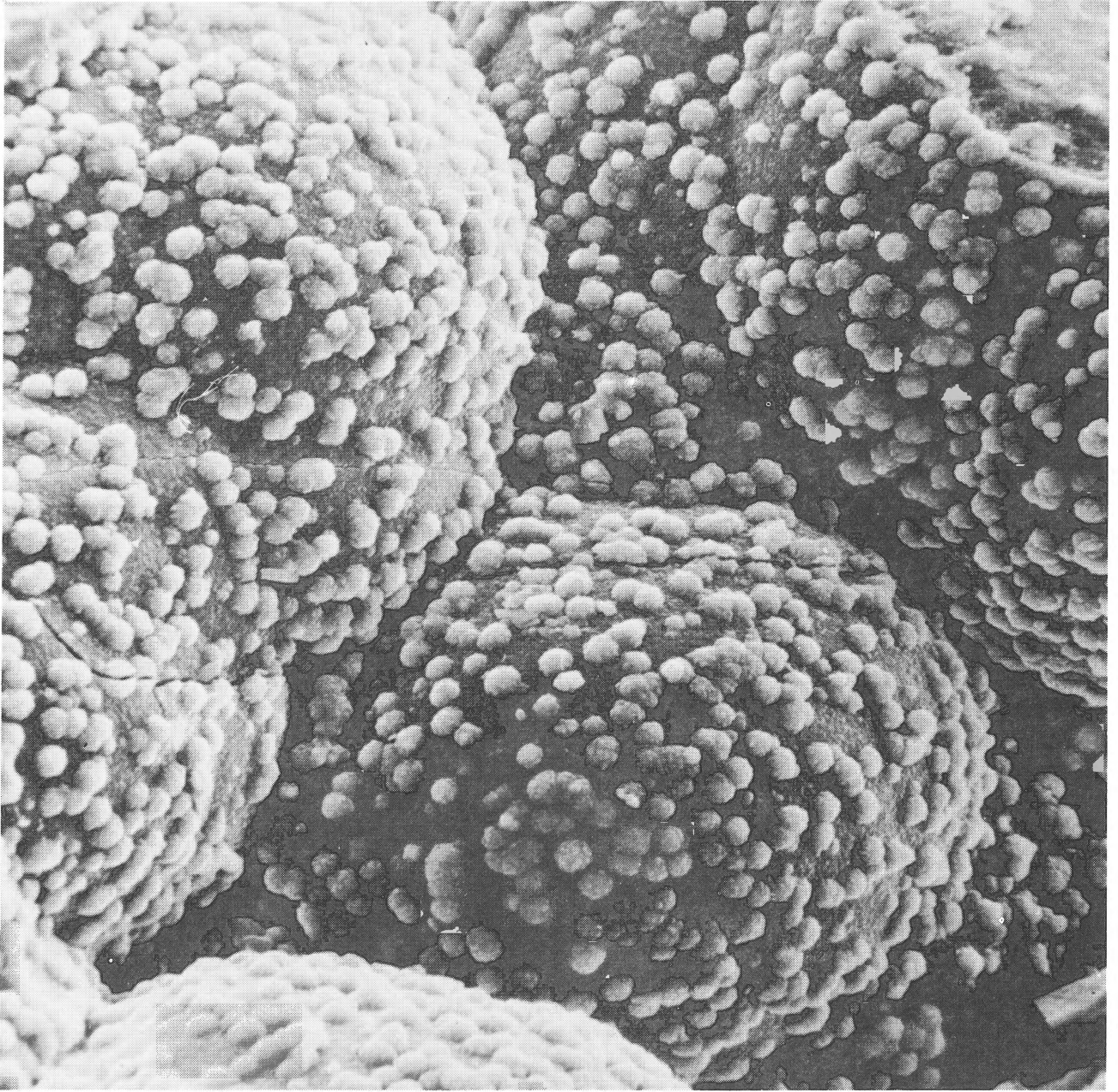


Fig. 8
Scanning electron micrograph of the inner part of concretion type 3. (TFDL 410-26) Magnification 700 x

CHEMICAL ANALYSIS

Total chemical analyses of the samples gave the results tabulated in Table 2. Most of the samples contain about equal amounts of alumina and silica.

Concretions type 3 (samples 23 and 25) show very high alumina contents in the inner parts. CaO contents may be attributed to CaCO_3 in some samples and to adsorbed Ca in samples where no carbonate was detected. The analyses of

sample 20 showed a strong consistence in chemical composition (see Table 2).

SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy was carried out on material of types 1 through 4. None of these materials showed distinctly crystalline structures.

Type 1 showed cracks in the material and, upon higher magnifications, initiation of hexangular structures on the surface; types 2,3 and 4 showed botryoidal structures (Fig. 8) and occasional sharp, platy fragments without crystal outlines.

HEATING

Sample 20 was heated at steps of 100°C up to 1200°C, in order to obtain crystalline substances. Crystallization started above 900°C. Between 900°C and 1100°C, high-cristobalite and mullite were found; above 1200°C mullite was perfectly crystalline and a calcium silicate glass was formed.

OTHER ANALYSES

Because the amorphous material of concretion type 1 showed characteristics very close to those of allophane, two tests, commonly used for this group of minerals were carried out.

Fluoride is known to disrupt OH bonding and to release OH from allophane (Furkert & Fieldes, 1970). Half a gram of sample 20 was added to 15 ml 1M NaF at 20°C. After one hour the pH had risen to 10,9. This is about the same rise as is induced by allophane in Andosols (volcanic ash).

An other method to characterize allophane in soils is the Cation Exchange Capacity delta value (delta CEC) (Aomine & Jackson, 1959). The CEC of allophane depends, among others, on the pH of the extract in which it is measured.

The delta CEC gives the difference in CEC values at buffered pH 10.5 and 3.5, respectively. In the present case, CEC values were: 155 meq/100 gram at pH 10.5 and 88 meq/100 gram at pH 3.5. Thus the delta CEC is about 67 meq/100 gram, which is close to the value for soil allophane (100 meq/100 gram).

DISCUSSION

Karst galleries. Felder (1974) recently reported the presence of horizontal karst galleries from southern Limburg. He describes a karst gallery on top of a dense flint layer. The galleries described in this paper (Fig. 2,6) were either formed on top of the hardground that marks the contact between Maastrichtian and Danian limestones, or on top of a hardground in the Maastrichtian limestones. The galleries may have developed at former ground water levels. The fact that the galleries described here are filled with pure calcarenite matter suggests that they might have formed before the deposition of post-Danian sediments. Clayey infillings as described by Felder were not found.

Source and accumulation of alumina and silica. It is

obvious that the alumina and silica that were found as concretions in the limestone or as accumulations on top of the limestone do not originate from the limestone itself. Minerals such as gibbsite and halloysite maf form in soils of tropical regions, where intense weathering results in high alumina and silica contents of percolating water, e.g. on volcanic ash soils.

Icole (1971, 1973) described accumulation of halloysite in soils on terrace deposits of Günz age, and accumulation of gibbsite in terrace deposits of Mindel age, and he attributes these accumulations to weathering in a climate warmer than the actual. Wilson (1969) on the contrary, described the formation of gibbsite on ultrabasic rocks in a cool atlantic climate (Scotland).

Recent weathering in soils in The Netherlands, however, will not result in excessive liberation of silica and alumina, and we will probably have to ascribe this process to Late Tertiary or Early Pleistocene soil formation. Sources of silica and alumina can be found in the clay minerals and feldspars of the Tertiary deposits overlying the limestone, although most of the weathering mantle of these deposits was since removed by erosion. The Oligocene strata that are now covering the Danian limestones, have not been affected by severe weathering.

Alumina and silica, once in solution, were transported downward either through the pore system in the chalk, or along vertical planes, and accumulated at some depth, presumably by stagnation of the water transport. The interface limestone/sand at a dolina wall acts as such a transport barrier, and it is quite logical to find accumulation of dissolved material here.

Accumulation in deeper parts of the limestone can also be explained by stagnation.

The concretions that occur along bedding planes in the limestone (Type 1 and 3) have lighter colours than those along cleavage planes. These differences in colour are probably due to small amounts of organic matter, that is filtered out upon transport through the limestone pore system, but not upon transport along cleavage planes. All accumulations were probably formed in preexisting open spaces in the limestone, because concretions hardly ever contain appreciable amounts of calcium carbonate.

Crystallization. The amorphous component of the materials ranges within the allophane minerals (viz. Grim, 1953). This is made clear by its chemical composition, dehydration characteristics, OH-bonding and delta CEC value. It is very similar to the material first described as allophane, by Strohmeyer & Hausmann (1816), who found their mineral in copper bearing marl. The other components are early crystallization products of allophane, that are frequently encountered in e.g. volcanic ash soils.

When ascribing the accumulation of the material to Tertiary soil formation, we have to account for the fact that the material is still not well crystalline. It is known (Lippens, 1961) that the crystallization of alumina gels is strongly influenced by the presence of anions, the absence of anions

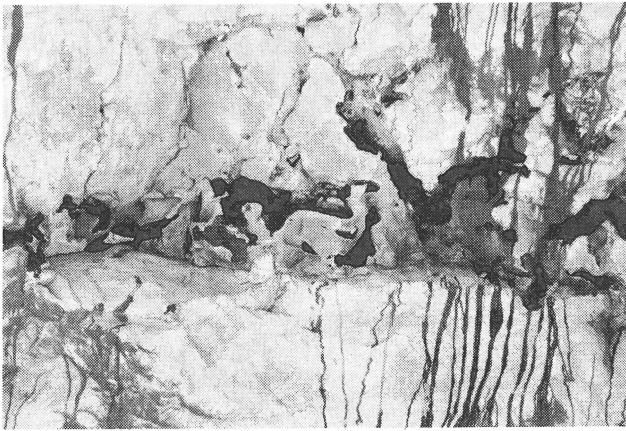


Fig. 9
Holes from which the concretions (type 3) were dissolved (width of the picture about 1 metre)

favouring crystallization. McHardy and Thompson (1971) found that gibbsite is precipitated from gels that are slightly acid and positively charged. In the present case, the composition of the chalk pore waters may well have inhibited crystallization. The presence of silica induced the formation of halloysite. The process of crystallization is still active.

Recently, material of type 1 was found in the top of the Kunrader Limestone (Maastrichtian) near Welten (South of Heerlen, viz. Fig.1), while concretions of type 5 were found in the quarry Blom near Berg en Terblijt (east of the Curfs quarry).

Although apparently accumulations of materials described above occur quite frequently in the top of the limestone (the Curfs quarry may easily yield several hundreds of kilograms), we don't think it strange that discovery was made only recently. The material is very soluble in water and is only

found in fresh rock faces in dry weather. A washed-out occurrence is shown in Fig.9. More occurrences can be expected in the Cretaceous rocks of Holland and Belgium.

ACKNOWLEDGEMENTS

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