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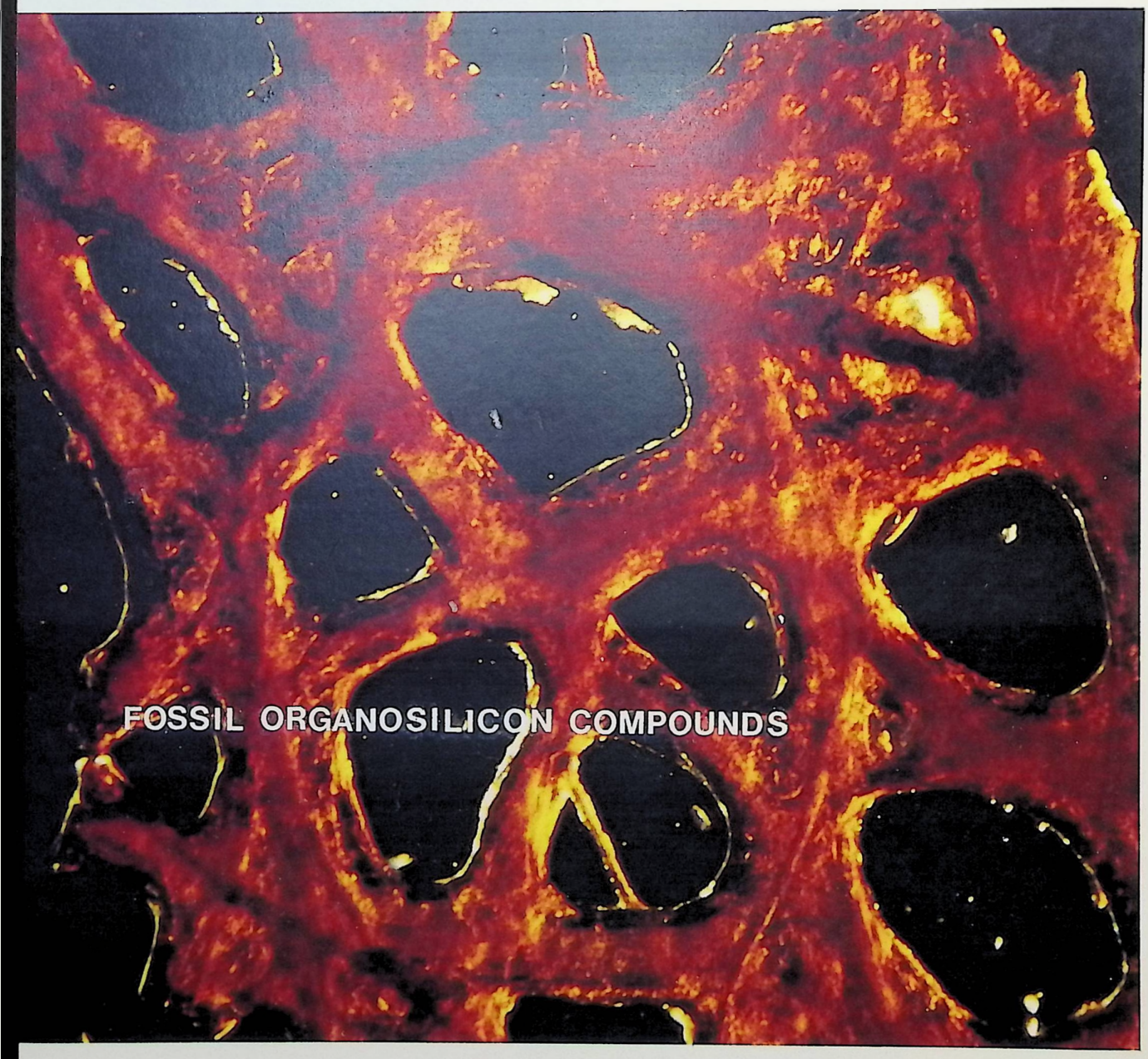

FOSSIL ORGANOSILICON COMPOUNDS

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1997

Für

Klaus - Peter Kelber

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Fossil Organosilicon Compounds -

a type of silicification diagenetically developed in Triassic vascular plant cuticles and thallophytes

by

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CONTENTS

A) ABSTRACT

Fossil vascular plant cuticles and fossil thallophytes* from the Carnian of Lower Franconia exhibit a very similar fossil appearance, which could be classified with the so called kerogens. They consist of a hyaline, yellow to red, flexible and burnable mass. On combustion a characteristically structured silica ash is formed. This observation indicates a silicification of these fossils. The original substances are diagenetically transformed into organosilicon compounds. The cuticles and thalli are preserved not only due to the resistance of their original matter, e.g. cutin, cutan, chitin, substances presumed to persist unaltered for millions of years. In addition these biopolymers have been involved in a silicification process resulting in a yellow to red substance extraordinarily resistant to chemical degradation. It was formed during the humification process as a complex condensation product derived from a mixed gel of humic substances and gelatinous silica. This matter is termed: fosicom (fossil organosilicon compound) with respect to its chemical bondage. Biopolymers, like cutin or chitin, are embedded in fosicom and are covalently bound to it. Thus they were protected from further coalification and remained preserved.
Fosicom is a polymerized substance with remarkable physical and chemical properties: a flexibility depending on moisture content, the ability to swell in polarized and unpolarized fluids and a high resistance to caustic agents and to heat. Fosicom combines traits characteristic of organic matter and of minerals. It is a diagenetical developed organosilicon compound with about 80% organic and 20% mineral components. Due to its chemical nature the formation of fosicom has the capability to stop the coalification process, thus preserving delicate cell structures and even biomolecules, e.g. lichen substances, for millions of years. This type of silicification provides evidence towards the lichen nature of the Triassic thallophytes and may open up a new way of understanding the formation and chemical nature of kerogens.

**Intended herewith are fossil fungoid thallophytes, some of which represent a consortium and anatomically resemble extant foliose lichens (Ziegler, 1992,a,b).*

B) INTRODUCTION

1. Vascular plant cuticles and lichens in the fossil report.

Cuticles are frequently found in fossil plant material. According to Kerp (1991), the study of fossil plant cuticles dates back to 1841 and yields numerous specimens from many localities. Extant lichens today can be found in a wide range of habitats (Lange, 1992). Considering their frequency in plant communities it surprises that there are only a few substantiated reports of fossil lichens although many of them have tissues capable of preservation (Taylor, 1993). In sharp contrast, reports of fossilized fungi are frequent. Numerous families of fungi have already been reported back in the Devonian (Hirmer, 1927). The lack of fossil reports also astonishes if one considers the compact fungal body of foliose lichens. Taylor (1993) supposes major problems in the identification of lichens whose fragile phycobionts and mycobionts may be difficult to recognize in permineralizations. Only a few sites, e.g. the Rhynie chert (Taylor et al., 1995), allow an observation of cellular structures which is a prerequisite for recognizing the lichenoid organization of a thallophyte.

2. Controversial origin of the Triassic thallophytes

The taxonomical origin of the fossil objects, described here as thallophytes, is controversial. They are often reported to appear in fossil cuticle assemblages. According to Manum (1996), these objects were first recorded by Ludwig (1857) and since then have been described by many authors. The taxonomical interpretations range from algae, megaspores, seed coats or other plant matter to animal objects like eggs or clitellate cocoons. Manum et al. (1991) and Manum (1996) give a general review, which need not be repeated here. The extreme diversity of interpretations is due to a lack of extant analogues. Based on predominantly morphological features Manum (1996) considers extant clitellate cocoons to be the most convincing analogues for these mysterious fossil organisms resp. objects, which are known to be associated with vascular plant cuticles in many localities from

Triassic to Tertiary. Ziegler (1992,a,b) describes them as fungoid thallophytes some of which resemble present foliose lichens.

3. Fossil matter of unknown chemical consistence

Besides the taxonomical origin of the thallophytes, also the compound of the fossil matter of which they consist is unknown. Horst (1954) tried to analyse the chemistry of these fossils with chemical and spectroscopical methods. Since he assumed a fungoid origin he mainly searched for chitin, but could not find any significant indication for this substance. Concerning my own observations it is remarkable that Horst (1954, p. 611) reports a spectrochemical proof of Si in these fossils. Irrespective of the origin and chemistry of these enigmatic fossils, the fact is that they consist of a matter which is very similar to that of the fossil vascular plant cuticles with which they are taphonomically associated. In this connection it is remarkable that fossil cuticles which have been obtained from diverse localities are presumed to consist predominantly of their original matter: cutin and or cutan (Bornemann 1856, Stach 1982, De Leeuw et al. 1991).

4. Fossil cutin

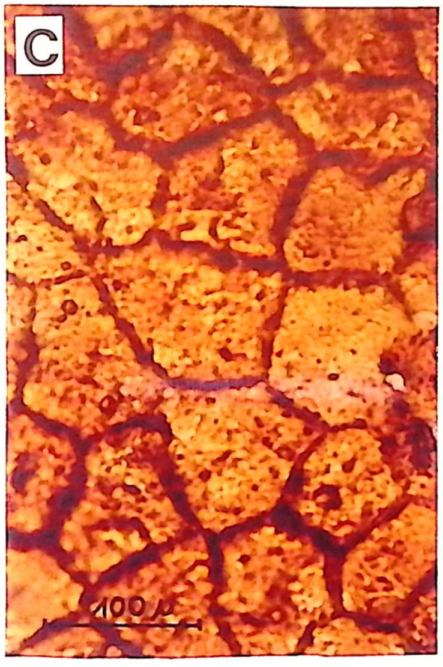
The cuticle of extant plant leaves is very resistant to environmental extremes and biological decomposition. For example it did not desintegrate when treated with hot concentrated mineral acids like H_2SO_4 or HNO_3. In this way Bornemann (1856) examined the durability of extant cycadaceae cuticles. This because he wanted to demonstrate that the cuticles of fossil cycadaceae, which he found in Thuringia`s Lettenkeuper, had endured a period of over two hundred million years unaltered due to the chemical resistance of cutin. In maceral terminology cuticles are termed 'cutinite' whose basic substance is still cutin (Stach, 1982). According to De Leeuw et al. (1991) aliphatic biomacromolecules like cutin are selectively preserved in the geosphere. Repeated attempts have been made to prove chemically the existence of cutin or chitin in fossils. Hence in the past diverse methods have been developed to macerate the fossil substance and to identify the fragments with the help of chemical detection (Jurasky, 1931). Modern procedures, for example the combination of pyrolysis, gas chromatography and spectrometry also desintegrate the fossil material and identify the molecular fragments (Tegelaar et al., 1991).- Even if one succeeds in identifying molecular fragments of the biopolymer precursors, this fact does not neccessarily mean that these substances have survived solely on account of their original chemical structure. According to Vavra (1993) often more than 90% of the preserved organic molecules in fossils are transformed into „kerogen", a high molecular insoluble substance. The term „kerogen" refers to all purely characterized, highly hydrogenious, amorphous, insoluble polymeric material, found in the geological record (Logan et al. 1991). In addition it has long been recognized that fossil cutin or chitin are subject to chemically unknown diagenetic alterations (Schopf, 1975). E.g. Potenie' (1924) finds that treatment with concentrated K0H corrodes extant cuticles more than fossil ones, an observation he cannot explain, and he continues with the quotation that Gümpel (1883) had traced back the preservation of fossil cutin to its content of $Si0_2$.

Fig. 1 Explanations

A) Almost completely intact fossil fern frond
B) Fragmentary lichenoid thallus
C) Pattern of epidermis cells on a fossil cuticle
D) Meshwork of tubular cells forming a plectenchymatous tissue.
E) Honeycomb-like structure of the fossil material (SEM)
F) Crystal in a fossil lichenous thallus colouring yellow to reddisch with KOH (Shape and colouring identical to stictic acid, see 1/G).
G) Stictic acid crystal (illustration, see Hale, 1967, plate 15 B), colouring yellow to reddish with KOH (Santesson, 1974)
H) Silica ash of a fossil plectenchyma (SEM)
I) Carbonate ash of the extant Hypogymnea physodes (Bertsch, 1964) plectenchyma (SEM)

FIGURE 1


A
0,3 cm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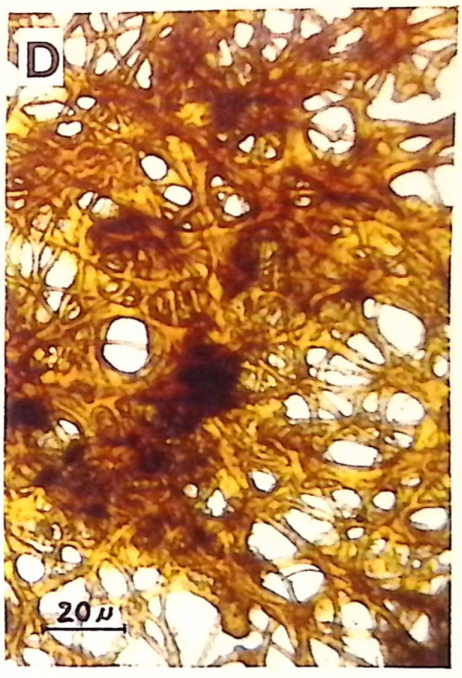
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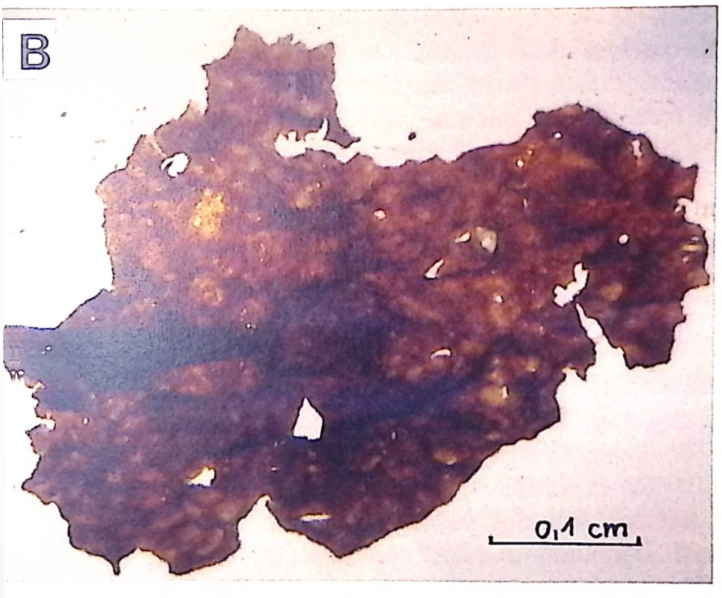
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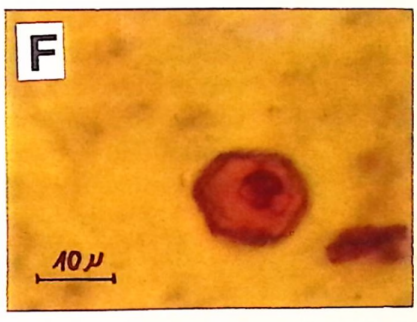
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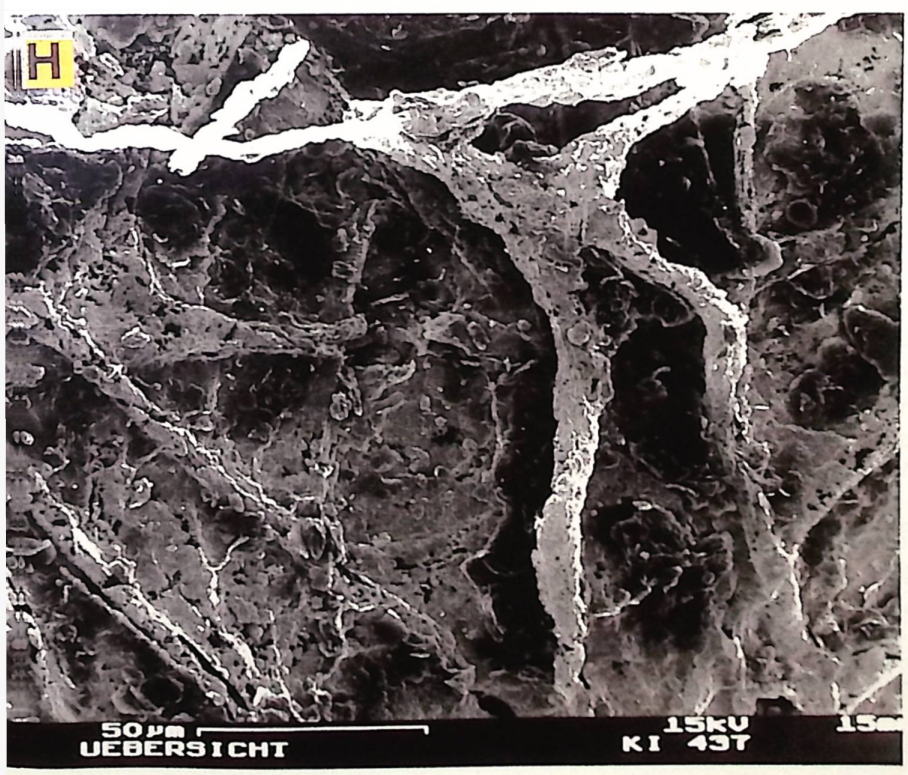
G
B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UEBERSICHT
15kV
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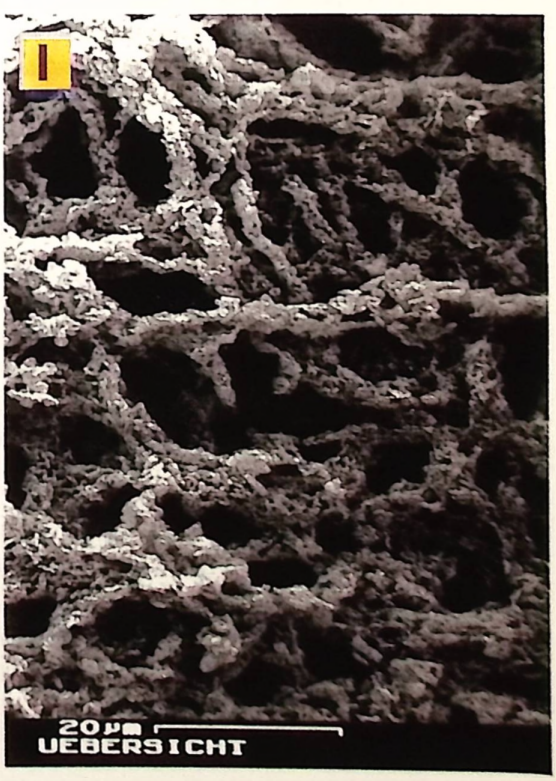
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20 µm
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5. Objectives of this paper

a. To present fossil vascular plant cuticles and fossil thallophytes, objects of very different taxonomical and substantial origin, which consist today of a very similar fossil material and can be classified with kerogens.

b. To demonstrate that the fossils described here no longer consist of their original matter but have been altered diagenetically by permineralization with silicic acid.

c. To describe a silicification process, in the course of which biopolymers like cutin or chitin were embedded in a chemical compound, which chemically is similar to a mixture of organosilicon compounds and silica gel.

d. To demonstrate the diagenesis of the convergent structures hidden in the corpora of higher vascular plant leaves and the thalli of folious lichens, in other words, to show as a model the connections between the original structures and substances, the course of the diagenesis and the fossil remains.

e. To provide evidence for the lichen nature of the described thallophytes due to their fossil preservation.

f. To contribute to the understanding of the chemistry and formation of kerogens.

"Although fossil structures essentially speak for themselves and an explicit statement about preservation is not demanded of any author, a conscious effort to consider more specifically how the fossils are preserved will be beneficial. We perceive correctly the ancient organisms only to the extent that we see through the murky pervasive patina of age that obscures every site of palaeontologic interest." (Schopf, 1975, p. 49).

C) METHODS; TECHNIQUES; MATERIAL STUDIED AND AREA DESCRIPTIONS

1. Recovering of the fossils

Fossil vascular plant cuticles in an excellent state of preservation were obtained from upper Triassic (Carnian, approx. 220 million years old) of Lower Franconia. The cuticles are locally associated with remnants of plectenchymatous tissues which obviously belong to fungous or lichenous thallophytes. The fossils were recovered in various quarries of the "Schilfsandstein", which in the local stratigraphy, is a series of strata compiled of sandstone and clay sediments (Wurster, 1964; Emmert, 1985). A typical situation of finding are local allochthonous plant communities (Kelber, 1990). The embedding sediments are fluviatile and were deposited under different speeds of current (Mader, 1990). The salvage of the fossils is best carried out by removal of the sediment which should be kept as compact as possible. In the laboratory the blocks of sediment are cut into thin sheets and the exposed surfaces are examined using a dissecting microscope (40x). The objects are isolated from the sediment using destilled water and a fine brush. Smaller leaves and thalli (2cm) are preserved intact and may well reveal the original appearance of the organisms. However, most objects are fragmented (Fig. 1A/B). Depending on the coal content the colours of the fossils range from light yellow hyaline to red and black opaque. The degree of coalification may vary within the stratum or even within the fossil. At best the fossils are hyaline and can be examined without further preparation. Example are shown in Figs. 1C/D. The cell and hyphae structures are more delicate than the sandy sediment in which they were embedded. The surrounding coarser material has left imprints in the fossil corpus, e.g. of sand grains. The fact that the embedding material is coarser than details of the fossil structures may well give rise to the notion that the original structure has been preserved. This may be one of the reasons why Bornemann (1856) and others presumed fossil cuticles to consist of their original cutin.

2. Taxonomy of the fossils

The fossil cuticles dealt with in this paper are the remnants of vascular plant leaves of the Keuper flora. Most significant plant elements of this ancient flora were several ubiquitous members of the vegetation in different stratigraphical stages: The horse tail Equisetites arenaceus and the conifers Voltzia coburgiensis and Widdringtonites keuperianus (Mader 1995). With the exception of

Bornemann (1856) who described epidermal cell patterns of several higher plants from Thuringias Lettenkeuper (Lower Keuper) the previous collections of Keuper plant fossils do not report the plant cuticles. Though many species of the Keuper vascular plant flora are well known by their macro fossils (Mader, 1995, Kelber 1995), the fossil report is lacking cuticles classed with their plant origin. A taxonomic classification of the cuticles would have been desirable but considering their very uniform chemical appearance and the objectives of this paper taxonomical investigations were not carried out.

The fossil thallophytes dealt with in this paper offer a wide range of complexity with regard to their anatomy and histology. There are simple net-like thalli comparably to the specimen reported by Horst (1954), who presumed an algal origin. And indeed also the present fossils in their simple filamentous forms exhibit an algal or fungal affinity. Further specimen occurre with a thallus closed all around covered by diverse types of tissues as reported by Manum et al. (1991), who emphasize the differentiation in the so-called "hapsine and alytine" as characteristic and coincident with the basic wall construction of clitellate cocoons, and particularly with certain members of the Hirudinea. One can only understand this interpretation as long as one is not familiar with the more complex forms of this fossil class as released by the Keuper, which show characteristic features of extant foliose lichens (Fig.1B, 2C/G). In view of the lichen interpretation the "hapsine and alytine" (Manum et al., 1991) appear as epicortex and cortex or rather as plectenchymatous, paraplectenchymatous and pseudoparenchymatous cortical tissues. Manum (1996) tries to disprove the lichen interpretation since it "implies an inverted concept of lichen morphology: a felt of hyphae on the outside of a dense cortical layer facing an empty interior." Concerning the morphology and the paleoenvironment some Keuper representatives of this type of fossils (fig.1,D) are very similar to those figured in Manum et al.(1991). Hence we presumably are dealing with the same class of fossil objects, but the Keuper collection exhibits more anatomical variety. There are samples with a smooth outside and a complex inner lining (Fig. 2C/G) and my own observations on these fossils suggest a development by cellular growth and not by animal gland activity. From simple fungoid to complex lichenoid forms all transitional stages were found among the Keuper samples. The present findings allow a rough differentiation into two informal taxa which morphologically can be characterized each comprising several species-like groups. Basing on today's 650 samples the same morphological groups as I described in Ziegler (1992,b) are still to be classified as informal groups. (A detailed morphological and anatomical description will be the objectives of another publication.)

Irrespective of their taxonomy and importance as Triassic lichens these objects are remarkable because of their fossil preservation and the physical and chemical properties of the fossil matter. The fossil appearance is very similar to the one of the fossil vascular plant cuticles with which they are associated. This fact indicates similarities according to the palaeoenvironment, conditions of burial, diagenesis and even anatomy. To throw light on the mysterious chemistry of these fossils will also help to illuminate their taxonomical affinity.

3. The fossil material and its precursors

The chemical consistence of the fossil thallophytes is indeed unknown, but both, fossil cuticles and thalli, externally consist of a very similar yellow to red mass in spite of the fact that the precursor substances were completely different: If we proceed from today, the extant cuticle mainly consists of cutin, a high-molecular-weight polyester composed of various interesterfied hydroxyalkanoic acids, and/or cutan, an insoluble, non-hydrolyzable polymethylenic biopolymer (Tegelaar et al, 1991). The cell walls of fungi and lichens mainly consist of polysaccharides: fungi/chitin (Schlegel, 1969), lichens/lichenin or isolichenin (Santesson, 1974). It seems surprising that substances of such diverse chemical origin may exhibit a similar appearance when preserved in the fossil record. This fact is not consistent with the concept that the original substances, e.g. the cutin of the cuticles, have remained unaltered and suggests that chemical transformations took place during the fossilization process.

In the following I will discuss the chemical nature of these fossilization processes. The basis for all my studies reported here was the observation that both kinds of fossils, cuticles and thalli, are burnable and will leave a grey ash which is insoluble in
hydrochloric acid but soluble in hydrofluoric acid. This was a chemical indication of the presence of silica within the fossils due to a silicification process during diagenesis.

In order to obtain further information about the chemical nature of the fossil material, microscopical investigations and a series of experiments were conducted:

a) anatomical observations on cross sections with the light microscope,
b) mechanical and chemical treatment,
c) combustion (Differential Thermic and Thermographimetric Analysis),
d) chemical and microscopical (SEM) analysis of the ash.

(As far as possible the same methods were applied on extant plant material.)

D) RESULTS

1. Anatomical observations

The fossil cuticles often resemble the fossil thalli in their outer appearance to such an extent that they can only be distinguished by an examination with the help of a light microscope. But the similarity between the fossil remains of leaves and thalli is only superficial. Cross sections show internal differences: The fossil cuticles only consist of the originally cutinized layers of the former epidermis cell walls featuring the anticlinal walls and epidermal protuberances like papillae (see Kerp, 1991, p.553, and Fig.3) whereas the fossil thalli contain cell corpora and can show plectenchymatous structures with several layers up to a thickness of about 100 µ and more (Fig. 2C and Fig. 3).

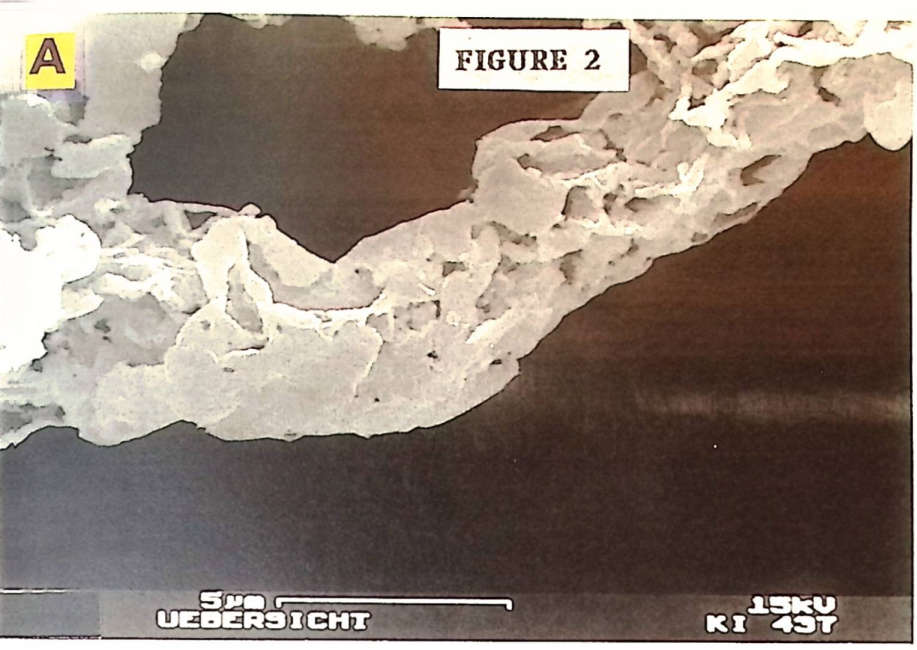
2. Physical properties of the fossil samples

The fossil cuticles and thalli are elastic. When folded in a dry state they will initially crease and finally break. The fossil material will soak up fluids like a sponge. It absorbs polar (e.g. water, ethanol, acetone) and non-polar (e.g. paraffin oil, gasolin, benzene) fluids and becomes soft and flexible in the soaked stage. When felt the fossil material develops a microscopical pattern of fissures. Soaked fossils are plastic and can be cut with a razor blade or can be mashed under a microscopic cover slide. Dry fossils are lighter than water and heavier than water when wet, which indicates a porous interior. In addition Scan Electron Microscopy exhibits a honeycomb-like structure of the fossil material (Fig. 1E and 2H). The hydration is reversible. The isolated cuticles and thalli are flat when soaked. They bend and predominantly the cuticles curl on drying up.

Fig. 2 Explanations

A) Hypha (detail of 1/H) in the silica ash of a fossil thallophyte. The organic component of the fossil matter has been burned up, the polysilicic acids condensed and formed an ash which distinctly differs from the carbonate ash of an extant lichen hyphae (see 2/B)
B) Hypha (detail of 1/I) in the carbonate ash of an extant lichen (Hypogymnea physodes)
C) Cross section of a fossil thallophyte with a lichenous arrangement of tissues (Compare with 2/G):Compact plectenchyma of the upper and lower cortex, spongy medullary layer and coalified remains of the algae layer below the upper external layer.
D) Hyphae in the plectenchyma of a fossil lichenoid thallophyte
E) Crystals of lichen substances on hyphae of the extant lichen Menegazzia terebrata.
F) Crystals which colour red with KOH on hyphae of a fossil lichenoid thallophyte.
G) Cross section of the extant lichen Parmelia caperata with the typical arrangement of tissues in a heteromerous folious lichen.
H) Coaly imprint of an algae shape inside the upper external layer of a fossil thallus showing also the porous structure of the fossil matter (SEM).

FIGURE 2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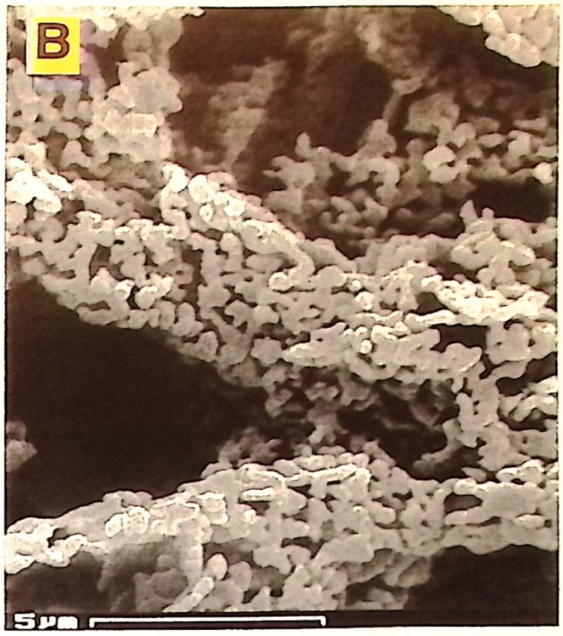
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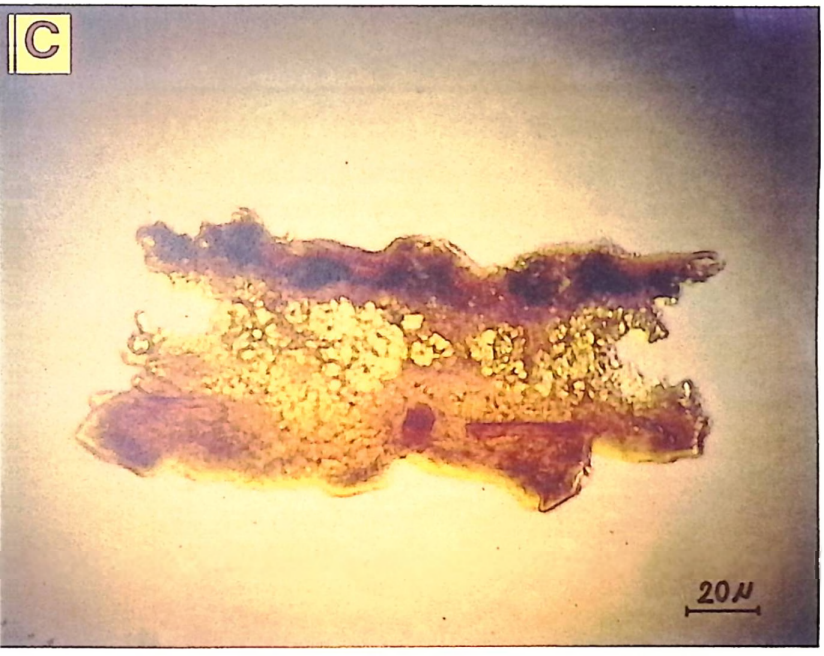
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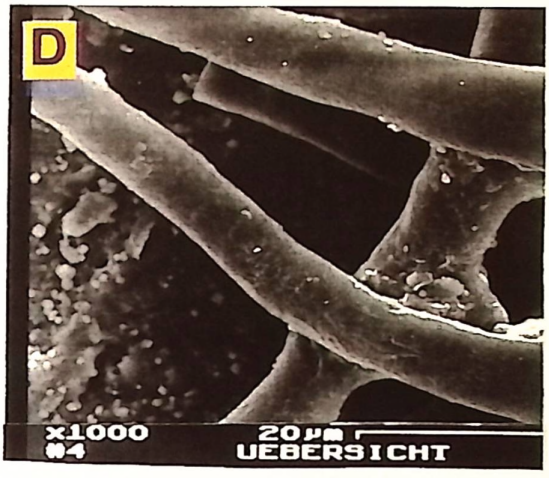
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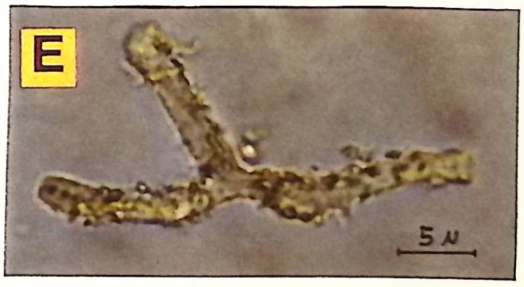
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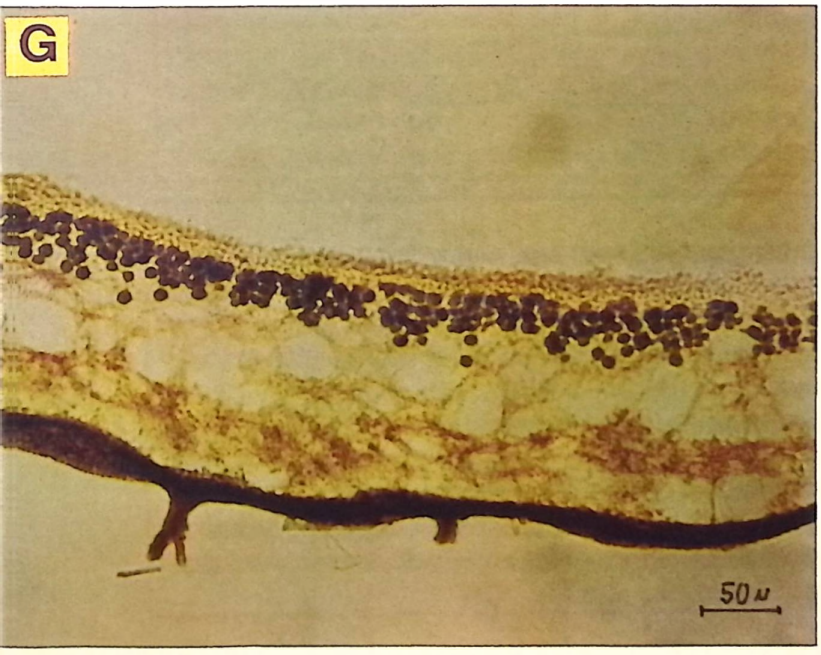
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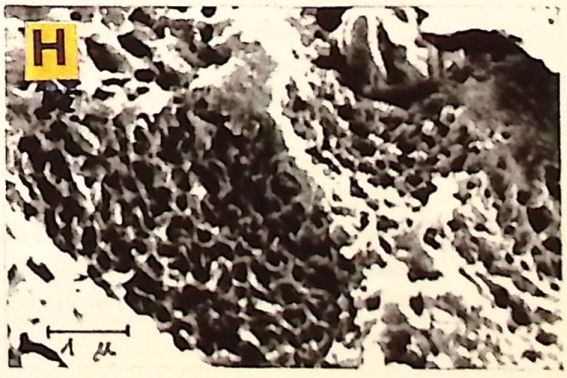
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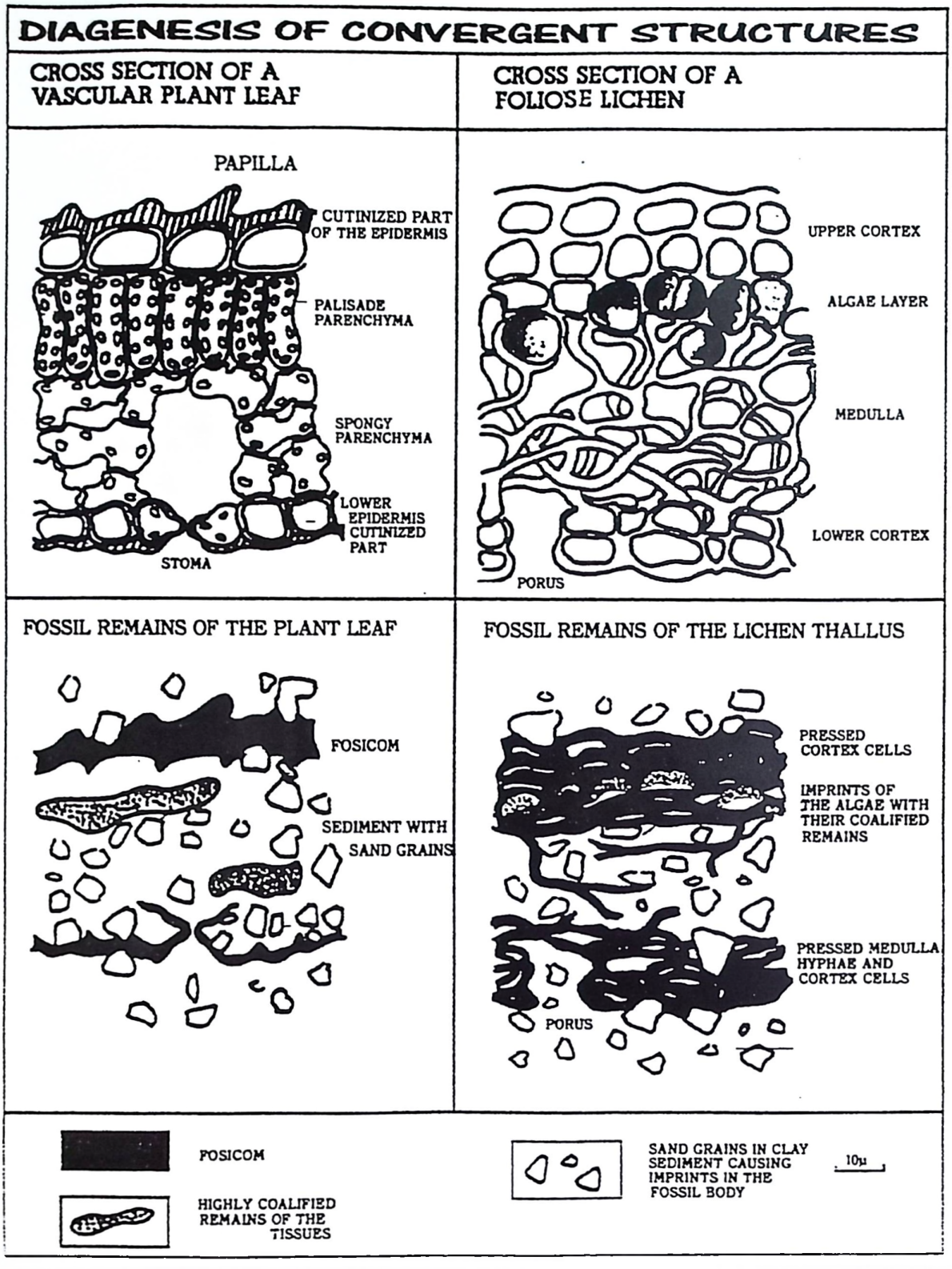


Fig. 3 Explanations

Diagenesis of convergent structures in a higher vascular plant leaf and a lichen thallus:

The figure shows in its upper part generalized cross sections of a typical extant leaf and an extant foliose lichen in comparison. This illustration also shows the generally known structural and functional similarity between a typical leaf of vascular plants and the thallus of a foliose lichen with the characteristic arrangement of the tissue layers.

Below there are cross sections of the cuticle and the lichen thallus resulting from diagenetical alterations which are described in this paper.

Some tissues are able to copy each other where in mutual contact. Thus the fossils of cuticles and lichens preserved the shapes of decomposed cells. The anticlinal walls of the fossil cuticle record the pattern of the epidermal cells and the original position and shape of the algae cells are recorded as a pattern of coaly imprints in the cortex of the fossil lichen (see also Fig. 2/H)

3. Chemical properties

3.1. Response to acids and oxidants:

When boiled in concentrated HNO_3, HCl and H_2SO_4 (and mixtures of these acids) the fossil material does not desintegrate. (14 days treatment with hydrofluoric acid (HF) had no visible effect). Contrary thalli of extant foliose lichens desintegrate completely in hot concentrated H2S04. Treating with Schultz agent, an oxydativ mixture of $KClO_3$ with HNO_3 (Schaarschmidt, 1993), the fossil material becomes light yellow and fragile. Subsequent treatment with NH_3 makes the material smooth and almost achromatic.

3.2. Response to alkali and ammonia:

Aqueous solutions of NH_3, NaOH, or KOH cannot dissolve the fossils either, but make it softer. With KOH the matter becomes darker, which is a chemical indication for humic substances (Stach,1982). There is an additional remarkable response to KOH. Some of the fossil thalli comprise crystallized substances (Fig. 2F) which exhibit a typical staining with KOH. Thus crystals could be obtained which have a colour and form very similar to stictic acid crystals (Compare Fig. 1F and 1G).

3.3. Response to acetone:

Stictic acid and anthraquinone, known as specific substances of extant lichens (Santesson, 1974), where extracted out of crystal bearing fossil thalli with the help of acetone and then subsequently identified using High Performance Liquid Chromatography. (This investigation was made in the Institut für Biowissenschaften, Universität Würzburg).

4. Response to heat

Using wet chemical techniques as described the fossil matter cannot be dissolved, whereas it desintegrates under treatment with thermic energy.
All samples produced a typical course of combustion, which was observed and analysed with different methods: With unarmed eyes, microscopical (light microscope and SEM) and with Differential Thermic and Thermographimetric Analysis:

4.1. Visible course of the combustion

With increasing temperature the fossil material initially bends, shrinks and darkens to a black opaque substance. Under supply of oxygen the fossils will start burning with a white flame. Rapid heating will produce a blast flame or even an audible deflagration. After burning, one may observe red heat starting at points and spreading through the material as a red glow but only as long as energy is supplied. Without external heating, the glow will disappear immediately, although the matter has not completely been burnt and burnable substances are still left. A coaly compound results from the glowing. If this remaining substance is further heated (up to about 1100°C) the coal disappears and a grey, partly reddish, and structured mineral ash forms, which finally melts to an amorphous mass.

4.2. Microscopical observation of the combustion

The temperature response of the fossil material was also observed under a light microscope with simultaneous measurement of temperatures:

150°C	darkening of cell walls, cell pattern more distinct
400°C	material becomes dark and opaque
500°C	material shrinks and develops fissures brown fluid is distilled and the matter becomes lighter in colour
800°C	melting begins
1100°C	partly melted hyaline ash with black and reddish inclusions

4.3. Differential Thermic (DTA) and Thermographimetric (TGA) Analysis

The combustion processes were further analyzed under controlled conditions using a temperature increase of 5°C min-1 while registering changes in weight, and by comparing the sample temperature with Al203 as standard in order to identify endogenous thermic
processes. During this analysis different kinds of fossil cuticles and thalli were heated up to 600°C. The course of the reaction is quite characteristic (Fig. 4A):
Several exothermic reactions will take place successively and simultaneously within the fossil cuticle: At circa 150°C the reaction starts and is finished around 500°C. This reaction is overlaid by additional reactions which peak between 150°C and 350°C and between 350°C and 500°C. The weight loss of the material correlates with the thermal reactions. The course of energy release is similar for the fossil cuticles and thallophytes, except that the thalli release energy at higher temperatures (Fig. 4 A/B). The experiment with controlled heating was also carried out with Hypogymnia physodes (all lichen determinations according to Bertsch 1964), a common lichen of the local flora, using only the lower cortex (without algae) because it is very similar to the fossil thallophytes . Weight and energy loss of extant lichen material was more rapid than in fossils. In the case of the fossil matter the exothermic processes were less violent but spread over a wider range of temperature (Fig.4,B).

4.4. The ash of the fossils

The ash still preserves the original form of the fossil, i.e. the outlines of the hyphae can still be recognized (Compare Fig. 1H/D), although the material has considerably shrunk. The method of preparing plant ashes called "Spodograms" was introduced into Botany by Molish (1927), who derived information about the anatomy and the chemical consistency of plant material from its ashes. According to Kräusel (1950) spodograms are appropriate to anatomical observations of those plant parts which tend to become carbonized or silicified. Spodograms were prepared from the fossils and, as a comparison, from some extant plants (e.g. Quercus, Betula, Fagus, Hypogymnea, Peltigera).

Some striking differences between the ashes of the fossils and the ashes of extant samples studied:

COLOURING:
fossil: grey with reddish inclusions
extant: white

SOLUBILITY:
fossil: insoluble in hydrochloric acid, soluble in hydrofluoric acid,
extant: soluble in hydrochloric acid

ASH WEIGHT:
fossil: about 15-25% of dry weight
extant: less than 10% of dry weight

MICROSTRUCTURE:
As the SEM pictures demonstrate, hyphae are still recognizable in both of them, the ashes of extant and fossil plectenchyma, but they strikingly differ in their microstructure. The ashes of the fossils are bulkier, more compact and less uniform than the ashes of the extant samples.

STABILITY:
The microstructures of the fossils ash proved to be more stable towards mechanical concussion than those of extant plant ash.

In all cases distinctly structured ashes were obtained whereby the ashes of the fossils chemically and morphologically differ from the ash of living plants.

E) DISCUSSION

1. Comparisons: Cuticles/thallophytes, fossil/extant samples

An extant plant cuticle and an extant lichen cortex differ considerably in some physical properties, e.g. in their behaviour towards water. Contrary to plant cuticles which are water repellent and by deposition of wax protect the plant from evaporation, a desiccated lichen gradually absorbs water through its cortex. In the fossil state both, cuticle and cortex, soak rapidly water, a behaviour which indicates a constitution different from the original. Moreover fossil cuticles and fossil thalli are largely identical concerning their response to the chemicals applied and their response to heat. All observations suggest a very similar fossil compound. In addition both types of fossils form a silica ash during combustion but the comparably high percentage of silica in the ash (15-20% of the dry weight) cannot be explained with an equivalent original silica content. According to Schuhmacher (1971) often $Si0_2$ is a component of extant plant ashes but seldom exceeds 1% of the plant's dry weight. Extant higher plants differ in their capacity to take up $Si(0H)_4$ out of soil solutions. Depending on their $Si0_2$ content in the dry weight they can be divided into three major groups: Cyperaceae (up to 15%), Gramineae (1-3%) and all others < 0,5% (Marschner, 1989, p. 417). Hence the high silica content of all fossil ashes is not explainable with the silica content of the original plant material.

2. Permineralization of the fossils by silicic acid

The chemical and thermal responses show differences between extant and fossil samples and provide a major insight into the chemical nature of the fossil matter: Obviously the chemical bonds in the fossil matter are strong enough to resist even very caustic agents. The matter only disintegrates under the influence of high temperatures. The reaction starts with a coalification process which proceeds exothermically. The substance releases flammable gases which accelerate the burning process. The first peak (Fig. 4A) represents a fraction of burnable gases with low boiling point, which originate from rapid breaking of weak chemical bonds. These substances volatilize and may produce the blast flame during rapid heating and probably consist mainly of methane. Stach (1982) reports of methane release during artificial peatification at 160 to 200°C. In contrast to this initial combustion, the further reaction (glowing) will only continue with a supply of external heat. This behaviour of the matter is remarkable. The reaction yields an exothermical response only as long as energy is supplied. Obviously the reaction does not produce enough energy to continue by itself. This is an indication that in the fossil substance stable chemical bonds exist which prevent the further release of burnable substances . Only when set free from these bonds by a supply of energy the fossil substances can continue the exothermic coalification process. On this occasion the matter becomes coal-black while shrinking. According to Stach (1982) during coalification more complex compounds emerge by condensation and aromatisation.
As a final reaction the material left burns up exothermically to CO_2 and H_2O if enough oxygen is supplied. This is reflected by the peak around 450 °C. While the organic components aredecomposed by heat the mineral constituents form the grey and reddish ash, which finally starts to melt. According to Kisser (1931) a grey colouration of ash is typical when coal particles are enclosed in SiO_2. Reddish colouration indicates Fe0 derived from the reaction between FeS and O_2. Even a white heat lasting hours is not able to eliminate the coaly rests. The coal is enclosed in the melted SiO2 and thus protected from further combustion. The persistence of the grey colour is considered a measure of the concentration of $Si0_2$ (Kisser, 1931). In contrast to the fossils the extant plant material burns out to a white, HCl-soluble ash. According to Schuhmacher (1971) the white ashes of extant plants predominantly consist of carbonates which do not preserve coal. Irrespective of the substantial difference and even taking into account alterations of forms and displacement during glowing, the ashes of the fossils structurally differ from extant plant ashes to such an extent that we are surely not dealing with the same matter (compare Fig.2A/B). The high $Si0_2$ content of the fossil substance suggests that the original organic material has been permineralized with silicic acid. This means that the fossil material results from chemical transformations, during which $Si0_2$ has become incorporated. This may explain why the chemically different original plant materials

FIGURE 4 DIFFERENTIAL THERMIC AND THERMOGRAPHIMETRIC ANALYSIS

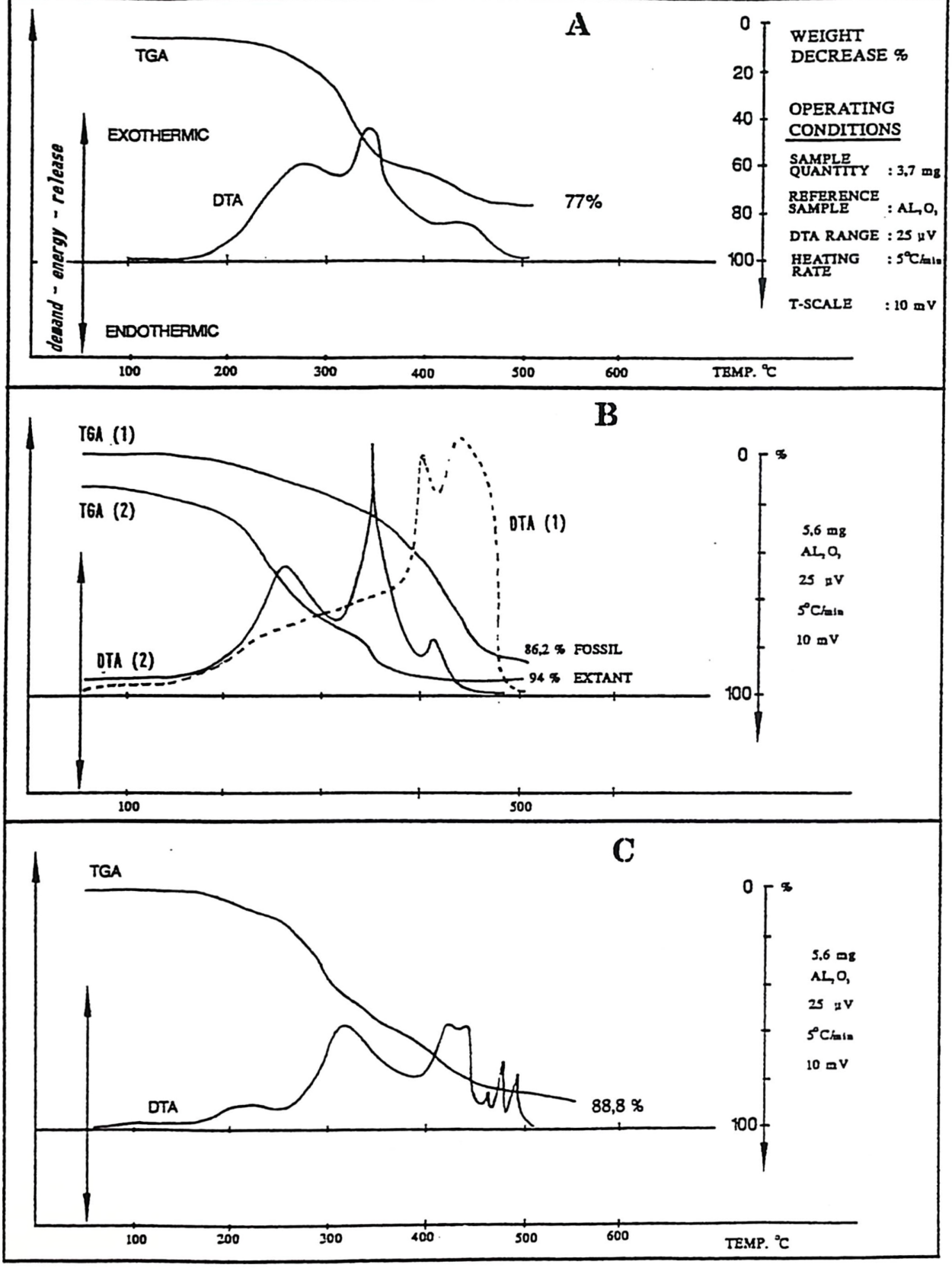


Fig. 4 Explanations:

Differential Thermic Analysis (DTA) and Thermographimetric Analysis (TGA)

A: DTA and TGA of a fossil vascular plant cuticle
B: DTA and TGA of a fossil thallophyte (1) and of the extant lichen Hypogymnea physodes (2)
C: DTA and TGA of a technical silicone

cutin or chitin are transformed into a fossil substance which is rather similar today. It must be viewed as a kind of "permineralization /petrifaction" (Schopf, 1975).
The silicification of wood may serve as an example (Leo and Barghoorn, 1976) where hydroxyl groups formed during decay may react with invading silicic acid creating hydrogen bonds. This process preserves some tissue structures of the original wood. This model can be adopted with some variation. The thermal stability of the present fossil material indicates that it is not solely linked by hydrogen bonds as Leo and Barghoorn (1976) report concerning silicified wood. These bonds between polarized atomic groups are comparatively weak, 8-32 kJ mol-1, (Schmidt 1967) and are not able to account for the high resistance of the fossil matter. An explanation could be covalent bonds which are much stronger (200-500 kJ mol-1). Further the plasticity and high percentage (about 80%) of organic components of the present fossils suggest a chemical structure different from silicified woods which are very hard and compact due to their high percentage of silica. The comparison of a not glown fossil hypha (Fig. 2D) with its ash (Fig. 2A) may give an impression of how $Si0_2$ is incorporated in the present fossils.

3. The fossil matter, a diagenetically developed organosilicon compound

The higher thermal energy necessary to mobilize substances in the fossil matter indicates strong covalent bonds. The combustion of the extant Hypogymnia demonstrates that extant lichen material disintegrates at lower temperatures and more rapidly. So we can consider the organic components in the fossil to be chained with covalent bonds to a mineral component. This could be traced back to silicic acid which accumulates during permineralization in the fossil body. A covalent linkage between organic substances and silicic acid would signify the existence of Si-0-C and Si-C bonds. Present synthetic substances containing this kind of bonds are termed Organosilicon Compounds (Römpp, 1983). Following this characterization the fossil matter must be regarded as a diagenetically developed organosilicon compound.

4. Comparison with synthetic organosilicon compounds

The bondage between organic groups and silicic acid, the flexibility and the heat resistance of the fossils are qualities we also find in silicones, a group of synthetic organosilicon compounds of major technological importance. In silicones organic groups are bound with Si-C linkages to a meshwork of Si-0-Si polymers (Fig. 5). Chemically they have an intermediate position between organic and anorganic substances. Silicones are stable to an extent that these substances do not corrode under the influence of acids or oxidants, which results from the strength of the Si-0-Si and Si-C bonds (Schmidt, 1967). The siloxane bonds Si-0-Si easily bend which explains the elasticity of the silicones (Elschenbroich and Salzer, 1986). Depending on the length and state of netting of their Si-0-Si framework the physical properties may vary (fluids, elastomers, resins). Because of its physical and chemical similarities with the fossil material the DTA and TGA was also carried out with industrial silicone. Elastic industrial silicone was cut into thin sheets of the same dimensions as the fossil samples. The thermal response of silicone was more similar to the response of the fossil matter than to that of the actual lichen (compare Fig. 4B/C).
All facts together suggest a comparable chemical structure of the fossil material and silicone, both containing a Si-0-Si framework with a strong linkage to organic components (Fig. 5). One could deduce from these coincidences that the fossils consist of diagenetically developed organosilicon compounds.

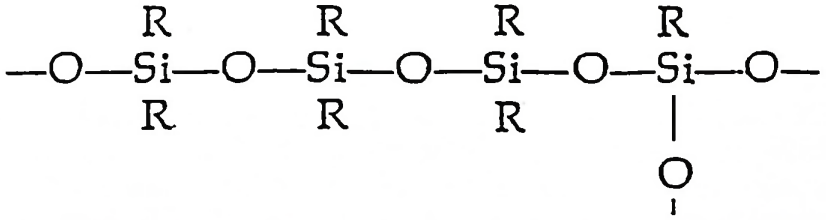


Fig. 5: Molecular structure of silicone (S = various organic groups (Römpp 1983)

5. Comparison with silica gel

There is however an essential difference between the fossil matter and silicone, namely in their respective behaviour towards water. Silicones are water repellent, unlike the fossils, which soak water, and are more flexible in a moist than in a dry state. Such behaviour is more typical for a gelatinous silica gel which precipitates in a colloidal solution and is able to develop a plastic and flexible consistency with a porous inner structure (Hofmann and Rüdorff, 1966). In addition, the plasticity of the fossil material is not typical for silicified fossils which are usually very hard due to their content of SiO_2. However if we assume the chemical structure of a silica gel both the content of silica and the flexibility of the fossils could be explained. Like silicones silica gel also has a network of siloxane bonds Si-0-Si (Fig. 6). According to Hofmann and Rüdorff (1966) a honeycomb-like structure is typical for silica gels which are used as absorbents in dry state because of their fine pores. Scan Electron Microscopy reveals a porous structure in the fossil matter (Fig. 1E/2H) which may account for its absorptive capacity and underlines the origin from a silica gel.

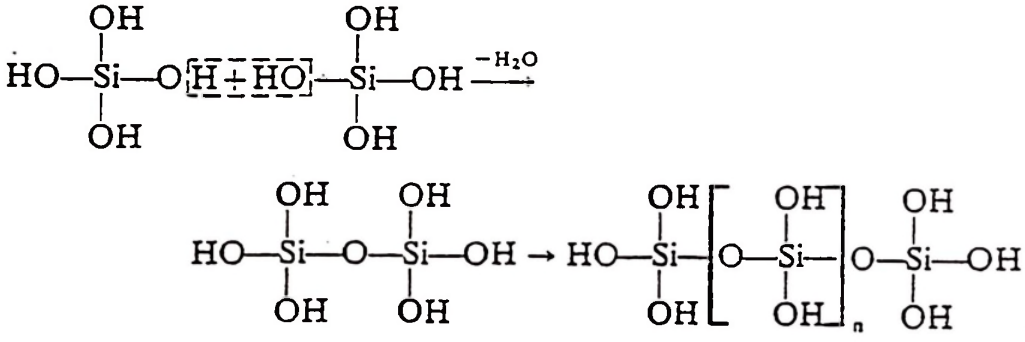


Fig. 6:
Development and molecular structure of polysilicic acid (Römpp 1983)

6. Original organic substances in the fossil material

Various observations indicate the presence of original organic substances or at least components of them in the fossil matter. The colouration as a response to KOH is a simple chemical method to distinguish between brown coals and bituminous coals. This is based on the solubility of humic acids in KOH. Brown coals still contain humic acids which can be extracted with KOH causing its colouration. In bituminous coals, humic acids have condensed to alkali insoluble humines. Extraction of humines is not possible and the colouration of the KOH will not occur (Stach, 1982). The fossil matter does not colour the KOH but becomes distinctly darker when treated with KOH. This could well be caused by a reaction with humic acids, which have been protected from coalification and now are enclosed in the silica gel. KOH is not able to dissolve the humic acids out of the present fossils. This immobility is another indication for the chemical bonding of the humic acids to the silica gel, whereas the molecules of H20, K+ and 0H- are able to advance to the enclosed humic acids and release the colouration. There is another indication for humic substances in the fossil matter: The fossil matter also absorbs unpolar fluids. This indicates the presence of unpolarized molecular groups, which could be traced back to the humic acids.
Lichens are known to contain specific substances, typical secondary plant products, which can crystallize on the hyphae. (Fig. 2E). Figure 1G (Hale, 1967) shows stictic acid of an actual lichen, in a crystallized form that stains yellow to red with KOH. This reaction is commonly used in lichen taxonomy for identification purposes (Santesson, 1974). Figure 1F shows a very similar crystal in a fossil lichen colouring yellow to red upon the treatment of KOH. This is a clear indication for stictic acid which is substantiated by the detection of this compound using HPLCR. Stictic acid contains stable benzene rings and various functional groups (Fig.7). Aromatic compounds are considered

stable enough to outlast millions of years (Aihara, 1992). Hence, the chance of lichen substances to pass through biochemical decomposition and get conserved by a subsequent silicification can be regarded as high.

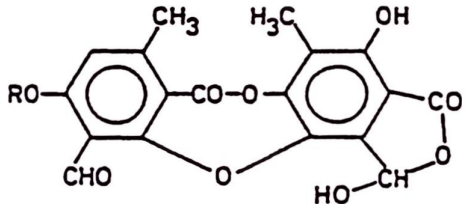


Fig. 7: Molecular structure of stictic acid R = $-CH_3$, (Santesson, 1974)

7. A possible course of the diagenetical tranformations

The chemical changes of the fossils are considered a result of peatification, coalification and silicification and may proceede as follows:
The degradation of plant detritus by fungi and bacteria is initially an aerobic process which subsequently may become an anaerobic process. Various microbes successively attack cell substances with the help of different enzymes. According to Logan et al. (1991) in acidic environments only a reduced diversity of decomposers can survive the low-pH conditions, which enhance the preservation of certain macromolecules. Microbial attack continues until all easily degradable substances such as sugar, starch, cellulose, hemicelluloses, lipids, pectines or proteins are decomposed.
According to Stach et al. (1982) during peatification, also called biochemical coalification, humic acids form, which are a mixture of decomposed cell substances. They constitute the raw material for the following coalification processes together with more resistant and therefore to a large extent unaltered biopolymers of the cell walls, like cutin, cutan or chitin. Coalification proceeds with condensation, polymerization and reducing reactions. At an early stage the humic substances may develop a gel with plastic consistency. This biochemical gelification in the case of the present fossils concurs with invading silicic acid. According to Willstätter (1931) ortho- and di-silicic acid are only stable at a pH of about 3,2 and only then are able to pass through the mashes of the remaining cell wall biopolymers. Depending on pH alterations, e.g. caused by coalification silicic acid condensates to polysilicic acid (Fig.7) forming a gel which is then - owing to its molecular size - unable to leave the cell wall structures by diffusion. Thus the largely degraded plant tissue works like a silica trap and finally is interspersed with a mixed gel of hydrated polysilicic acids and humic substances. Both of them have the ability for further polymerization, which process depends among others on moisture content. Decreasing hydration, caused by sediment pressure will initiate chemical interactions between functional groups. Numerous possibilities for bond-formation occur between free hydroxyl groups of the polysilicic acids and various groups of the humic substances.
The chemical reactions between the silica gel and the gel of the humic substances consume unbound functional groups and thus prevent a further coalification of the organic substances. Coalification normally leads to a opaque mass with increased carbon content. This process is stopped due to the linking with polysilicic acid. Depending on environmental conditions (pressure, temperature) from these interactions within the polymerizing mixed gel a hyaline and plastic mass results which is very resistant owing to its stable Si-C, Si-0-C and Si-0-Si bonds.

8. Comparison with natural organosilicon compounds

Marschner (1995,p.421) reports on a cell wall-bound silicon, presumably present as an ester-like derivative of silicic acid (R1-0-Si-0-R2). In addition, silicic acid also forms polymeric silicon complexes (Fig. 8). These natural organosilicon compounds affect the stability of higher plants not only as an inert deposition in lignified cell walls but might also increase cell wall elasticity during extension growth. The compounds reported by Marschner (1995) contain Si-0-C bonds and are of high stability and low solubility, properties which are prerequisites for the fossil preservation. Hence this compounds originally may be preserved in plant fossils. However these natural organosilicon compounds cannot explain the high silica content of the present fossils, because of their low quantity in living plants. This fact does not exclude their participation in the formation of organosilicon compounds during diagenesis. In this sense the term fosicom would comprise both: Fossilized, biologically developed, organosilicon compounds and those which have been developed by diagenesis.

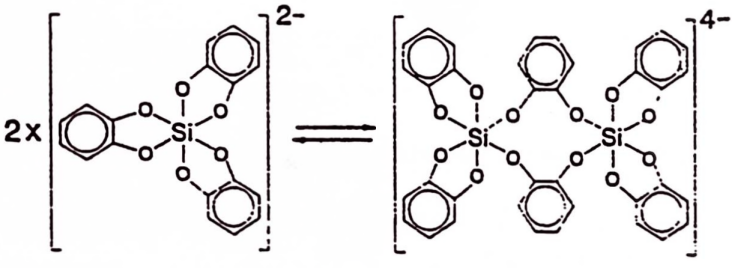


Fig. 8: Natural organosilicon compounds of vascular plant cell walls (Marschner,1995,p.421)

F) CONCLUSIONS

1. Fossil organosilicon compounds: Fosicom

Summarizing the results, the fossils evidently do not consist of their original material but have been altered diagenetically by a permineralization with silicic acid. The fossil matter is obviously a substance of a complex construction, the molecular arrangements of which vary widely, depending on the conditions and substances that coincided during its formation. Chemically it can be characterized as fossil organosilicon compound (fosicom from now).
Fosicom is a substance with remarkable properties: Combustibility combined with a relatively high heat resistance, plasticity, flexibility and elasticity depending on moisture content, the ability to soak polarized and unpolarized fluids, porosity, a high resistance to acids, alkalies and oxydants, a high durability and the capability to preserve biomolecules for millions of years. Fosicom combines properties of silicone and silica gel. Some aspects of its behaviour are typical of organic matter, others are more mineral in character. This organic-mineral double nature of fosicom is due to its composition: It is composed of carbon and silicon with a share of approximately 80% organic and 20% anorganic matter. Fosicom developed whenever a mixed gel of humic substances and polysilicic acid merged. It has no specific form and penetrates all fossil structures and even the surrounding sediment which often appears impregnated and glued with this ground mass. If the coalification process was interrupted at an early stage by silicic acid infiltration, fosicom reaches a hyalin yellow, amber-like appearance. A red to black colouration results from an advanced coalification. (The characteristic of the molecular structure is illustrated in Fig.9, as a model which may explain the properties of fosicom.)

2. Fossil preservation of biomolecules

It is well known that biomolecules can be preserved over geological periods (Knoche et al. 1967, Tegelaar et al. 1989, Logan et al. 1991, De Leeuw et al. 1991, Vavra, 1993) but in many cases it is

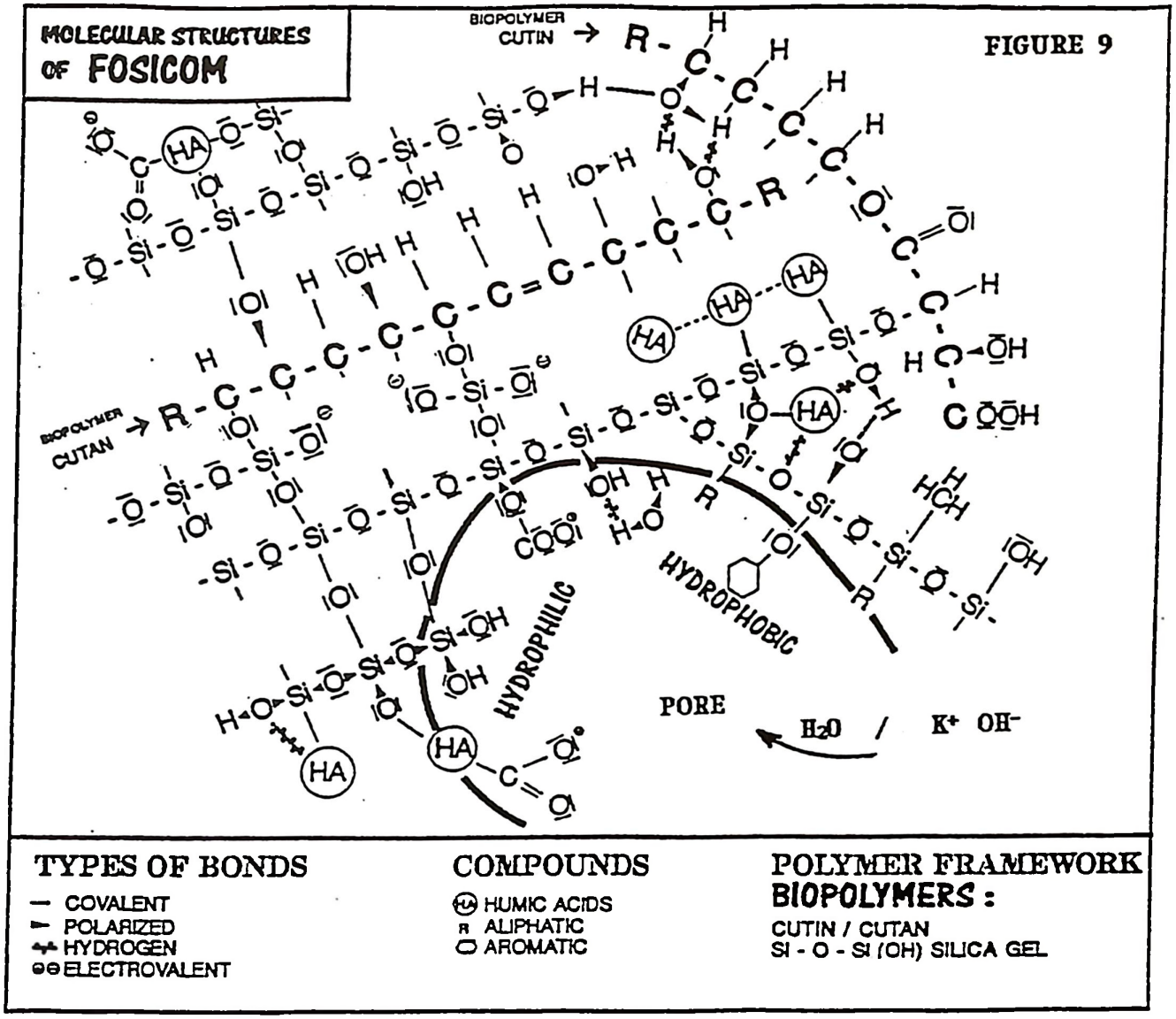


Fig. 9: Explanations

Fosicom consists of a brittle to plastic ground mass, the components of which are a gelatinous silica gel and the products of the humification and coalification processes. The humic substances are netted with each other and chemically bonded to the Si-O-Si framework of the porous silica gel. The physical properties of this fosicom ground mass are influenced by the organic nature of the enclosed cell wall remains like cutin or cutan. The fibrills of these biopolymers lie covalently bonded to the ground mass, fosicom, somewhat comparable to steel in reinforced concrete and make it flexible. When folded in a soaked state, the fossils will become fissured, caused by the braking ground mass, but do not brake asunder, possibly due to the enclosed biopolymers.

controversial or remains open as to what causes this enormous durability. The processes described in this paper are a model and suggest evidence for silicification processes which lead to the formation of extremely resistant fossil organosilicon compounds. Otherwise this substance is capable of mummifying chemical structures in their original arrangement. The morphology of the tissue is maintained. The formation of fosicom is a process which stops the coalification of plant matter and thus preserves original structures of tissues and cells and even biomolecules. In this sense fosicom mimics the original organism preserving the biology over millions of years in a joint structure of carbon and silicon. Important prerequisites for this kind of preservation are; 1) a certain chemical resistance to microbial decomposition, 2) a subsequent isolation to any biological activity and 3) functional groups which enable a linkage to polysilicic acids.

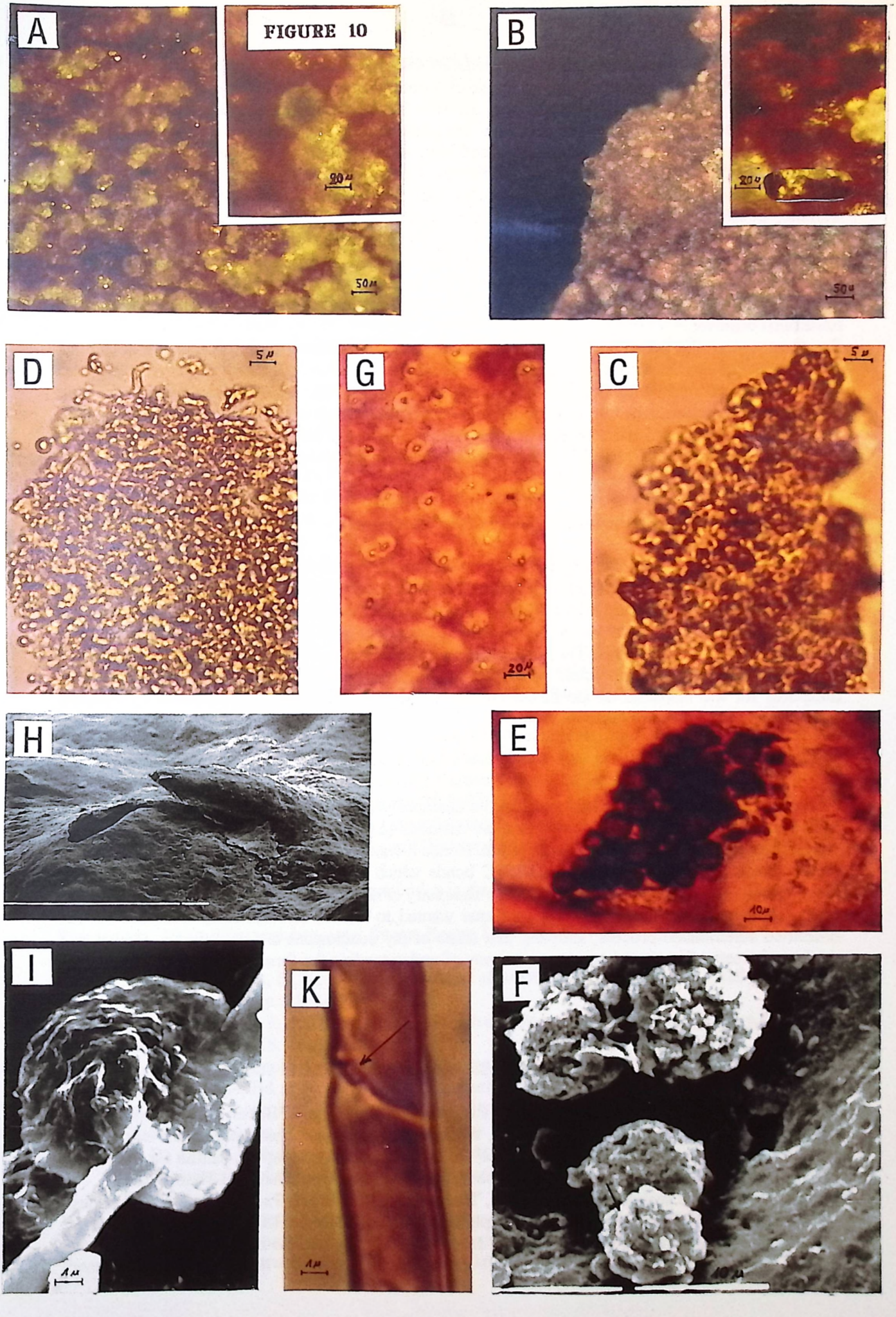
Beside plant cuticles and thallophytes the Keuper site in Lower Franconia yields in addition other fossils which are preserved in a similar manner, especially spores, fungi or drop-shaped masses containing biological objects. All these fossils are characterized by transparency and amber-like colouration. They are most likely preserved by silicification processes.

3. Diagenesis as key to a taxonomic mystery

The origin and taxonomical classification of the fossil objects described in this paper as thallophytes is controversial. Manum et al. (1991) try to disprove all elder interpretations of these enigmatic fossils and describe them as clitellate cocoons, thus transferring these objects to the zoological kingdom classified under Clitellata (phylum Annelida). Not to mention the anatomical and cytological facts, e.g. septated tubular cells (Fig. 10K), which suggest a thallophytic origin of these fossils (A detailled description is in preparation), the state of the fossil preservation contradicts an origin from animal glands. How should keratinous cocoons of Clitellata and vascular plant cuticles come to acquire such a similar fossil preservation?
According to De Leeuw et al. (1991) resistant kerogens mainly consist of aliphatic biomacromolecules. Manum et al. (1991) report that the cocoon substance of extant clitellate is a keratin-like protein. According to Logan et al. (1991) the biodegradation and chemical hydrolysis rapidly destroy even structural proteins. They also report that fossil proteins mainly concern molecules enclosed within or stabilized by biominerals. Hence the chance of complete keratinous cocoons to become fossilized must be regarded as low.
On the contrary, it is not pure chance that fossils of plant cuticles and foliose lichens are frequently associated yielding a similar appearance, rather this can be traced back to:
The same palaeoenvironment, a content of biopolymers with a high resistence to biochemical decay, a burial under the same environmental conditions und therefore similar fossilization conditions and an analogue arrangement of tissues by convergence (Fig. 3). Both of them have: a dense upper and lower external layer (epidermis/cortex), a tissue for photosynthesis (palisade cells/algae layer) and a

Fig. 10: Explanations

A. Surface of an extant lichen (Pelticera rufescens) covered with masses of soredia assuming a powdery appearance (detail: single soredia, magnified from the same sample)
B. Powdery surface of a fossil lichen surface (detail:single soredia, magnified from the same sample)
C. Squeezed fossil soredium taken from the surface of sample B featuring thin hyphae(1µ) and algae comparable to the extant sample (see D)
D. Squeezed soredium of an extant lichen (A) consisting of a tuft of hyphae investing algae cells
E. Soralium of a fossil lichen releasing soredia
F. Fossil soredia coming out of a soralium featuring hyphae (arrowed) investing globular cells (detail of sample E, SEM)
G. Pores dispersed on a fossil lichen cortex
H. Isidium on a fossil lichen surface, to the left a break of another isidium (SEM)
I. Contact between hypha and alga in a fossil lichen (SEM)
K. Septated hypha in a fossil plectenchyma, septum with pore (arrowed).


A
FIGURE 10
20μ
50μ
B
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D
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spongy interior tissue (spongyparenchyma/medulla) that allows together with special pores in the external tissue(stomata/cyphellae) the exchange of gases for photosynthesis (Fig. 10G).
The chemistry of the original cell walls was decisive for the diagenesis and the appearance in the fossil state. Only those parts of the plant leaf are preserved that originally were interspersed with cutin which means the cuticle and the cutinized layer of the epidermis cell walls (periclinal walls) and the cuticular ledges (anticlinal walls). The major rest of the cells coalified. In comparison the whole cell walls of the fossil thallophytes are preserved due to cell wall substances, which have been durable, possibly a polysachharide, like chitin. Hence the fossil lichens contain the whole cell corpora and thus are more voluminous and richer in structure than the fossil cuticles. The typical structures of cortex and medulla plectenchyma are preserved. Algae cells are of plant origin and their walls are chemically different from those of the fungal hyphae. In most objects they obviously were not durable enough to outlast the biological and geochemical alterations through diagenesis and have been coalified.
For to recognize the lichen nature of the present fossils it is decisive to understand the diagenetic alterations. The formation of fosicom enabled the preservation of even delicate lichen tissues which are composed of tightly arranged algae cells and fungal hyphae. The understanding of how fosicom is formed is a prerequisite for recognizing the fossil plectenchyma with its patterns of coalified algae. Thus in the fossil state we find fosicom-cuticles with the patterns of the former epidermis cells (Fig.1C/ and Fig.3) and as lichenous analogues fosicom-plectenchymas with the patterns of former algae cells (Fig.2H and Fig.3).

4. Evidence for the lichen nature of the Triassic thallophytes

In order to prove the lichen nature of any fossil thallophyte, it is necessary to find the fossil remains of the consortium. Of particular interest are cellular structures that are unique to the symbiosis, e.g. contacts between the lichen symbionts like closely appressed fungal hyphae (Fig.10G) or haustoria (Peveling, 1973). Best proof would be the identification of fossil consortium products like lichen substances (Fig. 1F/G) or isidia (Fig. 10H) and soredia(Fig. 10A-F). Isidia and soredia are unique vegetative structures that are found in foliose lichens. They consist of both symbionts serving as diaspores for the dispersal of the lichen (Jahns, 1973.p.37). The fossil preservation by fosicom provides all of these lichen characteristics.

G) FINAL REMARKS

The material of the present fossils could not be chemically dissolved which is a prerequisite for the application of special molecular spectroscopic methods (e.g. Infrared Spectroscopy). In addition I am not provided with the technical equipment. Hence it was not possible for me to furnish evidence for the presence of Si-0-Si, Si-0-C and Si-C bonds which would prove the existence of fosicom. Nevertheless I tried to light up the mysterious chemistry of the fossil matter with the help of, in some cases, elementary methods. This way I at least wanted to furnish circumstantial evidence for the described silicification process, knowing that some of my conclusions are speculative. However, I think my investigations may open up a new way of understanding the formation and chemical nature of kerogens.

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