DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 1998/23

Amorphous silica and hydrous aluminosilicates for production of contruction materials

INCO - Copernicus projekt No. ERBIC15CT960712

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MINISTRY OF ENVIRONMENT AND ENERGY

G E U S

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1st year Progress Report of Partner No. 5: GEUS

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G E U S

Contents

Abstract

The project **The usage of amorphous silica and hydrous aluminosilicates for the production of building materials with improved properties,** *INCO-Copernicus project ERBIC15CT960712,* aims at providing a catalogue over diatomite deposits, including geological models for the deposits, specification of their raw material properties, and description of the utilizations for the diatomaceous materials. Furthermore the project aims to identify a series of industrial minerals suitable for additive in building material which includes zeolites for cement and vermiculite for concrete. Finally the production of synthetic wollastonite for asbestos substitution based on calcareous diatomites will be investigated.

The project is divided in three phases with a number of associated tasks. In the 1st yearly period GEUS was involved in two of these phases, namely phase 1: Evaluation of geological data and field work, and phase 2: Material characterisation.

Phase 1: Evaluation of Geological Data and Field Work

Task 1.1. Literature review

An extensive pile of literature on the mo-clay (clayey marine diatomite) deposits and formation has been investigated, and a historical review is given as well as a full list of references.
Results: It is evident that the literature on the geochemistry of the diatomite is sparse. The opal - quartz transformation within the diatomite has not been studied, and the supergene alterations have not been investigated. This is obviously a target for the future investigations concerning the mo-clay in the project, and necessitates a comparison with similar deposits in other parts of the world.

Task 1.2. Reconnaissance and detailed field work and rock sampling

1.2.1. Field work in the mo-clay area

The samples analysed from the clayey diatomite in Denmark were collected from two reference profiles in the Limfjorden area, namely the island of Mors (Ejerslev mo-clay pit) and the island of Fur (Manhøj mo-clay pit). The field work was carried out prior to the beginning of the project in the autumn 1996 so that the laboratory work could be initiated in the early spring 1997 at the beginning of the first project period.

Results: A representative reference collection of clayey, marine diatomite, the mo-clay, consisting of 26 samples from two localities were collected to see the stratigraphical as well as the lateral variation of the diatomite composition within the mo-clay basin. The samples are prepared for further laboratory investigations.

1.2.2. Fieldwork on Samos

Field work was carried out in Samos in September 1997 with the aim at studying the transition of the diatomite opal A into C/T opal and further into quartz.

Results: A reference section of 15 samples have been collected and a detailed sedimentological study was carried out on the calcareous diatomite known as the Chora Beds in the Pythagorion Formation to support the interpretation of the depositional setting of these diatomites.

1.2.3. Reconnaissance field work on Aegina and in Elasson

Reconnaissance field work was carried out on the clayey diatomite deposits at Aegina and in the Elasson. The Aegina diatomite is situated in a local lacustrine basin in an andesitic volcano centre of the island Aegina. The Elasson deposit is situated in a broad intermontaneous lacustrine basin in the northern part of central Greece without a direct connection to volcanic centres.

Results: Reference samples of chertified concretionary beds from the Aegina clayey diatomite will provide an example of a perfect transition from unaltered opal into quartz. The investigations of the clayey diatomite from Elasson have indicated that this diatomite shows a marked similarity to the mo-clay. Additional samples from this deposit have been collected for clay mineral determination, and detailed work on the geological setting is envisaged.

Phase 2: Material characterization

Task 2.1. Laboratory analyses

On the samples collected in Phase 1 a number of analyses have been carried out. First a general identification of the minerals was carried out with X-ray diffraction (XRD) on the samples. Secondly certain samples were selected for detailed investigations. These included clay mineralogical identification for the clay minerals and DTA-analysis of selected samples of mo-clay. Finally the calcite content of the calcareous diatomites was determined and the opal A composition described in detail.

Results: The geochemistry, bulk mineralogy and clay mineralogy has been established for the marine clayey diatomite. This set of analyses may serve as a reference in future comparisons and classifications of various diatomaceous deposits.

Task 2.2. Investigation of the texture

The texture of the diatomite material has been studied in the scanning electron microscope (SEM) with an attached element analysis facility (EDAX). A large number of SEM microphotographs from a large number of diatomite samples form the basis for the selection of illustrations of the various diatomite textures.
Results: A photo data archive has been obtained for the documentation of the texture of diatomites. These photo data will be organized and may provide a reference for the identification of the diatomite textures.

Introduction

Amorphous silica and hydrous aluminosilicates have gained increasing importance in industrial application during the last twenty years. This is mainly due to the broad spectrum of applications which span from filters, fillers, chemical carriers to high-tech ceramics, constructional materials and insulation materials. The focus of the present project is on three specific types of material: **diatomite, vermiculite and zeolites**.

Diatomite has a high porosity and low permeability which makes it a good insulator. Granules of the clayey diatomite which in Denmark is known as moler have a high absorption capacity. The granules are therefore used in environmental protection, in drilling mud and as cat litter. The admixture of diatomite in concrete can eliminate excess water, improve water tightness and strength by implementing an equal distribution of voids in the mixture. It is foreseen that the diatomaceous rocks could be used as pozzolanic additives in cement for the improvement of the fresh and hardened concrete. Calcareous diatomite, which occurs in Greece, is expected to constitute a raw material for future production of synthetic wollastonite applicable for asbestos compensation material.

In the project the utilization of **zeolites** as a cement additive will be investigated. It is expected that zeolites will improve the workability and durability of cement.

Vermiculite is utilized in the production of lightweight aggregates and insulation materials. Several deposits of diatomite, zeolites and vermiculite occur in Romania, Hungary and Greece. Some of them are large in size, but few have been studied in detail or exploited on a large scale.

The **target of the project** focuses on three items:

1) Classification of the diatomite, zeolite and vermiculite deposits including a description of the depositional environment and diagenetic changes, raw material quality and utilization.

2) Investigation and evaluation of the inspected raw materials applied as cement additive.

3) Production of synthetic wollastonite ($CaSiO_3$) and testing its qualities.

GEUS provides the project with detailed geological information on Danish diatomite deposits (moler) and advanced analyses of the naturally occurring amorphous silica and hydrous aluminosilicate deposits as well as the raw material products and their behaviour during production. In this first year of the project the focus has been on the natural materials and investigation of the mineralogical composition and material structure. GEUS has concentrated on the characterization of the clayey diatomite from Denmark, the moler (mo-clay), and in addition we have carried out reconnaissance investigations on samples from selected localities in Greece.

Mo-clay investigations

Mo-clay (or moler as the companies prefer the trade name to be) is a clayey diatomite of Paleocene-Eocene age. It is unique in having suffered very slight diagenetic alterations after its deposition. It is exposed in the Limfjorden area whereas coeval deposits in Jutland are diatomaceous clays. The diatomite unit has a thickness of about 60 m mirroring a palaeo-oceanography with recurring blooms of plankton restricted to a special geological setting in the eastern part of the North Sea.

For about a hundred years the mo-clay has been used as a raw material for insulation bricks and granulates. The production amounts to about 200.000 cubic metre per year. The excavation takes place in some of the most beautiful hills on the islands Mors and Fur. Consequently a potential conflict exists between the landscape conservation and the raw material utilisation.

A large effort is therefore put into planning and recultivation of the excavation areas. GEUS provides the geological mapping and conducts the raw material investigations in the areas, and is consulted by the companies as well as by the environmental authorities.

Due to the very intense glaciotectonic deformation of the area predictive models for the occurrence of mo-clay deposits are founded on structural geological investigations.
The complexity of deformation involves buckle folding as well as shear folding. The buckle folds are interpreted as proglacial deformation. The shear folds, which generally superposes the buckle folds, are interpreted as the result of subglacial deformation. The succession of these two types of folds is interpreted as a sequential development of deformation during the ice advance. The shear deformation in the top of the deformational stockwerk may develop into a tectonic breccia - the glacitectonite - which may even be integrated in the lodgement till.

The complexity of deformation involves superimposed folding creating interference dome folds and the classic arrow head structures. The superimposed folding demonstrates that the area was transgressed by several ice advances.

The mo-clay unit is named Fur Formation. Interbedded in the diatomite are ca. 180 volcanic ash layers, which mirror the regional upwelling of magma during the initiation of the opening of the North Atlantic. The ash is well preserved in the mo-clay, and geochemical investigations show that the ash layers originated from different magmas. Most ash layers are of tholeiitic composition as are the volcanic rocks of the ocean floor.

Many fish fossils have been recovered in the mo-clay. Several of these have very delicate skeletal parts preserved. Besides turtles, birds and numerous insects have been found, and petrified wood and plant debris is very common.

Historical review of research in the mo-clay

The geological research in the mo-clay dates back more than 150 years. During these years the emphasis of the studies have varied according to the personal interest of the geologists and to issues of special interest to certain period. Through the 1960 to 80ies we have seen a proliferation of studies and observed an increasing number of specialist studies and sophisticated analyses. An extended reference list is attached at the end of this report. It contains papers which are not necessarily commented on in the following.

Year 1809 - 13: coal

In the early part of the 19th century the Danish government initiated investigations into the natural resources in Denmark. The occurrence of layers of black sand in the mo-clay was known and the colour was attributed to coal. A search for coal began. In 1809 - 13 a number of boreholes, a well and an adit failed to demonstrate the presence of coal. The work was stopped when it became clear that the strike and dip of the beds changed and that individual beds were not continuous.

1835: a freshwater deposit, coaly sand.

The first description of the mo-clay was provided by G. Forchhammer, professor in mineralogy, in a survey of the geology of Denmark. He mentioned mo-clay, cementsten (calcareous concretions) and black layers of coaly sand. He mentioned finds of insects and fish, assumed to be fresh water species, and interpreted the mo-clay formation as a fresh water deposit. Apparently he had no knowledge of the diatoms and he neglected to provide himself with a chemical analysis which would have shown that the black sand was not coaly. Frochhammer argued that the mo-clay was younger than the chalk and older than the Quaternary. He suggested that it might be coeval with the brown coal deposits in central Jutland. The latter are known today to be Miocene.

1863: diatoms.

In a review of diatoms found in Danish deposits some species from the mo-clay were included (Heiberg 1863) which is the first indication of the mo-clay as a diatomite.

1883: diatoms and volcanic ash.

Two Belgian palaeontologists described volcanic ash in samples from Mors and Fur (Prinz & Ermengem 1883). This was eventually read by a Danish diatom researcher who passed the information on to the geologist O.B. Bøggild, later professor in mineralogy.

1903 - 1918: volcanic ash layers.

The volcanic ash layers were recorded at several localities by N.V. Ussing in the years 1902-1907. He noted that individual layers could be traced from one coastal cliff to the next and he established the numbers, which are still in use. The ash layer stratigraphy and description of the layers were completed and published by Bøggild (1918). A number of thin, pale ash layers in the lower part of the negative series were added by Gry (1940).

1899 - 1979: the age of the mo-clay.

The lack of calcareous microfossils in the mo-clay has prolonged and complicated the discussion of the age of the formation. A dating based on ash layer correlation to coeval Danish formations was likewise impossible until the dinoflagellate stratigraphy was established (Hansen 1979, Heilmann-Clausen 1982 and later papers). The age of the mo-clay was first determined as Eocene from leaves, *Macclintockia kanei* (Stolley 1899). Dinoflagellate cysts indicate a latest Paleocene to earliest Eocene age (Heilmann-Clausen 1994). In the years between 1899 and 1979 the mo-clay was regarded by some to be Paleocene, by others to be Eocene, while others again thought it spanned the boundary. A relative age of the mo-clay is difficult to obtain because glacially undisturbed exposures are rare, and because the mo-clay in most outcrops is erosionally truncated and overlain by Quaternary deposits.

1937 - 1944: where were the volcanoes?

The volcanic ash layers at Ølst (central part of Jutland) were described by Andersen (1937), who also drew isopach maps of characteristic ash layers. The ash layers are thickest at Mors and Fur and gets gradually thinner towards the south and south-east. Andersen (1937) concluded that the volcanoes were located in Skagerrak. Older studies had proposed that the ash came from volcanoes in Scotland or in Scania or on islands (later submerged) close to Mors and Thy. Calculations on the grain-size of the ash layers supported a volcano in Skagerrak (Norin 1940).

1940 - present: glaciotectonics.

Gry (1940) focused the attention on the glaciotectonics of the mo-clay and the importance of glacial stratigraphy.
The glaciotectonic studies have been continued and are among the best documented case studies in Denmark (Pedersen 1987, Pedersen 1993, Klint & Pedersen 1995, Pedersen 1996).

1960 - present: fossils in the mo-clay.

Systematic as well as preliminary descriptions of major groups of fossils have been published:
Plant macrofossils (Koch 1960, Larsson 1975).
Diatoms (Benda 1972, Homann 1991).
Silicoflagellates (Perch-Nielsen 1976).
Insects (Larsson 1975, Wilmann 1977 and later papers, Freiwald 1991, 1992).
Birds (Hoch 1975, 1983, Hoch & Pedersen 1983, Kristoffersen 1997).
Fish (Bonde 1966 and later papers).

1975 - 1982: the volcanic ash.

The ash layer petrology was studied by Pedersen, Engell and Rønsbo (1975, 1977). It has been demonstrated that the ash which fell on land weathered to clays which retained their trace-elements during transport and deposition in marine environments (Nielsen & Heilmann-Clausen 1988). The shape of the ash particles show that some eruptions were subaqueous while other were subaerial (Pedersen & Jørgensen 1981).

1975 - present: geophysics.

A wide range of geophysical methods have contributed to studies of the Fur Formation. Three palaeomagnetic reversals were recorded by Sharma (1969) who estimated the duration of mo-clay deposition to c. 3 m.y. The volcanic ash layers are recognizable on gamma-ray logs and the wells in the North Sea documented the stratigraphic position of the ash layers (Jacques & Thouvenin 1975, Knox 1983, 1984 and later papers). Reflection seismics across Northern Jutland and Skagerrak documented the thickness and distribution of the Tertiary deposits (Jensen & Michelsen 1992). Recently the seismic velocity of the deposits have provided insight in the amount of uplift during the Neogene (Japsen 1992, 1993, Jensen & Schmidt 1993). Shallow seismic surveys illustrate the latest Tertiary and Quaternary tectonics (Lykke-Andersen 1992).

1975 - present: the margin of the North Sea Basin.

Hydrocarbon exploration in the North Sea began around 1970 (Andersen & Doyle 1990). Significant papters on the North Sea geology have been presented at the Conferences on Petroleum Geology of Northwest Europe (Woodland 1975, Illing & Hobson 1981, Brooks & Glennie 1987, Perker 1993). Ziegler (1 990 and earlier papers) have provided widely used palaeogeographic maps. The seismic data, the wire line logs and the cores document very thick Tertiary deposits in the North Sea and the micropalaeontology, volcanic ash markers and clay mineralogy tie them to the outcrops in Denmark (Nielsen et al. 1986, Knox 1984, 1 992, 1993). It has recently been recognized that the geological history of northern Jutland also involves early Tertiary inversion tectonics in the Fennoscandian Border Zone and regional Neogene uplift (Jensen 1992, Japsen & Langtoft 1991, Jensen & Michelsen 1992, Jensen & Schmidt 1993, Mogensen & Jensen 1994).

The volcanic center was formerly suggested to be situated in the Skagerrak, where Sharma (1 970) outlined a potential geomagnetic anomaly. Seismic surveys for hydrocarbon exploration in the 90ies have documented that no volcanic activity characterized Skagerrak during the Tertiary time (L. Jensen, Statoil, pers. comm.). At present most geologists agree that the ash layers reflect the eruption of volcanos along the Mid Atlantic Ridge near the Færø Islands at the time of the break up of the Greenland - Norway continental margin (Nielsen & Heilmann-Clausen 1988, Pedersen, Pedersen & Noe 1994).

1977 - present: sedimentology of the mo-clay.

The sedimentology of the mo-clay and the distribution of laminated versus structureless diatomite was studied by Pedersen (1981) who established an oxic-anoxic fluctuation model for the sedimentation in the mo-clay basin. The basin was described as related to the depocenter surrounded by salt diapir uplifts. The blooming of diatoms was related to the upwelling of nutrient oceanic water supplied from the opening Atlantic. The mo-clay was formally erected as the Fur Formation by Pedersen & Surlyk (1983). Water escape structures are known to occur in certain ash layers (Pedersen and Surlyk 1977). The calcareous concretions have been studied and demonstrated to be of early diagenetic origin (Pedersen & Buchardt 1996).

The diatomite of the Palaeogene Fur Formation

The clayey diatomite of the Fur Formation is a light yellowish weathering, almost white, diatomite in surface outcrops. Under wet conditions the hue turns grey brown and the surface becomes greasy. The diatomite occurs in the hilly landscape of the islands and peninsulas in the western Limfjord Region (Northern Jutland). Today operations are active on the islands of Mors and Fur (Fig. 1), and the investigated samples in this project are collected in two reference profiles exposed in open clay pits, one on Mors and one on Fur, respectively.

The 60 m thick Fur Formation comprises only about 25 m of the quality required for a raw material. This so called "excavation series" of the Fur Formation is devided into five units. The first unit is in the top of the mo-clay series and the last unit is in the bottom of the series. In addition samples from the series with the chertified beds in the lowermost part of the Fur Formation has been analysed to give information on the properties of these unusual sediments.

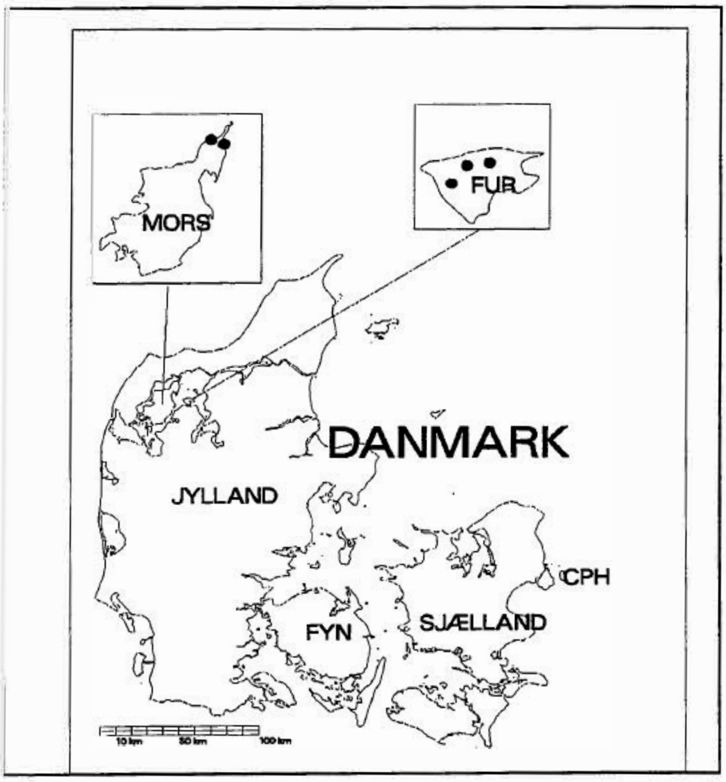


Figure 1. *Location map of the mo-clay pits on the islands of Mors and Fur in Denmark.*

Unit 1. This unit is 4 m thick and is bounded by the ash layer +1 at the bottom and +19 at the top. The unit comprises structureless yellow-white mo-clay intercalated with a few 5-8 cm thick black ash layers. Calcareous concretions are frequently present in the top of the unit.

Unit 2. This unit is 7.5 m thick and consist of mainly laminated, light yellow mo-clay. The upper boundary is ash layer +1, and the lower boundary is ash layer -13, both ash layers are about 8 cm thick. Apart from the three black ash layers -11 to -13 the unit is practically free of ash layers. In the middle part of the unit big (1-2 m in size) calcareous concretions appear (see Fig. 1).

Unit 3. This unit is 7.5 m thick and forms the main part of the lower half of the "excavation series". The upper boundary is the black ash layer -13 and the lower boundary is the 4 cm thick orange weathering ash layer -17. The unit is yellow brown weathering to greybrown in wet fresh excavations. Very few ash layers appear and only with a thickness of about 1 cm. The mo-clay is structureless with few intercalation's of laminated diatomite in the middle and in the lower part (Fig. 1).

Unit 4. This unit is about 1.5 m thick but may vary. It consist of the yellow brown mo-clay below ash layer -17. The lower boundary is the black mo-clay in the lowermost part of the "excavation series". The transition from unit 4 to unit 5 may vary within half a meter due to variation in oxidation level. The mo-clay is well laminated in the lower part of this unit and grades up into structureless diatomite.

Unit 5. This unit consist of the black mo-clay in the bottom of the "excavation series", which often costs the companies problems in the production. The unit is c. 3.5 m thick and consists of grey weathering, black mo-clay. It is mainly laminated, and in the middle part of the unit a c. 20 cm thick calcareous concretion appears. The lower boundary of the unit is the chertified layers which also forms the lower limit for exploitation.

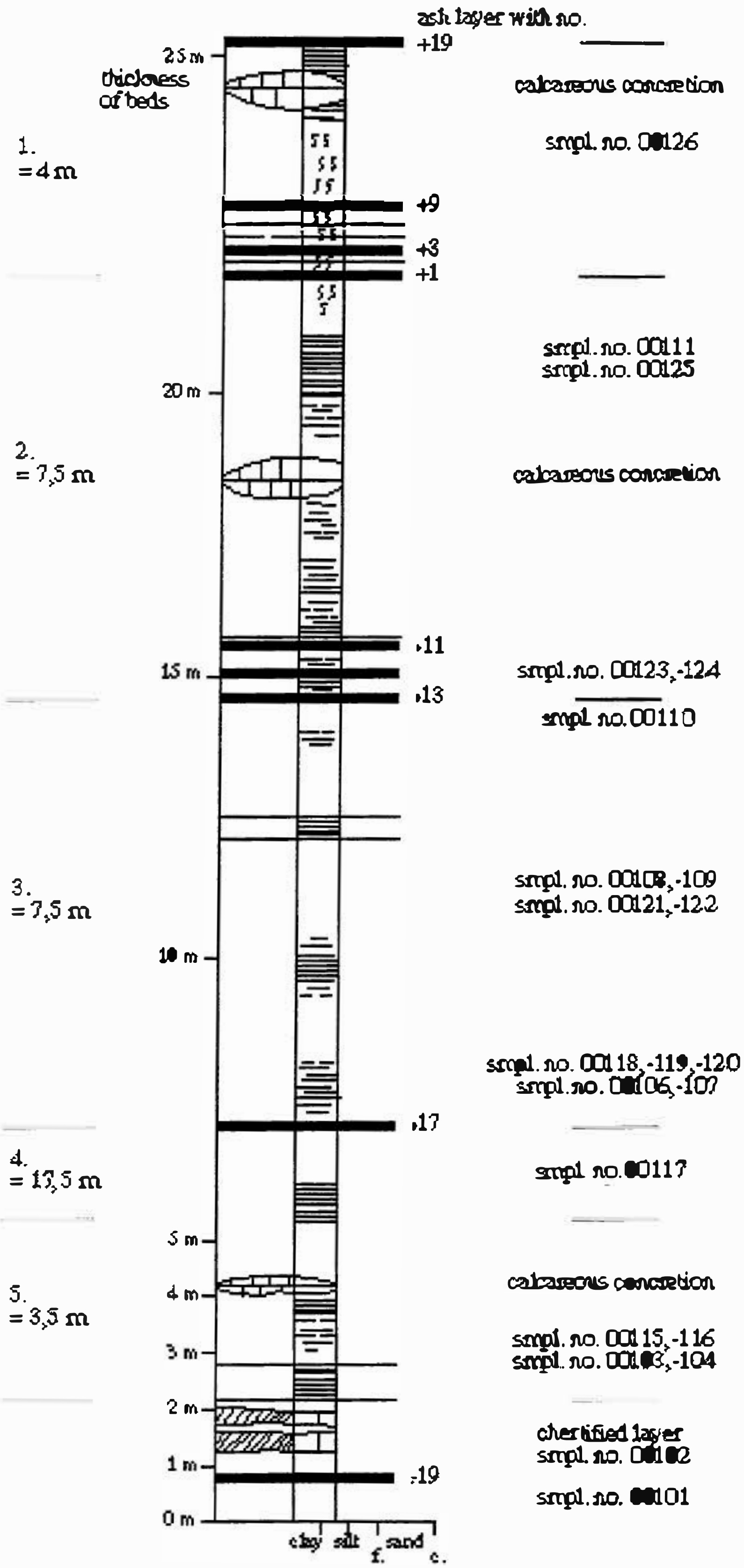


Figure 2. *Sedimentological log of the mo-clay section with indication sample numbers. the numbered units mentioned in the text are shown to the left of the log.*

X-ray identification of minerals in the mo-clay

The X-ray diffraction (XRD) analysis have been carried out on 26 samples from the Danish mo-clay area.
Randomly oriented specimens have been analysed for the bulk mineralogy of the samples. It must, however, be emphasised that opal A is poorly crystalline and therefore may be underestimated by X-ray diffraction.
For example, the X- ray diagram of the sample 00101 has been evaluated as following: The peaks of 14.3Å, 10.1Å, 7.68Å are due to clays (probably kaolinite and smectite, but these must be identified by analysis of oriented and saturated specimens, see below). The peaks at 4.29Å, 3.72Å (beta-line), 3.37Å, belong to Quartz and those at 2.72Å, 2.47Å, 2.22Å to Pyrite.
For all samples, the results are shown in Table 1.

Sample 00126 representing unit 1 is dominated by opal A.
Samples 00111 and 00123 - 00125 represent unit 2, the former taken from the island of Mors and the latter from the island of Fur. The samples are dominated by opal.
Samples 00106 - 00110 and 00118 - 00122 represent unit 3, taken from Mors and Fur, respectively. The samples are dominated by opal, and some clay occurs in the lower part of the unit.
Samples 00105 and 00117 (Mors and Fur, respectively) represent unit 4. The samples are rich in opal and contain some clay.
Samples 00103 - 00104 and 00115 - 00116 (Mors and Fur, respectively) represent unit 5. The samples are rich in opal and clay. Pyrite, gypsum and quartz are present in these samples.
Sample 00102 represent the chertified layer, sample from Mors. It is characterised by opal CT and contains quartz, pyrite, gypsum and clay.
Sample 00101 is a clayey unit below the chertified layers and is rich in quartz.
Sample 00113 and 00114 represents zeolitite from the lowermost part of the Fur Formation on Fur. The samples are dominated by zeolites.

Sample	Quartz	Pyrite	Gypsum	Clay min.	Opal
00101	XX	X	X	XX	
00102	X	X	X	X	XXX
00103	X	X	X	XXX	X
00104	X			XX	XX
00105	X			XX	XX
00106				X	XXX
00107				XX	XX
00108				X	XXX
00109				X	XXX
00110				X	XXX
00111				X	XXX
00112				XX	XX
00113	X			X	
00114	X			X	
00115	X	X	X	XX	XX
00116				XX	XX
00117				XX	XX
00118				X	XXX
00119				XX	XX
00120				X	XXX
00121				X	XXX
00122				XX	XX
00123				X	XXX
00124				X	XXX
00125				X	XXX
00126				X	XXX

XXX: dominant, XX: present in fair amounts, X: present in small amounts

Table 1. *Bulk mineralogy based on XRD. Note that the opal is opal A except for sample no. 00102 which contains opal CT. Samples 00113 and 00114 are dominated by zeolite.*

Clay mineral analysis

The clay mineralogical analysis was carried out on selected samples by X-ray diffraction after preparation and fractionation.

Alkali dissolution of poorly crystalline silica components

The chemical dissolution techniques were applied because the initial XRD showed the presence of disordered, through poorly ordered to well crystalline material.
Eight samples were selected. 5 g of each sample was added 50 ml (for the third treatment 100 ml) of a 0.5M NaOH solution and placed in a steam bath (~ 90°C) for ten minutes. After cooling and centrifugation the liquid was removed. The sample was washed in ethanol and dried over night at 40 degrees C. This procedure was repeated till constant sample weight.
The results are shown in Table 2.

Sample No	total (g)	1st treatment (g)	2nd treatment (g)	3rd treatment (g)	4th treatment (g)
00111	5.00	5.8o	4.00	3.60	3.60
00114	5.00	4.97	4.87		
00107	5.01	6.54	5.00	4.70	4.60
00119	5.00	5.22	4.22	3.80	3.80
00125	5.00	4.85	4.85		
00115	5.00	4.97	4.87		
00103	5.00	4.66	4.65		

Table 2. *Figures demonstrating the decrease in weight due to the removal of opal with NaOH.*

Fractionation and saturation with cations and glycerol

The samples were split by centrifugation into the following subfractions: <0.2μm, 0.2-2μm, >2μm. The amount of each subfraction is shown in Table 3. Each subfraction was saturated with K and Mg using 1 M chloride solutions. For each subfraction the following specimens were prepared: K-saturated, air dry; K-saturated, heated to 300 degrees C; Mg-saturated, air dry; Mg-saturated, glycerolated.
The clay mineralogy was determined from the d-spacings of the clay minerals following these treatments. The results are shown in Table 4.

	<0.2μ		0.2-2μ		>2μ	
S/No	**weight (g)**	**amount (g) %**	**weight (g)**	**amount (g)%**	**weight (g)**	**amount (g)%**
00115	0.35	7.0	0.44	8.8	3.23	64.6
00111	0.20	4.0	0.48	9.6	2.28	45.6
00113	1.02	24.0	0.74	14.8	1.95	39.0
00107	0.62	12.4	0.93	18.6	1.97	39.4
00125	0.45	9.0	0.87	17.4	2.46	49.2
00119	0.72	14.4	0.95	19.0	1.73	34.6
00114	1.60	32.0	0.50	10.0	2.05	41.0

Table 3. *Clay content in samples from the Mo-clay.*

Fraction 0.2-2 microns:					
Sample	vermiculite	smectite	chlorite	kaolinite	illite
00107		xxx		x	x
00115		xxx			
00111		xxx			x
00125		xxx			x
00119		xxx		x	x
00114		xxx			xx
00113		xxx			x

Fraction <0.2microns:					
Sample	vermiculite	smectite	chlorite	kaolinite	illite
00107		xxx		x	x
00115		xxx			
00111		xxx		x	x
00125		xxx			x
00119		xxx		x	x
00114		xxx			x
00113		xxx			x
xxx: dominant. xx: present in fair amounts. x: present in small amounts					

Table 4. *Amounts of clay minerals determined from analysis of oriented specimens by XRD.*

Material structure of the mo-clay

The examination of the mo-clay has been carried out on three different materials: 1) the main mo-clay from the middle part of the Paleogene Fur formation, 2) the chertified beds in the lower part of the formation, and 3) the zeolite rich layer situated at the lowest part of unit 5 at the base of the formation.

The main mo-clay material

The diatoms from the mo-clay are well known and have been described as the main constituent of the diatomite. In attempt to gain some informations on the aggregates in the diatomite the samples were crushed into the fraction less than 250 μ and analysed in the SEM using gold coating on the sample. In the samples (111, 115, 119, 125 and 126) the spherical frustules of the *Stephanopyxis* sp. were frequently observed. This is probably the most characteristic frustule in the crushed material and suggest that it has a high preservation potential. The *Coscinodiscus* which form the most prominent diatom in the mo-clay was mostly seen as fragments except for a few complete ones as for example the one seen in Fig. 3.

From the X-ray analysis it was expected that some diagenetic aggregates of opal C/T could be observed.

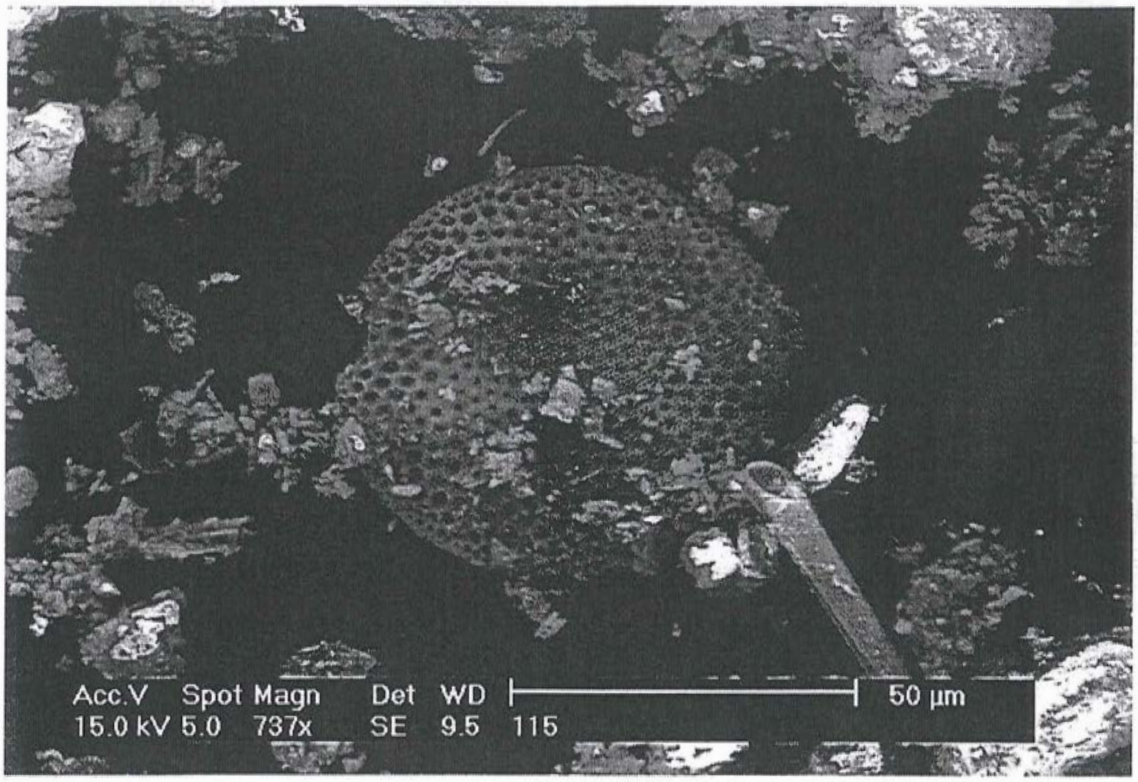


Figure 3. *SEM microphoto of diatomite from the mo-clay (sample 00115).*

Material from the chertified bed

The chertified beds are clearly distinguished from main mo-clay and play an important role as marker beds in the formation. However the origin of these characteristic beds have never been satisfactory explained. In this study we have attempted to give some descriptions that may provide some clues to the formations to the chertified beds.

The most characteristic microscopic feature of the chertified material is the small miarolitic balls. The balls have a smooth surface with a wall constituting of small spheroid aggregates surrounding a void cavity (Figs. 4). The spheroids are build of a mammalian like framework of small, platy opal CT particles.

Another characteristic feature of the cherty beds is the occurrence of framboidal pyrite. These framboids may be microcrystalline or pseudocrystalline (Fig. 5). It is obvious that the redbrown colour of the chertified beds derives from the oxidation of these pyrite framboids.

In the chertified beds diatoms have been recognised, and few fragments of an invertebrate fossil have been observed, probably representing an echinoderm.

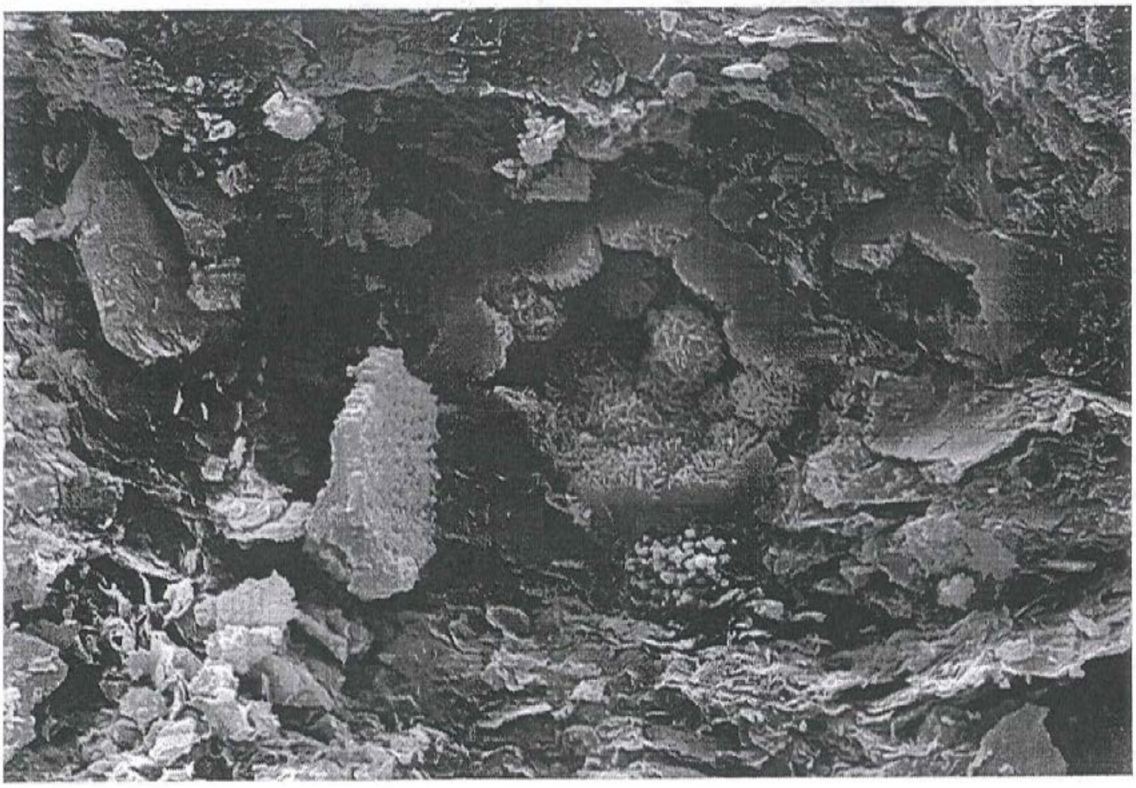


Figure 4. *SEM microphoto of botryoidal aggregate in a chertified bed. Size of spherical aggregate, ball shaped accumulation of lepisphere, is 10 my.*

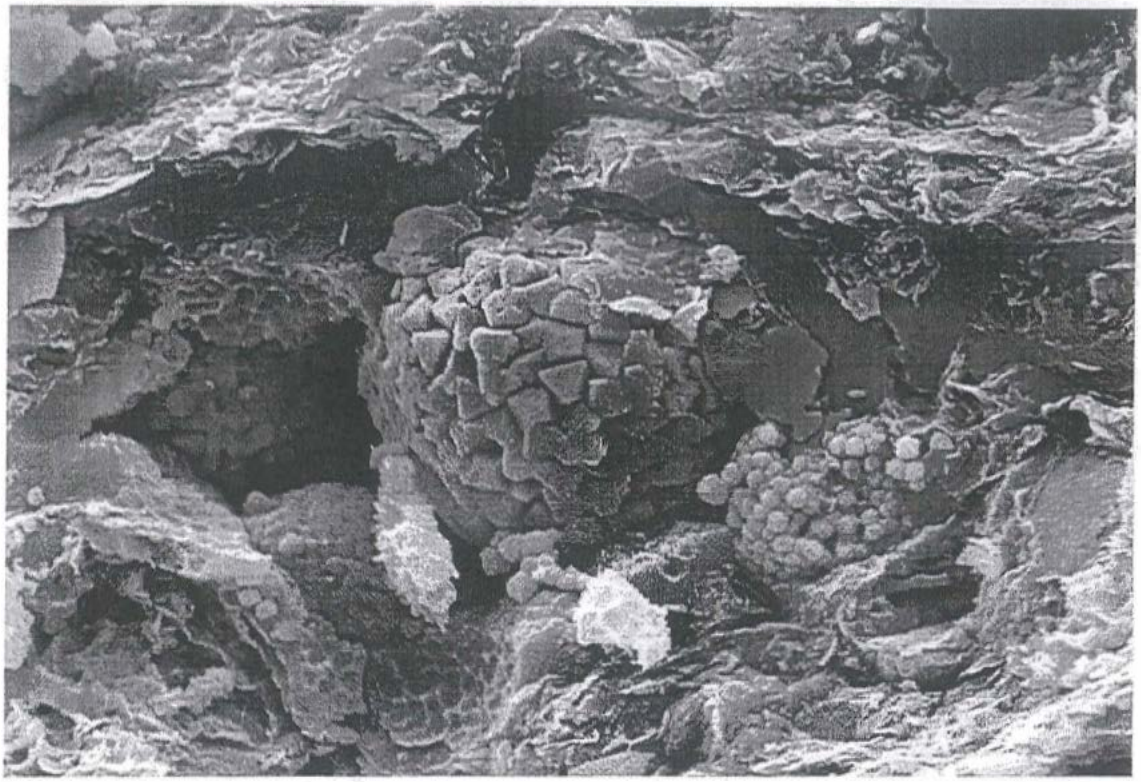


Figure 5. *SEM microphoto offramboidal pyrite in chertified layer. Note that the framboid in the center contain tetrahedral pyrite crystal while the framboid to the right only contains semicrystalline pyrite. Size of big framboid is 10 my.*

Zeolite material

The determination of the zeolitic material was primarily based on the XRD analysis. The zeolite material was subsequently investigated in the SEM microscope for the verification of the composition of the material. Although the lithology in hand specimen is very similar to diatomite no diatoms were recognised in the microscope. In Fig. 6 an example is given of the shape of particles interpreted to be zeolite.

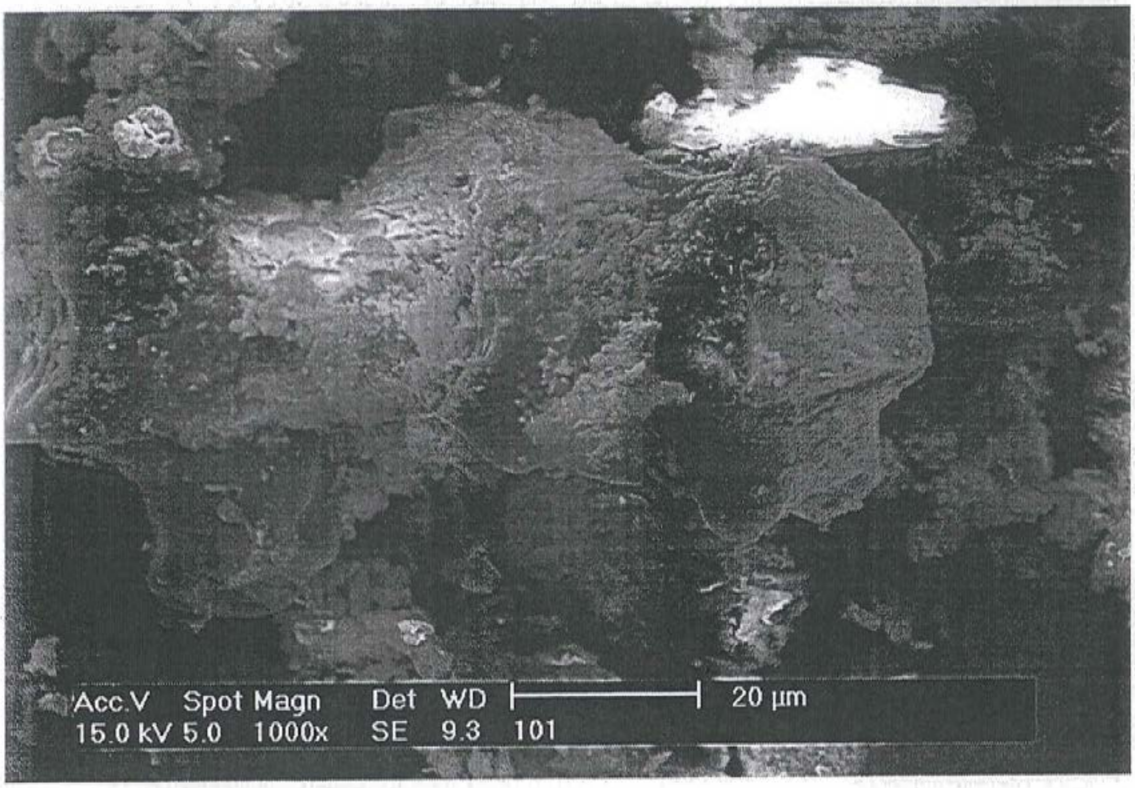


Figure 6. *SEM microphoto of zeolitic fragment from sample 00101.*

Clayey diatomite from Elasson, Greece

The geological setting and the main characteristics of the clayey diatomite in Elasson is described by the project partner 1, Stamatakis et al. 1998. In this report some additional analyses is given and some investigations of the texture are described.

Clay mineralogy

The analyses of the clay content follow the same procedure as described for the mo-clay. The results are given in the tables below:

	<0.2µ		0.2-2µ		>2µ	
S/No	**weight (g)**	**amount (g) %**	**weight (g)**	**amount (g)%**	**weight (g)**	**amount (g)%**
970.286	0.27	5.4	0.48	9.6	3.12	62.4

Table 5. Clay content in samples from the Elasson clayey diatomite.

In both the fine as well as the coarse clay fractions the dominating clay mineral is smectite.

Fractions 0.2-2 microns:			
Sample 970.286	smectite	kaolinite	illite
	xxx	x	x
Fraction <0.2 microns:			
	xxx	x	x
xxx: dominant, xx: present in fair amounts, x: present in small amounts			

Table 6. *Amounts of clay minerals determined from analysis of oriented specimens by XRD.*

Texture of the Elasson clayey diatomite

The lamination in the Elasson diatomite is only weak, and the diatomite contains a large number of plant fossils (leaves) which often are well preserved. The microstructure of the Elasson diatomite is characterised by a relative large variety of diatoms, varying both in shape and size.

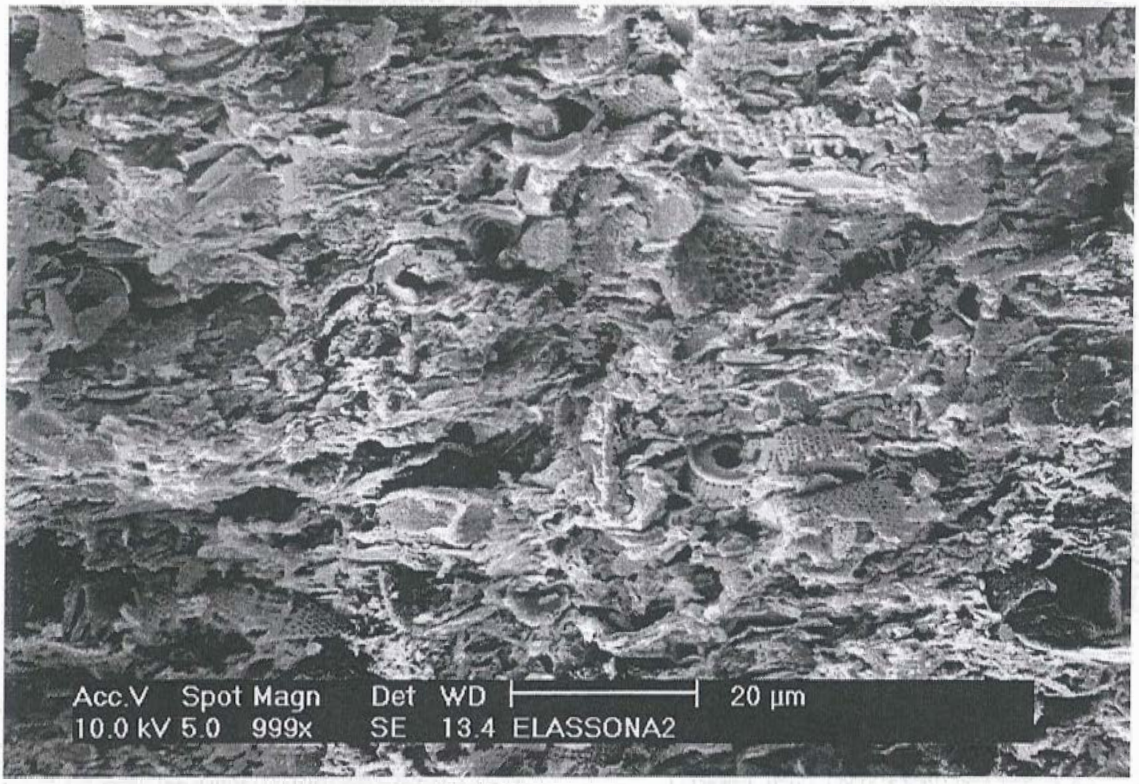


Figure 7. *Micro-lamination in the Elasson diatomite. Note the general small size of the diatoms in this part of the diatomite.*

Some of the diatom frustules are very big (*Actinocyclus sp.),Fig. 8.* However, these constitute less than a few percent of the sediment, whereas the majority of frustules belong to the small *Stephanodiscus* species only 10 micron in size, Fig. 7.

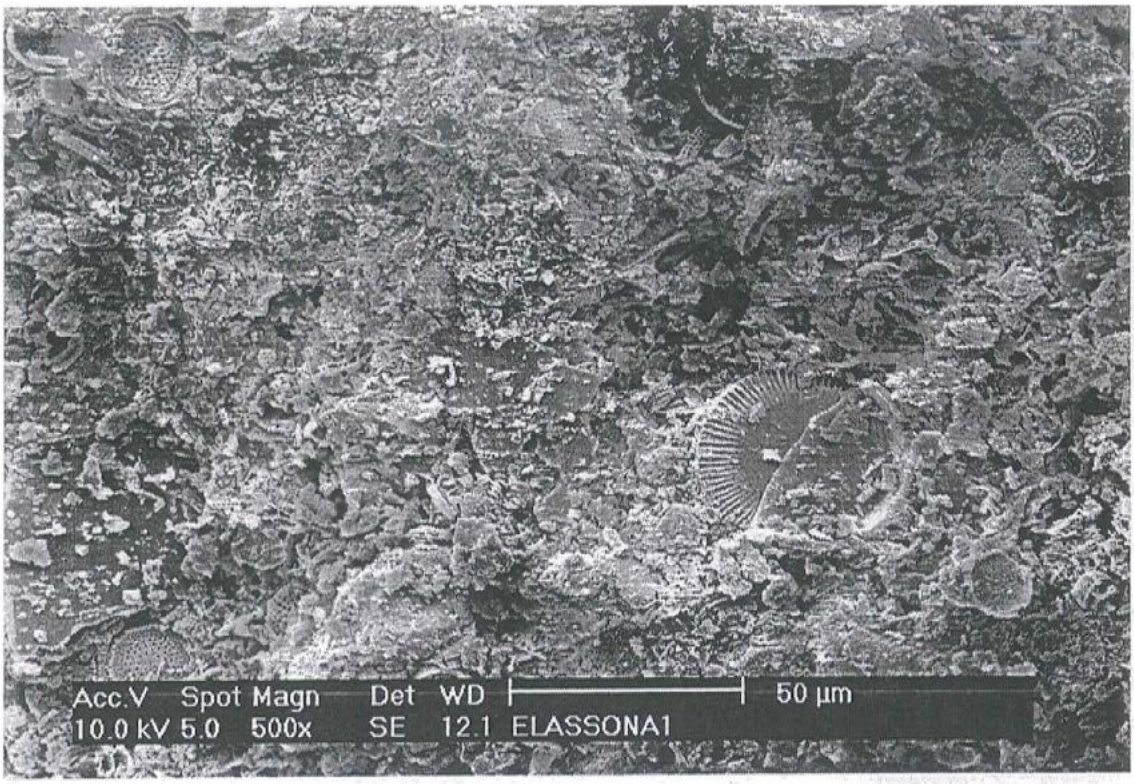


Figure 8. *One of the larger diatom species in a matrix of fragments of smaller skelletons.*

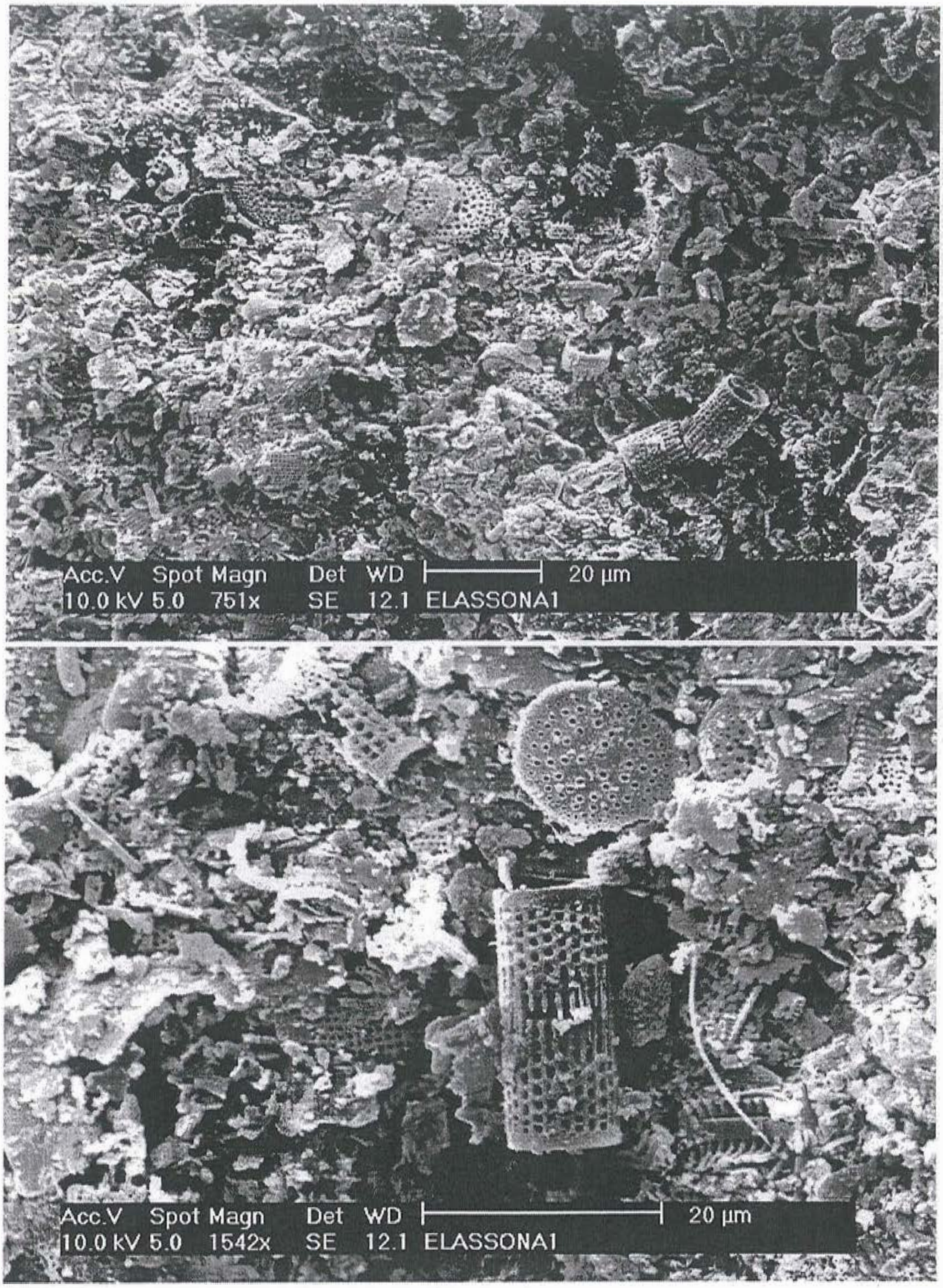


Figure 9. *The characteristic cylindric* ***Melosira islandica****, which is fairly abundant in the Elasson diatomite.*

Calcareous diatomite from Samos, Greece

A detailed investigation of the calcareous diatomite in the Pythagorion Formation on Samos, Greece, was carried out. The aim of this investigation was to study the transition of the opal A in the diatomite into opal C/T and further into quartz in what was taken to be the same primary sedimentary material: calcareous diatomite - just subjected to various degrees of diagenetic alteration.
The diatomite sequence in the Pythagorion Formation is known as the Chora Beds, and a detailed description is given in the partner 1 report, Stamatakis et al. 1998.

Removal of calcite from the calcareous diatomites:

From the XRD-analysis it was known that the diatomites from Samos contain a large amounts of calcite. In order to determine the amount of the remaining fraction, consisting predominantly of opal A, calcite was removed by dissolution in acetic acid at pH 3.0. During this dissolution, pH was carefully controlled so that pH was only allowed to stay below 5.0 for the short periods during addition of small amounts of acetic acid. Thus, amorphous Si is not expected to dissolve. After calcite dissolution, the samples were washed in ethanol-water, air-dried and weighted. The average amount of calcite in the first test sample from Samos was estimated to be 70.5%.
After the field work was concluded in September 1997 it was clear that the Chora Beds comprised a sequence of calcareous diatomite ranging from 1) porcelaenites, 2) C/T opal diatomite to 3) opal A diatomite. Therefore a detailed investigation was carried out to identify the various Si-phases in the sequence. In the following the XRD-diffractograms are given for the various types of diatomite and porcelaenite (Figs. 10, 11 & 12).

Figure 10. *XRD diffractogram of the calcareous diatomite from the middle and upper part of the Chora sequence. Note the well defined opal A pillow.*

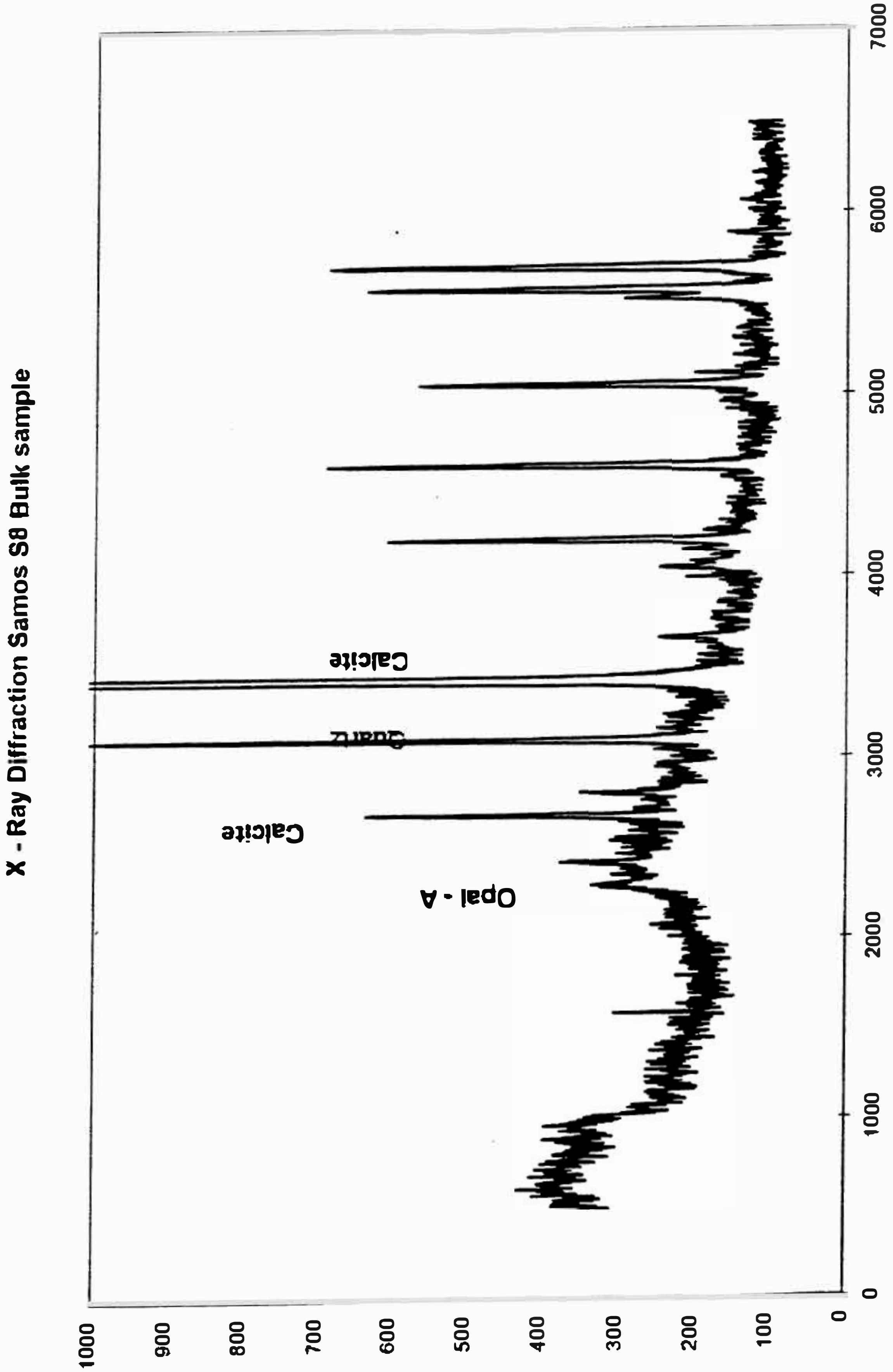


Figure 11. *XRD diffractogram of the calcareous diatomite from the lower middle part of the Chora sequence. Note the opal C/T peaks.*

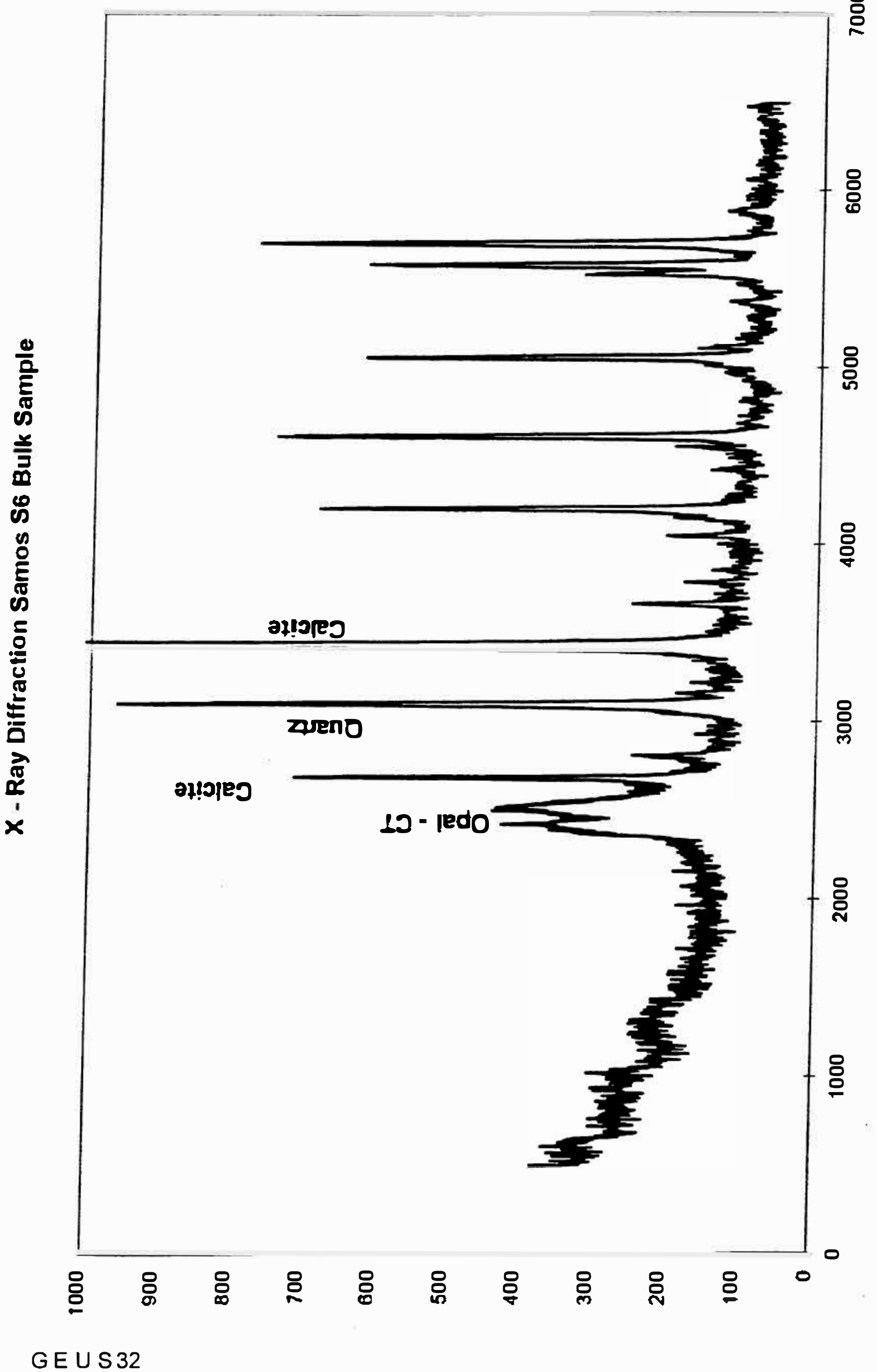
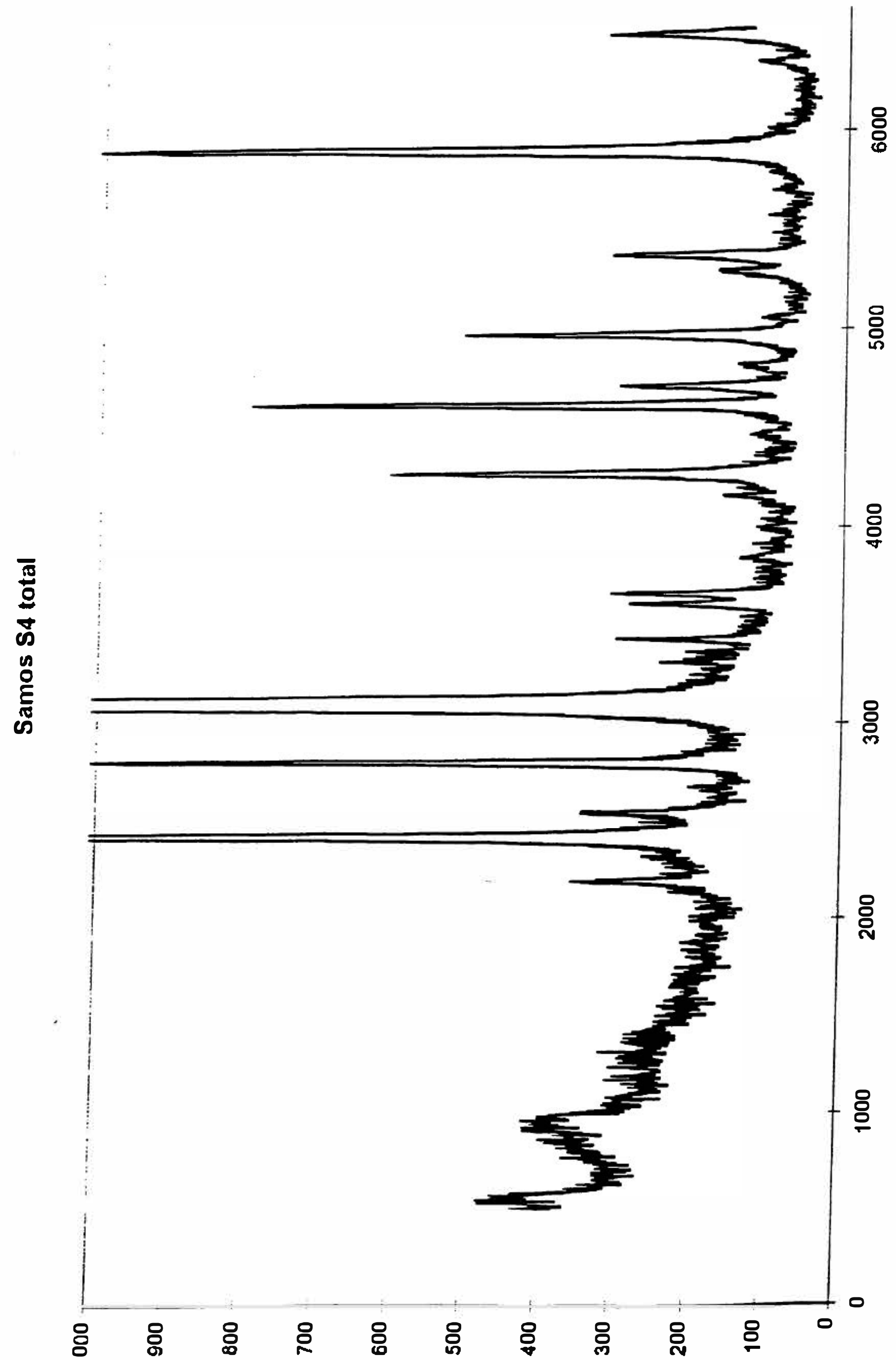


Figure 12. *XRD diffractogram of the calcareous diatomite from the lower part of the Chora sequence. Note the disappearance of opal A as well as opal C/T.*



Texture of the calcareous diatomite from Samos

The diatoms in the calcareous diatomite from Samos consisted mainly of one species, the small (10 my) dish shaped *Stephanodiscous astraea* (Figs. and).

The identified diatom species is characteristic of the freshwater environment of Early Miocene age (dr. Dave Jutson, pers. comm. 1997).

In the middle part of the sequence the diatomite is a very poor diatomite with an extreme well preserved opal frustule texture (Fig. 13). Further down in the sequence the opal C/T takes over and the lepisphere network starts to dominate (Fig. 14). In the lowest part of the sequence thin glassy chert bands occur in the calcite which marks the final transition into quartz and the porcelaenite lithology is formed. In the SEM microscope this is identified by a microcrystaline matix in which miraolitic voids with quartz crystals are visible (Fig. 15).

Figure 13. *SEM microphoto of the diatomite in the middle part of the Chora sequence. The material consists of opal A frustules, mono-floristic* ***Stephanodiscous astraea*** *which are 10 microns in size.*

Figure 14. *SEM microphoto of the opal C/T altered diatomite from the lower part of the Chora sequence. Frame is c. 100 microns.*

Figure 15. *Quartz crystals in porcelaenite from the lowest part of the Chora sequence. Size of crystals are c. 5-10 microns.*

Future activities

The coming project year will focus on sampling and textural analyses of representative diatomites from other parts of Greece as well as from Hungary and Rumania. Field work is planned to take place in June 1998.

Field meeting and field work will take place in the mo-clay area on the islands of Fur and Mors in Denmark in early September 1998 focusing on the clayey marine diatomites. This meeting will include visit to the companies processing the mo-clay.

In late September field work is planned to be carried out on the calcareous diatomite as well as on marine clayey diatomites in Crete.

Comparative studies on opal transition will be carried out in the laboratory on selected sequences containing relevant material for these studies. Further studies on the pyrite leaching is foreseen.

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