DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 1997/81

Mineralogical Composition of impure diatomites

Preliminary results of diatomite investigations for the EU Copernicus project ERBIC 15 CT960712

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Contents

Introduction

The investigations described in this report are contributions to the EU Copernicus project titled "The usage of amorphous silica and hydrous aluminosilicates for the production of building materials with improved mechanical properties", contract no. ERBIC 15 CT96 07 12.

The aim of this project is to study amorphous silica and hydrous aluminosilicates which in the last twenty years have gained increased importance in the industrial application. 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 this Copernicus project is on three specific types of material in the mentioned group, namely **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 mo-clay (moler in Danish) 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 an innovative raw material that can be used for the production of synthetic wollastonite applicable for asbestos compensation material.
In the project the use of zeolites as a cement additive will be investigated. It is expected that zeolites will improve the workability and durability of cement.
Vermiculite is applied in the production of lightweight aggregates and insulation materials.
Several deposits of the raw materials above occur in Romania, Hungary and Greece. Most of them are large in size, but have not 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 genetic model, raw material quality and application.
2) Investigation and evaluation of the inspected raw materials applied as cement additive.
3) Production of synthetic wollastonite ($CaSiO_3$) and testing its qualifications.

This report describes the preliminary investigations carried out to support the first item: the classification of diatomites and evaluation of the methods applied for the characterisation.

The investigation has been concentrated on mineralogical analysis of small clay fraction and opal compositions carried out using X-ray diffractometry, X-ray microscopy (SEM-EDAX). Furthermore differential thermal analysis (DTA) has been used for the investigation of the special properties of the clay-diatomit interaction during heating.

General description of samples and their geology

The investigation reported here has concentrated on the examination of the diatomite from the mo-clay region in northern Denmark. In addition three samples from three different places in Greece have been examined for comparative studies and for the future evaluation of the classification of diatomites.

Samples from the mo-clay

Mo-clay (or moler as the companies prefer the trade name to be) is a special clayey diatomite of Paleocene-Eocene age. 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. The national geological survey 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 a large effort is put into the structural geological investigation of the mo-clay deposits.

The glaciotectonic 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 subglacial deformation. The succession of these two types of folds are interpreted as a sequential development of deformation during the ice advance. The shear deformation in the top of the deformational stockwerk may even develop into a tectonic brecciation - the glacitectonite - which may even be integrated in the lodgement till (Pedersen 1996).

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 (Pedersen 1997).

The mo-clay unit is named Fur Formation (Pedersen & Surlyk 1983). Interbedded in the diatomite are 180 ash layers, which mirror the great volcanic activity in initiation of the opening of the North Atlantic (Pedersen, Pedersen & Noe 1994). The ash is well preserved in the mo-clay, and investigations of their composition show that they 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 are very common.

The samples from the mo-clay represent five units in the so called "excavation series" of the Fur Formation. 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 layer in the lowermost part of the Fur Formation has been analysed to give information of the properties of these unusual sediments.

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 almost 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 7.5 m thick 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 coloured 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.

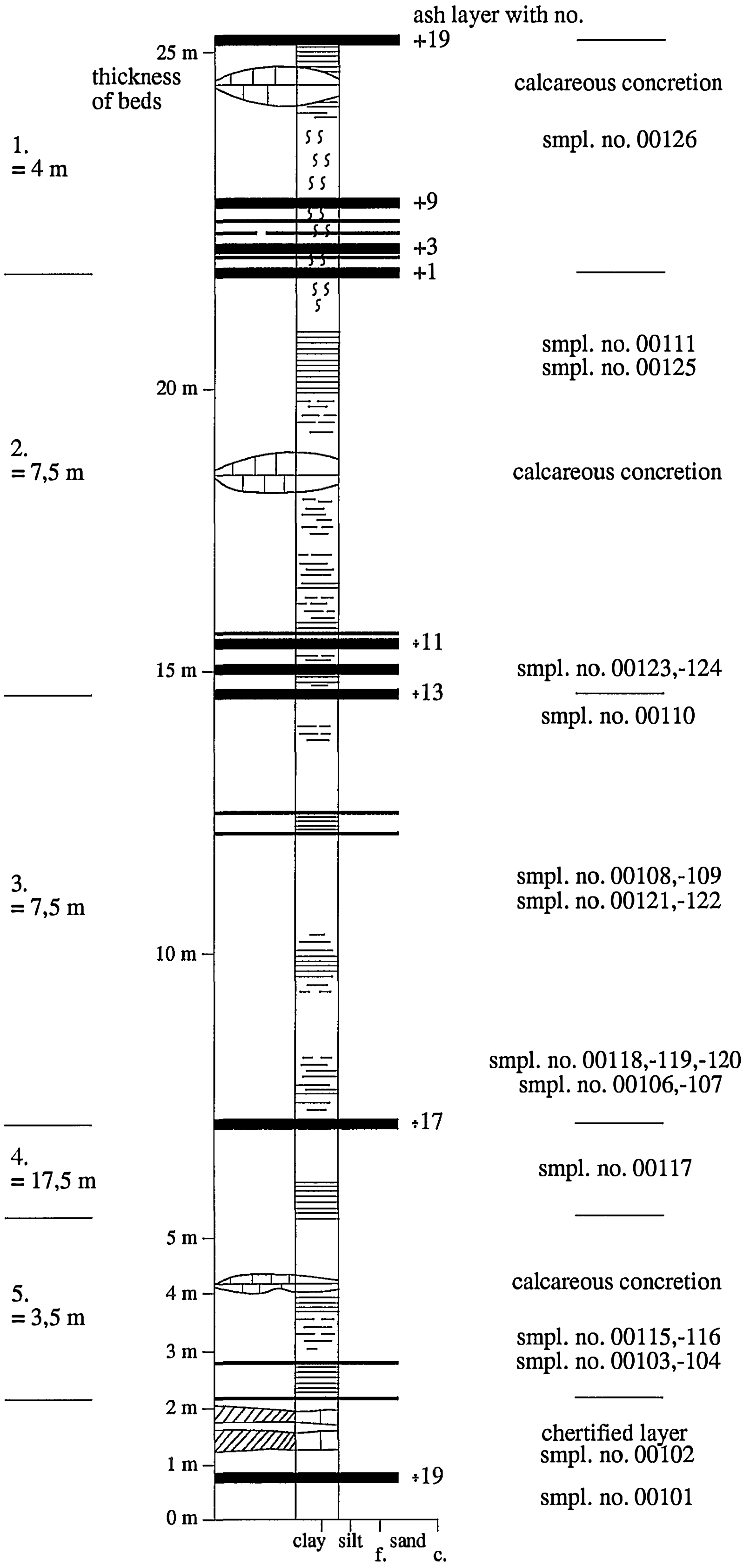


Figure 1. *Sedimentological log of the mo-clay section with indication sample numbers.*

The diatomites from Greece

Three samples of diatomites from Greece have been investigated, namely a clayey diatomite from Elasson, and two calcareous diatomites from Zakynthos and Samos, respectively. The Elasson diatomite is light grey to beige brown and laminated in structure. The calcareous diatomite are white, structureless or weakly laminated. The Greece diatomites are described by Stamatakis et al. 1989a and Stamatakis et al. 1989b.

General X-ray identification

The X-ray analysis have been carried out on 26 samples from the Danish mo-clay area and 3 samples from the Greek diatomite.

Randomly oriented specimens have been analysed for the detection of crystalline components 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	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
Elasson	X			XXX	
Zakynthos					X
Samos					X

Table 1. *General identification of minerals from the X-ray diffractograms. Note that the opal is opal A except for sample no. 00102 which contains opal CT. Samples 00113 and 00114 are dominated by zeolite. The samples from Zakynthos and Samos are from X-ray diffraction dominated by calcite.*

Clay mineral analysis

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

Preparation

Removal of calcite from the calcareous diatomites:

The diatomites from Samos and Zakynthos contained from X-ray diffraction 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.

Alkali dissolution of poorly crystalline silica components

The chemical dissolution techniques were applied because disordered, through poorly ordered to well crystalline material was detected by general X-ray diffraction.

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)
970.286	5.00	5.01	5.00		
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 by centrifugation fractionated into the following subfractions: <0.2µ, 0.2-2µ, >2µ. 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
970.286	0.27	5.4	0.48	9.6	3.12	62.4

Table 3. *Clay content in samples from the Mo-clay and from the Elasson clayey diatomite.*

Fraction 0.2-2 microns:

Sample	smectite	kaolinite	illite	vermiculite	chlorite
00107	xxx	x	x		
00115	xxx				
00111	xxx		x		
00125	xxx		x		
00119	xxx	x	x		
00114	xxx		xx		
00113	xxx		x		
970.286	xxx	x	x		

Fraction <0.2microns:

Sample	smectite	kaolinite	illite	vermiculite	chlorite
00107	xxx	x	x		
00115	xxx				
00111	xxx	x	x		
00125	xxx		x		
00119	xxx	x	x		
00114	xxx		x		
00113	xxx		x		
970.286	xxx	x	x		

xxx: dominating. xx: present in fair amounts. x: present in small amounts

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

SEM-investigations

Mo-clay examinations

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 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 crossed 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 species of the Stephanopyxis sp. was frequently observed. This is probably the most characteristic skeleton in the crushed material due to its high preservation potential. The Coscinodiscus which form the most prominent diatom in the mo-clay was mostly seen as fragmented parts of the material except for a few as for example the one seen in Fig. 2. From the X-ray analysis it was expected that some diagenetic aggregates of opal C/T could be observed.

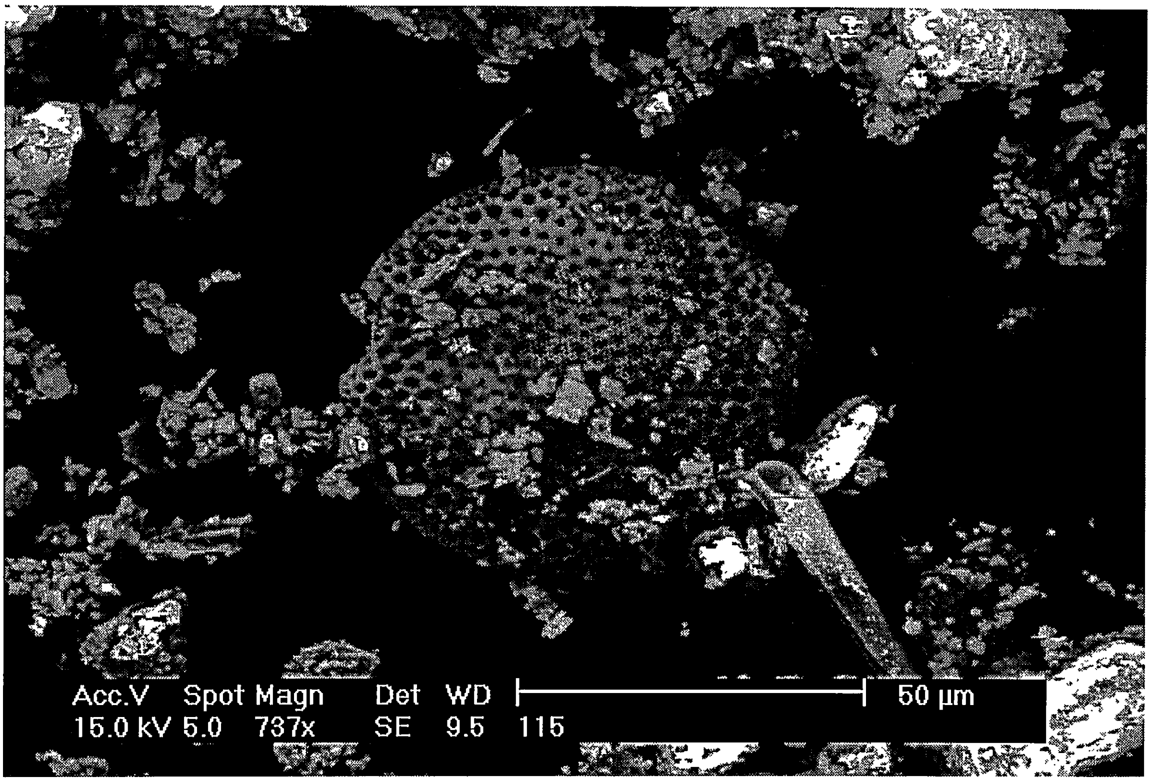


Figure 2. *SEM microphoto of diatomite from the mo-clay (sample 00115).*

Material from the chertified bed

The chertified beds are clearly distinguished from main mo-clay and play an important roll as marker beds in the formation. However the origin of these characteristic beds have never been satisfactory described. In this study we have attempted to give some descriptions that may indicate 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. 3). The spheroids are build of a mammalian like framework of small, platy opal CT particles.

An other characteristic feature of the cherty beds is the occurrence of framboidal pyrite. These framboids may be microcrystalline or pseudocrystalline (Fig. 4). It is obvious that the redbrown colour of the chertified beds derives from the oxidation of these pyrite framboids.

In the chertified layer diatoms have been recognised, and few pieces of a fossil fragment has been observed, probably representing an Echinoderm sp.

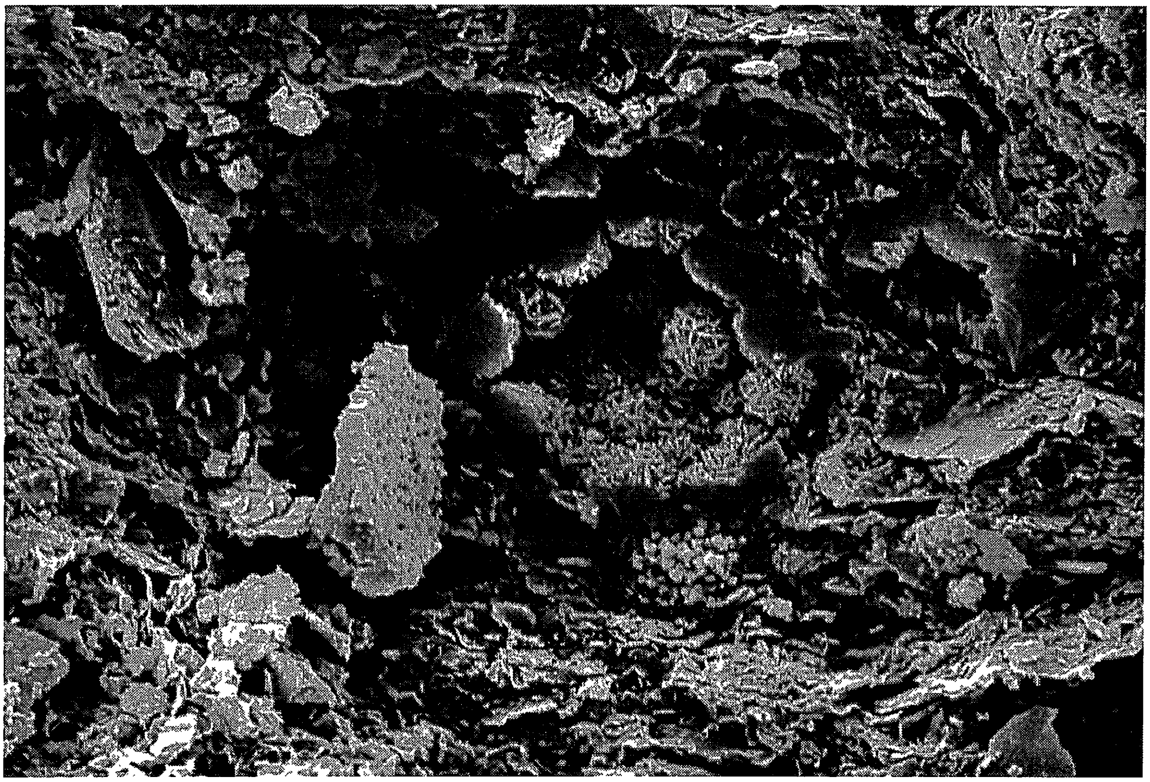


Figure 3. *SEM microphoto of botryoidal aggregate in chertyfied layer. Size of ball shaped aggregate is 10 my.*

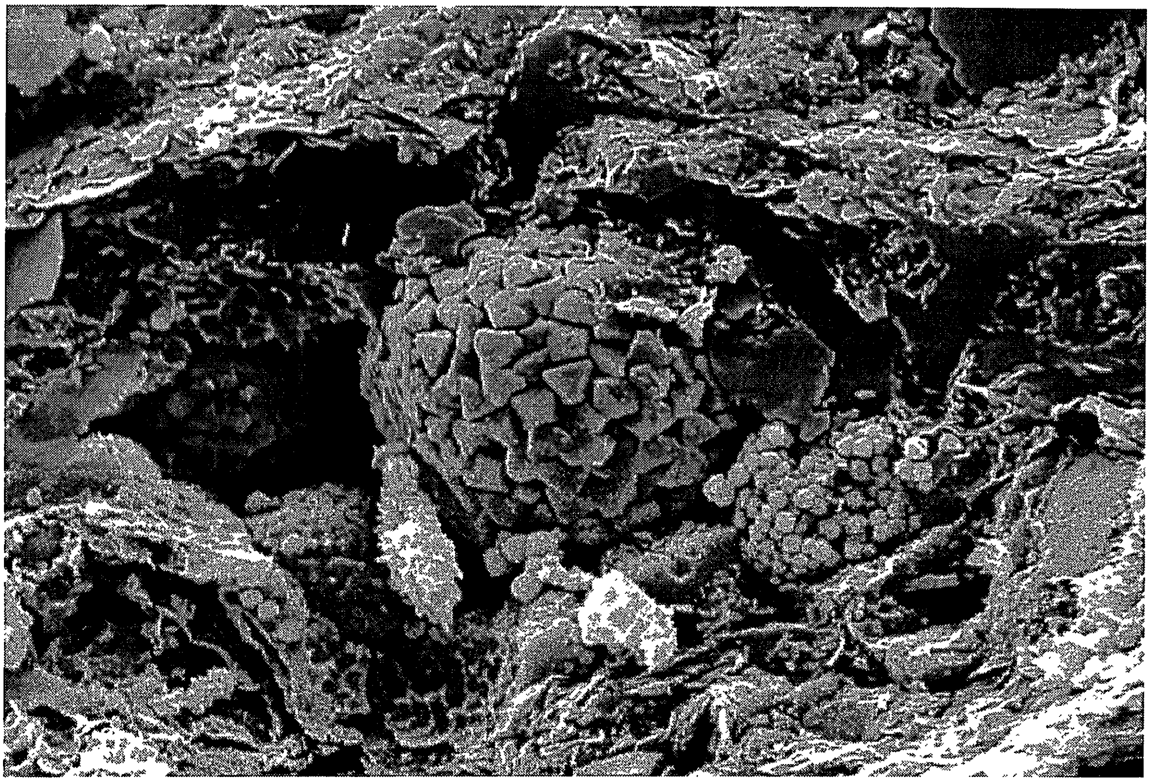


Figure 4. *SEM microphoto of framboidal pyrite in chertified layer. Note that the framboid in the center contain tetrahedral pyrite crystal while the framboid to the right only contains semicrystalline pyrite. Size of big framboid is 10 my.*

Zeolite material

The determination of the zeolitic material was primarily based on the X-ray 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. 5 an example is given of the shape of particles interpreted to be zeolite.

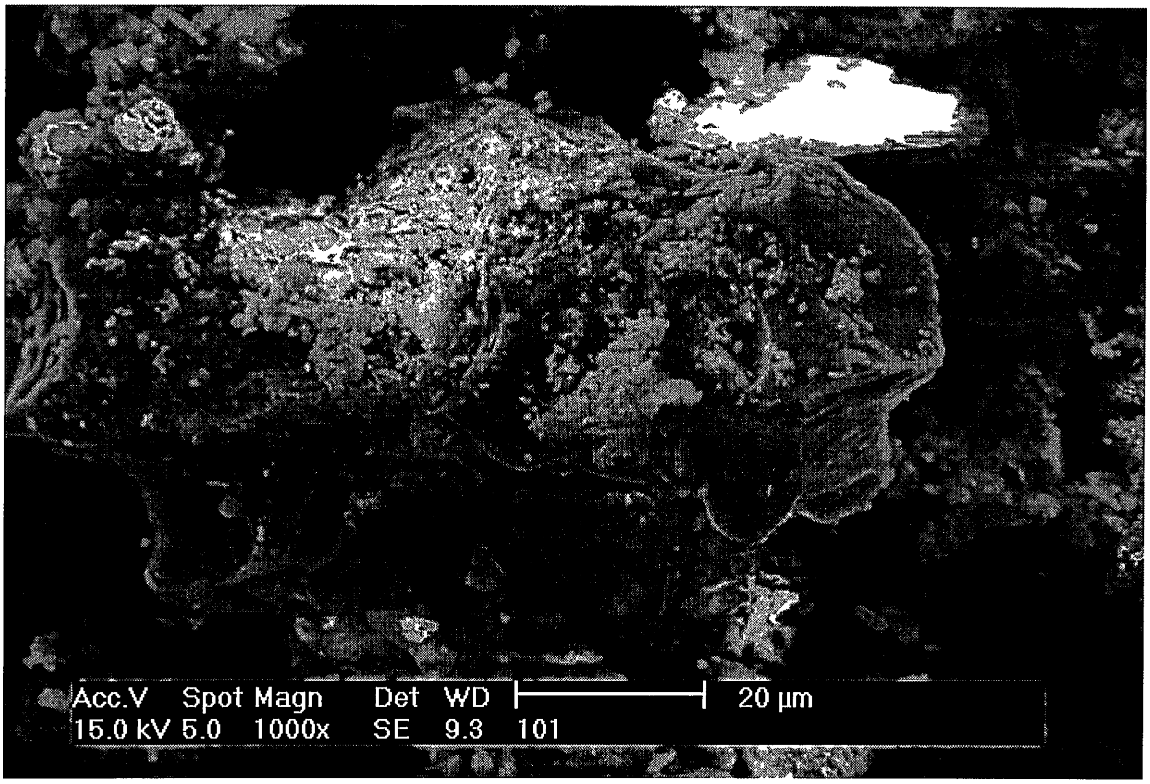


Figure 5. *SEM microphoto of zeolitic fragment from sample 00101.*

Greek diatomite

The three samples of Greek diatomites have been investigated in two steps, first the crushed material (250 my) was investigated, and secondly the surface of the rock sample was investigated. In addition the calcareous diatomite was examined after the calcite was removed with acid. The average amount of calcite in the sample from Samos was estimated to be 70.5%, and the sample from Zakynthos contained 60.7% calcite.

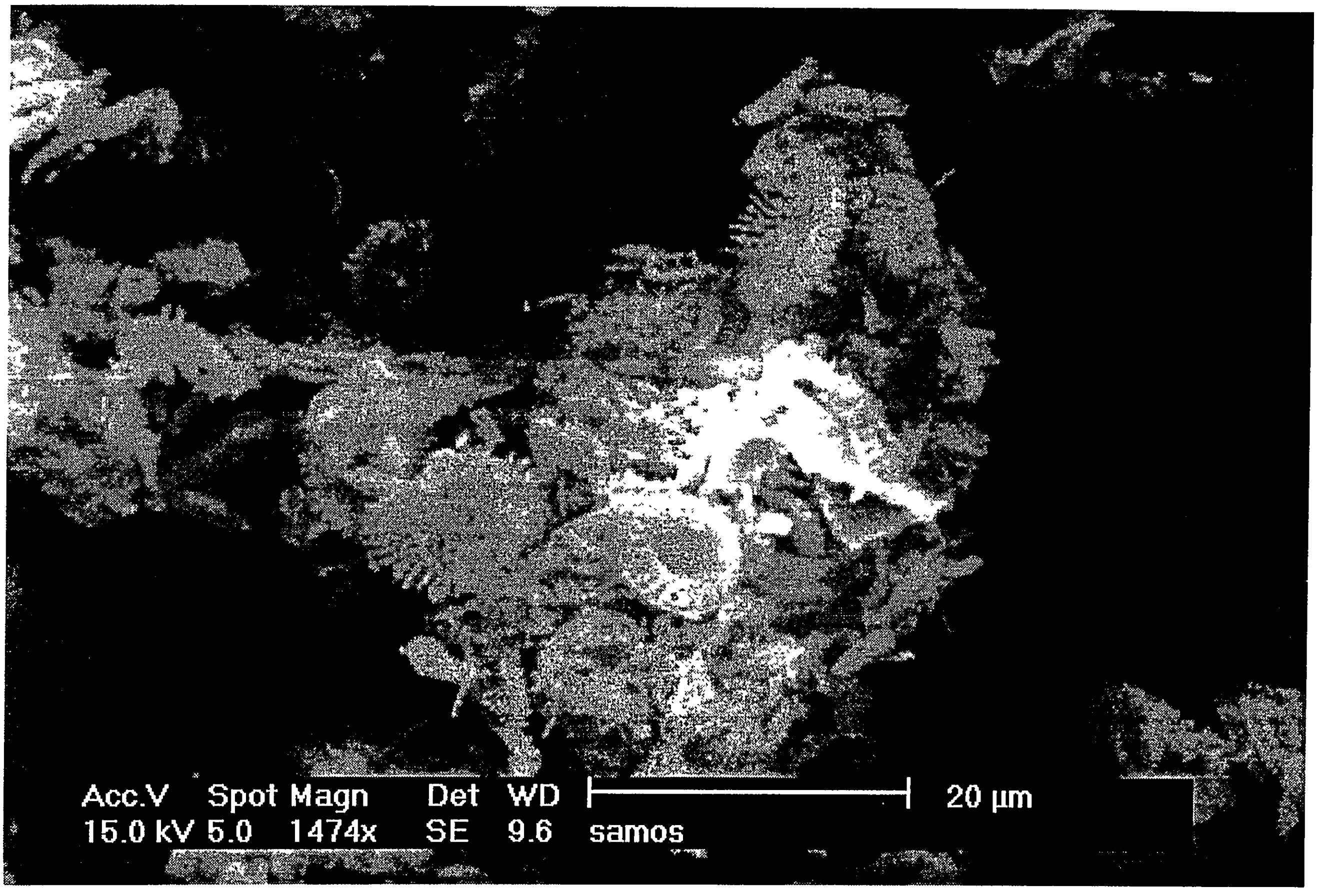


Figure 6. *Diatom skeletons of the Stephanodiscous astraea in the calcareous diatomite from Samos. The calcite was removed prior to this SEM investigation.*

Samos

The diatoms in the calcareous diatomite from Samos consisted mainly of one species, the small (10 my) dish shaped Stephanodiscous astraea (Figs. 6 and 7).

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

Figure 7. *SEM microphoto of the surface of the calcareous diatomite from Samos. Note that calcite had not been removed from this sample prior to this SEM investigation. The siize of the Stephanodiscous is about 10 my.*

Zakynthos

The calcareous diatomite from Zakynthos is more or less similar to the calcareous diatomite from Samos with the Stephanodiscous astraea being the dominant diatom species (Fig. 8). A few skeletons of Actinocyclus sp. have also been recognised (dr. Dave Jutson pers. comm.) (Fig. 9).

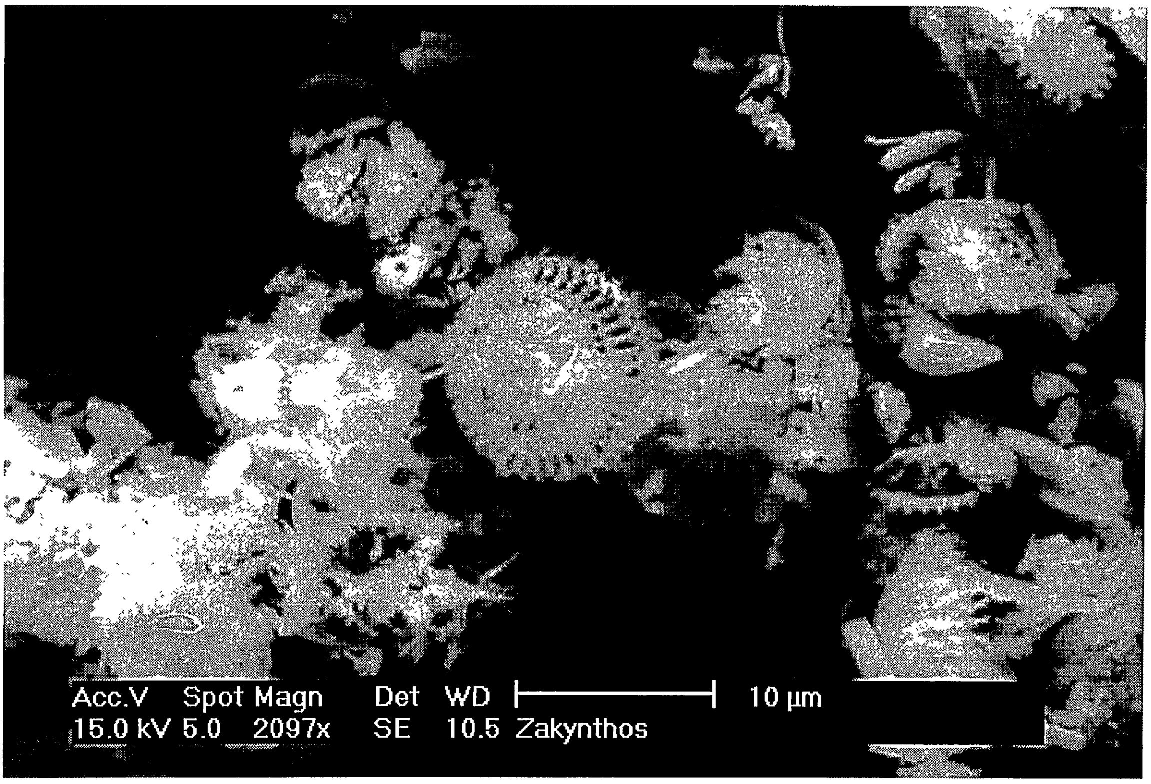


Figure 8. *SEM microphoto of diatoms from the Zakynthos diatomite (sample no. 697). The calcite was removed prior to this SEM investigation.*

Figure 9. *SEM microphoto showing the surface of large diatoms from the Zakynthos sample (Actinocyclus sp.?). Note that calcite had not been removed from this sample prior to this SEM investigation. Photo frame c. 100 my wide.*

Elasson

In the clayey diatomite of Elasson the tube formed diatom Melosia islandica was recognised (Fig. 10), and a number of silico-flaggelate was seen (Fig. 11).

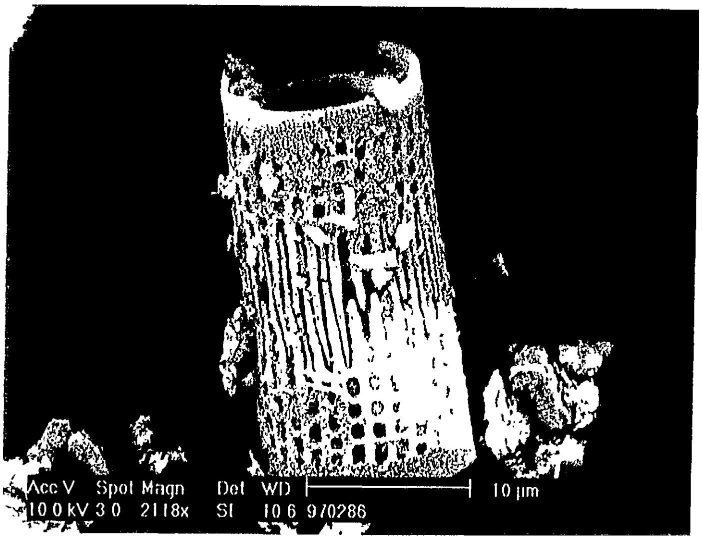


Figure 10. *SEM microphoto of Melosira islandica the Elasson diatomite.*

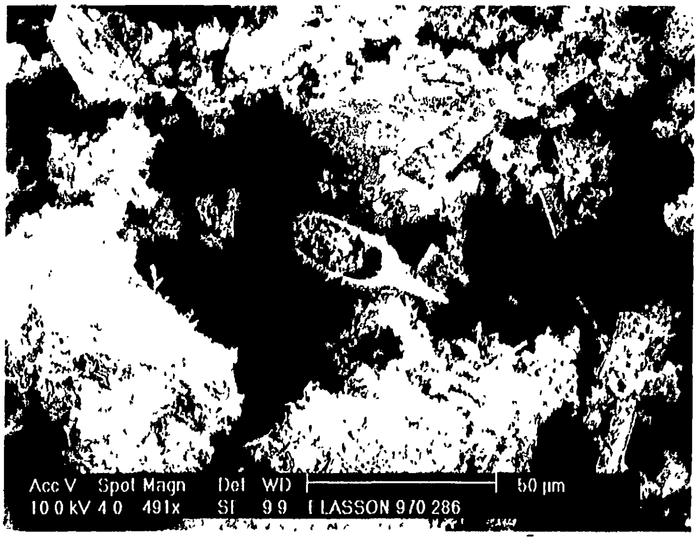


Figure 11. *SEM microphoto of silicoflagellate from the Elasson diatomite.*

DTA-analysis

Methods

The combined DTA -EGA equipment was developed at the British Geological Survey (Morgan, 1977) and is composed of a Stanton -Redcroft 673-4 DTA together with two Analytical Development infrared detectors for water and carbondioxide and a Whittaker electrochemical detector for sulfurdioxide.
The analytical gas was pure grade 40% oxygen in nitrogen at 300ml/min.

Results

Representative diagrams are shown in Figs. 12 - 15.
In the diagram Fig. 12 for sample 00101 an endothermic peak in the DTA curve at approximately 100°C corresponds to the large peak of the water release curve that is due to the water adsorbed on clay minerals. The weak exothermic peak at 200-500°C corresponds to the evolution of carbon dioxide and water and is due to the oxidation of organic matter. The strong exothermic peak at 400-450°C corresponds to the evolution of sulphur dioxide due to oxidation of the pyrite which can be quantified to 0.17% pyrite (Table 5). The slow and small evolution of sulphur dioxide from 750°C till the heating is stopped is due to decomposition of sulphates probably formed during weathering of the pyrite.
In the diagram Fig. 13 for the sample 00115 the amount of pyrite is significantly larger 7.5% (Table 5).
In the diagram for sample 00111 (Fig. 14) the DTA curve shows a small water release at 100°C due to release of adsorbed water. However this diagram is different from diagrams 1 and 2 in that the large water release at 300°C does from the lack of carbon dioxide evolution not correspond to oxidation of organic matter. Instead it must be a release of water from opal.
The same process can be followed in the diagram of sample 00119 (Fig. 15). In this sample, no pyrite can be detected from DTA-EGA .

Sample No	SO_2 curve (°C)	mg	FeS_2 %
00115	331-571	52.2	7.46
00102	396-556	84.7	0.11
00101	362-537	92.3	0.17
00113	352-563	82.9	0.32

Table 5. *The amount of pyrite calculated from DTA-EGA for four of the mo-clay samples.*

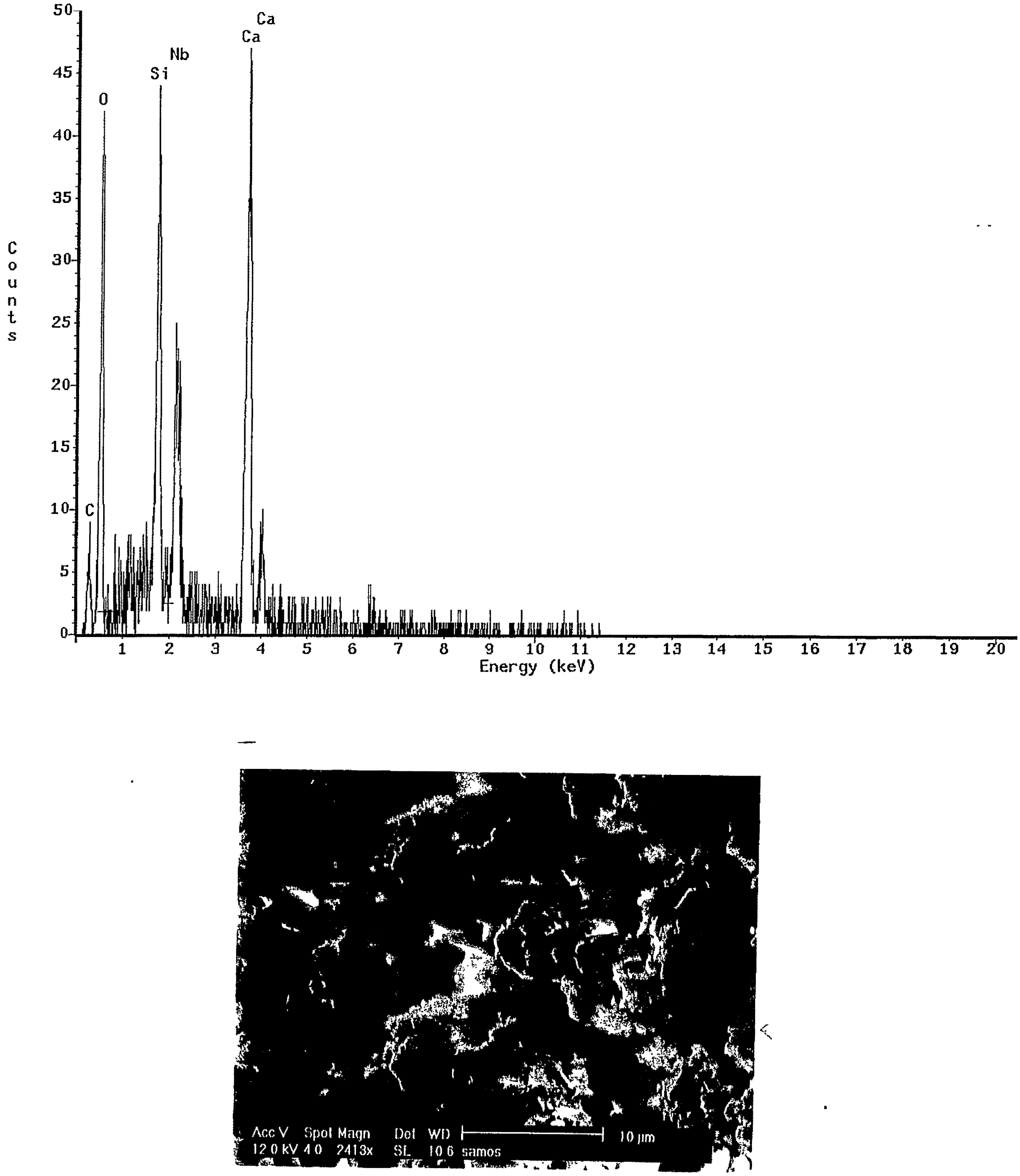


Fig. 11a. *Example of SEM-EDAX analysis of the chemical composition of calcareous diatomite form Samos.*

Figure 12. *DTA-EGA diagram of mo-clay sample 00101.*

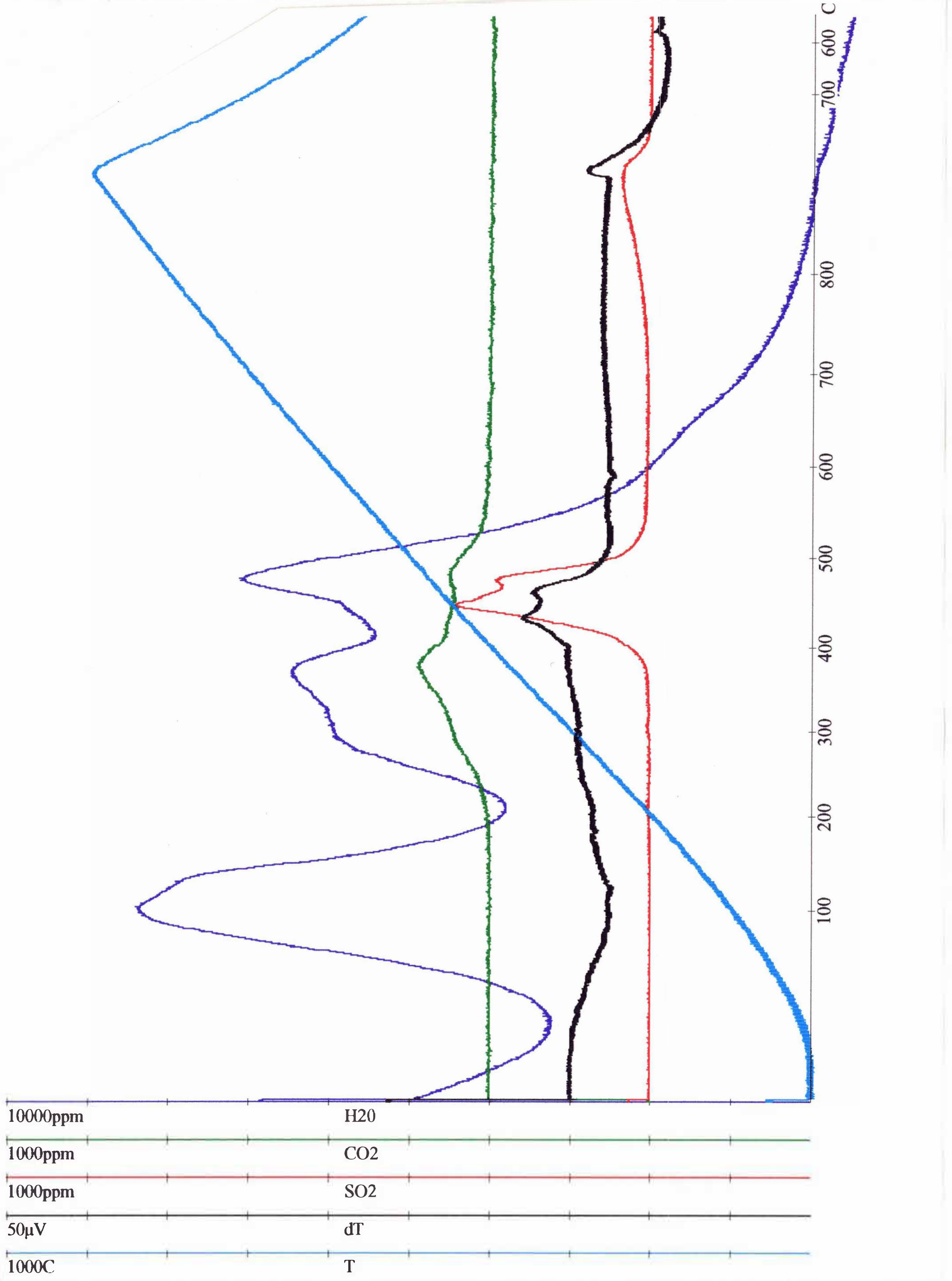


Figure 13. *DTA-EGA diagrams of mo-clay sample 00115.*

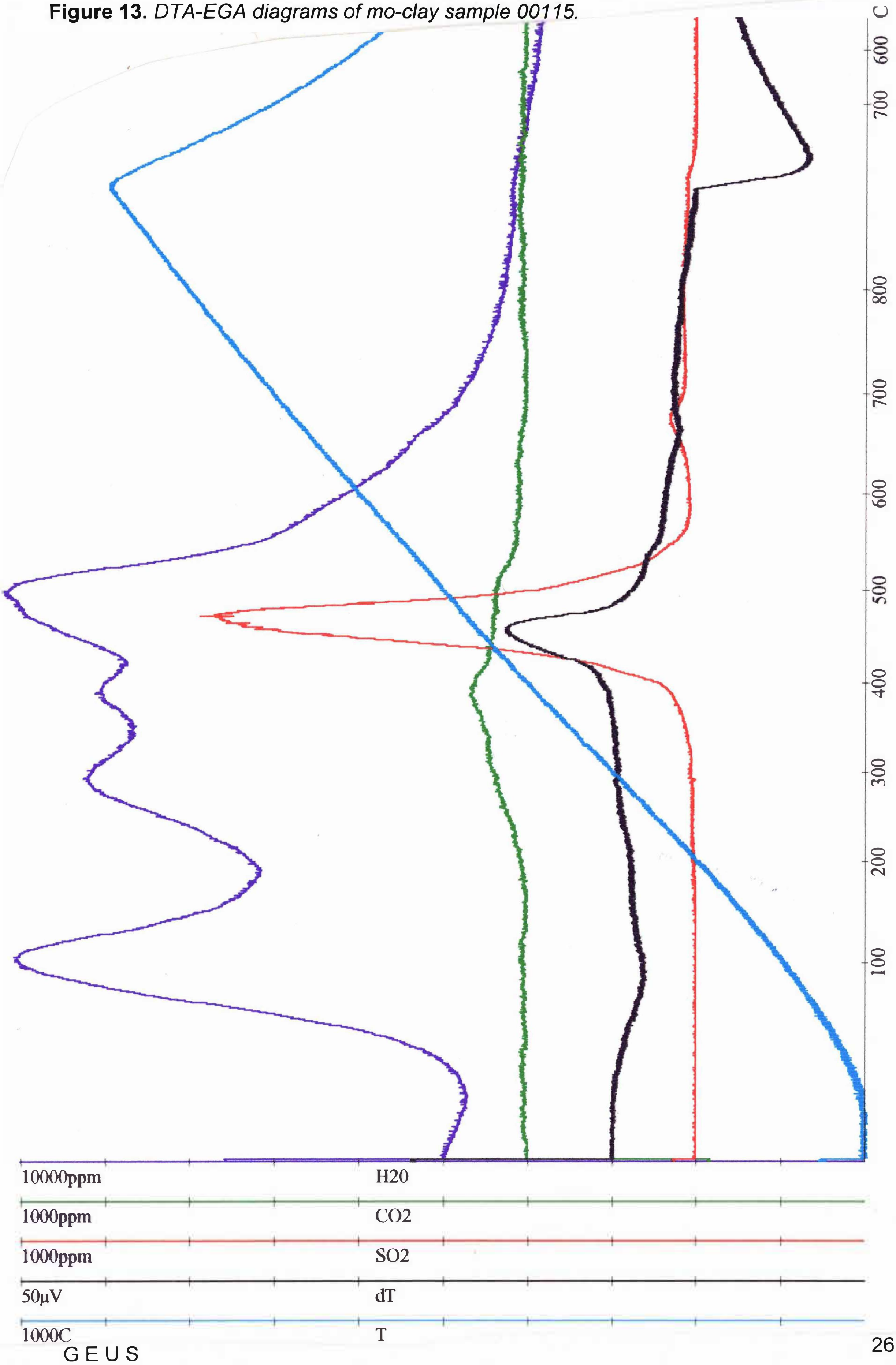


Figure 14. *DTA-EGA diagrams of mo-clay sample 00111.*

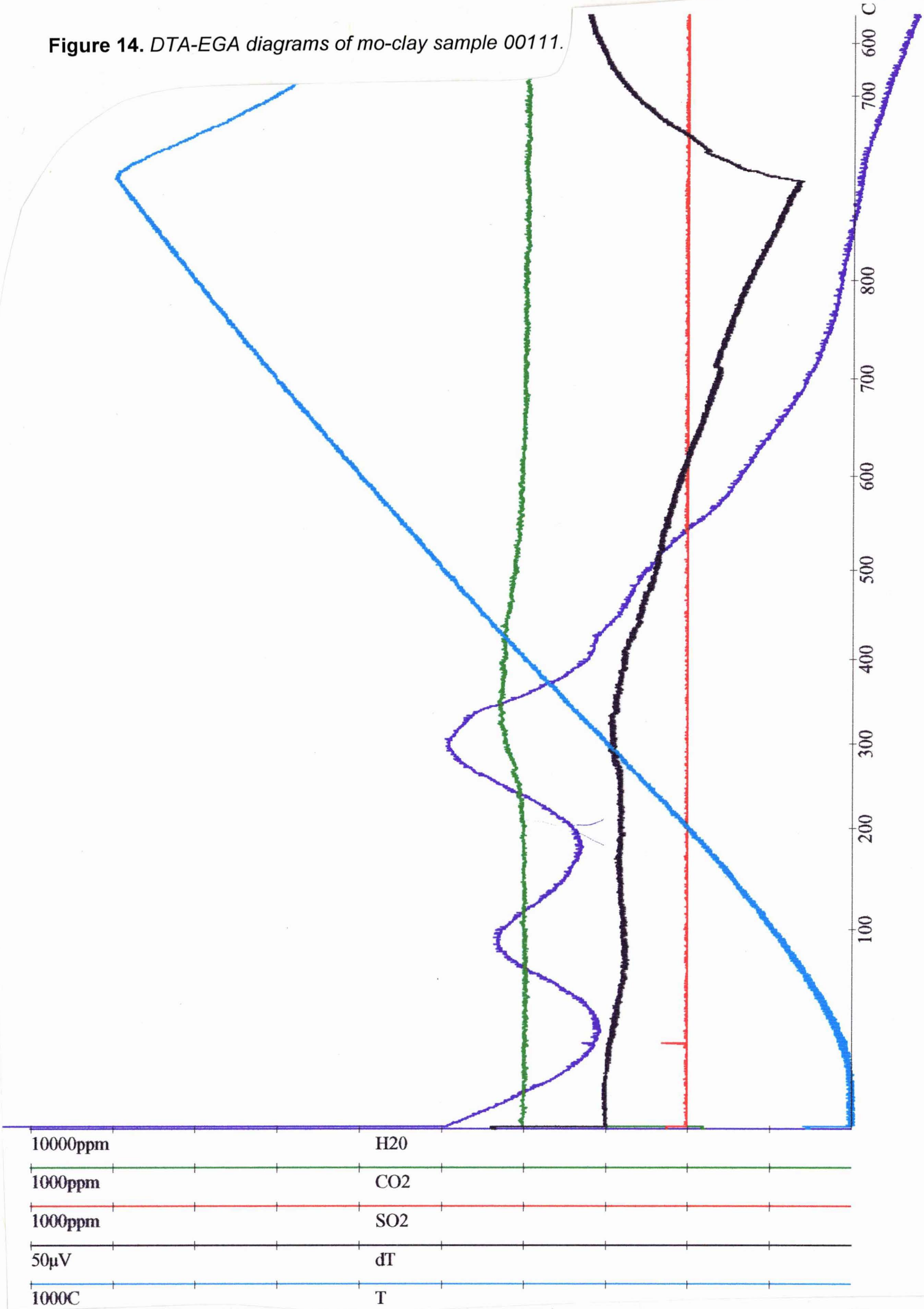
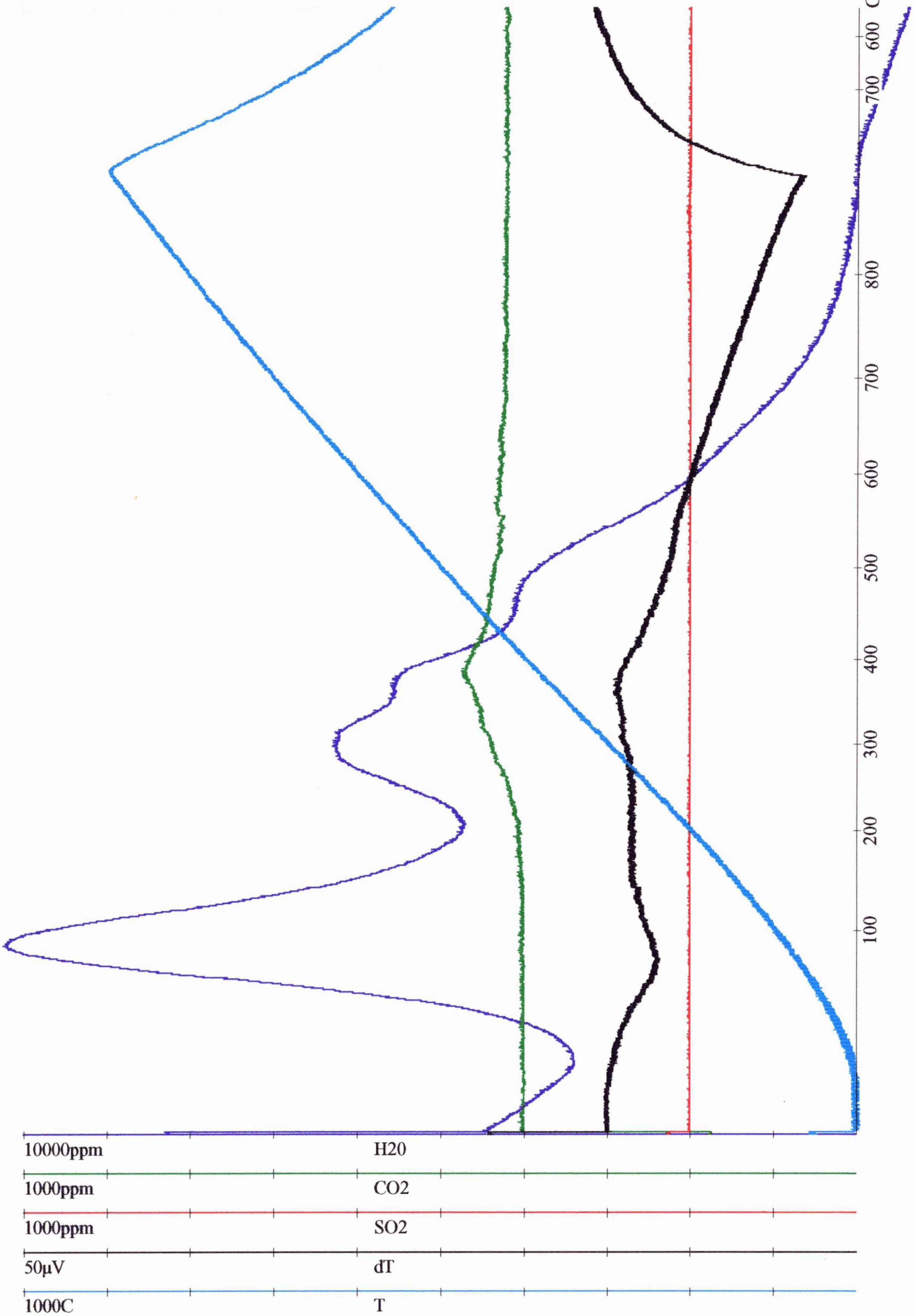


Figure 15. *DTA-EGA diagrams of mo-clay sample 00119.*



Discussion

For the determination of the clayey diatomite we considered the following two steps to be the proper way of progress in the analysis. Powder X-ray diffraction of a randomly oriented specimen provides the overall mineralogical composition of the material. The next important step is to do the detailed investigation of the clay minerals with a specialised clay preparation followed by X-ray diffraction of oriented specimens. This is especially important because the clay properties have a great influence of the behaviour of the material during the processing of the industrial material.

In the preparation of the calcareous diatomite it is well known that the opal is very hard to identify in the powder X-ray diffractogram (M. Stamatakis, pers. comm. 1997). Therefore it is necessary to remove the carbonates through dissolution in order to obtain pure opal skeleton material of the diatoms. The calcite-free residue of the material can be treated in two ways, either the residue can be investigated by X-ray diffraction or the material can be investigated in the SEM.

In our investigation both tests were applied, which we generally recommend for analysis of such materials.

For the further classification the DTA is important for determination of impurities like pyrite and organic material. In addition the DTA can give some indication of the presence of opal, since this method can be applied to all materials irrespectively of degree of crystallinity.

It is in addition important for impure diatomaceous raw materials to know the reactions during heating as most of these materials are used for roasted products and the DTA -EGA actually records the reactions during heating of a small powdered sample.

The SEM investigation reveals the structures of the material. To get the initial information of the structure of the material it is best to investigate the rock sample. In this type of examination the structures of diatom frustules and fine-scale sedimentary lamination can be determined. However, the investigation of samples from which impurities such as calcite have been removed can provide detailed information about the structure of the diatiomites. The small diatoms identified in the calcareous diatomite gave the clue to the opal origin in the samples, and no fragments of big diatom skeletons were observed.

Conclusion

Investigation of impure diatomites have demonstrated that combined chemical dissolution, X-ray diffraction, thermal analysis and scanning electron microscopy have provided an adequate characterisation of the materials. It is not possible to give a simple quantitative composition of diatomaceous material because of the wide range in crystallinity and elementary composition of the constituents.

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