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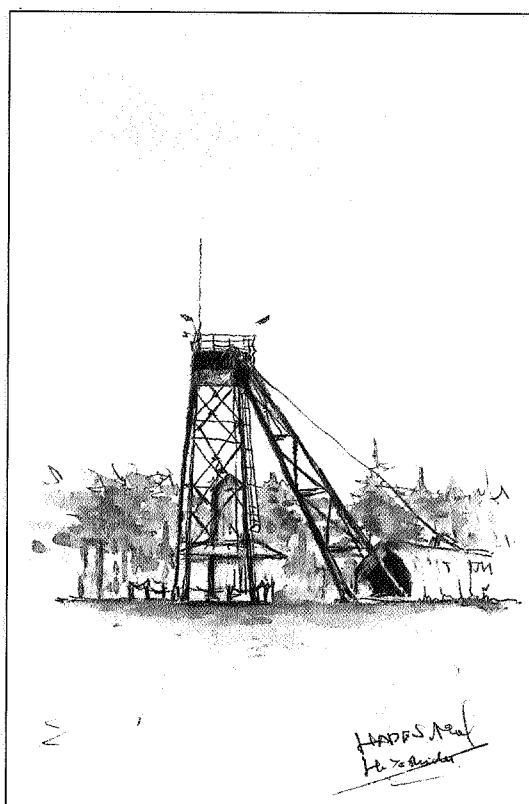
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GEOLOGICAL SURVEY OF BELGIUM
PROFESSIONAL PAPER 2003/1
N. 298

**CHARACTERISTICS
OF THE BOOM CLAY ORGANIC MATTER,
A REVIEW**

Maarten VAN GEET, Norbert MAES, Ann DIERCKX



SERVICE GEOLOGIQUE DE BELGIQUE
BELGISCHE GEOLOGISCHE DIENST



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SSN 0378-0902

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Maarten VAN GEET^{1*}, Norbert MAES¹, Ann DIERCKX²

1. SCK•CEN (Belgian Research Centre for Nuclear Energy), Waste & Disposal Department, Boeretang 200, B-2400 Mol, Belgium

* mvgeet@sckcen.be

2. NIRAS – ONDRAF (Belgian Agency for Radioactive Waste and Enriched Fissile Materials), Kunstlaan 14, B-1210 Brussel, Belgium

(23 pages, 10 figures, 5 tables)

Cover illustration : HADES underground laboratory access shaft, SCK•CEN in Mol.
Aquarel by Hidekazu Yoshida (°1962, Noveoka, Kyushu Island, Japan), geologist at Chubu Works, Power Reactor and Nuclear Fuel Corporation, PNC, Japan. Joined HADES research team at Mol from August 1987 until March 1990.

Comité éditorial: L. Dejonghe, P. Laga
Secrétaire de rédaction: M. Duser
Service Géologique de Belgique
Rue Jenner, 13 - 1000 Bruxelles

Redactieraad: L. Dejonghe, P. Laga
Redactiesecretaris: M. Duser
Belgische Geologische Dienst
Jennerstraat 13, 1000 Brussel

ISSN 0378-0902

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Guide for authors : see website Geologica Belgica (<http://www.ulg.ac.be/geolsed/GB>)

Editeur responsable: Daniel CAHEN
Institut royal des Sciences
naturelles de Belgique
29, rue Vautier
B-1000 Bruxelles

Verantwoordelijke uitgever: Daniel CAHEN
Koninklijk Belgisch
Instituut voor
Natuurwetenschappen
Vautierstraat 29
B-1000 Brussel

Dépôt légal: D 2003/0880/1

Wettelijk depot: D 2003/0880/1

Printed by : Federal Public Service Economy, SMEs, Selfemployed and Energy

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CHARACTERISTICS OF THE BOOM CLAY ORGANIC MATTER, A REVIEW

Abstract. This report gives an overview of all literature data available in 2002 on the organic matter present within Boom Clay. The report is split up into two parts. Part one discusses the data on the immobile organic matter. Literature data on this fraction comprises petrographical and chemical analyses. The second part discusses the literature on the mobile organic fraction. Here, it concerns very recent publications that focus on the use of new techniques to characterise this water dissolved organic fraction.

Keywords: organic matter, Boom Clay, Mol, Belgium

1. INTRODUCTION

Because of its specific characteristics Boom Clay is considered for the underground storage of nuclear waste in Belgium. Many research topics are focussed on the migration of radionuclides within this Boom Clay material and it has been stated that organic matter can have an important effect on the behaviour of radionuclides. Moreover, the radioactive waste produces quite some heat, which might affect the organic matter resulting in gas and bitumen generation. Finally, the diagenetic evolution of the organic matter present can provide information on the long-term behaviour of the Boom Clay, an essential topic concerning nuclear waste disposal. Therefore a thorough characterisation of the organic matter present within the Boom Clay is necessary.

Some data on this organic matter are already available, but much has to be done yet. This report aims to give an overview of the available literature data up to 2002.

2. NON-MOBILE ORGANIC MATTER

Most research already performed was focussed on the characterisation of the non-mobile fraction of the Boom Clay organic matter. This research can be divided into three major topics. The first one is a petrographical study of the present organic fragments and the interrelation of the organic matter and the surrounding clay. The second one is a bulk geochemical analysis of the organic matter. The third topic is focussed on the molecular organic geochemistry of the organic matter. It should be noted that most of this work was performed on samples from the outcrop region, except for the studies of Deniau *et al.* (2001) and Van Geet (2002). As a consequence, information on the upper part of the Putte member is missing, as this is not outcropping, and oxidation phenomena might have influenced the composition of the organic matter (Landais *et al.*, 1984).

Component	Interpretation
Poorly evolved material	Algae remnants Badly conserved liptinite
Liptinite	Vegetal resins and waxes
Inertinite (strongly evolved)	Residue of wood fire
Vitrinite	Cellular tissue of plants
Coal fragments	Coal layers

Table 1. Petrographically observed phytoclasts in Boom Clay and their interpretation (Vandenberghe, 1978).

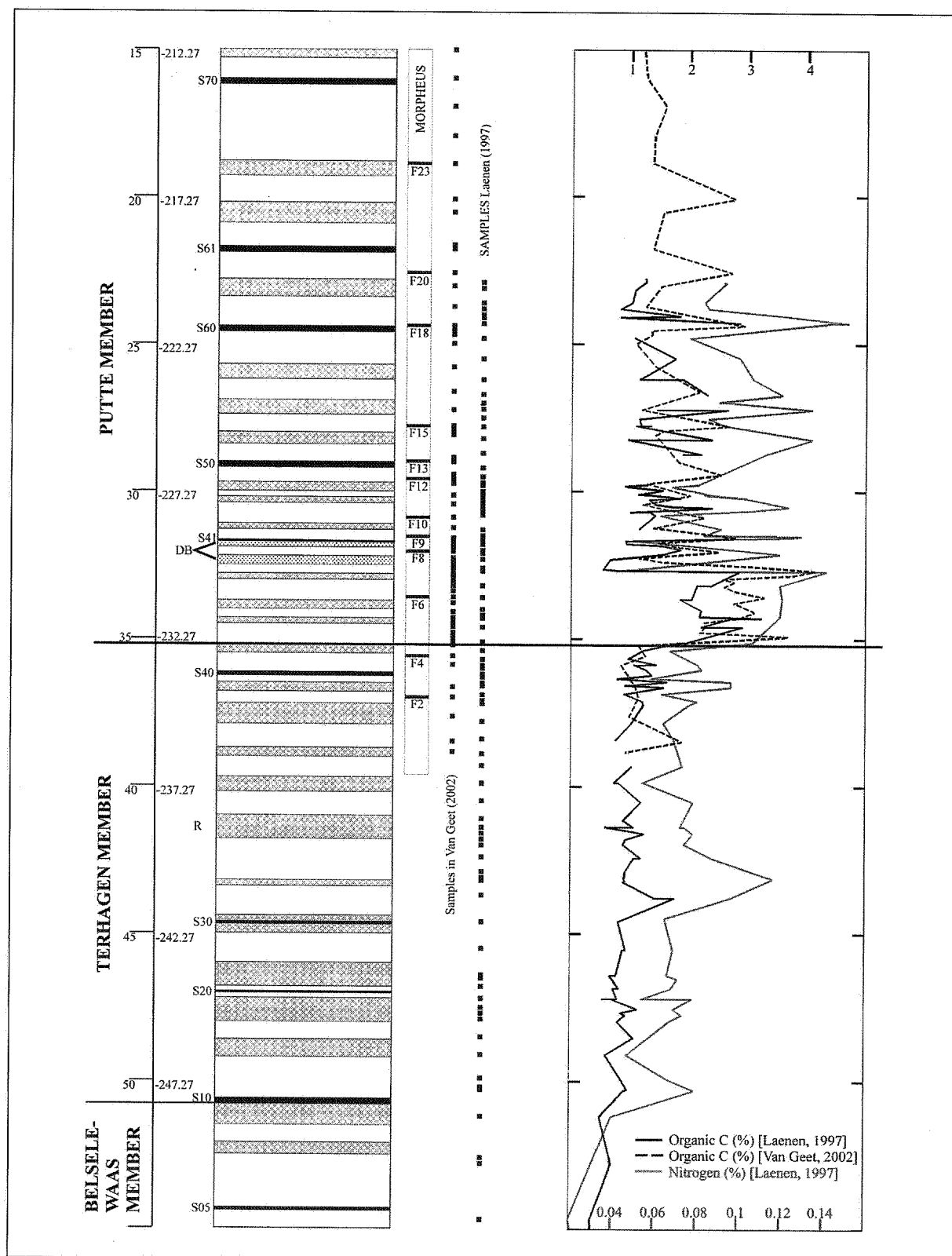


Figure 1. Stratigraphical distribution of the organic carbon and nitrogen through the Boom Clay section, marking the difference at the Putte/Terhagen boundary (Laenen, 1997 and Van Geet, 2002). Laenen studied outcrop samples, while the samples in the study of Van Geet originate from a cored interval starting from the underground research laboratory, Hades (Mol, Belgium). The stratigraphic positions of the filters of the MORPHEUS piezometer are indicated as well.

2.1. Petrography

Vandenberghe (1978) performed some petrography on the phytoclast fragments present in the Boom Clay. Five groups of fragments are distinguished and are summarised in Table 1.

Based on these petrographical data, the phytoclast fragments are divided in three groups, namely primary allochthonous grains, secondary allochthonous grains and coal fragments. The vitrinite reflectivity of the primary allochthonous particles ($R_0=0.2-0.83\%$) points towards an initial diagenetic stage with methane development, corresponding to a lignitic rank. The reflectivity of the secondary allochthonous particles ranges between 1.5 and 1.6%. The coal fragments have reflectivities ranging between 0.5 and 1.5%, pointing towards an origin from a Palaeozoic rock. From all potential source rocks, the British Coals have similar characteristics. During the Rupelian, the British coals were outcropping near the coast of what is now North England, which acted as a source area for the Boom Clay.

Deniau *et al.* (2001) studied a sample of the underground research laboratory and performed some scanning – and transmission electron microscopy of the organic matter of the Boom Clay. The SEM study reveals that the Boom Clay organic matter is mainly composed of aggregates of various sizes, ranging from 30 to 200 μm , without well-defined shapes. Some minor amounts of well-preserved terrestrial material are found as well. Back-scatter SEM (BSEM) of polished sections showed that the organic matter is mainly concentrated in small particles (3 to 10 μm) with regular outlines within the clay matrix. Some of these particles show a systematic association with pyrite framboids. A few structureless particles of 50 to 150 μm , but with less regular outlines interfinger with the mineral matrix. These might be assigned as faecal pellets and/or jellified terrestrial organic matter. However, the SEM studies show no tight association between the organic matter and the clay minerals. TEM observations showed that the Boom Clay organic matter is mainly amorphous. Two types are distinguished, namely granular and homogeneous. Some minor amounts of lamellar structures corresponding to cell walls inherited from biological precursors are detected in the kerogen. Neither regular organo-mineral organisation, nor a thin coating of mineral grains by organic matter is observed.

2.2. Bulk Geochemical analyses

Bulk organic geochemistry of the Boom Clay organic matter points towards a marked difference between the Putte member and the Terhagen and Belsele-Waas members concerning their C_{org} and N contents, as illustrated in Figure 1 (Laenen, 1997; Van Geet, 2002). Vandenberghe (1978) describes a C/N ratio varying between 5 and 23.8 through the Boom Clay. Nitrogen-rich OM originates from marine matter, while N-poor OM has a terrestrial origin. The measured range indicates at least two origins of OM input, namely a marine and a terrestrial input. Moreover, he concluded that the C/N ratio is increasing together with the C_{org} content. Consequently, the increase in C_{org} is explained as an increase of

	Tmax [°C]		HI [mg HC/g TOC]	
	Bulk samples	Isolated kerogen	Bulk samples	Isolated kerogen
Griffault <i>et al</i> (1996).	418 \pm 4	418 \pm 4	69.4 \pm 0.9	290 – 330
Laenen (1997)	358 – 429 mean = 416	-	19 – 181 mean = 92	-
Deniau <i>et al.</i> (2001)	425	414	120	300
Van Geet (2002)	418-428 mean = 422	-	50 – 283 mean = 139	-

Table 2. Comparison of the Rock-Eval analyses data of four studies.

terrestrial input, although high C/N ratios might also point towards a strong bacterial reworking of organic matter (Laenen, 1997). The conclusion of an increase of terrestrial input was consistent with the observation that phytoclasts (terrestrial plant fragments) are more concentrated in the black layers (rich in C_{org}) of the Boom Clay.

Laenen (1997) and Van Geet (2002) also performed Rock-Eval analyses to infer information on the amount of already produced bitumen (S_1), the amount of pyrolysable kerogen (S_2) and the level of maturation. A rearrangement of the data allows deducing the origin of the organic matter and maybe some first information on the diagenetic evolution path by means of the plot of the Oxygen index versus Hydrogen index (OI-HI plot). Although this Rock-Eval technique might suffer matrix effects, especially with clays, the studies of Laenen (1997) and Van Geet (2002) show this is negligible. However, other studies (Griffault *et al.*, 1996 and Deniau *et al.*, 2001) suggest some matrix effects, namely an underestimation of HI and an overestimation of T_{max} . The study of Deniau *et al.* is limited to one sample and the study of Griffault is limited to 5 samples coming from the underground research laboratory, Hades (Mol, Belgium) and thus are additional samples compared to the outcrop samples used by Laenen and the cored interval from Hades used by Van Geet. All studies obtain similar results of T_{max} , indicating a quite homogeneous index of maturity throughout the section, but different results on HI, which might be related to different sources of organic matter and not necessarily due to matrix effects (Tab. 2).

The stratigraphical distribution given in Laenen (1997) shows that the S_2 value slightly increases from the Belsele-Waas member up to the Terhagen/Putte boundary. Above it, the mean value and variance is increased (Putte member: $S_2 = 1.76 \pm 1.42$ and Terhagen member: $S_2 = 0.74 \pm 0.49$). The HI and OI values mirror each other in the stratigraphic distribution. In immature sediments, like the Boom Clay, the HI/OI index is chiefly a function of the degradation and type of organic matter. The average Boom Clay value of 1.08 ± 0.56 is low and points towards a large contribution of inert organic matter or towards a strong oxidative degradation. From the HI – OI plot (Fig. 2) it is clear that the Boom Clay data plot near the OI-axis, which might point towards a mixture of type III and type IV kerogens. The probable source of a type IV kerogen is a strongly oxidised, land derived organic matter reworked from older sediments. A type III kerogen is believed to originate from higher plants. However, apart from this mixing it might be possible to explain the data by oxidation of a type III and/or a type II kerogen, which is supported by a plot of HI – T_{max} (Fig. 2). Consequently, the Boom Clay organic matter probably originates a mixture of type II and type III kerogen derived from algae and higher plants. The HI – OI plot thus indicates strong oxic oxidation.

Due to a correlation of TOC and HI, it is suggested that organic-rich layers have the highest relative abundance of type II kerogen. Moreover, the pyrolysable oxygen compounds (S_3) increases as a function of TOC. Consequently, the black layers have the highest proportional contributions of type II organic matter, but at the same time the highest absolute concentrations of both pools of organic matter. The rise in flux of organic matter near the maximum flooding surfaces (mfs) is mainly due to an increase in the amount of type II kerogen. The concentration of organic matter of mixed continental and marine origin near mfs may be explained by the flooding of coastal plains, leading to the destruction of coastal soils, peat bogs and vegetation, resulting in higher fluxes of continental organic matter. The higher amounts of authigenic organic matter in these layers can be either due to a higher primary production caused by an increase of nutrients by the destruction of coastal soils, or due to a better preservation, caused by a change in redox conditions by a larger input of continental organic matter or by deposition of finer grained beds. The septaria layers contain more type II kerogen of marine origin.

Similar results were found in the study of Van Geet (2002). The stratigraphical distribution shows a sudden increase at Terhagen-Putte boundary (from 1.21 to 3.39 mean values) for the S_2 value. However, the HI/OI ratio is here 2.74, which is much higher compared to the study of Laenen and points towards less oxidative degradation. This might be related to the different sampling (clay pit versus fresh borehole). The detailed study of Van Geet also showed the presence of type II, III and IV kerogen. The type II kerogen seemed, however, mostly present in the organic-rich layers (TOC values above 2%). The additional information from the study of Deniau *et al.* (2001) points towards a kerogen of type II origin.

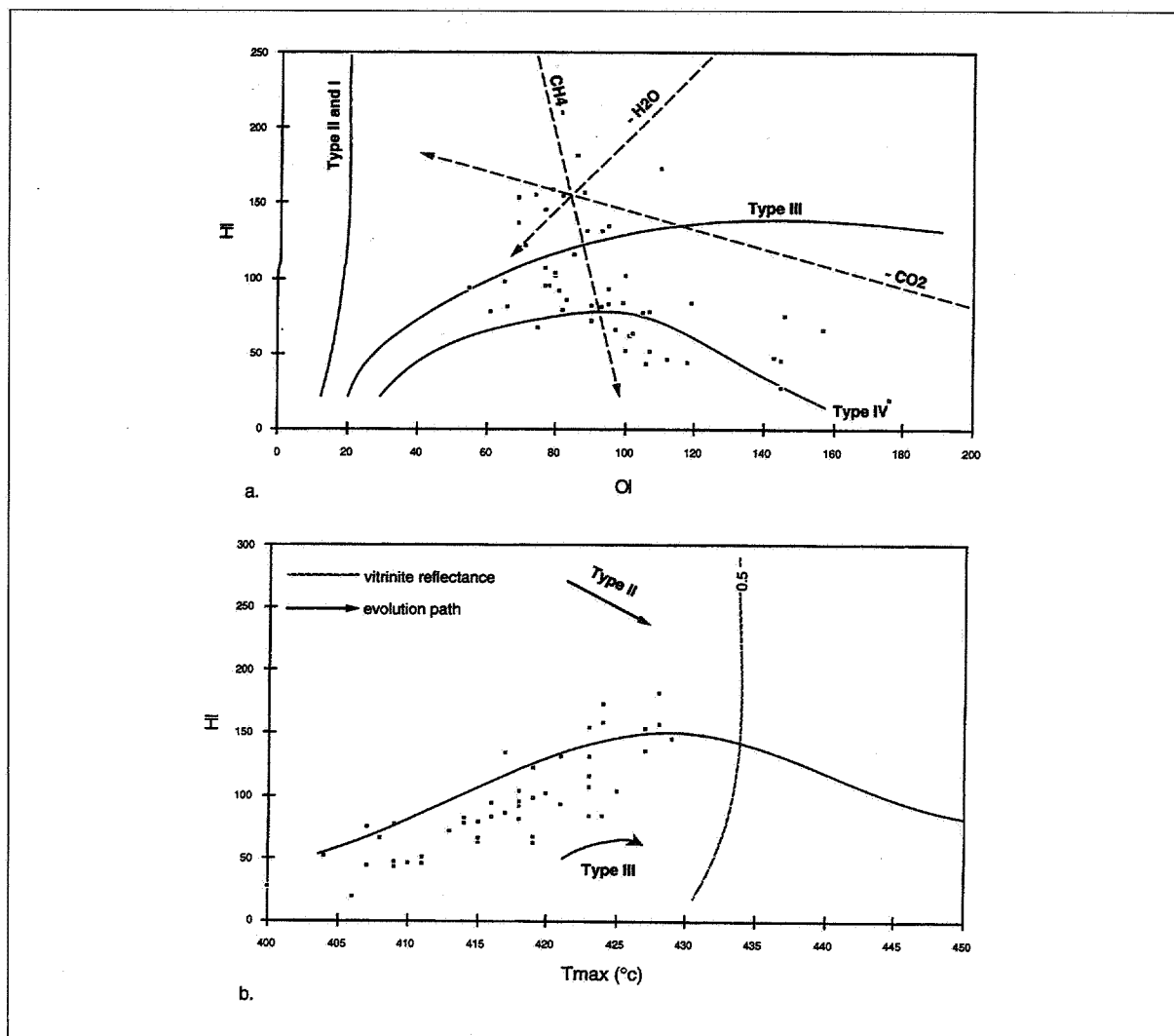


Figure 2. a. Tissot classification of the kerogen of the Boom Clay. The bold lines mark maturation pathways for the different types of kerogen, the dashed lines indicate the effects of the loss of H_2O , CO_2 and CH_4 . b. Plot of HI versus T_{max} . The bold line marks the boundary between the fields of type III and type II kerogens (Laenen, 1997).

The T_{max} values of about 420°C are typical for immature sediment (Tab. 2). Immature type II and type III kerogens have average T_{max} values between 425° and 430°C , but values of 400°C have been reported as well. Experimental studies of Landais *et al.* (1984) show that a bad preservation of samples (oxidation) leads towards higher T_{max} values. The quite low T_{max} values and the similarity with the samples from the underground laboratory, where the effects of oxidation are at least minimal, show that the effects of oxidation are negligible, even for the study of Laenen (1997).

Some spectroscopic analyses of the isolated kerogen have been performed as well, indicating considerable contributions of aliphatic chains (long polymethylenic chains), aromatic and olefinic carbons, hydroxyl groups, non-conjugated carboxyl groups and some C-O and/or C-N groups (Deniau *et al.*, 2001).

2.3. Molecular organic geochemistry

Next to these bulk analyses, a detailed molecular composition of the bitumen (fraction of organic matter, which is soluble in organic solvents) has been established for samples from the Boom Clay. An overview of the encountered molecules and their interpretation is given in Table 3.

reference	Component	Range	Max	Interpretation
Kiriakoulakis (1994)	n-alkanes	<C22		Marine origin
	n-alkanes		C16 C18	Origin from all organisms
	n-alkanes	>C22		Terrestrial origin
	Pristane Phytane Norpristane			Autophototrophical organisms and/or archaeobacteria
	Mono-unsaturated fatty acids		C16:1 C18:1	Microbial origin
	Branched components: iso- and anteiso carboxylic acids	C15-17		Anaerobic sulphate reducing bacteria
	Isoprenoid alkane		C30	Methanogenic archaeobacteria
	Hopanes and hopenes			Bacterial origin
Griffault et al. 1996	n-alkanes	C27-29		Terrestrial origin
	n-alkenes			
	aromatics			
	Hopanoids			Bacterial origin
	n-alkylbenzene	C19-20		Terrestrial origin and immature sediment
Laenen (1997)	n-alkanes	C21-33	C31	Higher plant waxes
	n-alkanes	C11-21	C17	Bacterial or algal origin
	Regular steranes	C27-29	C29	Higher plants origin
	Diasterenes			Acidic conditions
	Regular sterenes	C27-29		Low maturity
	Triaromatic steroids	C26-28		High maturity (reworking or progressive aromatisation in immature sediments)
	Steradienes	C27-29	All similar	Immature sediments and higher plants origin
	Aliphatic hopane	C27-33	C31	Bacterial origin and low maturity (configuration)
	Demethylated hopanes			Biodegradation
	Aliphatic HPPT			Angiospermal origin
	Aliphatic di- and sesquiterpenoids			Coal or gymnospermal origin
	Aromatic di- and sesquiterpenoids			Gymnospermal origin and low maturity
	PAH			Coal fragments and/or higher plants
	Chromans			Marine origin
Deniau et al. (2001)	n-alkanes	C13-30	C18	Especially marine origin
	Iso- and anteiso alkanes	C15-25	C17	Bacterial origin
	Hopanes	C27-31	C27	Bacterial origin
	PAH up to 4 rings			Strong resistant algal bio macromolecules with polyaromatic parts, selectively preserved in kerogen
	Saturated fatty acids	C12-28	C16 C18	Micro-algal, marine organisms, bacterial
	Long chain fatty acids	C20+		Terrestrial origin
	Branched acids	C14-17		Bacterial origin
	n-alkanols	C10-20	C16	Green algae
	n-alkanols	>C20		Higher plant waxes

Table 3. Overview of the recognised and easily interpretable organic molecules occurring within the Boom Clay as found in literature.

2.3.1. Source parameters

These data point towards a very homogeneous composition of the aliphatic fraction. The aromatic components seem to depend on the TOC. As all the compounds show a similar distribution throughout the section, a homogeneous composition of the organic matter throughout the section is supposed and indicates only small variations of sources of organic matter and diagenetic processes throughout the section.

According to Laenen (1997), the aliphatic fraction can be subdivided into 6 classes (hopanoids, sesqui- and diterpenoids, HPPT and A-ring degraded lupanoids, steranes, diasterenes, sterenes). The concentration of these six classes together with 3 classes of acyclic structures shows little variation. A maximum concentration can be found in the Lower Putte member. A factor analysis of this fraction distinguishes three groups of molecules. The first group is related to angiospermal material. This material has a terrestrial origin, probably coming from the Brabant Massif, south of the sedimentation basin of the Boom Clay (Fig. 3). This group also contains some molecules of autochthonous bacterial origin that probably lived from the angiospermal material. A second group is related to gymnospermal resins. The concentration of this group shows a positive correlation with TOC and consequently, high values of TOC are the result of an increase in supply of gymnospermal material. However, the increase in TOC might also be related with acidic early diagenetic pore water conditions. A third and last group contains autochthonous organic matter. The stratigraphical distribution of this group is related to grain size. This autochthonous material is most abundant in clay layers and on a larger scale shows an increase towards maximum flooding surfaces (mfs). The Boom Clay beneath the Putte/Terhagen boundary has low con-

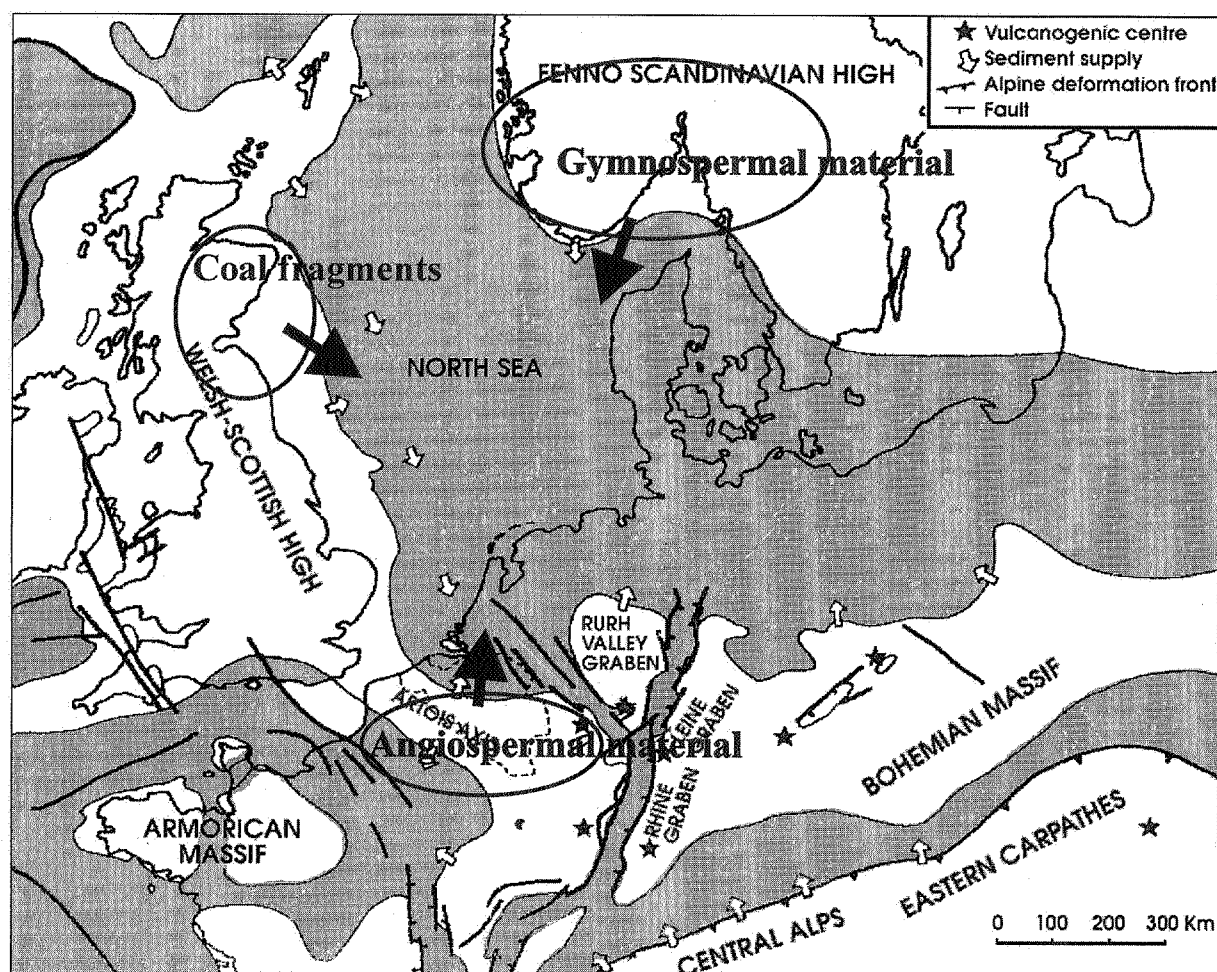


Figure 3. Palaeogeographical scheme of the Lower Oligocene (after Wouters & Vandenberghe, 1994) together with the sources of allochthonous OM present within the Boom Clay as interpreted by Laenen (1997).

centrations of gymnospermal material, which is limited to some black layers, and the organic matter in this part mostly consists of HPPT and ferenes. The ratio of n-alkanes with 31 and 17 carbon atoms (C_{31}/C_{17}) has a mean value of 6.6 in the Putte member and a mean value of 16.8 in the Terhagen member. This would point to more marine conditions in the Putte member and more terrestrial origin in the Terhagen member.

A factor analysis of the 14 aromatic compounds subdivides them in three groups (Laenen, 1997). A first group originates from higher plants. Once again indications are found that bacteria mainly lived on angiospermal material. A second group originates from gymnosperms. This group shows a correlation with TOC. As the highest concentrations are found in the Kruibeke quarry, this gymnospermal material is found deeper in the basin, indicating that an allochthonous, northern source must have been present (Fig. 3). A third group consists of thiophenes, which are related with sulphate reduction. Once again a correlation with TOC is found, so that organic-rich intervals must have been deposited during intense sulphate reduction. A sharp increase of the thiophenes above the Putte/Terhagen boundary points to a reduced oxygenation of the sediment. Moreover, during the sedimentation of the organic- and sulphur-rich sediments a better preservation of the organic matter is taking place.

The sample from the underground laboratory studied by Deniau *et al.* (2001) contains considerable amounts of hopanes, indicating a bacterial origin, and short chain fatty acids, indicating an autochthonous marine origin. The amount of long chain fatty acids, originating from terrestrial organic matter, is quite low in this sample. Moreover, the distribution of the n-alkanols in this sample suggest a considerable input of green algae, but only a minor input from higher plant waxes. This contradicts with the observations of Laenen (1997), but might be related to the stratigraphical distribution of the organic matter composition and would indicate a more marine input towards the top of the Putte member.

Many carbonate concretions are found within the Boom Clay at several distinct layers (Vandenberghe, 1978). These concretions are early diagenetic in nature (De Craen, 1998). A reconnaissance study of Kiriakoulakis *et al.* (1994) investigated possible differences in the organic matter within a Boom Clay concretion of S41 (one such distinct layer, see Fig. 1) and of its surrounding clay. Comparable with the study of Laenen (1997) the input of organic matter showed important amounts from terrestrial origin together with some limited autochthonous marine organic matter. Two possible explanations are given, namely a larger terrestrial input or a faster degradation of the autochthonous components (Haddad *et al.*, 1991). However, no significant difference between the clay and concretion material was found.

2.3.2. Maturity

All maturity parameters show a low maturity of the Boom Clay and do not show any variation throughout the section (Laenen, 1997). PolyAromaticHydrocarbons (PAH) normally are not present in immature sediments because they are formed by thermal maturation, although some may be originating from diagenesis and wood fires, etc. Some PAH-compounds present in the Boom Clay can only originate from highly mature organic matter and in the case of the Boom Clay probably come from coal fragments from the British Coalfields.

The study of Kiriakoulakis *et al.* (1994) also concludes a low maturity of the Boom Clay organic matter as for some components, like steranes and hopanes, the original biological stereo chemical configuration is still preserved.

2.3.3. Preservation and diagenesis

The presence of gymnospermal molecules coincides with acidic pore water conditions during early diagenesis (Laenen, 1997). All organic-rich layers seem to have had more acidic pore water conditions during early diagenesis, which might be the result of produced organic acids by aerobical bacterial degradation. The sulphate reduction was high, probably exceeded pyrite formation, during deposition of organic-rich layers. The ratio of two specific components (pristane/phytane) is high and quite con-

stant throughout the section, which shows that no suboxic but rather oxic water conditions were present during sedimentation of organic-rich layers. This means that only small changes in redox conditions took place between the sedimentation of the Terhagen and Putte member or that different input sources of these molecules (pristane and/or phytane) were present. Note, however, that Kiriakoulakis *et al.* (1994), and references therein, state that this pristane/phytane ratio is not recommended for low maturity samples.

Biodegradation from aerobic microbial activity might seriously hamper the interpretation of molecular organic geochemistry. In the Boom Clay section only little amounts of biodegraded molecules were found. Moreover, high concentrations of some other molecules (like n-alkanes) prove that hardly any biodegradation did occur. The found biodegraded molecules most probably come from a degraded source, like the reworking of older immature sediment, and have the same stratigraphical distribution as the angiospermal material.

As mentioned the sample from the underground laboratory contains considerable amounts of fatty acids, which are used as an alteration index as they are sensitive to microbial and physico-chemical degradation. As unsaturated fatty acids, which are the most reactive, are still present a low degree of alteration can be deduced (Deniau *et al.*, 2001). This indicates very early incorporation into the kerogen or efficient protection by organic macromolecules or by the mineral matrix. Nitrogen containing compounds, probably originating from proteins, are observed as well, also indicating a low degree of alteration. Concerning the general formation pathway of the kerogen, four possible pathways are studied. A natural sulphurisation was at most a minor preservation for the Boom Clay organic matter as the organic sulphur content decreases during pyrolysis. A selective preservation might have been important as the Boom Clay organic matter has a rather high aliphaticity. However, the morphological study reveals a predominance of amorphous organic matter, showing that the selective preservation did not play a major role. The third and fourth preservation pathways are degradation-recondensation and mineral protection. Both mechanisms result in similar observations of nanoscopically amorphous organic matter, as is the case in the Boom Clay (see petrography). As, however, no close interrelation between organic matter and clay minerals exists, the degradation-recondensation pathway is believed the main preservation pathway for the Boom Clay organic matter. A recently proposed preservation pathway of oxygen cross-linking would probably result in similar observations and thus should be taken into account as well.

Kiriakoulakis *et al.* (1994) found some evidence for bacterial activity during diagenesis and could indicate the activity of anaerobic sulphate reducing bacteria and methanogenic archaeobacteria. The early diagenetic formation of concretions probably lead to a better preservation as the sample showed higher TOC, higher extractable organic matter and higher concentrations of most biomarkers. Hopanes and hopenes of bacterial origin were the only biomarkers with a significant higher concentration in the clay compared to the concretion.

2.3.4. Provenance of the allochthonous OM (Laenen, 1997 and Fig. 4)

Two groups of allochthonous organic molecules have been distinguished in the Boom Clay. The first group is typical for angiospermal material (especially HPPT, ferenes, and aromatic structures of C3-oxidised precursors). This group has the highest concentration in the lower part of the section. As it shows a positive correlation with sediment supply, it most probably has a nearby southern source. The second group originates from gymnospermal material (resinous di- and sesquiterpenoids, α -cedrene, cedrane and cuparene) which probably has a more distant northern source. The amount of angiospermal material shows maxima near sequence boundaries, while the gymnospermal material shows maxima near the flooding surfaces. The ratio of gymnospermal material over angiospermal material is highest in the black layers. Moreover, the absolute concentration of angiospermal material is also highest in the black layers, but its relative contribution is low. Consequently, high fluxes of organic matter near the flooding surfaces are caused by a large input of allochthonous organic material. This can be explained

as follows. During fast sea level rise flooding destroys the coastal vegetation, which causes an increase of continental organic matter. As during this sea level rise more sedimentation space is created in the most marginal parts of the basin, sedimentation of especially angiospermal material will take place. High fluxes of continental organic matter and reduction of sediment supply leads to organic-rich layers. During a sea-level fall the sediment supply from the south fills up the accommodation and progrades basin wards. A minor influx of organic matter and an increase of sediment supply results in organic-lean layers. The strong increase organic carbon at the Putte/Terhagen boundary results from a reduction in sediment supply, an increase in flux of continental organic material, more acidic pore water conditions and probably some suboxic conditions, which leads to a better preservation. On a small scale a similar pattern might be observed, where every transition from silt to clay is seen as a transgressive system track.

2.3.5. Provenance of the autochthonous OM (Laenen, 1997 and Fig. 4)

Exclusively marine molecules are not found, although for some components such an origin is believed. The marine components covary with glacio-eustacy. At the maximum flooding surface (mfs) a strong marine signal is found. On a smaller scale the most important marine input is found during deposition of the clay layers. This might be interpreted as a small mfs in the middle of each clay layer or as a better preservation condition during clay sedimentation. The ratio of C_{31} over C_{17} n-alkanes provides information on the ratio of continental over marine input. The ratio is correlated with the angiospermal material. Two reasons for a higher marine input in black layers are provided. Firstly, this might result from a higher primary production by an increase of nutrients caused by the flooding and erosion of the coastal soils. Secondly, more acidic conditions and probably some suboxic eogenetic conditions in the organic-rich layers resulted in a better preservation. The amount of marine organic carbon is correlated with the N-content, where as TOC was not correlated with the latter. Marine TOC shows a third order pattern with high concentrations near the mfs and minima near glacio-eustatic low stands and near the double layer. The continental TOC shows a gradual increase in the Terhagen member and a sudden increase at the Putte/Terhagen boundary with a minimum near the double layer.

2.4. Conclusion on the non-mobile organic matter

The organic matter present in the Boom Clay is immature and originates from three different sources, namely angiospermal material (especially from the south), gymnospermal material (especially from a more distant northern source) and autochthonous marine material. Throughout the stratigraphy, all sources are always found, but in slightly different ratios. The organic-rich layers, however, are the result of an increase of the material from all sources. Moreover, a better preservation and a lower sediment supply enhanced the organic carbon content within these layers. The organic matter of the Boom Clay shows little effects of alteration, except for the reworked organic matter from older sediments. The organic matter within early diagenetic concretions is not very different from the one found in the surrounding clay matrix, but only better preserved. The degradation-recondensation pathway is probably the most important preservation way, although the oxygen cross-linking might have been important as well.

3. MOBILE ORGANIC MATTER

The study on the mobile organic matter, present within the pore water of the Boom Clay is studied with much less detail. Most of the research is performed by or by order of SCK•CEN in the framework of the study on the migration of radionuclides through the Boom Clay (Put *et al.*, 1992; De Brabandere *et al.*, 1994; Von Maravic, 1995; Put *et al.*, 1998; Dierckx *et al.*, 2000).

Mobile natural organic matter is commonly divided in three groups (Stevenson, 1982). The fraction, which is not soluble in alkali, is the humin fraction, whereas the humic and fulvic fractions are soluble

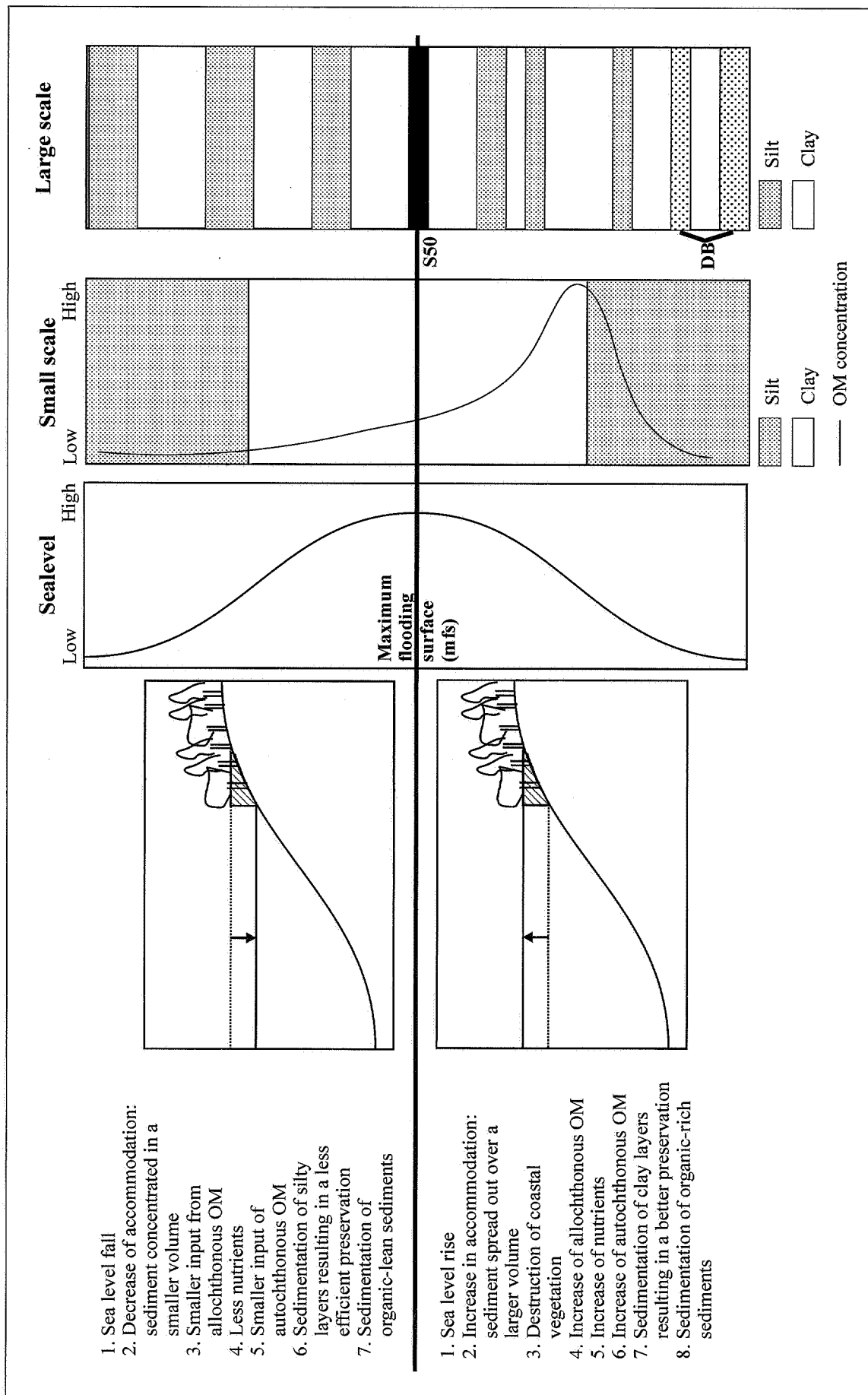


Figure 4. Schematic explanation of the rhythmic alternation of organic-rich and -lean sediment layers within the Boom Clay (after Laenen, 1997).

in alkali. The humic acids precipitate below pH 2, while the fulvic fraction remains in solution. The most important property of natural organic matter with respect to environmental chemistry is its polyfunctional structure. The various functional groups are responsible for the complexation of cations. Humic and fulvic acids are mostly classified as colloidal matter, with a size variation arbitrarily defined between 1 nm and 1 μ m. Because of their solubility at alkaline pH, and because of their relatively small molecular size, fulvic and humic acids are mobile in porous and fractured media.

The sampling of mobile organic matter from Boom Clay can be performed in three ways. Firstly, pore water can be extracted in-situ from the clay by means of piezometers. Secondly, Boom Clay samples can be squeezed to extract the water content. Finally, OM can be leached from Boom Clay samples at different solid/liquid ratios. Different amounts of TOC are measured for the three techniques. Piezometer water is thought to be the most representative and gives TOC values between 40 and 250 mgC/L (De Craen *et al.*, 2002).

3.1. Molecular size distribution

An impression of the molecular size distribution is an important first step in the characterisation of mobile OM. Different techniques have been proposed to study this distribution and many techniques have been criticised (Chin *et al.*, 1994, Thang *et al.*, 2001). From literature data it can be concluded that the determination of molecular size distribution is a complex matter. Here, an overview of the experiments performed on mobile organic matter present in Boom Clay water will be given, without discussing the technique as such.

The most obvious technique for the characterisation of the molecular size distribution of OM is the use of filtration and ultra filtration. Recently, such an experiment was performed on piezometer water at 9 different stratigraphical levels (Fig. 1 illustrates these positions as MORPHEUS piezometer. F23, F20 and F18 were not used.). The results are shown in Figure 6a, illustrating that about 45% of the mobile OM is smaller than 1000 Da and 45% is larger than 100,000 Da. This might correspond with the bimodal structure that is observed in GPC measurements (Fig. 6b) during the TRANCOM-clay project (funded by the EC and NIRAS/ONDRAF), although no calibration has been performed.

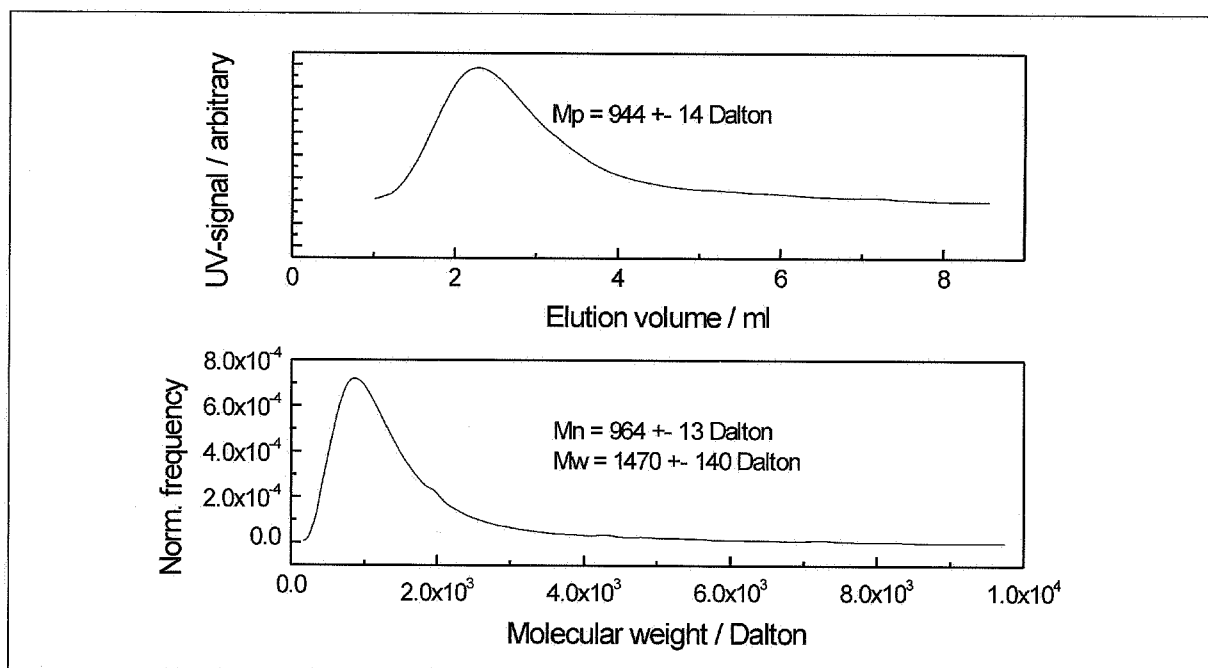


Figure 5. Molecular weight distribution of humic substances in Boom Clay pore water as measured with FFFF (Thang *et al.*, 2001).

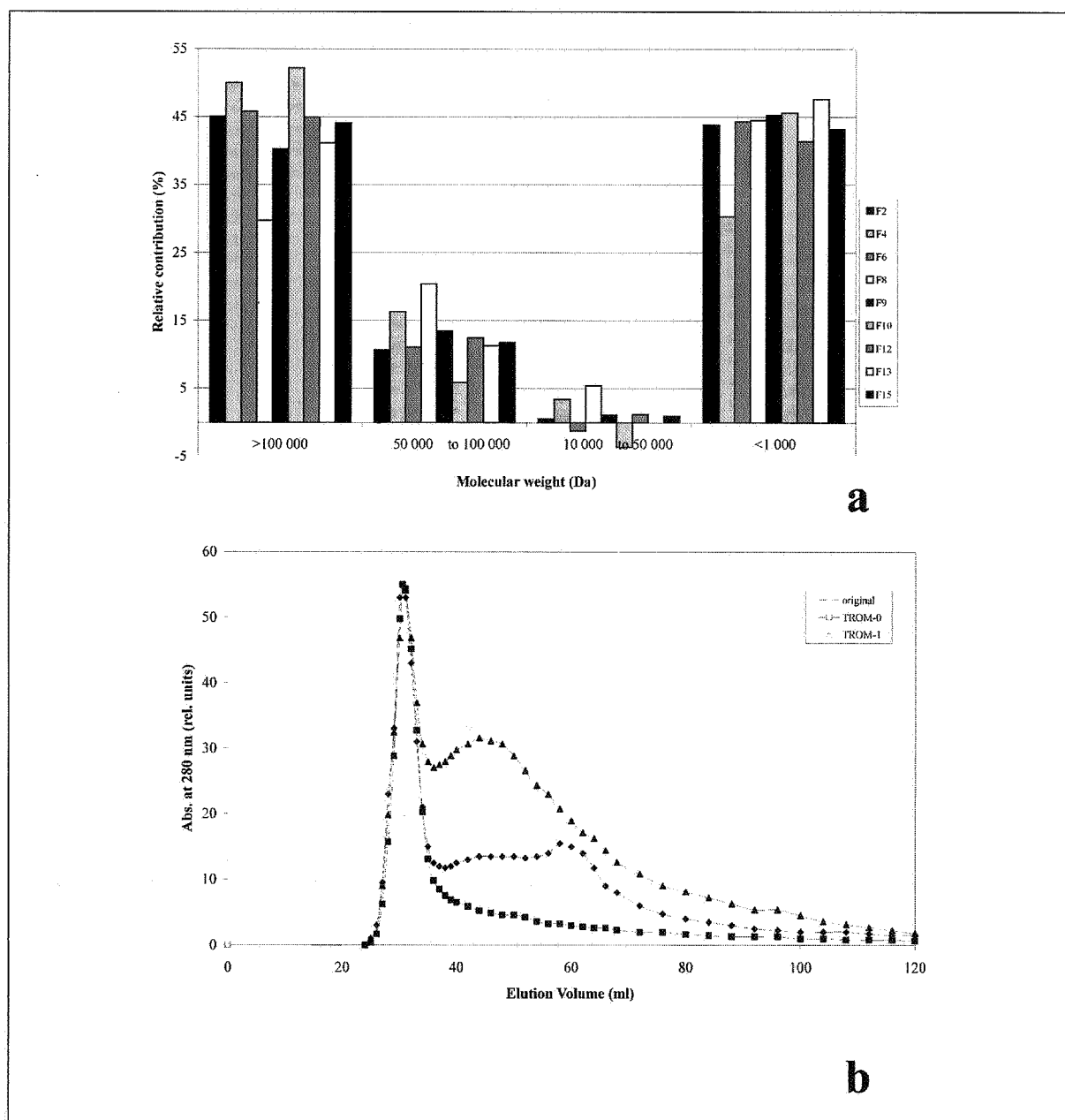


Figure 6. a. Molecular size distribution of the mobile organic matter from filters of the MORPHEUS piezometer (see figure 1), as determined by ultra filtration.
b. Molecular weight distribution with Gel Permeation Chromatography (GPC) of the original EG/BS clay water and concentrated samples of EG/BS, called TROM-0 and TROM-1 (Dierckx *et al.*, 1996).

	Boom Clay mobile organic matter
M_p : peak maximum molecular weight	1.0 ± 0.02 kDa
M_n : number averaged molecular weight	1.1 ± 0.03 kDa
M_w : weight averaged molecular weight	1.8 ± 0.04 kDa
M_w/M_n	1.6 ± 0.05 kDa
D_h : hydrodynamic diameter	1.8 nm

Table 4. Obtained values on the molecular size of the natural occurring mobile organic matter within Boom Clay (Thang *et al.*, 2001).

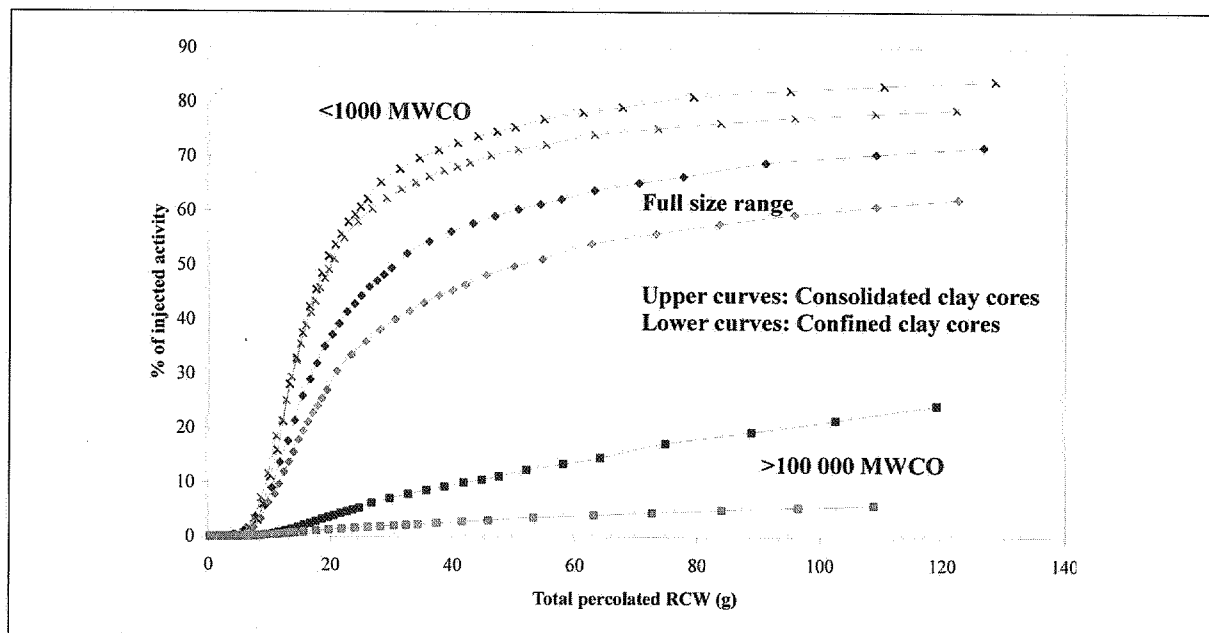


Figure 7. Cumulative recovery curves from the impulse injection experiments, showing the influence of the molecular size fractions of OM and the influence of the effective stress in the clay pores (Dierckx *et al.*, 2000).

A more quantitative analysis of the molecular size distribution of Boom Clay organic matter is performed by Thang *et al.* (2001). In their study they used flow field flow fractionation (FFFF) on EG/BS piezometer pore water (The EG/BS piezometer drains water over a thickness of about 14m of Boom Clay). A calibration of the technique with polystyrene sulphonate (PSS) was used to determine quantitatively the size fraction of the Boom Clay mobile organic matter. Their study illustrates that the most important fraction of the mobile organic matter has a molecular weight below 4000 Da (Fig. 5; Tab. 4). It should be noted, however, that the authors mention possible deviations of the exact values when using other calibration material.

Finally, it is most worthwhile to mention the results of migration experiments of ^{14}C labelled OM through Boom Clay samples. Figure 7 illustrates that low molecular size OM is more easily transported through the clay than high molecular weight OM. Boom Clay, consequently, seems to act as a non-perfect ultra filter itself. As a consequence, OM derived from piezometers, squeezing and leaching experiments might be quite different in composition, as noticed by De Craen *et al.* (2002).

3.2. Functional group capacity

In the framework of the TRANCOM-clay project, the functional group-capacity (CEC) of the organic matter was determined. The measurement of this parameter is a first necessary step in estimating the complexing capacity of the organic matter. This functional group capacity was measured on different sources of Boom Clay organic matter and by means of different techniques. The functional group capacity in the pH-range 7-8 was taken to be representative for the Boom Clay environment and used for comparison (Tab. 5). More details can be found in Dierckx *et al.* (1997) and Dierckx *et al.* (2000).

The obtained capacity curves over a pH-range 3.5-10 were used for modelling purposes as well (Pirlet *et al.*, 1998). This lead to the conclusion that three types of functional groups are needed to describe the titration curves within the studied pH-range. More functional groups could be added, but did not significantly improve the fit. Moreover, the extracted humic acid fraction has a two times lower total functional group concentration compared to the pore water fraction. This might indicate that natural organic matter from the pore water is smaller and thus exhibits more accessible functional groups. This might be related to the filtering effect of Boom Clay, as mentioned above.

Name	Extraction technique	Measuring technique	Capacity [Eq/mg]
EG/BS (V103)	Piezometer pore water	Titration	5.95
EG/BS (V3A)	Piezometer pore water	Titration	6.19
EG/BS (3)	Piezometer pore water	Titration	5.10
Total extracted Boom Clay	Leaching BC with SCW with an L/S ratio of 1/2	Titration	1.80
BCPHA	Concentration of EG/BS and then isolation, purification and transformation to the proton form of the HA	Titration	2.85
BCEHA	Successive extraction of HA from Boom Clay with NaHCO ₃ 0.015 M in air under close to in situ carbonate concentration conditions	Cobalt hexamine method	2.1
BCEHA (2)	Similar as for BCEHA with an additional extraction step consisting in bringing the Boom Clay to pH 3 to break salt bridges	Titration	1.65

Table 5. Comparison of the functional group capacity in the pH-range 7-8 for different organic matter samples (Dierckx et al., 2000).

3.3. Molecular organic chemistry

A detailed molecular characterisation of the mobile organic matter present in Boom Clay pore water has not been established yet. This is related to the experimental difficulty of such a characterisation. However, a recent technique of electrospray ionisation quadrupole time-of-flight mass spectrometry (ESI-Q-TOF-MS) has been proposed and tested. Boom Clay pore water has not been analysed yet, but water from a Mol aquifer was used in this study.

Plancque *et al.* (2001) examined the fulvic acids occurring in the aquifer below the Boom Clay by means of electrospray with quadrupole time-of-flight mass spectrometry. The direct analysis of the fulvic acids of the Mol aquifer yield a distribution of abundant series of peaks centred about m/z 350 (Fig. 8). The fulvic acid solution is a complex mixture of several hundred molecular structures. The mass spectrum shows about 1300 peaks in the range m/z 150-800. Two main families of peaks, representing singly charged ions, can be observed in the spectrum occurring at odd and even mass numbers, respectively.

The tandem mass spectrometry experiments demonstrated losses of 18 Da (water molecule) and of 44 Da (CO₂ molecule), which indicates the presence of carboxylic functions and confirm that the precursor-ion peaks correspond to singly charged ions. All precursor ions at odd mass numbers dissociate to give molecular substructure fragment ions with mass differences of 14, 15, 16 or 44 Da, corresponding to CH₃, NH₂, OH and COOH substituent groups, respectively.

The ESI(-) mass spectrum can be viewed as two series of ions: a $[M_1-H]^-$ series (odd mass numbers) representing compounds where the end group of the alkyl substituent is methyl, and a $[M_2-H]^-$ ion series

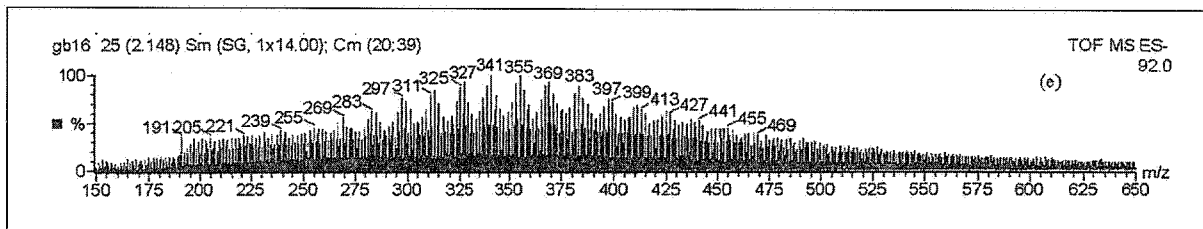


Figure 8. Negative-ion ESI mass spectra of fulvic acids from the Mol aquifer under optimised conditions (Plancque *et al.*, 2001).

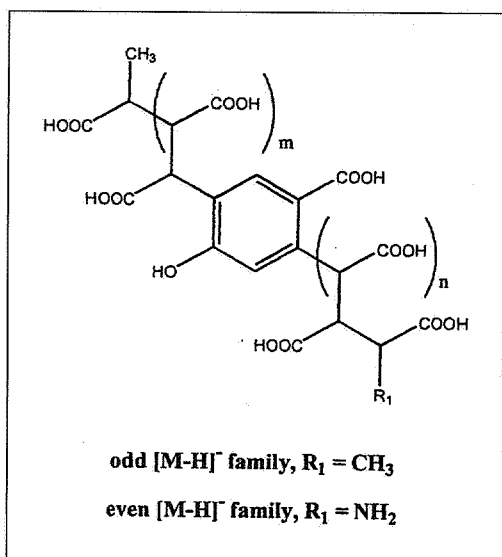


Figure 9. Representative molecular structure proposed for fulvic acid from the Mol aquifer (Plancque *et al.*, 2001).

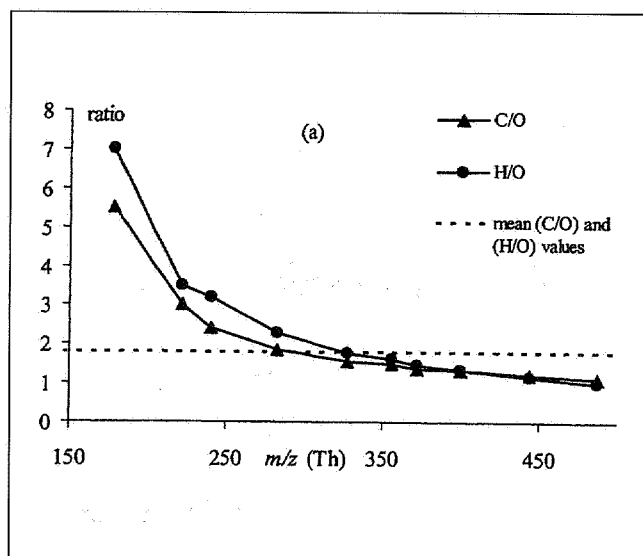


Figure 10. Modelled curve for H/O and C/O ratios as a function of *m/z* (Plancque *et al.*, 2001).

(even mass numbers) where the end group is amino (NH₂). A representative molecular structure of the molecules, which are most likely to be self-assembled in the fulvic acid samples, is given in Figure 9. Consequently, the fulvic acids of the Mol aquifer contain two families having homologous substructures with alkyl chains terminated in CH₃ or NH₂. Both families contain a mixture of species with a range of numbers of carboxyl functions, alkyl chain lengths and of numbers of substituents on the aromatic ring. Finally, the above mentioned findings were confirmed by comparing the ratios of C/O and C/H obtained by elemental analysis and obtained from modelling the ESI data. The latter models also show that the C/O ratio is decreasing with increasing molecular mass. So the small molecules have few oxygen atoms and the large molecules have numerous oxygen atoms (Fig. 10).

3.4. Conclusion on mobile organic matter

Up to now, little is known about the mobile organic matter present within the Boom Clay. Some attempts in describing the molecular size have been undertaken, showing that the size of the humic material is varying around 1000 Da. However, organic matter with sizes above 100 000 Da have been measured as well. Information on the possible spatial variation of the mobile organic matter is absent as well as its link with immobile organic matter. The technique of electrospray ionisation (ESI) Quadrupole Time-of-flight Mass Spectrometry (Q-TOF-MS) has been used to characterise the fulvic acids occurring in the aquifer underlying the Boom Clay. The technique seems very interesting in obtaining detailed information of the organic components. However, no information is available on the link between the organic matter present within the Boom Clay pore water and those present within the underlying aquifer.

Acknowledgment

Dr. Laenen is thanked for providing his digital data on organic matter within the Boom Clay. This report is produced in the frame of the project on Characterisation of Boom Clay organic matter: mobile and immobile fraction, funded by NIRAS – ONDRAF coordinating the National Belgian Waste Management Program.

4. REFERENCES

- CHIN, Y., AIKEN, G. & O'LOUGHLIN, E., 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environ. Sci. Technol.*, 28, pp. 1853-1858.
- DE BRABANDERE, J., MAES, A. & CREMERS, A., 1994. Radionuclide – humic acid binding in Boom clay. In: BEAUFAYS, R., BLOMMAERT, W., BRONDERS, J., DE CANNIERE, P., DEL MARMOL, P., HENRION, P., MONSECOUR, M., PATYN, J. & PUT, M. Characterization of the Boom clay and its multilayered hydrogeological environment. European Commission Nuclear Science and Technology. Final Report EUR 14961.
- DE CRAEN, M., 1998. The formation of septarian carbonate concretions in organic-rich argillaceous sediments. PhD-dissertation, K.U.Leuven, Leuven, Belgium.
- DE CRAEN, M., VAN GEET, M., WANG, L. & PUT, M., 2002. Natural organic matter in Boom Clay and its pore water (Mol, Belgium) obtained by different extraction techniques. International meeting on Clays in natural and engineered barriers for radioactive waste confinement, Reims, december 9-12.
- DENIAU, I., DERENNE, S., BEAUCAIRE, C., PITSCH, H. & LARGEAU, C., 2001. Morphological and chemical features of a kerogen from the underground Mol laboratory (Boom Clay Formation, Oligocene, Belgium): structure, source organisms and formation pathways. *Organic Geochemistry*, 32, pp. 1343-1356.
- DIERCKX, A., DE CANNIÈRE, P., FONTEYNE, A., MOORS, H., VAN GOMPEL, M., AERTSENS, M. & PUT, M. (1996). Transport of radionuclides due to complexation with organic matter in clay formations (TRANCOM-Clay). CEC contract FI4W-CT95-0013, Co-sponsored by NIRAS/ONDRAF. Extensive progress report covering the period January 96 – June 96, R-3134, November 1996.
- DIERCKX, A., MAES, A., HENRION, P. & DE CANNIÈRE P., 1997. Potentiometric titration of humic substances extracted from Boom Clay. In: DROZD, J., GONET, S.S., SENESI, N. & WEBER, J. (Eds.). *The Role of Humic Substances in the Ecosystems and in Environmental Protection*. IHSS – Polish Society of Humic Substances, Grunwaldzka 53, Wroclaw Poland, p. 573-578.
- DIERCKX, A., PUT, M., DE CANNIÈRE, P., WANG, L., MAES, N., AERTSENS, M., MAES, A., VANCLUYSEN, J., VERDICKT, W., GIELEN, R., CHRISTIAENS, M., WARWICK, P., HALL, A. & VAN DER LEE, J., 2000. Transport of Radionuclides due to Complexation with Organic Matter in Clay formations (TRANCOM-Clay). European Commission Nuclear Science and Technology. Final Report EUR 19135.
- GRIFFAULT, MERCERON, T., MOSSMANN, J.R., NEERDAEL, B., DE CANNIERE, P., BEAUCAIRE, C., DAUMAS, S., BIANCHI, A. & CHRISTEN, R., 1996. Archimede-Argile: Acquisition et Regulation de la chimie des eaux en milieu argileux pour le projet de stockage de déchets radioactifs en formation géologiques. Rapport Final, Contrat CCE N° FI2W-CT92-0117, 189pp.
- HADDAD, R.I., MARTENS, C.S. & FARRINGTON, J.W., 1991. Quantifying early diagenesis of fatty acids in a rapidly accumulating coastal marine sediment. *Organic Geochemistry*, 19, pp. 205-216.
- KIRIAKOULAKIS, K., WOLFF, G. & MARSHALL, J., 1994. Organic geochemistry of a Boom Clay concretion and its surrounding sediments. Internal report.
- LAENEN, B., 1997. The geochemical signature of relative sea-level cycles recognized in the Boom Clay. PhD-dissertation, K.U.Leuven, Leuven, Belgium.
- LANDAIS, P., MONTHIOUX, M. & MEUNIER, J.D., 1984. Importance of the oxidation/maturation pair in the evolution of humic coals. *Organic Geochemistry*, 7, pp. 249-260.
- PIRLET, V., VAN ISEGHEM, P., DIERCKX, A. & DESREUX, J.F., 1998. The investigation of the neptunium complexes formed upon interaction of high level waste glass and Boom Clay media. *Journal of Alloys and Compounds*, 271-273, pp. 267-271.

- PLANCQUE, G., AMEKRAZ, B., MOULIN, V., TOULHOAT, P. & MOULIN, C., 2001. Molecular structure of fulvic acids by electrospray with quadrupole time-of-flight mass spectrometry. *Rapid Communications in mass spectrometry*, 15, pp. 827-835.
- PUT, M., MONSECOUR, M. & FONTEYNE, A., 1992. Mobility of the Dissolved Organic Material in the Interstitial Boom Clay Water. *Radiochimica Acta*, 58/59, pp. 315-317.
- PUT, M.J., DIERCKX, A., AERTSENS, M. & DE CANNIERE, P., 1998. Mobility of the Dissolved Organic Matter through Intact Boom Clay Cores. *Radiochimica Acta*, 82, pp. 375-378.
- STEVENSON, F.J., 1982. *Humus Chemistry - Genesis, Composition, Reactions*. Wiley Interscience, John Wiley & Sons.
- THANG, N.M., GECKEIS, H., KIM, J.I. & BECK, H.P., 2001. Application of the flow field flow fractionation (FFFF) to the characterisation of aquatic humic colloids: evaluation and optimization of the method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 181, pp. 289-301.
- VANDENBERGHE, N., 1978. Sedimentology of the Boom Clay (Rupelian) in Belgium. *Verhandeling Koninklijke Academie voor Wetenschappen, Letteren en Schone Kunsten van België, Klasse Wetenschappen XL*, 147p.
- VAN GEET, 2002. Interpretation of Rock-Eval data on samples of core HADES 2001/4. Topical report in the frame of D.S. 2.82 Characterisation of Boom Clay organic matter: mobile and immobile fraction. SCK•CEN report, R-3605, Mol, Belgium, 12pp.
- VON MARAVIC, H., 1995. Migration of radionuclides in the geosphere. MIRAGE project – third phase. Proceedings of the final meeting, Brussels, Belgium, 15-17/11/1994. European Commission Nuclear Science and Technology. Eur 16218.
- WOUTERS, L. & VANDENBERGHE, N., 1994. *Geologie van de Kempen – Een synthese*. NIRAS/ONDRAF – 94 – 11.

5. ABBREVIATIONS

OM:	Organic matter
R₀:	Vitrinite reflectivity
SEM:	Scanning Electron Microscopy
BSEM:	Back-scatter Scanning Electron Microscopy
TEM:	Transmission Electron Microscopy
C_{org}:	Organic Carbon
S1:	The amount of hydrocarbons (mg / g sample) expelled at low temperature during a Rock-Eval analysis
S2:	The amount of hydrocarbons (mg / g sample) expelled at temperatures between 300°C and 550°C during a Rock-Eval analysis.
S3:	The amount of oxygenated organic components (mg / g sample) expelled during a Rock-Eval analysis.
OI:	Oxygen Index
HI:	Hydrogen Index
T_{max}:	The temperature at which the expulsion of S2-hydrocarbons reaches a maximum
mfs:	Maximum Flooding Surface
HPPT:	Higher Plant Pentacyclic Triterpenoids
PAH:	Poly-Aromatic Hydrocarbons
TOC:	Total Organic Carbon
EOM:	Extractable Organic Matter
TRANCOM:	Transport of Radionuclides due to Complexation with Organic Matter in Clay formations
EG/BS:	Experimental Gallery Bottom Shaft piezometer
BCPHA:	Boom Clay Pore water Humic Acids
BCEHA:	Boom Clay Extracted Humic Acids
L/S:	Liquid – Solid ratio
HA:	Humic Acid
CEC:	Cation Exchange Capacity
FFFF:	Field Flow Field Fractionation
PSS:	Polystyrene Sulfonate
Da:	Dalton
m/z:	Mass-over-charge ratio
ESI:	Electrospray ionisation
Q-TOF-MS:	Quadrupole – Time-Of-Flight – Mass Spectrometry
GPC:	Gel Permeation Chromatography