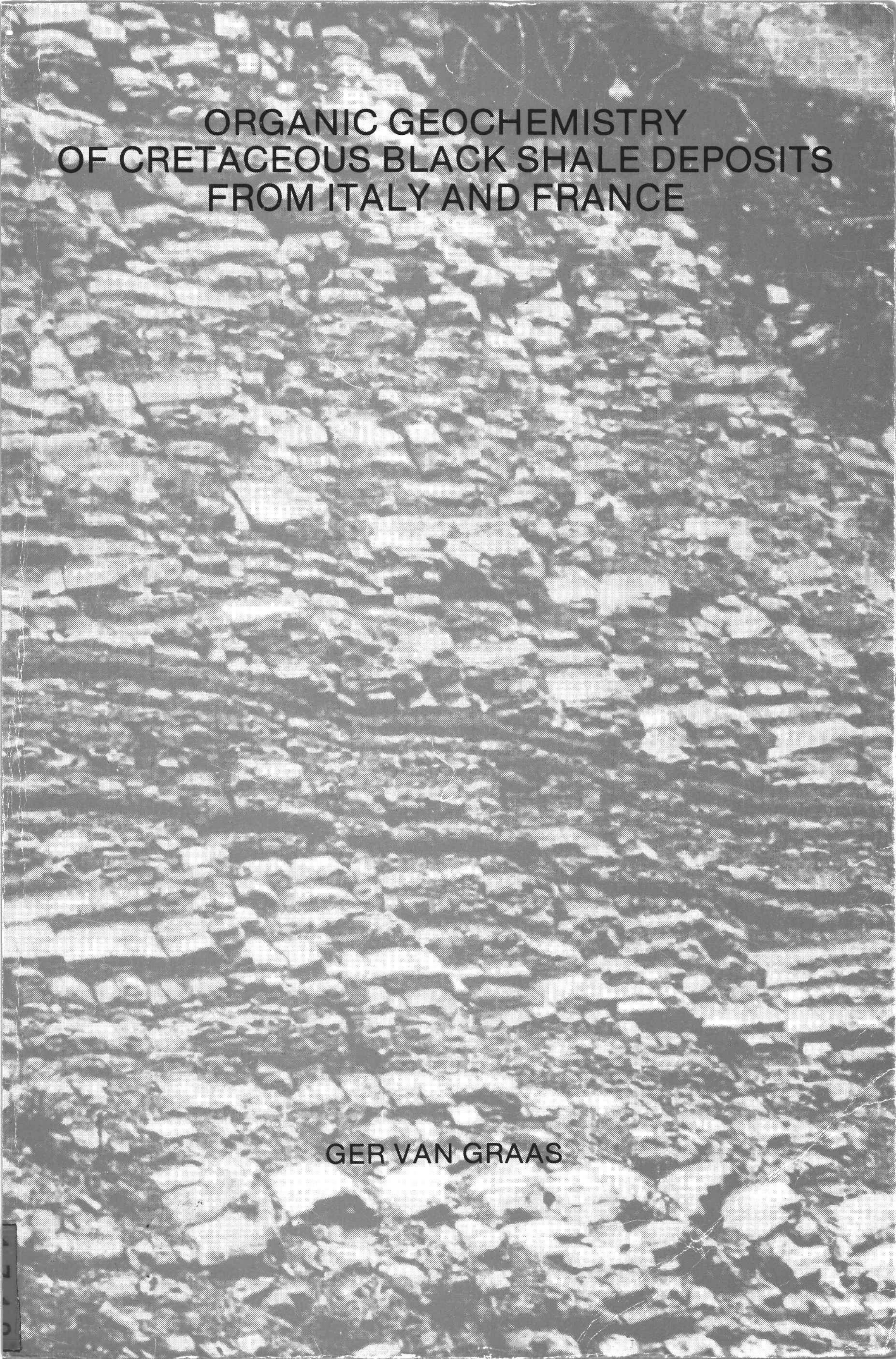


ORGANIC GEOCHEMISTRY OF CRETACEOUS BLACK SHALE DEPOSITS FROM ITALY AND FRANCE

GER VAN GRAAS

ORGANIC GEOCHEMISTRY OF CRETACEOUS BLACK SHALE DEPOSITS FROM ITALY AND FRANCE

ORGANIC GEOCHEMISTRY OF CRETACEOUS BLACK SHALE DEPOSITS FROM ITALY AND FRANCE

PROEFSCHRIFT

ter verkrijging van de graad
van doctor in de technische wetenschappen
aan de Technische Hogeschool Delft
op gezag van de rector magnificus,
prof. ir. B.P.Th. Veltman
voor een commissie
aangewezen door het college van dekanen
te verdedigen op
donderdag 7 oktober te 14.00 uur

DOOR

GERARDUS WIJNANDUS VAN GRAAS

Scheikundig ingenieur,
geboren te Gouda

Delft University Press/1982

Dit proefschrift is goedgekeurd door de promotor,
PROF. DRS. P.A. SCHENCK

Aan mijn ouders

Het tot stand komen van dit proefschrift is alleen mogelijk geweest dankzij de bijdragen van vele mensen. In de eerste plaats zijn dit de leden van de groep Organische Geochemie, maar daarnaast ook andere leden van de vakgroep Algemene Scheikunde en van de massaspektrometrische afdeling van de vakgroep Organische Chemie. Buiten de TH Delft betreft het de leden van de afdeling Biomoleculaire Fysica van het FOM-instituur voor Atoom- en Molecuulfysica te Amsterdam en de overige deelnemers aan het 'Black Shale' onderzoek, die voornamelijk werkzaam zijn op het Instituut voor Aardwetenschappen te Utrecht. Ik wil hen allen graag bedanken voor de prettige samenwerking, die ik heb ervaren en die het mij mogelijk maakt om met veel plezier aan de afgelopen jaren terug te denken.

The research described in this thesis was supported by the Netherlands Foundation for Earth Science Research (AWON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Cover photograph:
Albian part of the exposure near Moria, Italy (Chapter 2). The rhythmic alternation of limestones and marls can be easily observed.

CONTENTS

CHAPTER 1

CRETACEOUS BLACK SHALES: AN INTRODUCTION

OCCURRENCE

'Black shales' is an old term used by geologists to designate argillaceous rocks rich in organic matter (e.g. Howell, 1957). In the literature there is no unanimity concerning a more precise definition but Curtis (1980) summarized the essential characteristics as follows: a) high organic carbon content; b) low carbonate content; c) high pyrite content; d) fissility arising from lamination. This is still a rather vague description as it does not mention absolute amounts for the various constituents. Besides, there are many sediments which do not show all of these characteristics but should nevertheless be considered when discussing the origin of black shales (Arthur, 1979). The past decade has shown a revived interest for black shale deposits. This is principally due to their oil source rock potential (Arthur and Schlanger, 1979).

Attention is focussed mainly on Cretaceous black shales since the recognition of thick formations of these sediments in all major oceanic basins during the Deep Sea Drilling Project (DSDP) (Fig.1). The geographic distribution of the deposits - which were already known from land exposures in the Mediterranean area, England, the Caribbean area and California - proved to be substantially wider because of the presence of Cretaceous organic rich sediments in the North and South Atlantic (DSDP legs 1,11,14,36,40,41,43,44,47,48,50,51,52 and 53), the Indian Ocean (DSDP legs 25, 26 and 27), and the Pacific (DSDP legs 32 and 33). More information can be found in the appropriate *Initial Reports of the Deep Sea Drilling Project*.

The widespread distribution of Cretaceous black shales suggests that their formation is related to global oceanographic phenomena termed 'oceanic anoxic events' (Schlanger and Jenkyns, 1976). Three such events can be recognized during the Cretaceous (fig.2; Schlanger and Jenkyns, 1976; Ryan and Cita, 1977;

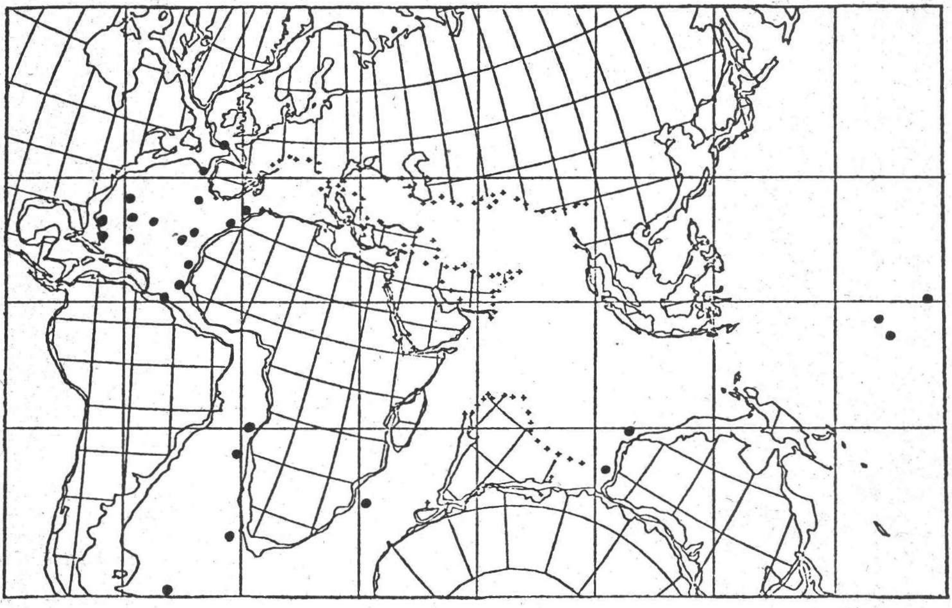


Fig. 1. Location of DSDP sites with recovery of organic rich Cretaceous sediments (compiled from various sources). Paleoreconstruction for 100 My B.P. (after Smith and Briden, 1977).

Arthur and Schlanger, 1979). The first one takes place from Late Barremian through Albian time (100-117 M yr B.P.). A second event located around the Cenomanian-Turonian boundary (90-95 M yr B.P.) is of higher intensity but more restricted in time. A third and less widespread event occurs during Coniancian and Santonian (78-86 M yr B.P.).

MODELS OF FORMATION

The formation of organic rich sediments is thought to occur when the environment of deposition becomes locally or fully anoxic. Two models of sedimentary environments are generally used to account for the development of anaerobic conditions (Schlanger and Jenkyns, 1976; Ryan and Cita, 1977; Thiede and Van Andel, 1977; Demaison and Moore, 1980) (fig.3).

In the first case a density stratification of the water column causes a stagnation thus inhibiting the transport of oxygen to deep waters. At the bottom the available oxygen is consumed by the oxydation of dead organic matter that rains down from the photic zone leading to an anaerobic environment of sedimentation. Such a density stratification can occur in several situations. The Black Sea is the classical example of a restricted basin which has only a shallow water connection to other parts of the ocean giving rise to stagnation in the deeper parts of the basin (Degens and Ross, 1974). Density stratification and the resulting stagnation can also be initiated by the influx of a dense bottom layer of water (Summerhayes, 1981) or a light surface layer (Rossignol-Strick *et al.*, 1982).

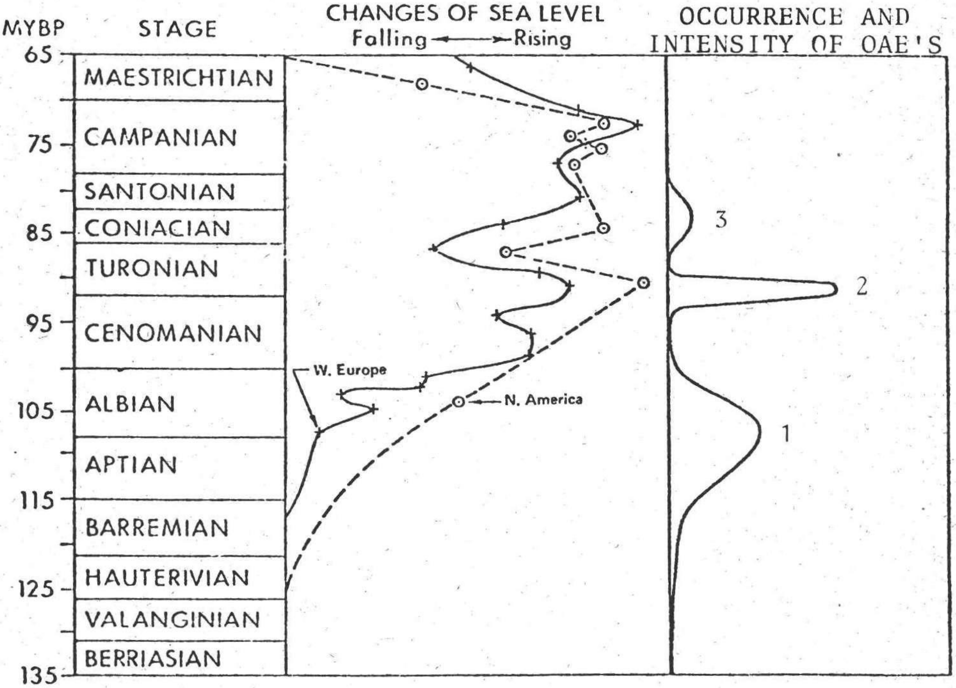


Fig. 2. Occurrence of 'oceanic anoxic events' in relation to sea level changes (after Arthur and Schlanger, 1979).

In the second case anoxic conditions of sedimentation are present at the interface of an expanded, oxygen-depleted oxygen-minimum layer and the sediment. In this model the deeper parts of the basin are oxygenated. Expansion of and oxygen depletion in the oxygen-minimum layer can be the result of upwelling of nutrient rich water which leads to a high productivity in the surface waters. The high oxygen demand for the recycling of large amounts of dead organic matter in the underlying water layers causes the development of anoxic conditions. A similar situation can also develop without a high productivity when the very large distance to a source of deep oxygenated water gives rise to a gradual exhaustion of oxygen. Present-day examples of these situations are found offshore Namibia influenced by the Benguela Current and in the Northern Indian Ocean respectively (Demaison and Moore, 1980).

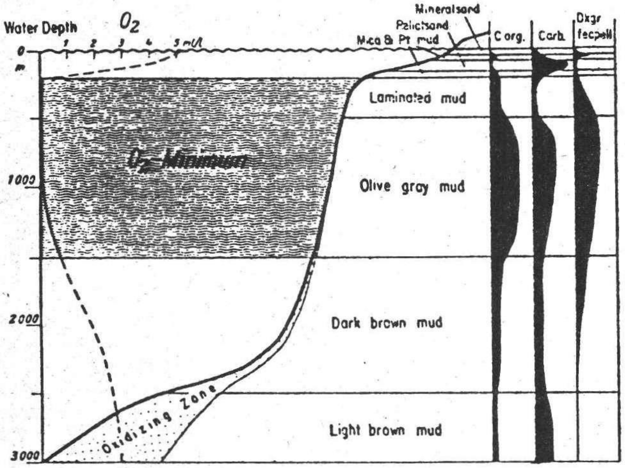
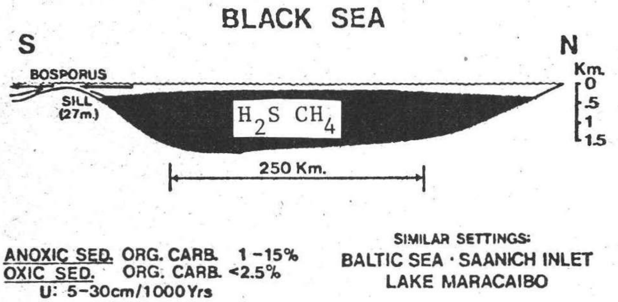


Fig. 3.
Present-day examples of anoxic environments of sedimentation (after Demaison and Moore, 1980).
a) The western shelf of India, interface with the oxygen-minimum layer.



b) The Black Sea, an anoxic silled basin.

The two models are not mutually exclusive. The development of fully anoxic conditions in the oxygen-minimum layer will be facilitated by a sluggish circulation and in case of a complete stagnation oxygen depletion is likely to start in the mid-water oxygen-minimum zone. It is not clear which model applies to the Cretaceous black shale deposits. In the Pacific the oxygen-minimum zone mechanism is very plausible since black shales are only found at the tops and flanks of seamounts and rises whereas in deeper parts of the basin oxygenated sediments occur (Schlanger and Jenkyns, 1976; Ryan and Cita, 1977). The restricted basin model is probably more applicable to the situation in the Cretaceous Atlantic Ocean which at the time was a young and relatively narrow ocean divided into several basins by sills, thresholds and ridges (Bernouilli, 1972; Ryan and Cita, 1977; Lancelot and Seibold, 1977; Tucholke and Vogt, 1979).

The simultaneous occurrence and the similarity of Cretaceous black shale deposits all over the world have initially led to the suggestion that their formation could be described by one generally applicable sedimentary environment. However, as more detailed studies were undertaken it became clear that conditions of sedimentation may vary significantly when comparing black shales from different locations and consequently several models for paleoenvironment are necessary. In general one can say that the Cretaceous has indeed been a period during which anaerobic conditions of sedimentation could easily develop depending on the local situation as will be discussed below.

PALEO-OCEANOGRAPHY

Several tectonic and climatic factors made the Cretaceous ocean as a whole more prone to the development of anoxic conditions. Schlanger and Jenkyns (1976) observed a coincidence of their 'oceanic anoxic events' and major transgressions (fig.2). These transgressions were caused by an enhanced rate of spreading of the oceanic plates and the related increase in the volume of the mid-oceanic ridges (Hays and Pitman, 1973). Due to the transgressions vast areas of coastal plains were flooded. During the Cretaceous the climate was mild and equable (Frakes, 1979) leading to a relatively low circulation velocity of oceanic water and hence a decrease in the replenishment of oxygen in deep waters can be expected.

The flooding of the coastal plains may have caused the seaward transportation of large amounts of terrestrial biomass thus promoting the formation of black shales. This mechanism, which is supported by the detection of significant amounts of terrestrial organic matter in a number of Atlantic black shales (Tissot *et al.*, 1980), has probably been only of local importance dependent of paleogeography. The suggestion of Jenkyns (1980) that 'much of the Cretaceous ocean was simply awash with wood' is not in agreement with the rate of the Cretaceous transgressions which were too slow to account for a catastrophic transfer of terrestrial organic matter into the ocean basins.

Besides being a potential source for terrestrial material the flooded plains are turned into highly productive shelf areas which can account for a large production of marine organic matter that can be transported towards the ocean. The extraction of large amounts of marine organic matter and its incorporation in the sediment would result in a higher $^{13}C/^{12}C$ ratio in the carbonates of the surface waters. Several authors (Fischer and Arthur, 1975; Scholle and Arthur, 1980) explain the occurrence of 'heavy' carbonates in sediments with a high organic carbon content by this mechanism. Another explanation for these 'heavy' carbonates is given by Weissert *et al.* (1979) who attribute the high $^{13}C/^{12}C$ ratio to a decreased upwelling of deep waters rich in light carbon isotopes. De Boer (1982b) suggests the 'heavy' carbonates in the organic rich layers to be the result of a diagenic process thus avoiding the necessity of a high productivity in the water column during the formation of black shales. Formation of black shales without an enhanced production of organic material is also suggested by the low rate of sedimentation in a number of cases (Tucholke and Vogt, 1979; de Boer, 1982a; Johnson Ibach, 1982).

ORGANIC GEOCHEMICAL INVESTIGATIONS

A major part of the research on Cretaceous black shales has been performed on sediments from the Atlantic Ocean that have become available through the Deep Sea Drilling Project. Whereas the first part of this project showed only little activity of organic geochemists (e.g. Simoneit *et al.*, 1972 and 1973), from leg 41 on the number of organic geochemical investigations has increased markedly. The Cretaceous black shales of legs 43,44,47/2, 48 and 50 have received the attention of several organic geochemists (see the appropriate *Initial Reports of the Deep Sea Drilling Project*).

Both the soluble and the insoluble organic matter have been investigated. Characterization of the insoluble material was carried out by microscopy (e.g. Dow, 1978; Cornford, 1980), elemental analysis (e.g. Erdman and Schorno, 1979), carbon isotope measurements (e.g. Stuermer and Simoneit, 1978), and various pyrolysis techniques (e.g. Claypool and Baysinger, 1978; Kendrick, 1979; Deroo *et al.*, 1979). Extracts were analyzed in detail after separation into several classes such as saturated and aromatic hydrocarbons, fatty acids, ketones, alcohols, and porphyrins (e.g. Baker *et al.*, 1978; Cardoso *et al.*, 1978; McIver and Rogers, 1978; Barnes *et al.*, 1979; Simoneit, 1979; Brassell *et al.*, 1980).

Several authors (Van Andel *et al.*, 1977; Arthur, 1979; Tissot *et al.*, 1980; Summerhayes, 1981) have summarized the results of the analyses of organic matter in Cretaceous black shales from the Atlantic Ocean. Their conclusions are generally in good agreement. No uniform model for the occurrence of all black shale deposits can be applied. The organic matter content varies over a wide range (from less than 1% up to more than 15% organic carbon). The relative amounts of marine and terrestrial organic matter depend on the paleolocation of the site with regard to the presence of landmasses and the occurrence of upwelling phenomena.

During Late Cenomanian-Early Turonian time high amounts of mainly marine organic matter have been incorporated in the sediments. This event which is identical to the second 'oceanic anoxic event' as identified by Schlanger and Jenkyns (1976) is suggested to have occurred after the realization of a deep water connection between the North and South Atlantic and the resulting northward transportation of dense saline bottom water. This dense water may have caused an upward transport of nutrient rich waters giving rise to an enhanced productivity of marine organic matter in the surface layer (Summerhayes, 1981).

At a number of locations the organic matter is of the right type to be a potential oil source but in all of these cases the sediments have not yet matured enough to generate oil (Tissot *et al.*, 1980).

CYCLICITY

A conspicuous feature of many black shale deposits is the rhythmic interbedding with lighter colored (green to gray) mud, marl or limestone (Arthur, 1979). Generally carbonate poor, organic rich, laminated or homogeneous sediments are alternated with carbonate rich, organic poor, bioturbated sediments. Several explications for the cyclicity have been offered (Berger and Von Rad, 1972; Dean *et al.*, 1977): 1) periodic influx of turbidites causing a redeposition of shallow carbonates in an anoxic environment below the carbonate compensation depth (CCD); 2) changes of diagenetic conditions inside the sediment such as redox potential and carbonate precipitation/dissolution; 3) variations in the CCD; 4) pelagic cycles of high marine productivity and/or a dilution by terrigeneous material. Several of the proposed mechanisms are thought to be related to climatic variations (Dean *et al.*, 1977; McCave, 1979; Mélières, 1979).

The rhythmicity in a set of pelagic limestones and marls of Aptian to Cenomanian age from the Umbrian Apennines near Moria, Italy, has been studied extensively by de Boer and Wonders (1981, 1982). They found a mean deposition time for a limestone/marl couplet of 21,000-23,000 years. This is within the range found for similar formations at other locations (17,00-50,000 years; Dean *et al.*, 1977; Arthur and Fischer, 1977; McCave, 1979). As the sedimentation rate of the non-carbonate material appears to be more or less constant in both limestones and marls (see also Tucholke and Vogt, 1979) and the foraminifera in the marly layers do not show signs of dissolution the cyclicity observed in the sediments must be the result of a variation in the surface productivity of biogenic carbonate (see also Arthur and Fischer, 1977). De Boer and Wonders (1981, 1982) suggest that the precession cycle, one of the so-called Milankovitch parameters influencing the earth's orbit (Kerr, 1981), with a period of 23,000 years causes a cyclic variation of the climate. As a consequence of these climatic variations the position of the 'high productivity equatorial zone' will vary in such a way that areas at 25 to 35 degrees of latitude will alternately fall inside and outside the influence of this zone. In case of the Moria sediments this implies that the carbonate rich beds were deposited when the area was within the influence of the 'high productivity equatorial zone' causing upwelling conditions, a high productivity and a good replenishment of oxygen in deep waters. The marly layers were formed during times of a sluggish circulation resulting in a low productivity and a situation in which oxygen depletion in deep waters could easily occur.

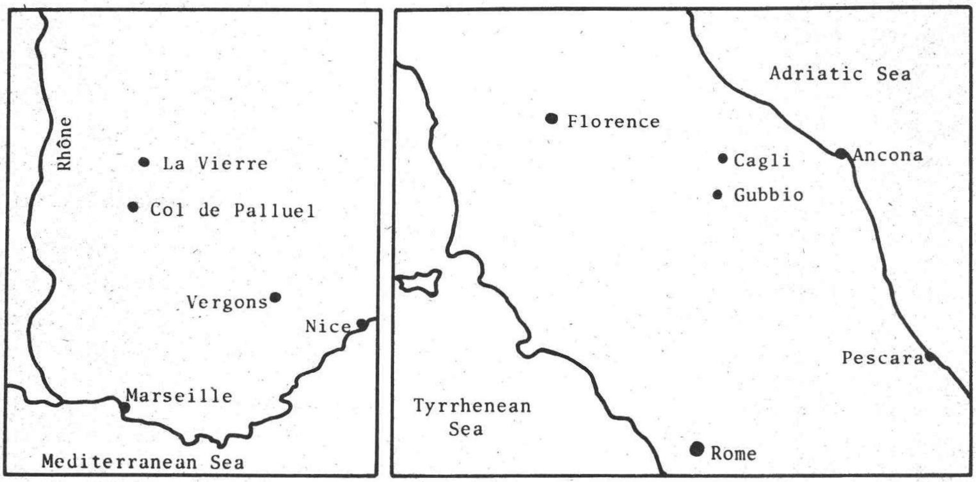


Fig. 4. Locations of the sampled sections in France and Italy.

SCOPE OF THIS THESIS

The organic geochemical investigations described in this thesis are part of a more extensive research project on the occurrence and formation of Cretaceous black shale deposits in northern Italy and southern France. This project combines the results of various disciplines such as sedimentology, paleontology, palynology, and organic geochemistry in order to obtain an integrated model for the formation of the black shales. The major part of the geological research has been performed by P.L. de Boer of the Comparative Sedimentology Division, Institute of Earth Sciences, Utrecht.

The sediments under investigation have been deposited in the now extinct Tethys Ocean of which the Mediterranean is a remnant. A series of tectonic events have occurred since the Cretaceous and have created several well-exposed outcrops of Cretaceous black shale deposits. The presence of these outcrops in Italy and southern France makes the area very suitable for our purposes. As the biostratigraphy and the geometry of the sedimentary basins are rather well-known a correlation of the sections from different locations is possible and the differences between samples from an open marine and a near-shore environment of sedimentation can be observed. The availability of outcrops also enables the collection of large samples. Hence it is possible to perform various studies on identical samples and the organic geochemical analysis of samples with a very low organic carbon content becomes feasible. These are important advantages of outcrop samples over the core samples that can be obtained from the Deep Sea Drilling Project. DSDP samples are generally limited in number and geographical distribution of the samples and in sample amount. The main disadvantage of the use of outcrop samples is the possible effect of weathering on the organic matter.

Our research has been focussed on sediments from two areas (fig.4): 1) the Umbrian Apennines near Cagli, Italy, and 2) the Alpes Maritimes in southeastern France.

The Umbrian Apennines are renowned for the presence of several continuous exposures of Cretaceous open marine pelagic facies (Arthur and Fischer, 1977; Wonders, 1980). Our samples come from a location near Cagli, Province of Pesaro and Urbino. This section, which ranges from the Albian into the Paleocene, is characterized by a rhythmic alteration of limestones and marls. Two intervals were sampled in detail: a) a section from the Albian part of the exposure comprising 13 limestone/marl couplets including several black colored marls (chapter 2); b) the Livello Bonarelli, a carbonate poor, laminated interval at the Cenomanian-Turonian boundary (chapter 3).

The French samples come from the 'Marnes Noires', grey to olive-black shales of Aptian to Albian age. This formation does show a rhythmic occurrence of more consistent beds with a higher carbonate content but it is much less

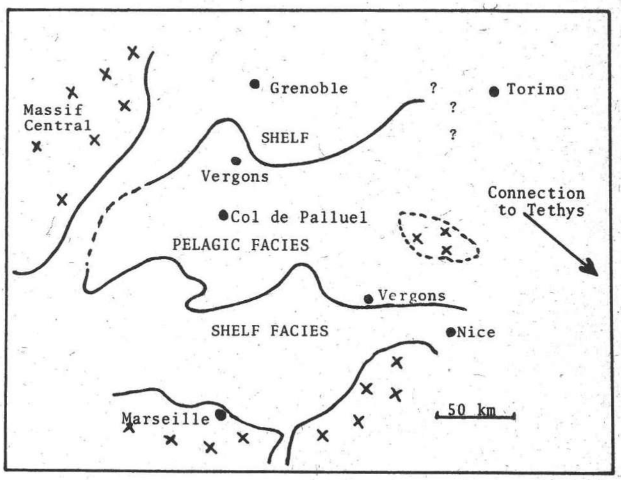


*Fig. 5.
Paleoreconstruction of the Vocontian Trough, a side-arm of the Tethys Ocean, and the location of the sampled sections.*

outspoken than in the Italian exposure. As the French sediments have also been altered by diagenetic processes (de Boer, personal communication) we limited ourselves to a study of two samples from Col de Palluel (chapter 4). These sediments have been deposited in the Vocontian Trough, a side-arm of the Tethys Ocean (fig.5). Due to this more near-shore location we expected to find a substantial terrestrial contribution to the organic matter of the samples from Col de Palluel.

ORGANIC GEOCHEMICAL RESEARCH DESCRIBED IN THIS THESIS

Both the soluble and the insoluble organic material have been investigated. Extracted sediments were characterized using Curie-point pyrolysis-mass spectrometry, Curie-point pyrolysis-gas chromatography, and Curie-point pyrolysis-gas chromatography-mass spectrometry. A substantial amount of research has been devoted to the development of data processing techniques for the interpretation of large series of pyrolysis mass spectra (van Graas *et al.*, 1980a, 1980b, 1981). For this purpose we used several model series among which a suite of samples from the Paris Basin, France (chapter 8).

The extracts were separated into a number of fractions such as saturated and aromatic hydrocarbons, ketones, acids, and alcohols. Our attention has been focussed mainly on the saturated hydrocarbon fractions because these appeared to be very useful for a comparison of the various samples.

In the course of the extract analyses several unknown compounds were encountered. Some of these could be identified through synthesis of reference compounds (chapters 5 and 6). The mass spectra of several other hitherto unidentified compounds are shown in the appendix.

Steroidal compounds play an important part in the sediments under investigation. Several stages of their diagenetic pathway can be recognized in our extracts. In order to obtain more information on the diagenesis of steroids we studied the possible prediction of the composition of mixtures of isomers at thermodynamic equilibrium through the application of molecular mechanics (chapter 7).

REFERENCES

Arthur M.A. (1979) North Atlantic Cretaceous black shales: the record at site 398 and a brief comparison with other occurrences. In *Initial Reports of the Deep Sea Drilling Project*, vol. 47, part 2 (Sibuet J.C., Ryan W.B.F. *et al.* eds.), pp.719-751. U.S. Govt. Printing Office.

Arthur M.A. and Fischer A.G. (1977) Upper Cretaceous-Paleocene magnetic stratigraphy at Gubbio, Italy. I. Lithostratigraphy and sedimentology. *Geol. Soc. Am. Bull.* 88, 367-371.

Arthur M.A. and Schlanger S.O. (1979) Cretaceous 'oceanic anoxic events' as causal factors in the development of reef-reservoired giant oil fields. *Am. Assoc. Pet. Geol. Bull.* 63, 870-885.

Baker E.W., Palmer S.E. and Huang W.Y. (1978) Miocene and Cretaceous tetrapyrrole pigments from leg 44, site 391. In *Initial Reports of the Deep Sea Drilling Project*, vol. 44 (Benson W.E., Sheridan R.E. *et al.* eds.), pp. 639-643. U.S. Govt. Printing Office.

Barnes P.J., Brassell S.C., Comet P., Eglinton G., McEvoy J., Maxwell J.R., Wardroper A.M.K. and Volkman J.K. (1979) Preliminary lipid analyses of core sections 18, 24 and 30 from hole 402A. In *Initial Reports of the Deep Sea Drilling Project*, vol. 48 (Montadert L., Roberts D.G. *et al.* eds.), pp. 965-976. U.S. Govt. Printing Office.

Berger W.H. and Von Rad U. (1972) Cretaceous and Cenozoic sediments from the Atlantic Ocean. In *Initial Reports of the Deep Sea Drilling Project*, vol. 14 (Hayes D.E., Pimm A.C. *et al.* eds.), pp.787-954. U.S. Govt. Printing Office.

Bernouilli D. (1972) North Atlantic and Mediterranean Mesozoic facies: a comparison. In *Initial Reports of the Deep Sea Drilling Project*, vol. 11 (Hollister C.D., Ewing J.I. *et al.* eds.), pp. 801-822. U.S. Govt. Printing Office.

de Boer P.L. (1982a) Cyclicity and the storage of organic matter in Middle Cretaceous pelagic sediments. In *Cyclic and Event Stratification* (Einsele G. and Seilacher A. eds.), pp.456-475. Springer.

de Boer P.L. (1982b) Cyclic climatic changes and the stable isotope composition in Cretaceous pelagic sediments. *Cretaceous Res.* (in press).

de Boer P.L. and Wonders A.A.H. (1981) Milankovitch parameters and bedding rhythms in Umbrian Middle Cretaceous pelagic sediments. I.A.S. 2nd Eur. Meeting, Bologna Abstracts, 10-13.

de Boer P.L. and Wonders A.A.H. (1982) Astronomically induced rhythmic bedding in the Cretaceous of Moria (Italy). Submitted to *Geology*.

Brassell S.C., Comet P., Eglinton G., McEvoy J., Maxwell J.R., Quirke J.M.E. and Volkman J.K. (1980) Preliminary lipid analyses of cores 14, 18 and 28 from Deep Sea Drilling Project hole 416A. In *Initial Reports of the Deep Sea Drilling Project*, vol. 50 (Lancelot Y., Winterer E.L. *et al.* eds.), pp. 647-664. U.S. Govt. Printing Office.

Cardoso J.N., Wardroper A.M.K., Watts C.D., Barnes P.J., Maxwell J.R., Eglinton G., Mound D.G. and Speers G.C. (1978) Preliminary organic geochemical analyses; site 391. Leg 44 of the Deep Sea Drilling Project. In *Initial Reports of the Deep Sea Drilling Project*, vol. 44 (Benson W.E., Sheridan R.E. *et al.* eds.), pp.617-623. U.S. Govt. Printing Office.

Claypool G.E. and Baysinger J.P. (1978) Thermal analysis/pyrolysis of Cretaceous sapropels: DSDP leg 44, hole 391C, Blake-Bahama Basin. In *Initial Reports of the Deep Sea Drilling Project*, vol. 44 (Benson W.E., Sheridan R.E. *et al.* eds.), pp.635-637. U.S. Govt. Printing Office.

Cornford C. (1980) Petrology of organic matter, Deep Sea Drilling Project site 415 and 416, Morrocan Basin, Eastern North Atlantic. In *Initial Reports of the Deep Sea Drilling Project*, vol. 50 (Lancelot Y., Winterer E.L. *et al.* eds.), pp.609-614. U.S. Govt. Printing Office.

Curtis C.D. (1980) Diagenetic alterations in black shales. *J. Geol. Soc.* 137, 189-194.

Dean W.E., Gardner J.V., Jansa L.F., Cepek P. and Seibold E. (1977) Cyclic sedimentation along the continental margin of northwest Africa. In *Initial Reports of the Deep Sea Drilling Project*, vol. 41 (Lancelot Y., Seibold E. *et al.* eds.), pp.965-989. U.S. Govt. Printing Office.

Degens E.T. and Ross D.A. eds. (1974) *The Black Sea - Geology, Chemistry and Biology*. Am. Assoc. Pet. Geol. Mem. 20.

Demaison G.J. and Moore G.T. (1980) Anoxic environments and oil source bed genesis. *Org. Geochem.* 2, 9-31.

Deroo G., Herbin J.P., Roucaché J. and Tissot B. (1979) Organic geochemisty of Cretaceous shales from DSDP site 398, leg 47B, Eastern North Atlantic. In *Initial Reports of the Deep Sea Drilling Project*, vol. 47, part 2 (Sibuet J.C., Ryan W.B.F. *et al.* eds.), pp.513-522. U.S. Govt. Printing Office.

Dow W.G. (1978) Geochemical analysis of samples from holes 391A and 391C, leg 44, Blake-Bahama Basin. In *Initial Reports of the Deep Sea Drilling Project*, vol. 44 (Benson W.E., Sheridan R.E *et al.* eds.), pp.625-634. U.S. Govt. Printing Office.

Erdman J.G. and Schorno K.S. (1979) Geochemistry of carbon: Deep Sea Drilling Project leg 43. In *Initial Reports of the Deep Sea Drilling Project*, vol. 43 (Tucholke B.E., Vogt P.R. *et al.* eds.), pp.651-655. U.S. Govt. Printing Office.

Fischer A.G. and Arthur M.A. (1975) Secular variations in the pelagic realm. In *Deep Water Carbonate Environments* (Cook H.E. and Enos P. eds.), pp.19-50. Soc. Econ. Paleontologists and Mineralogists Spec. Publ. 25.

Frakes L.A. (1979) *Climates throughout Geologic Time*. Elsevier.

van Graas G., de Leeuw J.W. and Schenck P.A. (1980a) Characterization of coals and sedimentary organic matter by Curie-point pyrolysis-mass spectrometry. Part I. *J. Anal. Appl. Pyrol.* 2, 265-276.

van Graas G., de Leeuw J.W. and Schenck P.A. (1980b) Analysis of coals of different rank by Curie-point pyrolysis-mass spectrometry and Curie-point pyrolysis-gas chromatography-mass spectrometry. In *Advances in Organic Geochemistry 1979* (Douglas A.G. and Maxwell J.R. eds.), pp. 485-494. Pergamon.

van Graas G., de Leeuw J.W., Schenck P.A. and Haverkamp J. (1981) Kerogen of Toarcian shales of the Paris Basin. A study of its maturation by flash pyrolysis techniques. *Geochim. Cosmochim. Acta* 45, 2465-2474.

Hays J.D. and Pitman W.C. (1973) Lithospheric plate motion, sea level changes and ecological consequences. *Nature* 246, 18-22.

Howell J.V. (1957) *Glossary of Geology and Related Sciences*. American Geological Institute.

Jenkyns H.C. (1980) Cretaceous anoxic events: from continents to oceans. *J. Geol. Soc.* 137, 171-188.

Johnson Ibach L.E. (1982) Relationship between sedimentation rate and total organic carbon content in ancient marine sediments. *Am. Assoc. Pet. Geol. Bull.* 66, 170-188.

Kendrick J.W. (1979) Geochemical studies of black clays from leg 43, Deep Sea Drilling Project. In *Initial Reports of the Deep Sea Drilling Project*, vol. 43 (Tucholke B.E., Vogt P.R. *et al.* eds.), pp.633-642. U.S. Govt. Printing Office.

Kerr R.A. (1981) Milankovitch climate cycles: old and unsteady. *Science* 213, 1095-1096.

Lancelot Y. and Seibold E. (1977) The evolution of the central North Atlantic - summary of results of DSDP leg 41. In *Initial Reports of the Deep Sea Drilling Project*, vol. 41 (Lancelot Y., Seibold E. *et al.* eds.), pp. 1215-1245. U.S. Govt. Printing Office.

McCave I.N. (1979) Depositional features of organic-carbon rich black and green mudstones at DSDP sites 386 and 387, Western North Atlantic. In *Initial Reports of the Deep Sea Drilling Project*, vol. 43 (Tucholke B.E., Vogt P.R. *et al.* eds.), pp.411-416. U.S. Govt. Printing Office.

McIver R.D. and Rogers M.A. (1978) Insoluble organic matter and bitumens in leg 44 samples. In *Initial Reports of the Deep Sea Drilling Project*, vol. 44 (Benson W.E., Sheridan R.E. *et al.* eds.), pp.645-649. U.S. Govt. Printing Office.

Mélières F. (1979) Mineralogy and geochemistry of selected Albian sediments from the Bay of Biscay. In *Initial Reports of the Deep Sea Drilling Project*, vol. 48 (Montadert L., Roberts D.G. *et al.* eds.), pp.855-875. U.S. Govt. Printing Office.

Rossignol-Strick M., Nesteroff W., Olive P. and Vergnaud-Grazzini C. (1982) After the deluge: Mediterranean stagnation and sapropel formation. *Nature* 295, 105-110.

Ryan W.B.F. and Cita M.B. (1977) Ignorance concerning periods of ocean-wide stagnation. *Mar. Geol.* 23, 197-215.

Schlanger S.O. and Jenkyns H.C. (1976) Cretaceous oceanic anoxic events: causes and consequences. *Geologie en Mijnbouw* 55, 179-184.

Scholle P.A. and Arthur M.A. (1980) Carbon isotope fluctuations in Cretaceous pelagic limestones: potential stratigraphic and petroleum exploration tool. *Am. Assoc. Pet. Geol. Bull.* 64, 67-87.

Simoneit B.R.T. (1979) Organic geochemistry of the shales from the northwestern proto-Atlantic, DSDP leg 43. In: *Initial Reports of the Deep Sea Drilling Project*, vol. 43 (Tucholke B.E., Vogt P.R. et al. eds.), pp.643-649. U.S. Govt. Printing Office.

Simoneit B.R.T., Scott E.S., Howells W.G. and Burlingame A.L. (1972) Preliminary organic analyses of the Deep Sea Drilling Project cores, leg 11. In: *Initial Reports of the Deep Sea Drilling Project*, vol. 11 (Hollister C.D., Ewing J.I. et al. eds.), pp.1013-1045. U.S. Govt. Printing Office.

Simoneit B.R.T., Scott E.S. and Burlingame A.L. (1973) Preliminary organic analyses of DSDP cores, leg 14, Atlantic Ocean. In: *Initial Reports of the Deep Sea Drilling Project*, vol. 14 (Van Andel T.H., Heath G.R. et al. eds.), pp. 575-600. U.S. Govt. Printing Office.

Smith A.G. and Briden J.C. (1977) *Mesozoic and Cenozoic Paleocontinental Maps*. Cambridge University Press.

Stuermer D.H. and Simoneit B.R.T. (1978) Varying sources for the lipids and humic substances at site 391, Blake-Bahama Basin, DSDP leg 44. In: *Initial Reports of the Deep Sea Drilling Project*, vol. 44 (Benson W.E., Sheridan R.E. et al. eds.), pp.587-591. U.S. Govt. Printing Office.

Summerhayes C.P. (1981) Organic facies of Middle Cretaceous black shales in deep North Atlantic. *Am. Assoc. Pet. Geol. Bull.* 65, 2364-2380.

Thiede J. and Van Andel T.H. (1977) The paleoenvironment of anaerobic sediments in the Late Mesozoic South Atlantic Ocean. *Earth Planet. Sci. Lett.* 33, 301-309.

Tissot B., Demaison G., Masson P., Delteil J.R. and Combaz A. (1980) Paleoenvironment and petroleum potential of Middle Cretaceous black shales in Atlantic basins. *Am. Assoc. Pet. Geol. Bull.* 64, 2051-2063.

Tucholke B.E. and Vogt P.R. (1979) Western North Atlantic sedimentary evolution and aspects of tectonic history. In: *Initial Reports of the Deep Sea Drilling Project*, vol. 43 (Tucholke B.E., Vogt P.R. et al eds.), pp.791-825. U.S. Govt. Printing Office.

Van Andel T.H., Thiede J., Sclater J.G. and Hay W.W. (1977) Depositional history of the South Atlantic Ocean during the last 125 million years. *J. Geol.* 85, 651-698.

Weissert H., McKenzie J. and Hochuli P. (1979) Cyclic anoxic events in the Early Cretaceous Tethys Ocean. *Geology* 7, 147-151.

Wonders A.A.H. (1980) Middle and Late Cretaceous planktonic foraminifera of the western Mediterranean area. *Utrecht Micropaleontol. Bull.* 24, 1-158.

CHAPTER 2

ORIGIN OF THE ORGANIC MATTER IN A CRETACEOUS BLACK SHALE DEPOSIT IN THE CENTRAL APENNINES (ITALY)*

Ger van Graas, T.C. Viets, J.W. de Leeuw and P.A. Schenck

Delft University of Technology
Department of Chemistry and Chemical Engineering
Organic Geochemistry Unit
De Vries van Heystplantsoen 2
2628 RZ Delft, The Netherlands

ABSTRACT

The organic matter in a Cretaceous sequence of alternating limestones and marls from the central Apennines, Italy, has been investigated microscopically and through detailed analysis of the extracts. Black layers are different from other layers in that they contain remains of bacteria in the insoluble material; the composition of the extracts points to a bacterial contribution too.

A paleoreconstruction based on chemical data shows a low productivity in the water column and an oxic environment of sedimentation for the black marls. Eolian input probably accounts for the presence of n-alkanes of terrestrial origin in all samples. This reconstruction is in agreement with paleontological and sedimentological data.

---

*In: *Advances in Organic Geochemistry 1981* (M. Bjorøy ed.), in press.

INTRODUCTION

During some intervals of the Cretaceous (140 to 65 My B.P.), dark coloured (black) shales, whether or not interbedded with lighter coloured, carbonate-richer beds, have been deposited more frequently and more abundantly than during any other geological period. Cretaceous black shales are encountered especially in the North and South Atlantic (e.g. DSDP leg 11, Hollister *et al.*, 1972; leg 40, Bolli *et al.*, 1978; leg 44, Benson *et al.*, 1978; leg 48, Montadert *et al.*,1979; etc.) but also in the Pacific at the flanks of seamounts and continents (e.g. leg 32, Larson *et al.*,1975; leg 33, Schlanger *et al.*, 1976).

Several authors have discussed the origin of the Cretaceous black shales. Schlanger and Jenkyns (1976) and Thiede and Van Andel (1977) suggest that the expansion of the mid-water oxygen minimum layer and its oxygen exhaustion caused the formation of the dark coloured, often organic rich layers, while Ryan and Cita (1977) emphasize the possibility of an ocean-wide stagnation. These theories are not conflicting; a full depletion of oxygen in the oxygen minimum layer will be favoured by a waning of circulation velocity. In case of complete stagnation (if possible), oxygen exhaustion is likely to start in the mid-water oxygen minimum zone.

The frequent depletion of oxygen in deeper parts of the Mid-Cretaceous oceans, which allowed the formation of organic rich sediments, is obviously related to both tectonic and climatic factors. The Mid-Cretaceous (110-85 My B.P.) is characterized by relatively high temperatures and low temperature differences between high and low latitudes (Frakes, 1979) as a consequence of a great rise of the sealevel (up to 350 m; Pitman, 1978) which in turn was caused by an increase of total volume of mid-oceanic ridges (van Straaten, 1973; Hays and Pitman, 1973). In such a situation a relatively low circulation velocity of oceanic water results and hence a decrease in replenishment of oxygen in deep water is expected. This depletion of oxygen has favoured the deposition of organic rich sediments in the oceans.

Depending on the place of deposition relative to the position of land areas, the organic matter in Mid-Cretaceous pelagic sediments is composed of varying ratios of terrestrial and marine organic matter (Tissot *et al.*, 1980). In spite of its large size, the rate of sealevel rise during the Cretaceous has been relatively small. Therefore , it is unlikely that the Cretaceous transgression would have caused a catastrophic transfer of terrestrially derived organic matter into the oceans, as was suggested by Jenkyns (1980).

Our current research is part of a project concerning sedimentological, paleontological and organic geochemical investigations of Middle Cretaceous black shale deposits from outcrops in Northern Italy and Southern France. In this paper we report about the results obtained on samples from a location in the north central Apennines, Italy, which covers a large part of the Cretaceous in this area. The sampled section forms part of a pelagic sequence. This sequence consists of a more or less regular alternation of carbonate-rich and carbonate-poorer beds, the latter of which are characterized by a grey to black colour and therefore are indicated as black shales.

The carbonate of the samples consists mainly of the remains of coccolithophores and to a smaller extent of planktonic and benthonic foraminifera (Wonders, 1980).

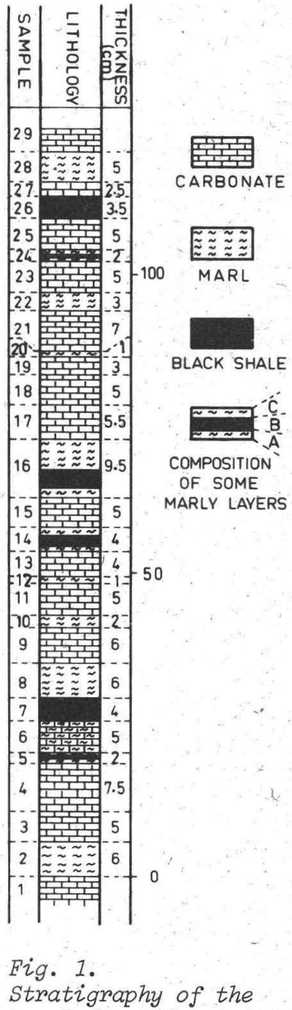


Fig. 1.
Stratigraphy of the sampled section.

De Boer and Wonders (1981) show the rhythmicity of the carbonate-marl alternations in the Albian-Cenomanian interval to be the result of a rhythmic variation of production of carbonate, which is related to the influence of astronomical parameters upon the earth's climate.

Analysis of the extractable organic matter from the limestones and marls, in combination with microscopic, sedimentological and paleontological data, made possible the construction of a model for the origin of this sedimentary sequence.

EXPERIMENTAL

The samples have been taken from a location along the Moria-Monte Petrano road near the cemetery of Moria (43°33'N, 12°41'S), 6.5 km southwest of Cagli in the north central Apennines, Italy (Wonders, 1980), from the lower part of the Scaglia Bianca Formation which is of Late Albian age (108-100 My B.P.). An interval of 1.30 m with 13 limestone/marl couplets was sampled (Fig. 1). In a number of couplets the marly layer is very thin. Several marly layers are partially or totally dark coloured. In case of partially dark coloured marls (samples 5, 14, 16 and 24) a subdivision was made as indicated in Fig. 1. In order to obtain fresh material about 30 cm of rock were removed before actual sampling.

In the laboratory six samples have been selected for a detailed analysis of the extracts: two carbonate layers (27 and 29); two integral marly layers, one with a black middle part (24-total) and one without a black middle part (28) and the black parts of two marly layers (24 B and 26). The samples were ground in a rotary disc mill and Soxhlet extracted with toluene/methanol (1/3 v/v) for 20 hrs. The organic carbon content of the extraction residues was measured after removal of carbonate with 2n HCl. The carbonate content of the samples was calculated from the weight loss upon 2n HCl treatment.

The total extracts were investigated by TLC using an Iatron Iatroscan TH-10 instrument equipped with Chromarods S II; hexane/diethylether/formic acid (95/5/1 v/v/v) was used as eluent (Kramer *et al.*, 1980). The hydrocarbons were isolated by preparative TLC on silicagel with petroleum ether 40-60/diethylether/acetic acid (89/10/1 v/v/v) as developer. Gas-chromatography (GLC) was performed using a Carlo Erba 4160 instrument equipped with a 25 m. glass WCOT column (I.D. 0.31 mm.) coated with SE-52.
Gas chromatography-mass spectrometry (GCMS) was carried out on a Varian 3700 gas chromatograph equipped with a 25 m. glass WCOT column (I.D. 0.25 mm.) coated with CP-sil-5, coupled to a MAT 44 quadrupole mass spectrometer operating at 70 eV with mass range m/z 50-500 and a cycle time of 2 s. In both GC and GCMS helium was used as carrier gas.

A blank procedure was carried out using quartz sand which was first heated for 16 hrs. at 900°C. Samples 26, 27, 28 and 29 have been investigated by incident light (UV, 365 nm.) microscopy.

RESULTS

Carbonate and organic carbon content of the samples are listed in Table 1. Extraction yields are in the order of magnitude of 10-100 ppm. Further quantitation was not attempted. TLC analysis showed that the extracts contain mainly saturated hydrocarbons (Rf 0.95-1.0) and highly polar material (Rf 0.0-0.1). Separate bands of aromatic hydrocarbons were not present.

The saturated hydrocarbon fractions of the extracts were analysed by GLC and GC-MS. The chromatograms of the hydrocarbon fraction of samples 26 and 28 are shown in Fig. 2. Identification of the numbered compounds is given in Table 2. Identification of hopanes and hopenes is based on mass spectral and GLC - retention data (Ensminger, 1974; Van Dorsselaer, 1974; Wardroper, 1979).

All samples contain n-alkanes with a moderate odd/even predominance* ($CPI_{24-34} \approx 2$) and squalene. The presence of the latter compound is due to

Table 1. Carbonate and organic carbon content of the samples.

SAMPLE	CARBONATE (% wgt)	$C_{organic}$ (% wgt)	SAMPLE	CARBONATE (% wgt)	$C_{organic}$ (% wgt)
3	73	.03	16C	68	.09
4	75	.02	17	78	.02
5A	75	.03	18	79	.01
5B	64	.08	19	77	.02
5C	69	.05	20	75	.05
6	71	.06	21	77	.02
7	71	.57	22	71	.02
8	75	.03	23	75	.02
9	75	.01	24-total	65	.14
10	74	.02	24A	72	.10
11	72	.03	24B	63	.26
12	71	.04	24C	54	.62
13	70	.03	25	73	.13
14	65	.08	26	67	.66
15	70	.04	27	73	.04
16A	65	.09	28	70	.23
16B	67	.21	29	77	.02

contamination from an unknown source, since it is the major compound showing up in the blank procedure. In the light layers (27, 28, 29) these alkanes were the only compounds that could be identified. The dark layers (24-total, 24B, 26) did also contain C27 and C29-32 hopanes. The major isomers are 17β(H), 21β(H)-hopanes, but 17α(H), 21β(H)- and 17β(H), 21α(H)-hopanes are also present. Other hopanoid compounds are present in some samples: hop-17(21)-ene was identified in sample 24 and 30-norneohop-13(18)-ene was tentatively identified in sample 26. Steroidal hydrocarbons were not detected in any of the samples. The saturated hydrocarbon fractions of samples 24-total and 24-B did not differ significantly.

The organic matter of sample 26, showing a brownish fluorescence under incident UV light is defined as structureless organic matter (SOM). This SOM - especially when it is associated with relatively large amounts of framboidal pyrite as in this case - is assumed to be the fossil form of bacterial biomass (Lijmbach, 1975). Moreover, this same qualitative analysis showed the presence of pelagic foraminifera and a fairly large amount of pollen and spores. Upon demineralisation (HCl/HF treatment) the pollen turned out to be of the bisaccate type (conifers).

The other samples (27, 28, 29) also contained SOM but in significantly smaller amounts.

* $$CPI_{24-34} = \frac{1}{2}\left(\frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}+C_{34}}\right)$$

DISCUSSION

The amounts of organic carbon in the black marly layers investigated (maximum 0.66%) are low as compared with values obtained for some Cretaceous black shales from the Atlantic Ocean (values up to 17%; e.g. Tissot *et al.*, 1980) or from other locations in the Apennines (values up to 14% at the Cenomanian-Turonian boundary; van Graas, unpublished results). However, on a number of other locations (e.g. DSDP leg 43, Tucholke *et al.*, 1979; leg 47B, Sibuet *et al.*, 1979) sediments occur which have been characterized as black shales and have organic carbon contents of less than 1%. Hence one might wonder whether it would be recommendable to reconsider the common definition of black shales being "organic-rich" dark-coloured marly or clayey sediments (e.g. Wonders, 1980). Microscopic studies indicate that pyrite instead of organic matter is responsible for the dark colour of the samples.

The hopanes exclusively present in the black layers probably are diagenetic products of bacteriohopanes (e.g. Van Dorsselaer *et al.*, 1974) which are present in bacteria (e.g. Rohmer and Ourisson, 1976). Two layers contain a hopene in addition to the hopanes. Hop-17(21)-ene is present in sample 24 and 30-norneohop-13(18)-ene in sample 26. These compounds were also found in Cretaceous black shales by Barnes *et al.* (1979) but together with their C_{27} and C_{29} or C_{30} homologues. They were thought to have arisen through rearrangement of the original double bond position. Recently Brassell *et al.* (1981) interpreted hop-17(21)-ene and neohop-13(81)-ene in Japan Trench samples as bacterial mar-

Table 2. Compounds identified by GC-MS in the hydrocarbon fractions of samples 26 and 28 (see Fig. 2).

1. n-hexadecane
2. 2,6,10-trimethylpentadecane
3. n-heptadecane
4. pristane
5. n-octadecane
6. phytane
7. n-nonadecane
8. n-eicosane
9. n-heneicosane
10. n-docosane
11. n-tricosane
12. n-tetracosane
13. n-pentacosane
14. phthalate ester (contaminant)
15. n-hexacosane
16. n-heptacosane
17. n-octacosane
18. squalene (contaminant)
19. 17α(H)-22,29,30-trisnorhopane
20. n-nonacosane
21. 17β(H)-22,29,30-trisnorhopane
22. unidentified hopane-like compound
23. n-triacontane
24. 30-norneohop-13(18)-ene
25. 17α(H),21β(H)-30-norhopane
26. 17β(H),21α(H)-30-norhopane
27. n-hentriacontane
28. 17α(H),21β(H)-hopane
29. 17β(H),21β(H)-30-norhopane
30. n-dotriacontane
31. 17α(H),21β(H)-homohopane
32. 17β(H),21β(H)-hopane
33. 17β(H),21α(H)-homohopane
34. n-tritriacontane
35. 17β(H),21β(H)-homohopane
36. n-tetratriacontane
37. n-pentatriacontane

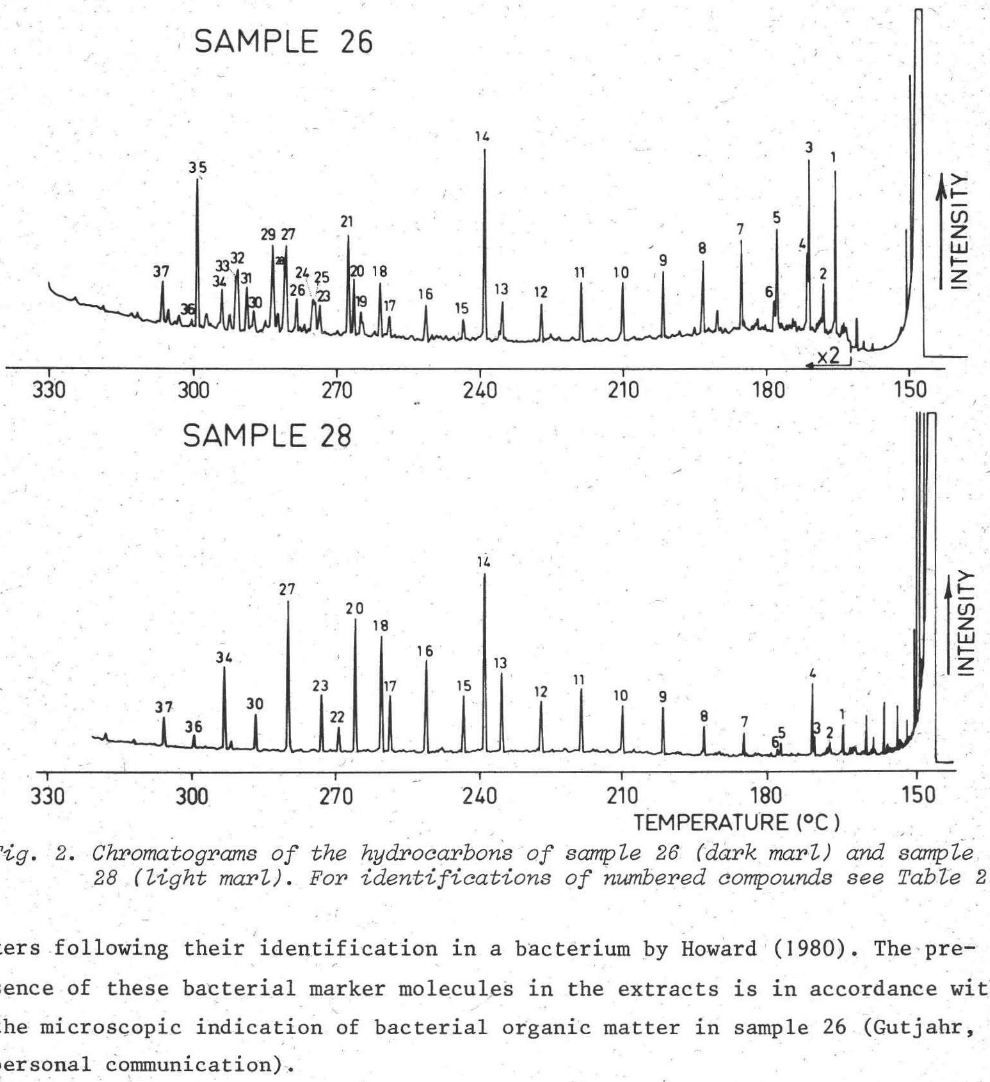


Fig. 2. Chromatograms of the hydrocarbons of sample 26 (dark marl) and sample 28 (light marl). For identifications of numbered compounds see Table 2.

kers following their identification in a bacterium by Howard (1980). The presence of these bacterial marker molecules in the extracts is in accordance with the microscopic indication of bacterial organic matter in sample 26 (Gutjahr, personal communication).

Three isomeric types of hopanes are present in the samples: 17β(H),21β(H), 17β(H),21α(H) and 17α(H),21β(H). The dominating presence of the 17β(H),21β(H)-type indicates a relatively low degree of maturation (Van Dorsselaer, 1974; Mackenzie *et al.*, 1980).

The n-alkane distribution in the samples (CPI ≈ 2) indicates an origin from higher plant material (e.g. Maxwell *et al.*, 1971). It also confirms the relatively low maturity of the sediments. Apart from the n-alkanes no other higher plant related compounds such as steroidal or diterpenoid hydrocarbons could be detected in the saturated hydrocarbon fractions. Since the TLC-analysis has shown the absence of aromatic hydrocarbon bands separated from the saturated hydrocarbons, partially or totally aromatized steroidal or diterpenoid hydrocarbons are also not present. The samples did not contain microscopically visible higher plant tissues although a number of spores and pollen were present. An explanation for the exclusive presence of n-alkanes as higher plant marker molecules could be the input of eolian dust into the sediments. The organic matter of eolian dust mainly consists of higher plant waxes (n-alkanes, n-alcohols, n-carboxylic acids) but does not contain diterpenoids or steroids (Simoneit, 1977; Simoneit and Eglinton, 1977). The supposed open marine environment of sedimentation of the samples (de Boer, 1982) does not at all exclude the possibility of eolian input since eolian transport can cover large distances (Simoneit,1977). The presence of bisaccate pollen (conifers) is also in agreement with eolian input since they can be airborne over large distances. In case of potamic input of terrestrial material one would expect to find diterpenoid hydrocarbons which are present in high concentrations in the resins of conifers (Thomas, 1969). The spores present in the samples are fairly large which makes eolian input unlikely. The way in which they reached the sediment remains uncertain at present.

The complete absence of steroidal hydrocarbons in the extracts and of visible organic algal remains in the sediments upon microscopic investigation indicate a low productivity in the water column and an aerobic environment of sedimentation. The low mean sedimentation rate (0.7 cm/1000 y; de Boer, 1982) agrees with the proposed low productivity.

In conclusion we can construct the following model for the origin of this sedimentary sequence. The low amounts of organic carbon and the absence of substantial amounts of algal related compounds, together with the low rate of sedimentation, indicate that the sediments have been deposited in a low productive environment with enough oxygen available in the water column to oxidize the algal products. Black marly layers were formed when enough organic material could reach the sediment surface to enable growth of bacteria as represented by the hopanes and the presence of structureless bacterial residues in the samples. This relatively high input of organic matter into the sediment probably is the result of a lower availability of oxygen. According to sedimentological evidence marly layers were deposited during times of low productivity (de Boer, 1982). Hence the presence of black layers is probably due to a lower availability of oxygen caused by a restricted water circulation. During such periods absence of oxygen in the top of the sediments gave rise to activity of sulfate-reducing bacteria which must have led to the formation of pyrite that causes the dark colour of the sediments. Eolian input explains the sole presence of n-alkanes as higher plant marker molecules and is in agreement with the paleoreconstruction of the site as being a pelagic environment located at a considerable distance from the mainland (de Boer, in preparation).

The relatively low maturity of the samples as indicated by the distribution of the hopanes and the n-alkanes is in agreement with the burial history which shows an overburden of ±500 m until the Miocene, an increase to 2000-2500 m during the Miocene, and upheaval and erosion afterwards (Wonders, 1980).

ACKNOWLEDGEMENTS

The authors are grateful to Mr. P.L. de Boer for valuable discussions and suggestions regarding the geological aspects of this investigation. Dr. C.C.M. Gutjahr (Koninklijke/Shell Exploratie en Produktie Laboratorium, Shell Research B.V., Rijswijk, The Netherlands) kindly performed the microscopic analyses. Mr. F. de Lange is thanked for technical assistance during the course of this investigation. This research is supported by the Netherlands Foundation for Earth Science Research (AWON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

REFERENCES

Barnes P.J., Brassel S.C., Comet P., Eglinton G., McEvoy J., Maxwell J.R., Wardroper A.M.K., Volkman J.K. (1979) 50. Preliminary lipid analyses of core sections 18, 24 and 30 from hole 402 A. In *Initial Reports of the Deep Sea Drilling Project*, volume XLVIII (Montadert L., Robert D.G. *et al.* eds.), pp. 965-975. Washington, U.S. Government Printing Office.
Benson W.E., Sheridan R.E. *et al.* (eds.) (1978) *Initial Reports of the Deep Sea Drilling Project*, volume XLIV. Washington, U.S. Government Printing Office.
de Boer P.L. (1982) Cyclicity and the storage of organic matter in Middle Cretaceous pelagic sediments (to be published).
de Boer P.L. and Wonders A.A.H. (1981) Milankovitch parameters and bedding rhythms in Umbrian Middle Cretaceous pelagic sediments. I.A.S. 2nd Eur. Meeting, Bologna Abstr., 10 - 13.
Bolli H.M., Ryan W.B.F. *et al.* (eds.) (1978) *Initial Reports of the Deep Sea Drilling Project*, volume XL. Washington, U.S. Government Printing Office.
Brassell S.C., Wardroper A.M.K., Thompson I.D., Maxwell J.R., Eglinton G. (1981) Specific acyclic isoprenoids as biological markers of methanogenic bacteria in marine sediments. *Nature* 290, 693-696.
Ensminger A. (1974) Triterpénoides du schiste de Messel. Thesis, University of Strasbourg.
Frakes L.A. (1979) *Climates throughout Geologic Time*. Elsevier, 310 p.
Hays J.D. and Pitman W.C. (1973) Lithospheric plate motion, sea level changes and ecological consequence. *Nature* 246, 18 - 22.
Hollister C.D., Ewing J.I. *et al.* (1972) *Initial Reports of the Deep Sea Drilling Project*, Volume XI. Washington, U.S. Government Printing Office.
Howard D.L. (1980) Polycyclic triterpenes of the anaerobic photosynthetic bacterium Rhodomicrobium vaniellii. Thesis, University of California, Los Angeles.
Jenkyns H.C. (1980) Cretaceous Anoxic Events: From Continents to Oceans. *J. Geol. Soc. London* 137, 171 - 188.

Kramer J.K.G., Fouchard R.C., Farnworth E.R. (1980) Effect of solvents on the resolution of neutral lipids on chromarods. *J. Chromatogr.* 198, 279 - 285.

Larson R.L., Moberly R.M. *et al.* (1975) *Initial Reports of the Deep Sea Drilling Project,* Volume XXXII. Washington, U.S. Government Printing Office.

Lijmbach G.W.M. (1975) SP 1. On the origin of petroleum In *9th World Petroleum Congress,* volume 2, pp. 357-374. London, Applied Science Publishers.

Mackenzie A.S., Patience R.L., Maxwell J.R., Vandenbroucke M., Durand B. (1980) Molecular parameters of maturation in the Toarcian shales, Paris Basin, France. -I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta,* 44, 1709 - 1721.

Maxwell J.R., Pillinger C.T., Eglinton G. (1971) Organic geochemistry. *Quart. Rev. Chem. Soc.* 25, 571 - 628.

Montadert L., Roberts D.G. *et al.* (1979) *Initial Reports of the Deep Sea Drilling Project,* Volume XLVIII. Washington, U.S. Government Printing Office.

Pitman W.C. (1978) Relationship between eustacy and stratigraphic sequences of passive margins. *Geol. Soc. Am. Bull.* 89, 1389 - 1403.

Rohmer M., Ourisson G. (1976) Structure des bacteriophopanetetrols d'Acetobacter xylinum. *Tetr. Lett.* 40, 3633 - 3636.

Ryan W.B.F., Cita M.B. (1977) Ignorance concerning episodes of oceanwide stagnation. *Mar. Geol.* 23, 197 - 215.

Schlanger S.O., Jenkyns H.C. (1976) Cretaceous oceanic anoxic events: causes and consequences. *Geologie en Mijnbouw* 55, 179 - 184.

Schlanger S.O., Jackson E.D. *et al.* (1976) *Initial Reports of the Deep Sea Drilling Project,* Volume XXXIII. Washington, U.S. Government Printing Office.

Sibuet J.C., Ryan W.B.F. *et al.* (1979) *Initial Reports of the Deep Sea Drilling Project*, Volume XLVII part 2. Washington, U.S. Government Printing Office.

Simoneit B.R.T. (1977) Organic matter in eolian dusts over the Atlantic Ocean. *Mar. Chem.* 5, 443-464.

Simoneit B.R.T. and Eglinton G. (1977) Organic matter of eolian dust and its input to marine sediments. In *Advances in Organic Geochemistry 1975* (Campos R., Goni J. eds.), pp. 415-430. ENADIMSA, Madrid.

van Straaten L.M.J.U. (1973) Eustatische zeespiegelbewegingen en verschuiving der continenten. *Kon. Ned. Akad. v. Wetensch.* 82, 6-8.

Thiede J., Van Andel T.H. (1977) The paleoenvironment of anaerobic sediments in the Late Mesozoic South Atlantic Ocean. *Earth Planet. Sci. Lett.* 33, 301-309.

Thomas B.R. (1969) Kauri resins - modern and fossil. In *Organic Geochemistry - Methods and Results* (Eglinton G., Murphy M.T.J. eds.), pp. 599-618. Springer Verlag, Berlin.

Tissot B., Demaison G., Masson P., Delteil J.R., Combaz A. (1980) Paleoenvironment and petroleum potential of Middle Cretaceous black shales in Atlantic basins. *Am. Assoc. Pet. Geol. Bull.* 64, 2051-2063.

Tucholke B.E., Vogt P.R. *et al.* (1979) *Initial Reports of the Deep Sea Drilling Project*, Volume XLIII. Washington, U.S. Government Printing Office.

Van Dorsselaer A. (1974) Triterpenes de sediments. Thesis, Univ. of Strasbourg.

Van Dorsselaer A., Ensminger A., Spyckerelle C., Dastillung M., Sieskind O., Arpino P., Albrecht P., Ourisson G., Brooks P.W., Gaskell S.J., Kimble B. J., Philp R.P., Maxwell J.R., Eglinton G. (1974) Degraded and extended hopane derivatives (C_{27} to C_{35}) as ubiquitous geochemical markers. *Tetr. Lett.*, 1349-1352.

Wardroper A.M.K. (1979) Aspects of the geochemistry of polycyclic isoprenoids. Thesis, University of Bristol.

Wonders A.A.H. (1980) Middle and Late Cretaceous planktonic foraminifera of the western Mediterranean area. *Utrecht Micropaleontol. Bull.* 24.

CHAPTER 3

A STUDY OF THE SOLUBLE AND INSOLUBLE ORGANIC MATTER FROM THE LIVELLO BONARELLI, A CRETACEOUS BLACK SHALE DEPOSIT IN THE CENTRAL APENNINES, ITALY*

Ger van Graas, T.C. Viets, J.W. de Leeuw and P.A. Schenck

Delft University of Technology
Department of Chemistry and Chemical Engineering
Organic Geochemistry Unit
De Vries van Heystplantsoen 2
2628 RZ Delft, The Netherlands

ABSTRACT

A suite of samples from the Livello Bonarelli, a thinly laminated carbonate-poor sedimentary unit at the Cenomanian-Turonian boundary, have been studied. Pyrolysis-mass spectrometry of the extracted sediments indicates the presence of significant differences between the samples. Microscopic investigations and pyrolysis-gas chromatography show a main contribution from marine organic matter for all samples. The composition of the extractable hydrocarbons becomes more complex with increasing organic carbon content of the sediments.

The results of the organic geochemical analyses combined with sedimentological and paleontological data enable us to draw some conclusions with regard to the environment of sedimentation of the Livello Bonarelli. The proposed paleoenvironment is compared with a model that has recently been described for the Pleistocene Mediterranean sapropels.

---

*Submitted for publication to *Geochim. Cosmochim. Acta* .

INTRODUCTION

The Livello Bonarelli is a carbonate-poor sedimentary unit deposited at the Cenomanian-Turonian boundary (Wonders, 1980). It is present over a large area in the Umbrian-Marchean Apennines (Bernouilli, 1972). Similar deposits from Late Cenomanian to Early Turonian age have been found at many other locations e.g. in Spain, England (Black Band), Colorado and at several North Atlantic DSDP sites (Schlanger and Jenkyns, 1976; Fischer, 1980; Summerhayes, 1981). These sediments generally have high amounts of organic carbon (up to 16%). They are thought to be the result of one of the so-called 'oceanic anoxic events' that have occurred during the Cretaceous (Schlanger and Jenkyns, 1976; Arthur and Schlanger, 1979; Jenkyns, 1980). As to the exact nature of these events several models have been proposed. In case of the North Atlantic sediments Summerhayes (1981) suggested that an influx of dense saline bottom water from the South Atlantic has been responsible for the formation of the organic rich deposits. A similar model has also been considered for the Livello Bonarelli but clear indications for the presence of highly saline bottom water have not yet been found (de Boer, personal communication).

In this paper we report the results obtained in organic geochemical analyses of a number of samples from the Livello Bonarelli. The insoluble organic material of the samples was investigated by Curie-point pyrolysis-mass spectrometry (Py-MS) and Curie-point pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)(e.g. van Graas *et al.*, 1981). Several samples have been studied microscopically. The extracted saturated hydrocarbons of six samples were analyzed in detail.

The geochemical data combined with sedimentological and paleontological results enable us to draw some conclusions on the origin of the organic matter in the sediments and on the conditions of sedimentation. The results obtained for the Livello Bonarelli are compared with data on samples from the Albian part of the same exposure (van Graas *et al.*, 1982b).

EXPERIMENTAL

The samples have been taken from the Livello Bonarelli, a carbonate-poor interval deposited at the Cenomanian-Turonian boundary (92 My B.P.). They come from a location along the Moria-Monte Petrano road near the cemetery of Moria (43°33'N, 12°41'E), 6.5 km southeast of Cagli in the north central Apennines, Italy (Wonders, 1980). In order to obtain fresh material about 40-50 cm of rock were removed before actual sampling.

In the laboratory the samples were ground in a rotary disc mill and Soxhlet extracted with toluene/methanol (1/3, v/v; 20 h). The organic carbon content of the extraction residues was measured after removal of carbonates with 2 n HCl. The carbonate content of the samples was calculated from the weight loss during the HCl treatment. Samples 9, 13, 31 and 32 have been investigated by incident light microscopy (365 nm).

Curie-point pyrolysis-mass spectrometry

The apparatus described by Meuzelaar *et al.* (1978) was used under the following conditions: pyrolysis temperature 510°C; pyrolysis time 1 s; ionisation energy 14 eV; number of scans 150; scanning velocity 10 scans/s; mass range m/z 16-169.

The ferromagnetic wires were coated with 80-100 μg of the extracted samples suspended in methanol. Each sample was analyzed in triplicate. Data processing of the pyrolysis mass spectra was performed using the programs for factor analysis and subsequent discriminant analysis from the *Statistical Package of the Social Sciences* (Nie *et al.*, 1975) as described by Windig *et al.* (1982). The resulting discriminant functions can be converted into mass spectra. Discriminant scores, the quantitative measures of a discriminant spectrum in the individual mass spectra, can be used to look for clustering in the data set. A similar approach based on the results of factor analysis was used on samples from the Toarcian shales of the Paris Basin, France (van Graas *et al.*, 1981).

Curie-point pyrolysis-gas chromatography(-mass spectrometry)

Pyrolysis-gas chromatography was carried out using a pyrolysis reactor similar to the one described by Meuzelaar *et al.* (1975) modified for the use at high temperatures (van de Meent *et al.*, 1980). The samples were pyrolyzed for 10 s at 610°C. The pyrolysis reactor was mounted on a Packard Becker 419 instrument equipped with a Packard 799 cryogenic unit and a 50 m glass capillary column (i.d. 0.5 mm) coated with CP-sil-5 (film thickness 1.25 μm). Helium (5 ml/min) was used as carrier gas.

Pyrolysis-gas chromatography-mass spectrometry was carried out under identical conditions on a Varian 3700 instrument equipped with a Packard 799 cryogenic unit and coupled to a MAT 44 quadrupole mass spectrometer operating at 80 eV with a cycle time of 2 s and a mass range of m/z 46-400. Identification of the pyrolysis products is based on mass spectral data (Stenhagen *et al.*, 1974) and gas chromatographic retention times (Svob and Deur-Siftar, 1974; Schröder, 1980).

Analysis of the extracts

The extracts of samples 6, 9, 13, 30, 31 and 32 have been analyzed. The saturated hydrocarbon fractions were obtained by preparative thin layer chromatography on silicagel with petroleum ether 40-60/diethyl ether/acetic acid (89/10/1, v/v/v) as a developer or by column chromatography over silicagel using hexane as an eluent. Gas chromatography was carried out on a Varian 3700 instrument equipped with a 24 m glass capillary column (i.d. 0.25 mm) coated with CP-sil-5 and on a Carlo Erba 4160 instrument equipped with a 25 m glass capillary column (i.d. 0.3 mm) coated with SE-52. Gas chromatography-mass spectrometry of the hydrocarbon fractions was performed on a Varian 3700 gas chromatograph equipped with a 25 m fused silica column coated with CP-sil-5 coupled to a MAT 44 quadrupole mass spectrometer operating at 80 eV with mass range m/z 50-500 and a cycle time of 2 s.

RESULTS

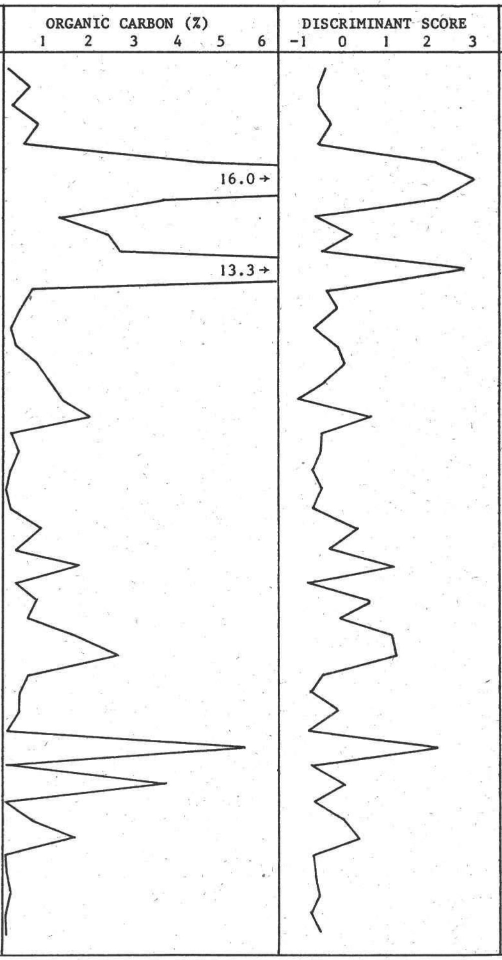
In the Livello Bonarelli about 28 couplets with different lithology and/or colour can be distinguished (de Boer, 1982) and from these 39 separate layers with some additional transitions and subdivisions have been sampled. Especially in the middle part the lithologic alternations were so small-scaled that no proper samples of individual layers could be taken. The inorganic part of the samples is composed mainly of clay minerals and biogenic silica (Radiolaria; de Boer, personal communication). Pyrite is present in various amounts. Carbonate content, organic carbon content and extraction yield of the samples are listed in Table 1.

The extracted samples have been subjected to Py-MS analysis to characterize the insoluble organic matter. The Py-MS data were processed using discriminant analysis. According to the first discriminant function the samples can be devided into several groups (Table 1): 1) samples 6 and 9; 2) samples 5, 6A and 30; 3) samples 20, 24 and 26; 4) samples 8A, 14D, 18, 22 and 34; 5) samples 11, 13, 14A, 23, 28B, 32 and 33B; 6)samples 1A, 2, 3, 4, 7, 8B, 10, 12, 14B, 15, 16, 17, 17A, 17B, 19, 21, 27, 28A, 29, 31, 33A, 35, 36, 37, 38 and 39; 7) sample 14C. This grouping is moderately correlated with the organic carbon content of the samples (r=0.82). Samples 8B, 14C and 32 are the main exceptions to this rule. Their organic carbon content is significantly higher than is suggested by their grouping based on the pyrolysis mass spectra.

Information on the chemical nature of the observed grouping can be found in the spectrum of the first discriminant function (Fig. 1). The negative part of the spectrum characterizing the high numbered groups (low organic carbon

Table 1. Carbonate and organic carbon content, extraction yield, discriminant score and grouping based on discriminant analysis of all samples.

SAMPLE	CARBONATE (%)	EXTRACT (ppm)	GROUP
1A	4	14	6
1B	1	58	6
2	6	53	6
3	4	113	6
4	2	98	6
5	6	1611	2
6	6	10174	1
6A	8	766	2
7	0	68	6
8A	0	119	4
8B	0	120	6
9	4	8570	1
10	3	573	6
11	1	69	5
12	4	127	6
13	1	39	5
14A	6	152	5
14B	6	407	6
14C	35	423	7
14D	8	193	4
15	4	10	6
16	2	343	6
17	1	24	6
17A	2	44	6
17B	4	50	6
18	3	194	4
19	1	40	6
20	3	657	3
21	2	261	6
22	3	243	4
23	2	758	5
24	3	1066	3
26	1	930	3
27	4	243	6
28A	4	205	6
28B	4	243	5
29	2	66	6
30	7	4149	2
31	2	26	6
32	8	1139	5
33A	3	33	6
33B	2	159	5
34	7	465	4
35	3	144	6
36	6	84	6
37	5	10	6
38	4	50	6
39	13	59	6



content) consists of masses representing alkenes, alkanes and benzene. The positive part of the spectrum characterizing the low numbered groups (high organic carbon content) is filled with masses that can tentatively be ascribed to various series of aromatic compounds such as phenols, benzenes ($\geq C_8$), indanes and indenes. Also present are m/z 34 (H_2S) and m/z 66, 79 and 80, probably related to cyclopentadiene and its methylated homologues. In case of the series of aromatic compounds the higher substituted members are more distinctly present in the spectrum.

Samples 5, 6, 6A, 7, 8A, 8B, 9, 30 and 32 have been analyzed by Py-GC and sample 9 also by Py-GC-MS (Fig. 2, Table 2). As the pyrograms of the samples are qualitatively similar with regard to the prominent peaks we considered the

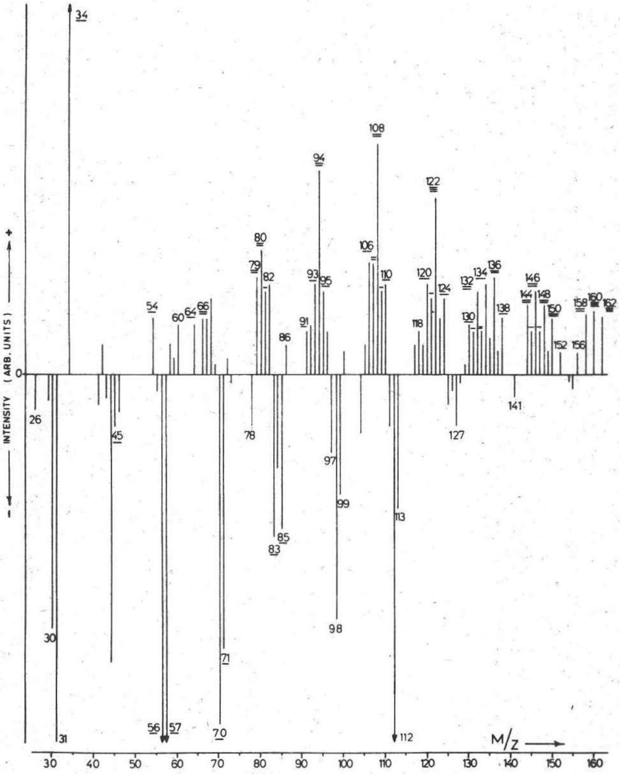


Fig. 1. Spectrum of first discriminant function. Underlining of mass numbers indicates the amount of correlation between the mass and the function. Triple underlined: correlation >0.9; double underlined: >0.8; single underlined: >0.6.

Py-GC-MS data of sample 9 sufficient for the identification of the major differences between the pyrograms of the samples.

Based on the Py-MS results and on the organic carbon contents six samples were selected for analysis of the saturated hydrocarbon fractions. The gas chromatogram of sample 9 is shown in Fig. 3. The results of the GC-MS analyses of the six samples are summarized in table 4.

Samples 9, 13, 31 and 32 have been analyzed by incident light microscopy. The results are shown in Table 4. All samples show signs of severe oxidation.

DISCUSSION

The grouping of the samples based on the Py-MS data (Table 1) shows the existence of significant differences between samples with low (group 6) and high (group 1) amounts of organic material as well as the presence of several groups of samples with intermediate characteristics. The mass spectrum of the first discriminant function (Fig. 1) together with the Py-GC results (Fig. 2) provide information on the chemical background of the observed grouping. In the pyrograms of group 6 samples (samples 8B and 7; Fig. 2b) the major peaks are from relatively short ($\leq C_8$) alkanes and alkenes and from short alkylbenzenes. These compounds can also be identified in the negative part of the discriminant spectrum that is characteristic for group 6 samples. In pyrograms of group 4 and 5 samples other series of compounds especially in the high molecular weight

Table 2. Identifications of numbered compounds in the pyrolysis gas chromatograms of samples 7 and 9 (Fig. 2).

1	Light products such as H_2S, SO_2, CH_4, C_2H_4, C_2H_6
2	Propene
3	Propane
4	Me-propane
5	Me-propene
6	But-1-ene + Buta-1,3-diene
7	*n*-Butane
8	*tr*-But-2-ene + Methanethiol
9	*ci*-But-2-ene
10	3-Me-but-1-ene
11	2-Me-butane
12	Pent-1-ene
13	2-Me-but-1-ene
14	*n*-Pentane
15	Isoprene
16	*tr*-Pent-2-ene
17	*ci*-Pent-2-ene
18	2-Me-but-2-ene
19	*tr*-1,4-Pentadiene
20	Cyclopentadiene
21	*ci*-1,4-Pentadiene
22	Cyclopentene
23	2- + 3-Me-pent-1-ene
24	2-Me-pentane
25	Hex-1-ene
26	*n*-Hexane
27	C6:1
28	C6:2
29	Me-cylopentane
30	2-Me-cyclopentadiene
31	1-Me-cyclopentadiene
32	Benzene
33	Thiophene
34	Cyclohexa-1,4-diene
35	Cyclohexene
36	Hept-1-ene
37	*n*-Heptane
38	C7:1
39	C7:2
40	Toluene
41	Me-thiophene
42	2-Me-heptane
43	Oct-1-ene
44	*n*-Octane
45	C8:1
46	C8:2
47	Et-benzene
48	*m*- + *p*-Xylene
49	C_2-thiophene
50	Heptan-2-one
51	Styrene
52	*o*-Xylene
53	Non-1-ene
54	*n*-Nonane
55	C_3-benzene
56	C_3-thiophene
57	Phenol
58	Octan-2-one
59	Dec-1-ene
60	*n*-Decane
61	Indane
62	Indene
63	C_4-benzene
64	C_4-thiophene
65	*o*-Cresol
66	*m*- + *p*-Cresol
67	Nonan-2-one
68	Undec-1-ene
69	*n*-Undecane
70	Me-indene
71	C_2-phenol
72	Dodec-1-ene
73	*n*-Dodecane
74	C_2-indene
75	2-Me-naphthalene + Me-benzothiophene
76	Tridec-1-ene
77	1-Me-naphthalene + 2,6,10-tri-Me-undec-1-ene
78	*n*-Tridecane
79	Tetradec-1-ene
80	*n*-Tetradecane
81	Pentadec-1-ene
82	*n*-Pentadecane
83	Contaminant
84	Hexadec-1-ene
85	*n*-Hexadecane
86	Heptadec-1-ene
87	*n*-Heptadecane
88	Prist-1-ene
89	Octadec-1-ene
90	*n*-Octadecane

C6:1 is an aliphatic hydrocarbon with 6 carbon atoms and one double bond equivalent; C_2-thiophene is dimethyl or ethyl substituted thiophene.

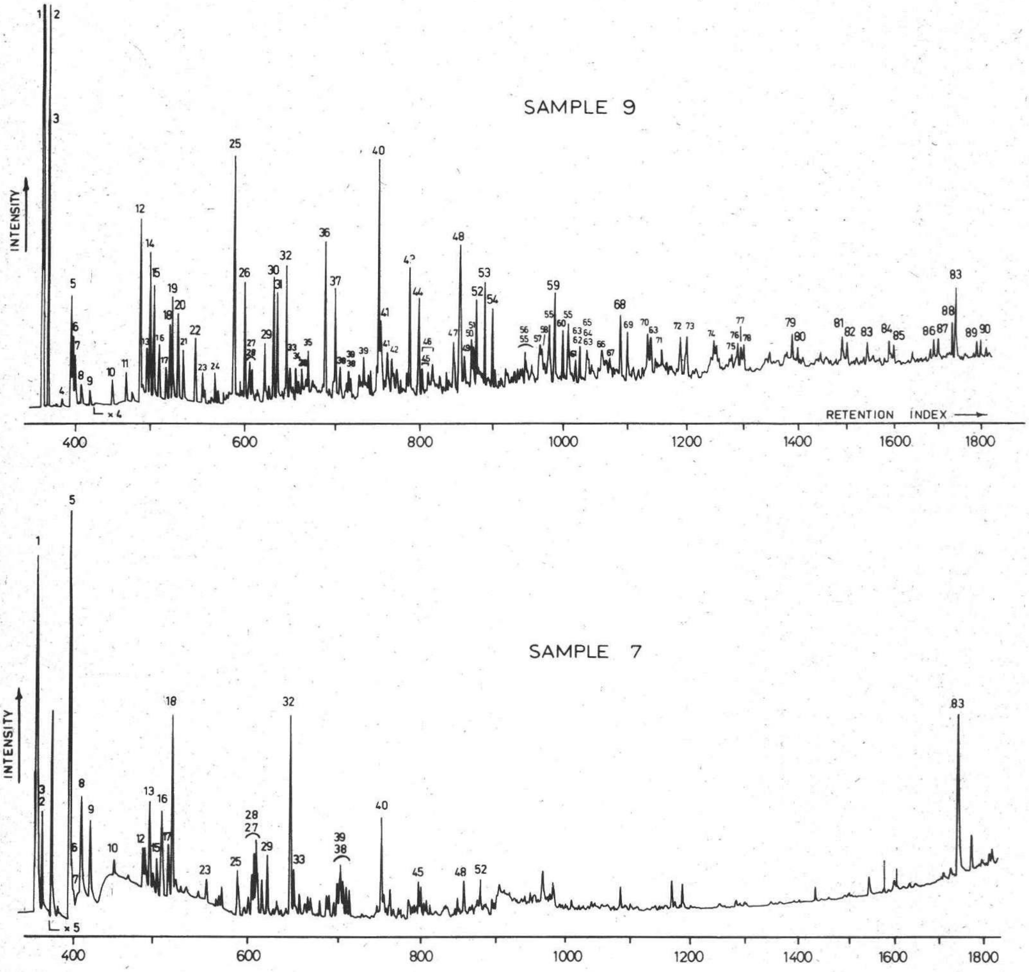


Fig. 2. Pyrolysis gas chromatograms of samples 9 and 7. Temperature program: -25°C (5 min) to 275°C at 3°C/min. Identification of numbered compounds is given in Table 2.

part of the chromatogram become relatively important. This phenomenon is even more outspoken in the pyrograms of group 1 and 2 samples (samples 5, 6, 6A, 9 and 30; Fig. 2a) containing alkylbenzenes, indanes, indenes, phenols and cyclopentadienes. These compounds are consistent with masses present in the positive part of the discriminant spectrum (Fig. 1). The samples of group 1 differ from those of group 2 because of a higher amount of prist-1-ene in the pyrograms and of H_2S in the pyrolysis mass spectra of the former. The significance of the fluctuation of the prist-1-ene concentrations is not clear. This compound also plays an important part in other series of samples (van Graas *et al.*, 1981).

Although the masses that characterize the organic rich samples originate

Table 3. Identifications of marked compounds in the gas chromatograms of sample 9 (Fig. 3).

a. 2,6,10-trimethyltridecane
b. 2,6,10-trimethylpentadecane
c. pristane
d. phytane
e. C_{27}-diasterene
f. C_{27}-diasterene
g. C_{28}-diasterene
h. unknown
i. C_{28} + C_{29}-diasterene
k. C_{29}-diasterene
l. 4-methyldiasterene
m. 5α(H)-cholestane
n. unknown
o. 22,29,30-trisnorhop-17(21)-ene
p. 4-methyldiasterene
q. 17β(H)-22,29,30-trisnorhopane
r. 30-nor-neohop-13(18)-ene
s. 5α(H)-24-cholestane
t. hop-17(21)-ene
u. 17α(H),21β(H)-hopane
v. neohop-13(18)-ene
w. 17β(H),21β(H)-30-nor-hopane
x. homohop-17(21)-ene
y. 17α(H),21β(H)-homohopane
z. 17β(H),21β(H)-hopane
A. 17β(H),21α(H)-homohopane
B. 17β(H),21β(H)-homohopane

mainly from aromatic compounds, the pyrograms do not have a predominantly terrigenous character because of the relatively low amounts of phenols and the absence of methoxyphenols and of long-chain (>C_{20}) alkanes and alkenes. The pyrograms of the organic rich samples resemble those of Cariaco Trench kerogens (van de Meent *et al.*, 1980) which are supposed to have mainly marine input material (Hoering, 1971; Simoneit *et al.*, 1973). Pyrograms of Atlantic Cretaceous black shales differ from our samples in the presence of a notably higher terrestrial component (van de Meent *et al.*, 1980).

The saturated hydrocarbon fractions of the samples show an increasing diversity with increasing organic carbon content (Table 4). All samples contain significant amounts of n-alkanes but these indicate various origins. In samples

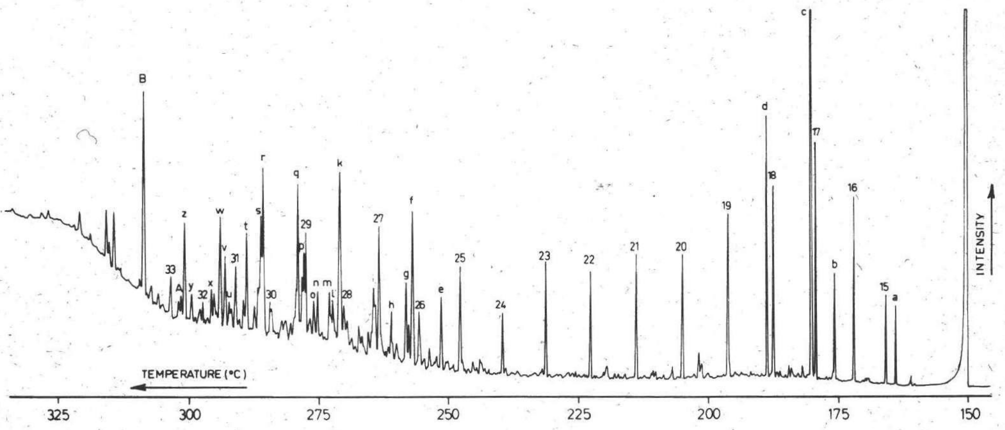


Fig. 3. Gas chromatogram of the saturated hydrocarbon fraction of sample 9. Stationary phase: CP sil 5; temperature program: 150-325°C, 4°C/min. Identification of marked compounds is given in Table 3; numbers indicate chain lengths of n-alkanes.

13 and 31 the distribution of the n-alkanes mainly indicates a higher plant origin (maximum at C_{27} and C_{31}; e.g. Maxwell *et al.*, 1971). The low CPI of sample 31 suggests a fairly advanced level of maturation. However, this is contradictory to observations in the extracts of other samples from the series which are of the same diagenetical stage (high CPI in samples 6 and 9; predominance of 17β(H),21β(H)-hopanes over other isomers; Van Dorsselaer *et al.*, 1974). Hence there must be another (unknown) contribution to the n-alkanes. The n-alkanes of sample 30 (maximum at C_{21}) are thought to represent the presence of bacterially altered marine material (Hatcher *et al.*, 1977). Samples 6, 9 and 32 have had a major marine input as can be judged from the n-alkanes (maximum at C_{16} or C_{17}; Simoneit, 1975). The high CPI of samples 6 and 9 indicates a distinct input of higher plant material (e.g. Maxwell *et al.*, 1971). The increasing amounts of hopanoid compounds when going from sample 31 to sample 9 indicate an increasing amount of bacterial input material (Van Dorsselaer *et al.*, 1974). The steranes and diasterenes, which are absent in samples 13 and 31, and show an increase parallel to the hopanoids in the other samples can be the result of both marine and terrestrial input material. Their presence indicates an environment of sedimentation which has been sufficiently anoxic for the preservation of these compounds.

In addition to the major compound series discussed above several compounds are present in trace amounts. Sample 30 contains A-nor-steranes which have recently been identified in a Cretaceous black shale and were suggested to be marker molecules for certain types of sponges (van Graas *et al.*, 1982a). In the GC-MS analyses of samples 6 and 9 spectra showed up which have tentatively been identified to be indicative for A-nor-diasterenes related to the A-nor-steranes (van Graas *et al.*, 1982a). The presence of diterpanes in sample 32 can be regarded as an indication for the input of terrestrial material (Simoneit, 1977). Sample 32 also contains compounds that have recently been identified as 17(21)-secohopanes which are possibly diagenetic products of hopanoid compounds (Trendel *et al.*, 1982).

The observed co-occurrence of diasterenes and neohop-13(18)-enes is of special interest (Table 4). Diasterenes are thought to arise through an acid-catalyzed rearrangement of sterenes (Rubinstein *et al.*, 1975). Barnes *et al.* (1979) suggested that the presence of neohop-13(18)-enes in sediments is caused by a similar rearrangement starting from hop-17(21)-enes (Berti and Bottari, 1968) but Brassell *et al.* (1981) indicated the possibility of a direct bacterial input of neohop-13(18)-ene. In our case the simultaneous occurrence of diasterenes and neohop-13(18)-enes supports the hypothesis of Barnes *et al.* (1979).

Table 4. Summary of GC-MS results of hydrocarbon fractions.

SAMPLE	C_{org} (%)	COMPOSITION OF HYDROCARBON FRACTION[1] n-alkanes	hopanes	Δ17(21)-hopenes	Δ13(18)-neohopenes	steranes	dia-sterenes	trace comp.	CPI[2]	Pr/Ph[3]	MACERAL DESCRIPTION SOM[4]	desmo-collinite	sporinite	lipto-detrinite	micrinite	pyrite
6	16.0	++++ C_{17}	+++ $\beta\beta C_{31}$	++ C_{30}	++ C_{29}	++ $5\alpha C_{29}$	+++ C_{27}	[6]	2.1	2.5	n.d	n.d	n.d	n.d	n.d	n.d
9	13.3	++++ C_{17}	++++ $\beta\beta C_{31}$	++ C_{30}	+++ C_{29}	++ $5\alpha C_{29}$	+++ C_{29}	[6]	2.3	2.3	+++	–	++	+++	+++	+++
30	5.6	++++ C_{21}	++++ $\beta\beta C_{27}$	++ C_{27}	+ C_{29}	++ $5\alpha C_{29}$	+ n.d[5]	[7]	1.6	1.6	n.d	n.d	n.d	n.d	n.d	n.d
32	3.8	++++ C_{16}	++++ $\beta\beta C_{27}$	++ C_{27}	–	++ $5\alpha C_{29}$	–	[8–9]	n.d	1.7	+++	+	+	+	+++	++
13	0.3	++++ C_{27}	++ $\beta\beta C_{31}$	–	–	–	–	–	1.7	1.2	+	+	–	+	–	++
31	0.1	++++ C_{31}	–	–	–	–	–	–	1.2	3.7	–	–	–	–	–	+

[1] Indicated are relative intensities of compound series (++++ abundant, +++ common, ++ minor, + trace, – not detected) and the member with maximum intensity.

[2] $$\mathrm{CPI} = \tfrac{1}{2}\left(\frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{24}+C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}+C_{33}}{C_{26}+C_{28}+C_{30}+C_{32}+C_{34}}\right)$$

[3] pristane/phytane

[4] structureless organic matter

[5] not determined

[6] A-nor-diasterenes as tentatively identified by van Graas *et al.* (1982a)

[7] A-nor-steranes as identified by van Graas *et al.* (1982a)

[8] 17,21-secohopanes as identified by Trendel *et al.* (1982)

[9] diterpanes

The results obtained by pyrolysis and by analysis of the saturated hydrocarbons are corroborated by microscopic observations. The inferred presence of predominantly marine organic matter in samples 9 and 32 agrees with the presence of common quantities of structureless organic matter (SOM) in these samples. The minor contribution of terrestrially derived organic matter is in accordance with the observed amounts of liptodetrinite, sporinite and desmocollinite. The absence of identifiable macerals in sample 31 matches with the composition of the hydrocarbon fraction containing only a small amount of alkanes and with the very low organic carbon content of the sample (0.1 %). Sample 13 contains relatively small amounts of both marine (SOM) and terrestrially derived (desmocollinite, liptodetrinite) organic matter.

The microscopic observation of severe oxidation features (oxidated pyrite, micrinite is thought to arise through postsedimentary oxidation of exinites) could result from the near-vertical orientation of the sediment layers in the sampled section. This orientation and the relative softness of the sediments makes this formation very suitable for water circulation. Hence the dissolved oxygen may have caused the observed oxidation features. The availability of oxygen also implies the possibility of biodegradation of the original organic material of the sediments. A contribution of recent biological material might also be expected to result from the water circulation. Both the pyrolysis data and the composition of the extracts did not indicate the presence of recent organic matter (humic material, proteins and carbohydrates are not revealed by the pyrolysis data and polyunsaturated fatty acids are absent in the extracts). Therefore we assume that biodegradation and/or recent contributions of organic matter have not been substantial.

Although the Livello Bonarelli as a whole seems to represent very different conditions of sedimentation with regard to the surrounding sediments, the differences that exist within the Livello itself also appear to reflect major changes in the paleoenvironment. The rhythmic alteration of limestones and marls that is a striking characteristic of the entire exposure (de Boer, 1982) seems to be continued in another form in the Livello Bonarelli. The conditions under which the organic rich members of the cycles were deposited have varied significantly. This is exemplified by the wide range of organic carbon contents and by the increasing complexity of the pyrograms and the hydrocarbon fractions with increasing amounts of organic matter. Outside the Livello Bonarelli the conditions of sedimentation have probably varied in a similar way but to a less extent. This is suggested by the fact that the largest differences present in the organic matter of the marls and limestones from the Albian part of the exposure (van Graas *et al.*, 1982b) are of the same order of magnitude as the differences between samples 13 and 31. The dark Albian marls (0.7 % C_{org}) were thought to have accumulated during times of low productivity and slightly anoxic conditions. Hence the extremely organic rich sediments (up to 16 % C_{org}) from the Livello Bonarelli are probably the result of more severe anoxic conditions and possibly of a higher productivity in the water column. Anoxic conditions are indicated by the presence of SOM and pyrite in the samples. It is interesting to notice that the pristane/phytane ratio (Table 4) does not show a clear pattern in these samples. It also does not reach values <1.0 which are thought to be indicative for deposition under anoxic conditions (Didyk *et al.*, 1978). Input of predominantly marine material in the dark samples is suggested by the pyrolysis results, the n-alkane distributions and the presence of SOM. A minor input of terrestrially derived detrital matter is evidenced by the maceral assemblages and the CPI of the n-alkanes.

Recently Rossignol-Strick *et al.* (1982) suggested that the Pleistocene Mediterranean sapropels were caused by the formation of a low salinity surface layer and the resulting stagnation. The low salinity surface layer could be the result of periods of high rainfall in Africa which would lead to a strongly enhanced water transport through the river Nile. The resulting fresh water fan would contain terrestrial detritus and high amounts of nutrients leading to a high productivity in the water column. A similar model could explain the variations we observed in the organic matter of the Livello Bonarelli, especially the - to a certain extent - simultaneous increase of marine and terrestrially derived organic matter in the anoxic sediments. Such a model is not conflicting with the ideas of de Boer (1982) and de Boer and Wonders (1982) based on a study of the entire Moria exposure (Albian to Turonian). They suggest the rhythmicity in the sediments to be the result of climatic changes due to cyclic variations in the earth's orbital parameters. These climatic variations would have their strongest effects at paleolatitudes of 20-30 degrees (paleolatitude of Moria is about 30°N; Smith and Briden, 1977). At these latitudes climatic changes would also have a significant effect on the precipitation pattern on land as can be deduced from the present location of the major desert zones which lie around 25°N or S. Therefore it seems possible that the climatic variations suggested by de Boer and Wonders (1982) give rise to precipitation patterns in the hinterland of the Moria section that cause a similar situation to that described by Rossignol-Strick *et al.* (1982) for the Pleistocene Mediterranean.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. P.L. de Boer for valuable discussions with regard to the geological aspects of this investigation. Mr. J.M.A. Buiskool Toxopeus (Koninklijke/Shell Exploratie en Produktie Laboratorium, Shell Research B.V., Rijswijk, The Netherlands) kindly performed the microscopic analyses. The F.O.M. Institute for Atomic and Molecular Physics, Amsterdam, is gratefully acknowledged for the permission to use its analytical and data processing instruments. Mr. F. de Lange is thanked for technical assistence during the course of this investigation and Mrs. A. Tom and B. Brandt for performing the Py-MS analyses.

This research is supported by the Netherlands Foundation for Earth Science Research (AWON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

REFERENCES

Arthur M.A. and Schlanger S.O. (1979) Cretaceous 'oceanic anoxic events' as causal factors in the development of reef-reservoired giant oil fields. *Am. Assoc. Pet. Geol. Bull.* 63, 870-885.

Barnes P.J., Brassell S.C., Comet P., Eglinton G., McEvoy J., Maxwell J.R., Wardroper A.M.K. and Volkman J.K. (1979) Preliminary lipid analyses of core sections 18, 24 and 30 from hole 402A. In *Initial Reports of the Deep Sea Drilling Project*, vol. 48 (Montadert L., Roberts D.G. *et al.* eds.), pp. 965-975. U.S. Govt. Printing Office.

Bernouilli D. (1972) North Atlantic and Mediterranean Mesozoic facies: a comparison. In *Initial Reports of the Deep Sea Drilling Project*, vol. 11 (Hollister C.D., Ewing J.I. *et al.* eds.), pp.801-822. U.S. Govt. Printing Office.

Berti G. and Bottari F. (1968) Constituents of ferns. *Progress in Phytochemistry*, vol. 1, pp.590-685.

de Boer P.L. (1982) Cyclicity and the storage of organic matter in Middle Cretaceous pelagic sediments. In *Cyclic and Event Stratification* (Einsele G. and Seilacher A. eds.), pp.456-475. Springer.

de Boer P.L. and Wonders A.A.H. (1982) Astronomically induced rhythmic bedding in the Cretaceous of Moria (Italy). Submitted to *Geology*.

Brassell S.C., Wardroper A.M.K., Thomson I.D., Maxwell J.R. and Eglinton G. (1981) Specific acyclic isoprenoids as biological markers of methanogenic bacteria in marine sediments. *Nature* 290, 693-696.

Didyk B.M., Simoneit B.R.T., Brassell S.C. and Eglinton G. (1978) Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature* 272, 216-222.

Fischer A.G. (1980) Gilbert-bedding rhythms and geochronology. *Geol. Soc. Am. Spec. Paper* 183, 93-104.

van Graas G., de Leeuw J.W., Schenck P.A. and Haverkamp J. (1981) Kerogen of Toarcian shales of the Paris Basin. A study of its maturation by flash pyrolysis techniques. *Geochim. Cosmochim. Acta* 45, 2465-2474.

van Graas G., de Lange F., de Leeuw J.W. and Schenck P.A. (1982a) A-nor-steranes, a novel series of sedimentary hydrocarbons. *Nature* 296, 59-61.

van Graas G., Viets T.C., de Leeuw J.W. and Schenck P.A. (1982b) Origin of the organic matter in a Cretaceous black shale deposit in the Central Apennines. In *Advances in Organic Geochemistry 1979* (Bjorøy M. ed.), in press.

Hatcher P.G., Simoneit B.R.T. and Gerkachov S.M. (1977) The organic geochemistry of a recent sapropelic environment: Mangrove Lake, Bermuda. In *Advances in Organic Geochemistry 1975* (Campos R. and Goni J. eds.), pp.469-484. ENADIMSA.

Hoering T.C. (1971) The benzene soluble organic matter, humic acids and insoluble organic matter in a core from the Cariaco Trench. *Carnegie Inst. Washington Yearb.*, 585-592.

Jenkyns H.C. (1980) Cretaceous anoxic events: from continents to oceans. *J. Geol. Soc.* 137,171-188.

Maxwell J.R., Pillinger C.T. and Eglinton G. (1971) Organic geochemistry. *Quart. Rev. Chem. Soc.* 25, 571-628.

van de Meent D., Brown S.C., Philp R.P. and Simoneit B.R.T. (1980) Pyrolysis-high resolution gas chromatography and pyrolysis-gas chromatography-mass spectrometry of kerogens and kerogen precursors. *Geochim. Cosmochim. Acta* 44, 999-1013.

Meuzelaar H.L.C., Ficke H.G. and Den Harinck H.C. (1975) Fully automated pyrolysis gas-liquid chromatography. *J. Chromatogr. Sci.* 13, 12-17.

Meuzelaar H.L.C, Kistemaker P.G., Eshuis W. and Boerboom A.J.H. (1978) Automated pyrolysis-mass spectrometry; application to the differentiation of microorganisms. In *Advances in Mass Spectrometry 7B* (Daly N.R. ed.), pp. 1452-1456. Heyden.

Nie N.H., Hull C.H., Jenkins J.G., Steinbrenner K. and Bent D.H. (1975) *Statistical Package for the Social Sciences*, 2nd edn. McGraw-Hill.

Rossignol-Strick M., Nesteroff W., Olive P. and Vergnaud-Grazzini C. (1982) After the deluge: Mediterranean stagnation and sapropel formation. *Nature* 295, 105-110.

Rubinstein I., Sieskind O. and Albrecht P. (1975) Rearranged sterenes in a shale: occurrence and simulated formation. *J. Chem. Soc. Perkin 1*, 1833-1836.

Schlanger S.O. and Jenkyns H.C. (1976) Cretaceous oceanic anoxic events: causes and consequences. *Geologie en Mijnbouw* 55, 179-184.

Schröder H. (1980) Retention indices of hydrocarbons up to C_{14} for the stationary phase squalane. *J. High Resolut. Chromatogr. Chromatogr. Commun.* 3, 39.

Simoneit B.R.T. (1975) Sources of organic matter in oceanic sediments. Thesis, Univ. of Bristol.

Simoneit B.R.T. (1977) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. *Geochim. Cosmochim. Acta* 41, 463-467.

Simoneit B.R.T., Howells W.G. and Burlingame A.L. (1973) Preliminary organic geochemical analyses of the Cariaco Trench, site 147. In *Initial Reports of the Deep Sea Drilling Project*, vol. 20 (Heezen P.C. *et al.* eds.), pp. 625-636. U.S. Govt. Printing Office.

Smith A.C. and Briden J.C. (1977) *Mesozoic and Cenozoic Paleocontinental Maps*. Cambridge University Press.

Stenhagen E., Abrahamsson S. and McLafferty F.W. eds. (1974) *Registry of Mass Spectral Data*. Wiley.

Summerhayes C.P. (1981) Organic facies of Middle Cretaceous black shales in deep North Atlantic. *Am. Assoc. Pet. Geol. Bull.* 65, 2364-2380.

Svob V. and Deur-Siftar D. (1974) Kovats retention indices in the identification of alkylbenzene degradation products. *J. Chromatogr.* 91, 677-689.

Trendel J.M., Restle A., Connan J. and Albrecht P. (1982) Identification of a novel series of tetracyclic terpene hydrocarbons (C_{24} - C_{27}) in sediments and petroleums. *J. Chem. Soc. Chem. Commun.*, 304-306.

Van Dorsselaer A. (1974) Triterpènes de sediments. Thesis, Univ. of Strasbourg.

Van Dorsselaer A., Ensminger A., Spyckerelle C., Dastillung M., Sieskind O., Arpino P., Albrecht P., Ourisson G., Brooks P.W., Gaskell S.J., Kimble B. J., Philp R.P., Maxwell J.R. and Eglinton G. (1974) Degraded and extended hopane derivatives (C_{27} to C_{35}) as ubiquitous geochemical markers. *Tetr. Lett.*, 1349-1352.

Windig W., Haverkamp J. and Kistemaker P.G. (1982) Chemical interpretation of sets of pyrolysis-mass spectra by discriminant analysis and graphical rotation. Accepted for publication by *Anal. Chem.*

Wonders A.A.H. (1980) Middle and Late Cretaceous planktonic foraminifera of the western Mediterranean area. *Utrecht Micropaleontol. Bull.* 24, 1-157.

CHAPTER 4

INVESTIGATION OF THE ORGANIC MATTER FROM THE 'MARNES NOIRES' AT COL DE PALLUEL, FRANCE

INTRODUCTION

The sampled section near Col de Palluel (44°25'N, 5°32'S) is located in the Albian 'Marnes Noires'. This formation consists of grey-black shales with a rhythmic occurrence of more consistent layers with a higher carbonate content. The differences between the various lithologies are relatively small but at the surface they are enhanced by weathering effects. The 'Marnes Noires' in southeastern France have been deposited in the Vocontian Trough, a side-arm of the Tethys Ocean (Chapter 1). Therefore we expected to find a substantial contribution of terrestrially derived organic matter in the samples from Col de Palluel.

Two samples were investigated: Pal-35, a homogeneous grey shale with 62% carbonate and 1.7% organic carbon, and Pal-49, a thinly laminated dark-grey paper shale containing 52% carbonate and 2.7% organic carbon. The latter sample is rich in ammonite remains. The insoluble organic matter of the samples was investigated by Curie-point pyrolysis-gas chromatography. The saturated hydrocarbon fractions of the extracts were analyzed in detail by gas chromatography-mass spectrometry.

We did not analyze a large suite of samples from this section by Curie-point pyrolysis-mass spectrometry (as described in Chapters 3 and 8) because of the apparently small differences between the various sediment layers. An earlier attempt to apply pyrolysis-mass spectrometry to a similar set of samples from the 'Marnes Noires' near Vergons, France, did not yield any useful information (van Graas, unpublished results).

EXPERIMENTAL

The analytical techniques used for the Col de Palluel samples have been described in Chapter 3.

RESULTS AND DISCUSSION

The pyrolysis-gas chromatograms of the two samples do not differ significantly. They contain abundant alkylbenzenes and somewhat lower amounts of alkanes and alkenes. Phenols are distinctly present but their intensity is too low to indicate a predominantly terrestrial input. This is corroborated by the absence of long-chain (>C_{20}) alkanes and alkenes. As a whole the pyrograms resemble those of Cariaco Trench sediments (van de Meent *et al.*, 1980) which are thought to contain mainly marine organic matter (Hoering, 1971; Simoneit *et al.*, 1973).

The extracted hydrocarbon fractions of both samples are qualitatively similar (fig. 1). They contain n- and isoprenoid alkanes, steranes, diasterenes (Rubinstein *et al.*, 1975), 13β(H),17α(H)-diasteranes (Ensminger *et al.*, 1978), C-ring aromatic steranes (eluted together with the saturated hydrocarbons; Schaefle *et al.*, 1978) and hopanes (17α(H),21β(H)- and 17β(H),21α(H)-hopanes dominate over 17β(H),21β(H)-isomers; Van Dorsselaer, 1974). A semi-quantitative comparison of Pal-49 and Pal-35 shows a significant decrease of steroidal compounds and a smaller decrease of hopanes relative to n-alkanes in the latter sample. These differences between the samples are similar to those observed in Italian samples (Chapters 2 and 3) where an increasing organic carbon content is parallelled by increasing amounts of hopanoid and steroidal compounds in the extracts. This similarity suggests that the deposition of the black shales in

Table 1. Identification of the compounds in Fig.1.

a. 2,6,10-trimethyl-tridecane
b. 2,6,10-trimethyl-pentadecane
c. pristane
d. phytane
e. diacholestene (20S)
f. C-ring aromatic sterane
g. diacholestene (20R)
h. 24-methyl-diacholestene (20S)
i. 20S-βα-diacholestane
k. desmethyl C-ring aromatic sterane
l. 20R-βα-diacholestane
m. 24-methyl-diacholestene (20R)
n. 20S-24-methyl-βα-diacholestane
o. 20R-24-methyl-βα-diacholestane
p. 24-ethyl-diacholestene (20R)
q. 20S-24-ethyl-βα-diacholestane
r. 5α-cholestane
s. 20R-24-ethyl-βα-diacholestane
t. 5α-24-methyl-cholestane
u. αβ-30-norhopane
v. 5α-24-ethyl-cholestane
w. βα-30-norhopane
x. αβ-hopane
y. βα-hopane
z. αβ-homohopane
A. βα-homohopane

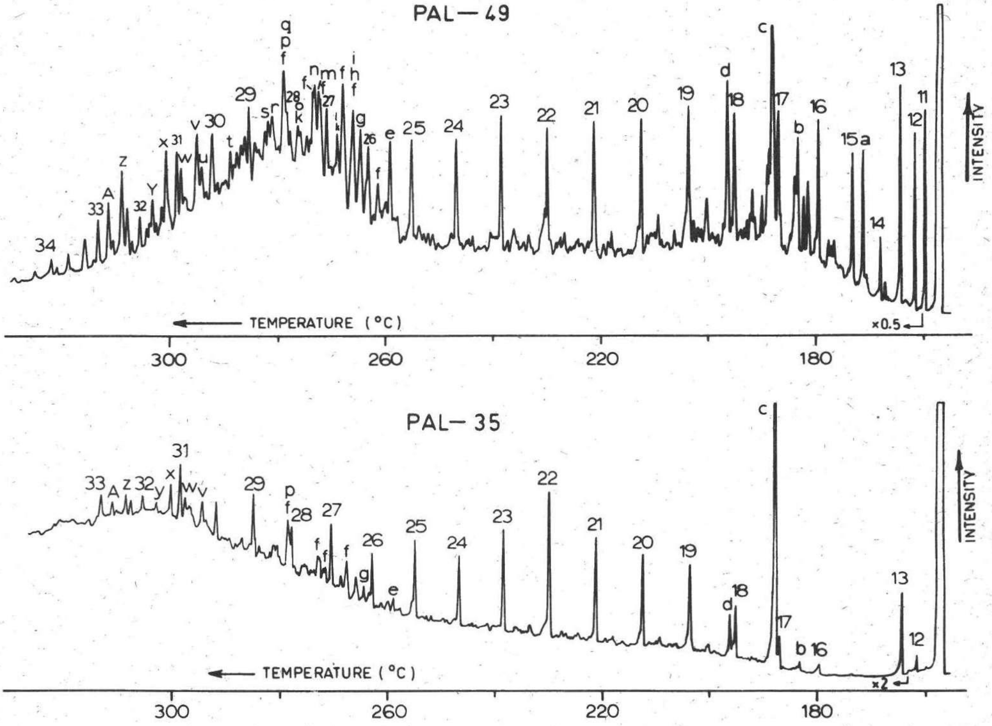


Fig. 1. Gas chromatograms of the saturated hydrocarbon fractions of samples Pal-49 and Pal-35. Stationary phase: OV-101. Temperature program: 150-300°C at 4°C/min.

Italy and France has occurred under fairly analogous conditions.

Contrary to our expectations no indications for a substantial input of terrestrial material in the samples from Col de Palluel could be found, neither in the pyrograms nor in the extracts (absence of diterpanes and of terrestrial triterpanes). Although the sediments have been deposited in a relatively near-shore environment the input of terrestrial matter has been minor.

However, the samples from Col de Palluel differ from the Italian samples (Chapters 2 and 3) as far as the degree of maturation is concidered. The Italian samples are very immature as evidenced by the predominance of ββ-hopanes over other isomers and the absence of diasteranes. In the Col de Palluel samples 20R- and 20S-βα-diasteranes are present and βα- and αβ-hopanes dominate over ββ-isomers. In Pal-49 the ratio of βα/αβ C_{30}-hopane is 0.4 and the ratio of 20S/20(R+S) diasteranes ranges from 0.5-0.6. When comparing these ratios with the values that Mackenzie *et al.* (1980) found in the Toarcian shales of the Paris Basin, France, it appears that the maturity of the Col de Palluel samples is of a level comparable to that of Paris Basin sediments from intermediate depths (500-2000 m). It is possible that the higher maturity of the French samples compared to the Italian sediments is responsible for the decrease of the differences between samples with high and low organic carbon content. There are several possible reasons for this higher maturity such as a higher overburden, a higher paleothermal gradient and diagenetic changes due to tectonic activity. To distinguish between these possibilities additional geological information is required.

REFERENCES

Ensminger A., Joly G. and Albrecht P. (1978) Rearranged steranes in sediments and crude oils. *Tetr. Lett.*, 1575-1578.

Hoering T.C. (1971) The benzene soluble organic matter, humic acids and insoluble organic matter in a core from the Cariaco Trench. *Carnegie Inst. Washington Yearb.*, 585-592.

Mackenzie A.S., Patience R.L., Maxwell J.R., Vandenbroucke M. and Durand B. (1980) Molecular parameters of maturation in the Toarcian shales, Paris Basin, France. I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta* 44, 1709-1721.

van de Meent D., Brown S.C., Philp R.P. and Simoneit B.R.T. (1980) Pyrolysis-high resolution gas chromatography and pyrolysis-gas chromatography-mass spectrometry of kerogens and kerogen precursors. *Geochim. Cosmochim. Acta* 44, 999-1013.

Rubinstein I., Sieskind O. and Albrecht P. (1975) Rearranged sterenes in a shale: occurrence and simulated formation. *J. Chem. Soc. Perkin I*, 1833-1836.

Schaefle J., Ludwig B., Albrecht P. and Ourisson G. (1978) Aromatic hydrocarbons from geological sources. VI. New aromatic steroid derivatives in sediments and crude oils. *Tetr. Lett.*, 4163-4166.

Simoneit B.R.T., Howells W.G. and Burlingame A.L. (1973) Preliminary organic geochemical analyses of the Cariaco Trench, site 147, DSDP leg 15. In *Initial Reports of the Deep Sea Drilling Project*, vol. 20 (Heezen P.C. *et al.* eds.), pp.625-636. U.S. Govt. Printing Office.

Van Dorsselaer A. (1974) Triterpènes de sediments. Thesis, University of Strasbourg.

CHAPTER 5

A-NOR-STERANES, A NOVEL CLASS OF SEDIMENTARY HYDROCARBONS*

Ger van Graas, F. de Lange, J.W. de Leeuw and P.A. Schenck

Delft University of Technology
Department of Chemistry and Chemical Engineering
Organic Geochemistry Unit
De Vries van Heystplantsoen 2
2628 RZ Delft, The Netherlands

As part of our investigations of Cretaceous black shales[1] we have analysed samples from a location near Aqualagna in the north central Apennines, Italy (43°39'N, 12°43'E). The saturated hydrocarbon fraction of one sample, a dark-grey shale of Upper Barremian age (115 Myr BP), contains novel series of steranes, which have been identified as C_{26}-C_{28} 5β(H)- and 5α(H)-A-nor-steranes. Because these compounds are structurally related to 3β-hydroxymethyl-A-nor-steranes which have been found in some sponges, we suggest here that these steranes might be biological markers for certain types of sponges.

The Upper Barremian sample has an organic carbon content of 9% and was Soxhlet extracted with toluene/methanol (1/3, v/v; 20h). The hexane-soluble part of the extract was separated by column chromatography over silica/alumina using hexane, toluene and toluene/methanol (1/1, v/v). The saturated hydrocarbons were isolated from the hexane fraction by Ag^+-TLC (Merck silicagel impregnated with a 3% solution of silver nitrate in water/methanol) using pentane as a developer. Gas chromatography-mass spectrometry was performed on a Varian 3700 gas chromatograph equipped with a 25-m glass capillary column (i.d.

---

*Published in *Nature* 296, 59-61 (1981).

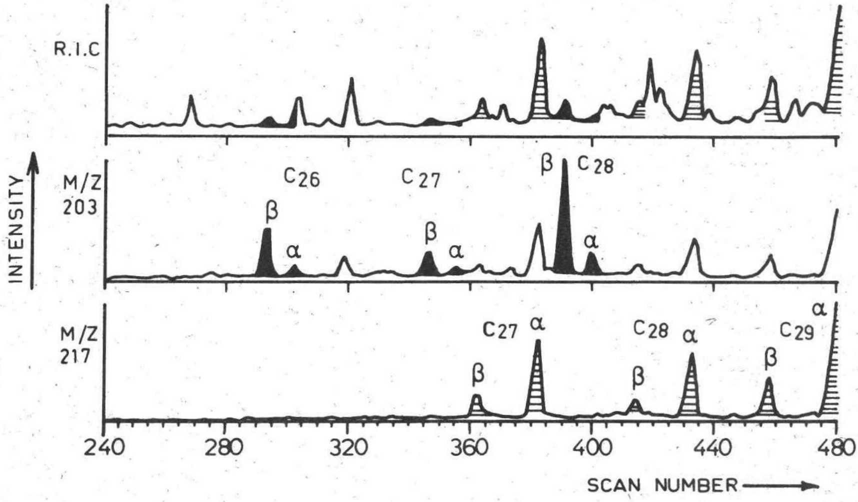


Fig.1 Part of the reconstructed ion chromatogram (RIC) and of mass fragmentograms of m/z 203 (indicative of A-nor-steranes) and m/z 217 (indicative of steranes). Temperature programme: 150-280°C (4°C/min).

0.25 mm) coated with CP-sil-5 coupled to a MAT 44 quadrupole-mass spectrometer operating at 70 eV (mass range: m/z 50-500; cycle time, 2s).

The saturated hydrocarbon fraction of the shale sample contains series of n- and isoprenoid alkanes, steranes, 4-methylsteranes and hopanes. Also present are a series of compounds with mass spectra that show a main fragment ion at m/z 203 (Fig. 1) and molecular ions at m/z 358 (Fig. 2a), 372 and 386. These mass spectra are similar to those of steranes with m/z 217, 218 shifted to m/z 203, 204 respectively and m/z 149 shifted to m/z 135.

Based on the mass spectra we assumed the unknown compounds to be a series of modified C_{26}, C_{27} and C_{28} steranes with 14 mass units missing from the nucleus and with side chains comparable to the common C_{27}, C_{28} and C_{29} steranes. From the shift of the fragment ion m/z 217 -in steranes representing the ABC-ring part of the molecule[2]- to m/z 203 and the shift of the fragment ion m/z 149 -in steranes ascribed to an AB-ring fragment[3]- to m/z 135 it can be deduced that a methylene group from ring A or B or the C_{19} methyl group is not present in these compounds. The presence of a characteristic peak at m/z 262 in the spectrum of the C_{26} unknown compound suggests that the missing carbon atom is the 19-methyl group or a methylene group of ring A. Ion m/z 262 in the spectrum of cholestane results from B-ring cleavage[4] and therefore a substantial change in the intensity of m/z 262 should be expected in the case of a B-norsterane.

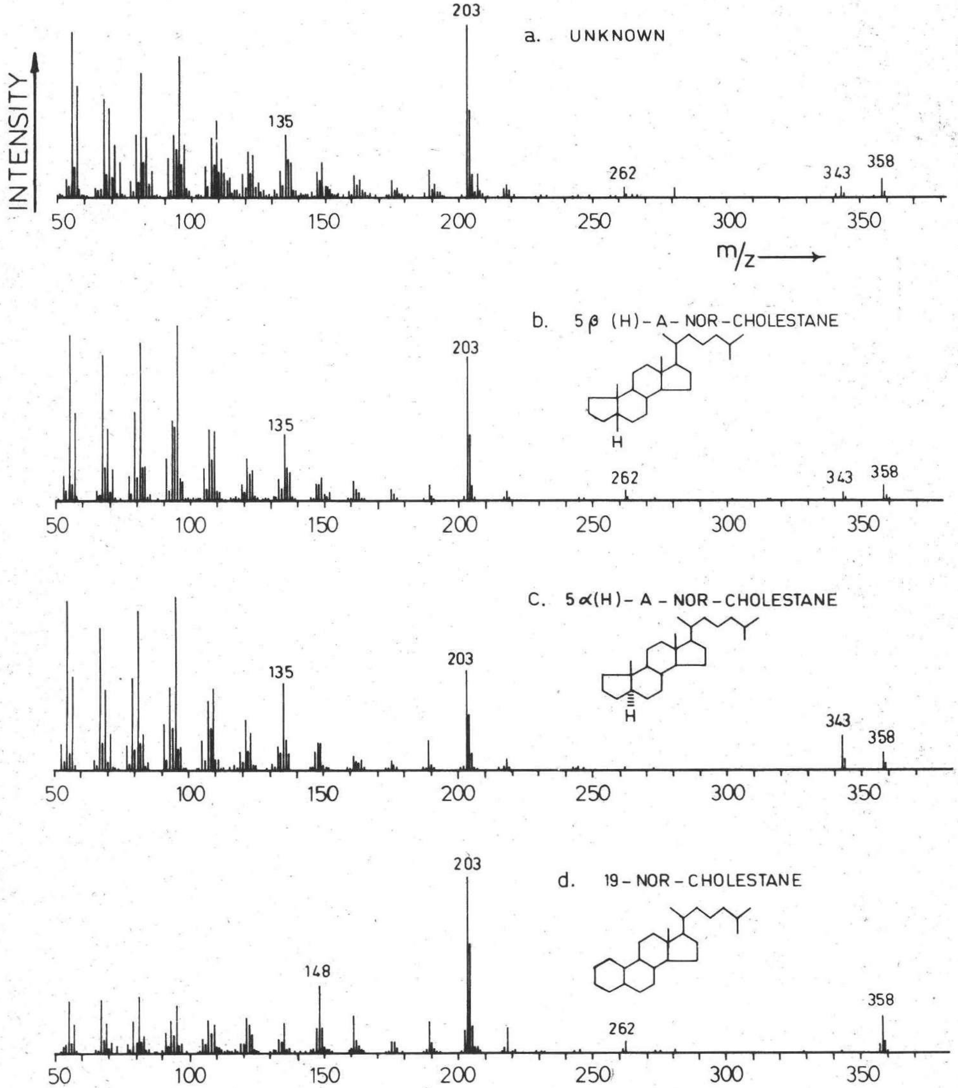


Fig.2 Mass spectra of a) the first eluting C_{26}-compound (scan 293, Fig.1); b) synthetic 5β(H)-A-nor-cholestane; c) synthetic 5α(H)-cholestane; d) synthetic 19-nor-cholestane.

To test our hypothesis the following compounds were synthesized$^{5-9}$ (conversion of 19-hydroxycholest-4-en-3-one into 19-nor-cholesterol was achieved according to a reaction scheme obtained from Organon) (Fig. 3): 19-nor-cholestane (the synthesis yielded three compounds with identical mass spectra, probably A-B ring junction isomers), 5α(H)-A-nor-cholestane and 5β(H)-A-nor-cholestane. The mass spectra of the 19-nor-cholestanes differed from those of

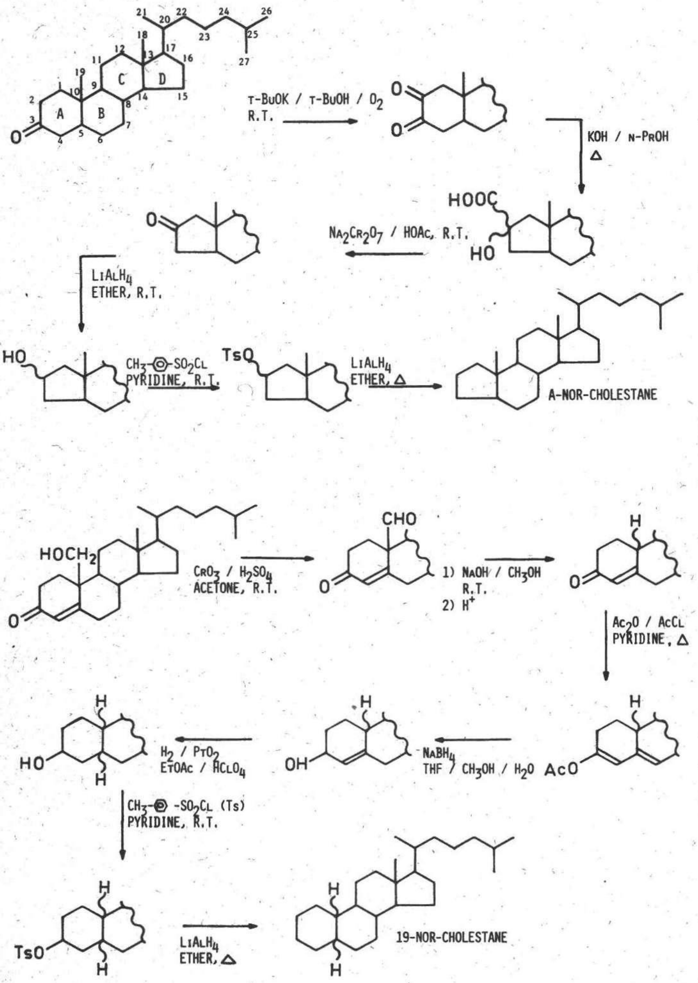


Fig. 3.

Synthetic pathways for

a) A-nor-cholestane (5α(H) and 5β(H)) from cholestanone (5α(H) and 5β(H))$^{6-9}$.

b) 19-nor-cholestane from 19-hydroxy-cholest-4en-3-one$^{6-8}$.

the A-nor-cholestanes in the presence of a prominent peak at m/z 148 (Fig. 2d). The mass spectra of the 5α(H)- and 5β(H)-isomers of A-nor-cholestane are different with regard to the ratios of M^+ and $M^+ - 15$ (Fig. 2b,c).

Mass spectrometry (Fig. 2) and coinjection on a capillary column coated with SE-52 showed that the first eluting C_{26}- unknown compound (Fig. 1) is identical to 5β(H)-A-nor-cholestane. The second unknown C_{26}-compound coeluted with 5α(H)-A-nor-cholestane but the mass spectrum of this less abundant unknown was not intense enough to compare it in detail with the spectrum of the synthetic compound. Therefore the second eluting C_{26}-compound is tentatively identified as 5α(H)-A-nor-cholestane. From these results it seems likely that the hydrocarbon fraction of the shale sample under investigation contains series of C_{26}, C_{27} and C_{28} 5α(H)- and 5β(H)-A-nor-steranes.

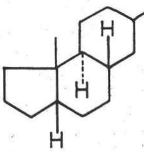
In addition to these 5α(H)- and 5β(H)-A-nor-steranes there is one other relatively intense peak in the fragmentogram of m/z 203 (Fig. 1, scan 318). The mass spectrum of this compound does indeed show an intense peak at m/z 203 but its identity is unknown at present. An assignment of this compound to a C_{20}-epimer of an A-nor-sterane, seems very unlikely as the regular steranes in this sample are exclusively present in the natural 20R configuration.

It is now clear that the nor-steranes in DSDP sediments previously assigned tentatively as 19-nor-components[10] are in fact A-nor-steranes (J. McEvoy, personal communication).

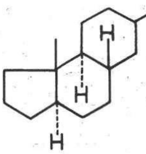
The unsaturated hydrocarbon fraction of the sample contains diasterenes, hopenes and in addition a series of compounds with mass spectra similar to those of diasterenes but with a base peak at m/z 243 instead of m/z 257 (ref. 11). Considering the presence of A-nor-steranes in the saturated hydrocarbon fraction we suggest that this series of unsaturated compounds is a series of A-nor-diasterenes. However, this suggestion has to be confirmed through the synthesis of the proper compounds.

As abiotic ring contraction of six-membered rings has not been reported in sediments, the presence of A-nor-steranes in the sample under investigation is thought to be the result of the input of related compounds showing this skeleton.

Sterols with a 5α(H)-A-nor-nucleus and a 3β-hydroxymethyl group have been found as major sterols in several sponges[12-14]. With one exception the sponges all belong to the family Axinellidae[14]. It is not known, however, whether these sponges already existed during the Cretaceous. The A-nor-sterols are formed by the sponges through ring contraction of the dietary sterols[15]. It seems possible that the A-nor-steranes present in this Cretaceous sample are the ultimate diagenetic products of 3β-hydroxymethyl-A-nor-steranes, assuming that the 3β-hydroxymethyl group is removed (through microbial action?) and that isomerization at C_5 occurs at some stage of diagenesis resulting preferentially in the more stable 5β(H)-isomer. Molecular mechanics calculations



I



II

using the EAS force field[16] by J.M.A. Baas (Delft University of Technology) showed that model compound I(A-B *cis*) is thermodynamically more stable than model compound II(A-B *trans*) by 1.9 kcal mol^{-1}. See also calculations on the 8-methyl-hydrindanes in ref. 17. The presence of sponges seems to contradict the supposedly anoxic environment of sedimentation of black shales. However, some sponges are tolerant of very low levels of oxygen[18]. Moreover, black shale formation does not necessarily imply the existence of a thick anoxic water layer but can also occur when anoxic conditions are restricted to the sediment itself or to a thin (few millimetres) water layer at the bottom. We therefore suggest that these novel series of sedimentary hydrocarbons might be useful markers for certain types of sponges.

We thank P.L. de Boer for the sample and Dr. F.J. Zeelen (Organon, Oss) for 19-hydroxycholestenone. This research is supported by the Netherlands Foundation for Earth Science Research (AWON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (ZWO).

1. van Graas G., Viets T.C., de Leeuw J.W. & Schenck P.A. in *Advances in Organic Geochemistry 1981* (ed. M. Bjorøy) (in the press).
2. Ryhage R. & Stenhagen E. *J. Lipid Res.* 1, 361(1960).
3. Tökes L. & Amos B.A. *J. Org. Chem* 37, 4421-4429(1972).
4. Tökes L., Jones G. & Djerassi C. *J. Am. Chem. Soc.* 90, 5465-5477(1968).
5. Blatt A.H. (ed.) *Organic Synthesis* Vol. 2, 191-193 (Wiley, London, 1961).
6. Espie J.C., Giraud A.M. & Rassat A. *Bull. Soc. Chim. Fr.*, 809-815(1967).
7. Strating J. & Backer H.J. *Recl. Trav. Chim. Pays-Bas* 69, 638-648(1950).
8. Bailey E.J., Barton D.H.R., Elks J. & Templeton J.F. *J. Chem. Soc.*, 1578-1591(1962).
9. Nace H.R. & Inaba M. *J. Org. Chem.* 27, 4024-4027(1962).
10. McEvoy J., Eglinton G. & Maxwell J.R. *Init. Rep. DSDP Leg 63*, 763-774 (1981).
11. Rubinstein I., Sieskind O. & Albrecht P. *JCS Perkin I*, 1833-1836(1975).
12. Minale L. & Sodano G. *JCS Perkin I*, 2380-2384(1974).
13. Bohlin L., Gehrken H.P., Scheuer P.J. & Djerassi C. *Steroids* 35, 295-304 (1980).
14. Bohlin L., Sjöstrand U. & Djerassi C. *JCS Perkin I*, 1023-1028(1981).
15. Bibolino L., Minale L. & Sodano G. *JCS Chem. Commun.*, 524-525(1978).
16. Engler E.M., Andose J.D. & Schleyer P. von R. *J. Am. Chem. Soc.* 95, 8005-8025(1973).
17. Allinger N.A., Hirsch J.A., Miller M.A., Tyminski I.J. & Van-Catledge F.A. *J. Am. Chem. Soc.* 90, 1199-1210(1968).
18. Tunnicliffe V. *Nature* 294, 354-356(1981).

CHAPTER 6

DE-A-STEROID KETONES AND DE-A AROMATIC STERANES: POSSIBLE INDICATORS FOR A NEW DIAGENETIC PATHWAY OF STEROIDAL COMPOUNDS*

Ger van Graas, F. de Lange, J.W. de Leeuw and P.A. Schenck

Delft University of Technology
Department of Chemistry and Chemical Engineering
Organic Geochemistry Unit
De Vries van Heystplantsoen 2
2628 RZ Delft, The Netherlands

Recent investigations of Cretaceous black shales have led to the identification of several hitherto unknown steroidal compounds[1,2] thus providing more information on some diagenetic pathways of steroids. In this letter we report the identification of ring A degraded steroids in a Cretaceous black shale from the Livello Bonarelli, a carbonate-poor interval deposited at the Cenomanian-Turonian boundary. The ketone fraction of the extract contains a series of compounds which have been identified as 10α(Me)-de-A-cholestan-5-one and homologues. Correspondingly the presence of mono- and diaromatic de-A-steranes in the aromatic fraction of the extract is suggested. The occurrence of these degraded steroids can be explained by a degradation pathway similar to that suggested for 3-oxygenated triterpanes such as β-amyrin and lupeol[3-7].

The shale sample under investigation was taken from an exposure (43°33'N, 12°41'E) near the cemetery of Moria, a small village near Cagli, province of Pesaro and Urbino, Italy[8]. The sediment which has an organic carbon content of 13.3% was Soxhlet extracted with toluene/methanol (1/3, v/v; 20 h). The hexane-soluble part of the extract was separated by column chromatography over silica-

---

* Accepted for publication by *Nature*.

gel. Elution with 50 ml portions of hexane containing increasing amounts of diethyl ether (0,1,3,5,7,10,20%) yielded several fractions including aromatic hydrocarbons (1 and 3% diethyl ether) and ketones (7 and 10% diethyl ether). Gas chromatography-mass spectrometry was performed on a Varian 3700 gas chromatograph equipped with a 25 m fused silica column coated with CP-sil-5, coupled to a MAT 44 quadrupole mass spectrometer operating at 80 eV (mass range m/z 50-500, cycle time 2s).

The ketone fraction contains series of n- and isoprenoid methyl ketones, steroidal and hopanoid ketones. Also present are a series of three compounds the mass spectra of which exhibit a characteristic peak at m/z 177 (Fig. 1).

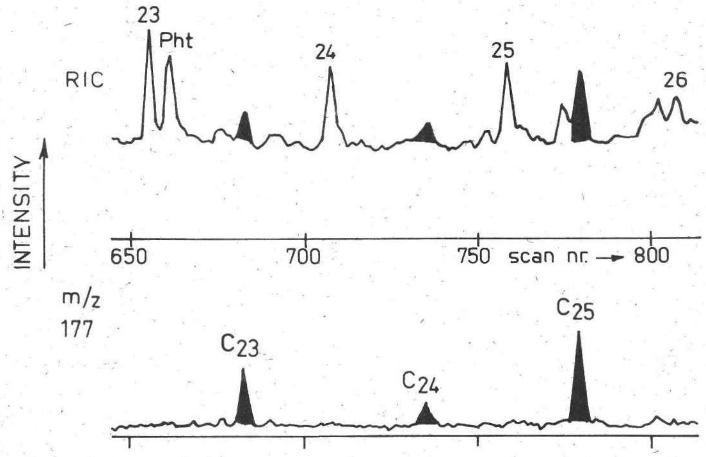


Fig. 1. Part of the reconstructed ion chromatogram (RIC) and of the mass chromatogram of m/z 177. Numbered compounds in RIC are n-alkan-2-ones. Pht = phthalate. Temperature program: 150-300°C (4°C/min).

The distribution pattern of these compounds is similar to that often encountered in case of steroidal compounds. As the main fragment ion at m/z 177 and the molecular ions at m/z 332 (Fig. 2a), 346 and 360 of the unknown compounds are 54 mass units lower compared to the corresponding ions in the mass spectra of C_{27}, C_{28} and C_{29} cholestan-3-ones (m/z 231, 386, 400 and 414 respectively) we assumed that we were dealing with a series of de-A-steroid ketones. In order to test this hypothesis we synthesized de-A-cholestan-5-one (3aα,6β-dimethyl-3α-(1,5-dimethylhexyl)-perhydro-benz(e)inden-7-one) starting from cholest-4-en-3-one (Fig. 3)[9-11]. During the removal of ring A the orientation of the C-19 methyl group is changed from β into the more stable α configuration[10].

The synthetic compound coeluted with the C_{23} unknown compound on two stationary phases (OV 101 and SE 52). These coelutions and a comparison of the mass spectra (Fig. 2a,b) showed that the C_{23} unknown compound is identical to

10α(Me)-de-A-cholestan-5-one. The C_{24} and C_{25} unknown compounds are most likely the 24-methyl and 24-ethyl substituted homologues.

The aromatic fraction of the extract contains C_{23}, C_{24} and C_{25} compounds the mass spectra of which show a resemblance to those of ring A monoaromatic steranes (4-methyl-24-ethyl-19-nor-cholesta-1,3,5(10)-triene m/z: 394(M^+, 85%), 253(M^+-sidechain, 5%), 226(13%), 211(100%), 197(8%), 158(66%), 157(32%))[1] but with a shift of 54 mass units for the prominent ions (Fig. 2c). Therefore it seems possible that we are dealing with a series of Δ5,7,9-de-A-steratrienes (3aα,6β-dimethyl-3α-(1,5-dimethylhexyl)-2,3,3a,4,5,9b-hexahydro-benz(e)indene). Also present in the aromatic fraction are compounds the mass spectra of which show a base peak at m/z 195 and weak molecular ions (among others at m/z 322 and 336). These compounds could very well be diaromatic de-A-steranes. Unambiguous identification of these mono- and diaromatic compounds can only take place after synthesis of the proper reference compounds.

As ring A degraded steroidal compounds have not been reported to occur in living organisms, it seems likely that they are formed through diagenetic degradation of steroids. This degradation could proceed along a pathway that has been proposed for 3-oxygenated triterpenoids such as β-amyrin and lupeol[3-7].

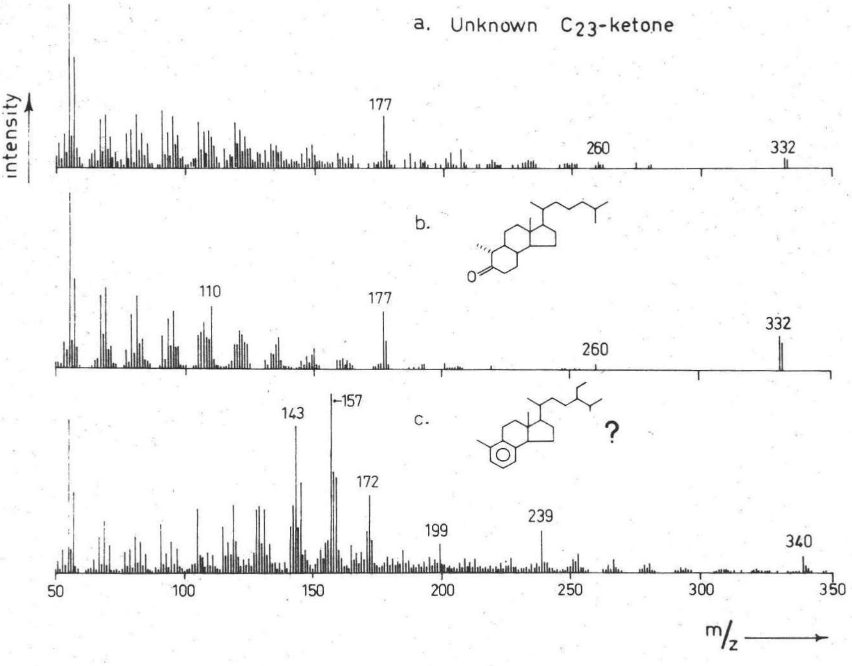


Fig. 2. Mass spectra of a) unknown C_{23} ketone, b) synthetic 10α(Me)-de-A-cholestan-5-one, c) C_{25} monoaromatic de-A-sterane (tentative identification. Spectra a) and c) are not pure due to contributions from other compounds.

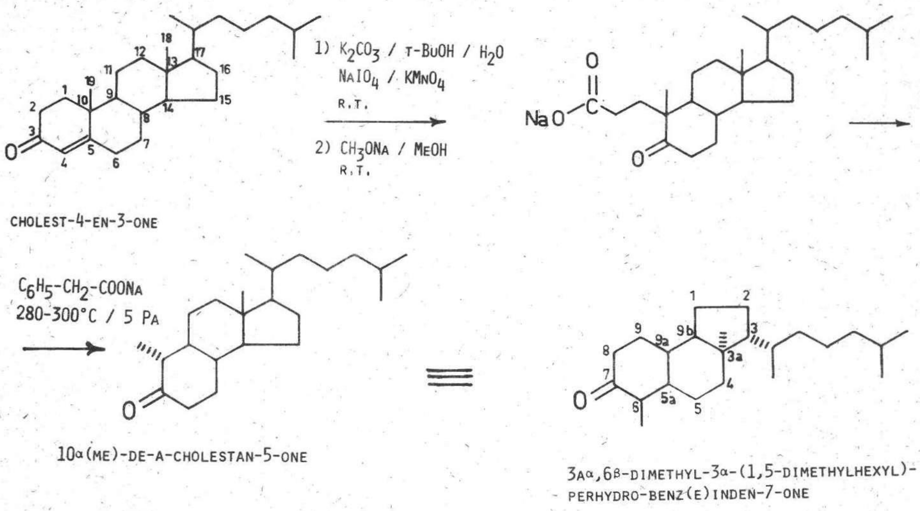


Fig. 3. Preparation of 10α(Me)-de-A-cholestan-5-one from cholest-4-en-3-one[9-11].

Cleavage of the C-3/C-4 bond is proposed to occur through a photochemical or a microbial oxidation yielding 3:4 seco acids[6]. Further steps imply the removal of the ring A remains yielding de-A-triterpanes[7]. The formation of di-[4,5] and triaromatic[3] de-A-triterpanes is also possible. The occurrence of ring A degraded steroids in the sediment under investigation is compatible with the described degradation pathway. The likeliness of this pathway in case of steroids would be greatly enhanced by the identification of 3:4 seco steroidal acids in recent sediments.

This research is supported by the Netherlands Foundation for Earth Science Research (AWON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

1. Hussler G., Chappe B., Wehrung P. & Albrecht P. *Nature* 294, 556-558(1981).
2. van Graas G., de Lange F., de Leeuw J.W. & Schenck P.A. *Nature* 296, 59-61 (1982).
3. Spyckerelle C., Greiner A.G., Albrecht P. & Ourisson G. *J. Chem. Res.*, (S) 330-331, (M) 3746-3777(1977).
4. Spyckerelle C., Greiner A.G., Albrecht P. & Ourisson G. *J. Chem. Res.*, (S) 332-333, (M) 3801-3828(1977).
5. Laflamme R.E. & Hites R.A. *Geochim. Cosmochim. Acta* 43, 1687-1691(1979).
6. Corbet B., Albrecht P. & Ourisson G. *J. Am. Chem. Soc.* 102, 1171-1173 (1980).
7. Schmitter J.M., Arpino P.J. & Guiochon G. *Geochim. Cosmochim. Acta* 45, 1951-1955(1981).
8. Wonders A.A.H. *Utrecht Micropaleontol. Bull.* 24, 1-157(1980).
9. Edward J.T., Holder D., Lunne W.H. & Puskas I. *Can. J. Chem.* 39, 599-600 (1961).
10. Edward J.T. & Lawson N.E. *J. Org. Chem.* 35, 1426-1430(1970).
11. Hartshorn M.P. & Jones E.R.H. *J. Chem. Soc.*, 1312-1313(1962).

CHAPTER 7

THEORETICAL ORGANIC GEOCHEMISTRY. I. THE THERMODYNAMIC STABILITY OF SEVERAL CHOLESTANE ISOMERS CALCULATED BY MOLECULAR MECHANICS*

Ger van Graas[+], Jan M.A. Baas[†], B. van de Graaf[†] and J.W. de Leeuw[+]

[+]Delft University of Technology
Department of Chemistry and Chemical Engineering
Organic Geochemistry Unit
De Vries van Heystplantsoen 2
2628 RZ Delft, The Netherlands

[†]Delft University of Technology
Department of Chemistry and Chemical Engineering
Laboratory of Organic Chemistry
Julianalaan 136
2628 BL Delft, The Netherlands

ABSTRACT

The thermodynamic stabilities of thirteen cholestane isomers have been computed using molecular mechanics. The calculated composition of a mixture of these isomers at thermodynamic equilibrium is in agreement with the composition of a cholestane isomerate. From the calculated stabilities the extent to which isomerisation reactions can proceed during maturation can be predicted. The GLC retention order on non polar phases of 20R/S isomeric pairs has been estimated from the preferred geometries of the molecules which are also obtained by molecular mechanics.

* Accepted for publication by *Geochim. Cosmochim. Acta*.

INTRODUCTION

Steranes encountered in sediments and crude oils are the diagenetic products of sterols and stanols which occur widely in organisms. These sterols and 5α(H)-stanols (Fig. 1) almost exclusively have the 14α,17α,20R configuration (Nes *et al.*, 1977; α and β refer to the hydrogen atoms). The conversion of sterols and stanols to sterenes and steranes with a non-rearranged skeleton is an early diagenetic process (e.g. Gagosian *et al.*, 1980). The steranes found in immature sediments have mainly the original 14α,17α,20R configuration. There is no conclusive evidence as to the significance of a 5α or 5β configuration. This configuration is determined by several parameters such as input, environment of sedimentation and hydrogenation of the intermediate sterenes (Gaskell and Eglinton, 1976; Giger and Schaffner, 1981).

During maturation the original 14α,17α,20R steranes undergo a number of isomerisation reactions. Several isomers have been identified (Fig. 1): 5α,14α,17α,20S steranes and 5α,14β,17α,20(R+S) steranes (Mulheirn and Ryback, 1975) and 5α,14β,17β,20(R+S) steranes (Petrov *et al.*,1976; Seifert and Moldowan, 1979). These compounds are also present in a cholestane isomerate (300°C, 50 hr, 50 kg/cm^2 H_2, Pt(C) catalyst) along with 5β,14α,17α,20(R+S); 5β,14β,17β,20(R+S); 5β,14β,17α,20(R+S) and 5α,14α,17β,20R steranes (Petrov *et al.*, 1976; Seifert and Moldowan, 1979).

Seifert and Moldowan (1979) drew a number of conclusions with regard to the relative thermodynamic stability of several sterane isomers based on Petrov's isomerate and their observations on the composition of crude oils and bitumens.

The progressive isomerisation of steranes has been used as an indicator for the maturation of sediments. In a study of samples from the Toarcian shales of the Paris Basin Mackenzie *et al.*(1980) found increasing amounts of 20S relative to 20R,5α,14α,17α C_{29}-steranes, of 5α,14β,17β,20(R+S) relative to other non-rearranged C_{29}-steranes and a decreasing amount of 5β,14α,17α C_{29}-steranes relative to their 5α counterparts with increasing maturity. Similar observations were made by Seifert and Moldowan (1981) with regard to the ratios of 20S relative to 20R,5α,14α,17α C_{29}-steranes and of 5α,14β,17β,20R to 5α,14α,17α,20R C_{29}-steranes in crude oils and bitumens.

For a better understanding of the observed relationship between isomerisation and maturation thermodynamic data on the stabilities of the compounds involved are required.

The present paper describes the use of molecular mechanics to provide thermodynamic data for a number of sterane isomers. With these data a prediction can be made of the extent to which certain isomers can be formed during maturation (based on thermodynamic and not on kinetic considerations; see also van Graas *et al.*, 1982). Molecular mechanics also yield information on the preferred geometries of the molecules.

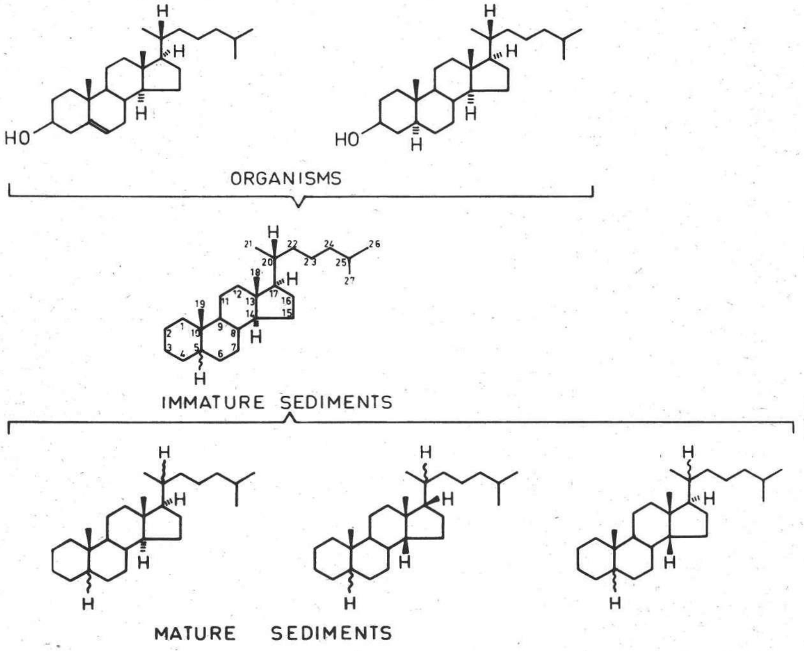


Fig. 1. Cholestanes encountered in mature sediments and their origins.

MOLECULAR MECHANICS

Molecular mechanics can be characterised best as a mathematical molecular model using empirical energy functions. The heat of formation of a compound (298 K, 1 atm, ideal gas phase) is derived from the constitution and the geometries of its molecules. The geometry of a molecule is expressed in the internal coordinates: bond lengths, valency angles, torsion angles, and non-bonded distances. The relation between the internal coordinates and the heat of formation is described by various energy functions containing a great number of parameters: strainless values of internal coordinates and force constants. Such a set of functions and parameters is developed using a 'training set' of compounds and is called an empirical force field.

A computer program for energy minimisation is required to locate favourable geometries with respect to the internal coordinates.

For each energy minimum the thermodynamic functions can be calculated using the harmonic oscillator approximation for the vibrations. In this way the heats of formation have been extrapolated from 298 K to other temperatures. Although the force fields we used have not been designed to reproduce entropy values, these can be calculated using a harmonic oscillator approximation. The resulting entropy values contain rather large uncertainties with regard to the differences between the various isomers. Therefore entropies have not been taken into account in the calculations of isomerate compositions.

The calculations were carried out with the Delft computer program for molecular mechanics (van de Graaf *et al.*, 1980) using the MM2 empirical force field (Allinger, 1977). For this force field the standard deviation between the calculated and the experimental values of the heats of formation of a training set of 42 hydrocarbons (including several compounds such as decalin and hydrindane with structures resembling part of the sterane skeleton) amounts to 1.72 kJ/mol, compared with an average reported experimental error of 1.67 kJ/mol. For comparison some values have also been calculated using the older EAS force field which has a reported standard deviation of 3.5 kJ/mol for a training set of 39 hydrocarbons (Engler *et al.* 1973). The calculations also yield the geometries of the molecules in the energy minima.

The calculations on large molecules like cholestane (75 atoms) consume large amounts of computing time. Hence, the influences of several structural variations were studied on partial structures of the cholestane molecule. The effects of the configuration at C-14 and C-17 and of the rotational isomerism around the C-17 to C-20 bond were studied in 1-isopropyl-9-methylhydrindane. 1-*sec*-Butyl-9-methylhydrindane was used to investigate the effects of 20R/20S epimerisation and the 9-methyldecalins gave an estimate of the differences between the 5α and the 5β isomers.
The large number of rotational isomers originating from the different conformations of the side chain were avoided by confining the calculations to the rotational isomer found in the X-ray structures of three 2,3-dihalocholestanes (Geise and Romers, 1966; Geise *et al.*, 1966) and 5α-cholest-2-ene (Kemlo *et al.*, 1979). The C-17/C-20/C-22/C-23/C-24/C-25/C-26 chain adopts an all-anti zigzag with C-27 and H-20 pointing in the same direction. The connection of the side chain is such that H-17 and H-20 are anti. This observed preference with respect to the orientation around C-17 to C-20 and C-20 to C-22 bonds is in accord with the calculated stabilities of the 1-*sec*-butyl-9-methylhydrindane rotamers. Detailed results of the calculations on partial structures of cholestane will be published elsewhere.

RESULTS AND DISCUSSION

The calculations have been carried out for the 13 cholestane isomers present in Petrov's isomerate (Petrov *et al.*, 1976; Seifert and Moldowan, 1979) using two different force fields (MM2 and EAS). They are listed in Table 1 together with the energy differences relative to the most stable isomer and the corresponding rank number. The energy differences within the series of compounds show a fairly good correlation between the two force fields whereas the calculated heats of formation show differences of 11-16 kJ/mol. Although the calculated values of the heats of formation may be wrong by several kJ/mol, it appears that the energy differences within a group of structurally related compounds are considerably more accurate. The results obtained with the Allinger MM2 force field were used to calculate the composition of mixtures of isomers at thermodynamic equilibrium (Table 1). This table also shows the composition of a cholestane isomerate (Petrov *et al.*, 1976; Seifert and Moldowan, 1979). The calculated values are generally in good agreement with the isomerate assuming that the latter represents a situation of thermodynamic equilibrium. However, the largest differences between the two sets of data, the amounts of the 5β,14β,17β isomers can be explained by suggesting that the

Table 1. Calculated energy differences and relative stabilities of thirteen cholestane isomers. Composition of mixtures of isomers at various temperatures.

Cholestane isomer	$\Delta\Delta H_f^\circ$(298 K) (kJ/mol)		Stability rank		Composition of equilibrium mixture(mol %)					
					Results from MM2 force field[1] data					Exp[3]
	MM2[1]	EAS[2]	MM2[1]	EAS[2]	298 K	375 K	450 K	525 K	573 K	573 K
5α14β17β20R	0[4]	0[5]	1	1	29.8	24.4	21.1	18.8	17.0	20
5α14β17β20S	1.12	0.48	2	2	19.0	16.9	15.4	14.3	13.7	20
5β14β17β20R	2.41	1.39	3	3	11.2	11.4	11.2	11.0	10.7	5
5β14β17β20S	3.53	1.87	6	4	7.2	7.9	8.2	8.4	8.6	6
5α14α17α20R	3.37	5.18	5	8	7.6	8.2	8.5	8.6	8.5	12
5α14α17α20S	2.89	5.28	4	9	9.3	9.7	9.8	9.7	9.5	14
5β14α17α20R	6.17	6.95	10	11	2.5	3.4	4.1	4.6	5.0	4
5β14α17α20S	5.68	7.03	8	12	3.0	4.0	4.7	5.2	5.5	4
5α14β17α20R	6.08	4.84	9	7	2.6	3.6	4.3	4.9	5.3	5
5α14β17α20S	4.39	2.22	7	5	5.1	6.1	6.7	7.1	7.6	6
5β14β17α20R	8.69	6.47	12	10	0.9	1.6	2.2	2.7	3.2	1
5β14β17α20S	6.99	3.85	11	6	1.8	2.7	3.4	4.0	4.6	2
5α14α17β20R	10.97	14.59	13	13	0.1	0.2	0.4	0.6	0.8	1

[1] Allinger, 1977

[2] Engler et al., 1973

[3] Experimental values were estimated from the total ion current of Petrovs isomerate (Seifert and Moldowan, 1979)

[4] Steric energy = 205.25 kJ/mol; ΔH_f = -464.10 kJ/mol

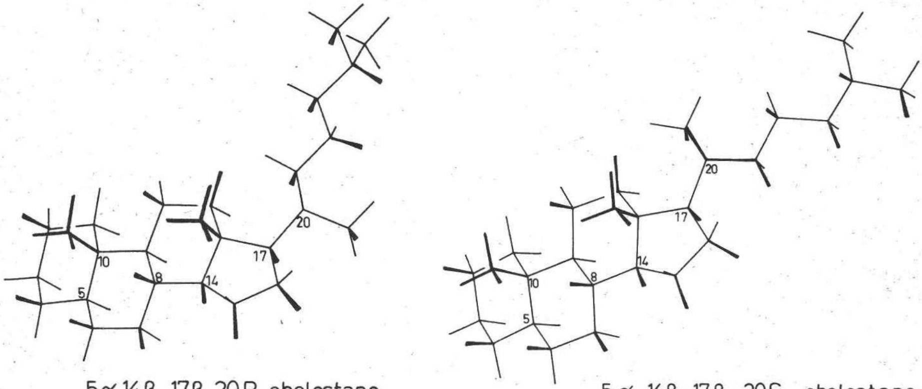
[5] Steric energy = 185.46 kJ/mol; ΔH_f = -450.17 kJ/mol

isomerate has not yet completely reached equilibrium.

The data in Table 1 correspond with a number of other observations mentioned in the literature.

1. The change in the ratio of 20S/20R 5α,14α,17α C_{29}-steranes from 0 to 1 with increasing maturity as noted by Mackenzie *et al.* (1980) and the range of this ratio in crude oils and bitumens (20S/20R between 0.2 and 1.1; Seifert and Moldowan, 1981) are in agreement with the calculated stabilities of 20R and 20S, 5α,14α,17α cholestane.
2. The greater stability of 14β,17β relative to 14α,17α steranes as noted by Seifert and Moldowan (1979) and supported by the work of Dreiding (1954) on 8-methylhydrindanes and of Patterson *et al.* (1977) on Δ^8-11-keto-steroids also agrees with our results. The observed ratios of 5α,14β,17β,20(R+S) to 5α,14α,17α,20(R+S) C_{29}-steranes in the Toarcian shales of the Paris Basin (up to 3.3 in mature sediments; Mackenzie *et al.*, 1980) and in crude oils and bitumens (up to 2.0; Seifert and Moldowan, 1981) match with the calculated ratios which vary between 1.7 (573 K) and 2.9 (298 K). These data also suggest that the samples of Mackenzie *et al.* (1980) have experienced a relatively low maximum temperature (Tissot *et al.*, 1971).
3. The calculated stability of 14β,17α steranes is comparable to that of the 14α,17α isomers. Hence these compounds can be formed during maturation as was suggested by their occurrence in petroleum (Mulheirn and Ryback, 1975).
4. 14α,17β steranes are relatively unstable as was suggested by Hanack (1965). This rationalizes why they have never been reported to occur in geological samples.
5. The decrease with increasing maturity of 5β,14α,17α steranes relative to their 5α counterparts as observed by Mackenzie *et al.* (1980), and indicated by the results of Mitra and Elliot (1969), is in agreement with their calculated stabilities.

As our calculations are valid for molecules in the gaseous state one has to be careful in comparing the results with isomer ratios established in the liquid phase in sediments because in the latter case several other processes such as solvation and adsorption can be of importance. In a first approximation we assumed these effects to have a relatively small influence on our results since we are dealing with a series of closely related non-polar compounds. The good correlation between our calculations and experimental values indicates that this assumption is indeed justified. When using thermodynamic stabilities in calculating the extent to which isomerisation reactions can proceed one has to keep in mind that the activation energy of the reaction determines the reaction rate. Calculations of this activation energy cannot be carried out



5α,14β, 17β, 20R cholestane

5α, 14β, 17β, 20S cholestane

Fig. 2. Preferred geometries of 20R and 20S 5α,14β,17β-cholestane.

without detailed information on the transition state and the development of force fields that can handle radicals and ions. Furthermore, determination of the extent to which isomerisation reactions can proceed does not necessarily imply a unique product-precursor relation between the original steranes in immature sediments and the mixture of isomers in more mature sediments and petroleum.

Force field calculations also provide information on the preferred geometry of the molecules. In this case the configuration at C-20 is of interest since this will greatly influence the overall length of a sterane molecule (fig. 2). The overall lengths of 20R/S isomers can be calculated and hence their GLC retention order can be predicted since it is known that in case of structural isomers the molecule with the larger overall length generally has the longer elution time on non polar phases. In Table 2 the predicted elution orders of several 20R/S isomer pairs are compared with data from the literature. For 5α,14α,17α; 5β,14α,17α and 5α,14β,17β isomers our results are in agreement

Cholestane isomers	First eluting C-20 epimer	
	predicted	experimental
5α14α17α	S	S[1]
5β14α17α	S	S[2]
5α14β17β	R	R[3,4]
5β14β17β	R	?[3]
5α14β17α	S	R[2]
5β14β17α	S	R[2]

[1] Mulheirn and Ryback, 1977.
[2] Seifert and Moldowan, 1979
[3] Moldowan et al., 1980
[4] Mackenzie et al., 1980

Table 2.
Retention order of 20R/S epimers of cholestane isomers.

with the literature. The first eluting 5β,14β,17β cholestane first assigned to be the 20S isomer (Seifert and Moldowan, 1979), an assignment which was later doubted by Moldowan *et al.* (1980), is in fact the 20R isomer according to our interpretation. In the case of 5α and 5β,14β,17α cholestanes our predictions yield the reverse retention order than that reported by Seifert and Moldowan (1979).

ACKNOWLEDGEMENT

One of us (G. van G.) gratefully acknowledges support by the Netherlands Foundation for Earth Science Research (AWON) with financial aid from The Netherlands Organization for the Advancement of Pure Research (ZWO).

REFERENCES

Allinger N.A. (1977) Conformational analysis. 130. MM2. A hydrocarbon force field utilizing V_1 and V_2 torsional terms. *J. Am. Chem. Soc.* 99, 8127-8134.

Dreiding A.S. (1954) The conformations of hydrindanes and the relative stabilities of the cis- and trans- configurations at the C/D ring junction in steroids. *Chem. Ind. (London)*, 992-994.

Engler E.M., Andose J.D. and von R. Schleyer P. (1973) Critical evaluation of molecular mechanics. *J. Am. Chem. Soc.* 95, 8005-8025.

Gagosian R.B., Smith S.O., Lee C., Farrington J.W. and Frew N.M. (1980) Steroid transformations in recent marine sediments. In: *Advances in Organic Geochemistry 1979* (eds. A.G. Douglas and J.R. Maxwell) pp. 407-419. Pergamon Press.

Gaskell S.J. and Eglinton G. (1976) Sterols of a contemporary lacustrine sediment. *Geochim. Cosmochim. Acta* 43, 1221-1228.

Geise H.J., Romers C. and Rutten E.W.M. (1966) The conformation of non-aromatic ring compounds. XVI. The crystal structure of 2β,3α-dichloro-5α-cholestane (modification β) at -120°C. *Acta Crystallographica* 20, 249-257.

Geise H.J. and Romers C. (1966) The conformation of non-aromatic ring compounds. XVII. The crystal structure of 2α,3β-dichloro- and 2α,3β-dibromo-5α-cholestane. *Acta Crystallographica* 20, 257-263.

Giger W. and Schaffner C. (1981) Unsaturated steroid hydrocarbons as indicators of diagenesis in immature Monterey shale. *Naturwissenschaften* 68, 37-39.

van de Graaf B., Baas J.M.A. and van Veen A. (1980) Empirical force field calculations. VI. Exploration of reaction paths for the interconversion of conformers. Application to the interconversion of the cyclohexane conformers. *Recl. Trav. Chim. Pays-Bas* 99, 175-178.

van Graas G., de Lange F., de Leeuw J.W. and Schenck P.A. (1982) A-norsteranes: a novel class of sedimentary hydrocarbons. *Nature* 296, 59-61.

Hanack M. (1965) *Conformation theory*. Academic Press.

Kemlo W.S., van Niekerk J.C. and Nassimbeni L.R. (1979) 5α-cholest-2-ene, $C_{27}H_{46}$. *Cryst. Struct. Commun.* 8, 107-114.

Mackenzie A.S., Patience R.L., Maxwell J.R., Vandenbroucke M. and Durand B. (1980) Molecular parameters of maturation in the Toarcian shales, Paris

Basin, France. I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta* 44, 1709-1721.

Mitra N.N. and Elliot W.H. (1969) Bile acids. XXVII. Mechanisms of allomerisations of steroids with Raney nickel. *J. Org. Chem.* 34, 2170-2175.

Moldowan J.M., Seifert W.K., Haley M.J. and Djerassi C. (1980) Proof of structure by synthesis of 5α,14β,17β(H)-cholestane (20R) a major petroleum sterane. Correction of previous assignment. *Geochim. Cosmochim. Acta* 44, 1613.

Mulheirn L.J. and Ryback G. (1975) Stereochemistry of some steranes of geological sources. *Nature* 256, 301-302.

Mulheirn L.J. and Ryback G. (1977) Isolation and structure analysis of steranes from geological sources. In: *Advances in Organic Geochemistry 1975* (eds. R. Campos and J. Goni) pp. 173-192. ENADIMSA.

Nes W.R., Varkey T.E. and Krevitz K. (1977) The stereochemistry of sterols at C-20 and its biosynthetic implications. *J. Am. Chem.Soc.* 99, 260-261.

Patterson D.G., Djerassi C., Yuh Y. and Allinger N.L. (1977) Factors governing the relative stabilities of the C/D cis and trans ring junctures in Δ^8-11-keto steroids. *J. Org. Chem.* 42, 2365-2370.

Petrov A.A., Pustil'nikova S.D., Abriutina N.N. and Kagramonova G.R. (1976) Petroleum steranes and triterpanes. *Neftekhimiia* 16, 411-427.

Seifert W.K. and Moldowan J.M. (1979) The effect of biodegradation on steranes and terpanes in crude oils. *Geochim. Cosmochim. Acta* 43, 111-126.

Seifert W.K. and Moldowan J.M. (1981) Paleoreconstruction by biological markers. *Geochim. Cosmochim. Acta* 45, 783-794.

Tissot B., Califet-Debyser Y., Deroo G. and Oudin J.L. (1971) Origin and evolution of hydrocarbons in Early Toarcian shales, Paris Basin, France. *Am. Assoc. Pet. Geol. Bull.* 55, 2177-2193.

CHAPTER 8

KEROGEN OF TOARCIAN SHALES OF THE PARIS BASIN. A STUDY OF ITS MATURATION BY FLASH PYROLYSIS TECHNIQUES*

Ger van Graas[+], J.W. de Leeuw[+], P.A. Schenck[+] and J. Haverkamp[†]

[+]Delft University of Technology
Department of Chemistry and Chemical Engineering
Organic Geochemistry Unit
De Vries van Heystplantsoen 2
2628 RZ Delft, The Netherlands

[†]F.O.M. Institute for Atomic and Molecular Physics
Kruislaan 407
1098 SJ Amsterdam, The Netherlands

ABSTRACT

A set of 14 samples - both extracted and unextracted - from the Toarcian of the Paris Basin have been investigated using Curie-point pyrolysis-mass spectrometry and Curie-point pyrolysis-gas chromatography-mass spectrometry. The relative amount of *n*-alkenes and *n*-alkanes in the pyrolyzates increases with increasing maximum burial depth of the samples. Comparison of the pyrolysis data of extracted and unextracted samples shows that generation of hydrocarbons from the kerogen starts at a maximum burial depth of ∿ 1000 m. The increase of pristane and phytane in the extracts of the deeper samples is correlated with the gradual decrease of the characteristic pyrolysis product prist-1-ene. Three samples yield pyrolyzates with high relative amounts of aromatic compounds. This phenomenon probably reflects a different type of contributing organic matter and/or a different environment of sedimentation.

---

*Published in *Geochim. Cosmochim. Acta* 45, 2465-2474 (1981).

INTRODUCTION

The Toarcian shales of the Paris Basin have been studied extensively over the past two decades by organic geochemists (Louis, 1966; Tissot *et al.*, 1971; Durand *et al.*, 1972; Espitalié *et al.*, 1973; Tissot *et al.*, 1974; Mackenzie *et al.*, 1980). They offer a very attractive opportunity for organic geochemical investigations since they were deposited under relatively uniform conditions. Their organic matter is generally assumed to be homogeneous although recent studies by Huc (1978) point to differences in type of organic matter in the north-eastern part of the Basin. The relatively simple geological history and structure of the basin have allowed a reliable reconstruction of the burial history of the Toarcian shales. Type of organic matter and maturation have been determined on the kerogen and on compositional parameters of the extracts. Recently Mackenzie *et al.* (1980) have published a detailed study on molecular indicators for the degree of maturation.

In the study reported in this paper attention is focussed on the kerogen in the same series of samples from the Toarcian shales that Mackenzie *et al.* have used, thus making a future comparison of the results much more valuable.

It is known from literature that pyrolytic degradation techniques in combination with gas chromatography (Py-GC), mass spectrometry (Py-MS) and gas chromatography-mass spectrometry (Py-GC-MS) can be successfully applied to the characterization of insoluble organic matter from various types of sedimentary samples such as soils (Bracewell and Robertson, 1977; Saiz-Jimenez *et al.*, 1979), coals (Larter, 1978) and sediments or their isolated kerogens (Maters *et al.*, 1977; Larter, 1978; Jones and Vanderborgh, 1979). Van Graas *et al.* (1980b) showed the existence of a distinct relation between coal rank and the relative amounts of certain pyrolysis products by studying a series of humic coals ranging from high volatile bituminous coal to anthracite using pyrolysis-low eV EI-MS and factor analysis to process the data. By applying Py-GC-MS these compounds could be identified as being indenes, indanes, benzofurans and phenolic compounds. Furthermore differences in maceral composition of the coals could be recognized from the pyrolysis data.

In an analogous study dealing with a series of Liassic samples of the same diagenetical stage several groups related to differences in input material and/or environment of sedimentation, could be distinguished in general accordance with paleontological and other geochemical data (van Graas *et al.*, 1980a).

We have used the methods mentioned above in studying the kerogen in samples from the Toarcian of the Paris Basin.

EXPERIMENTAL

Samples

This study deals with a set of 14 samples from the Lower Toarcian Shales from the Paris Basin, France. They are listed in Table 1 together with their maximum burial depths. They were analyzed both before and after ultrasonic extraction with toluene/methanol (2/1, v/v; 20 min) with the exception of COUR of which only the extracted sample was investigated.

Curie-point pyrolysis-mass spectrometry

The apparatus described by Meuzelaar *et al.* (1978) was used under the following conditions: pyrolysis temperature 510°C; pyrolysis time 1 s; ionisation energy 14 eV; number of scans 150; scanning velocity 10 scans/s; mass range m/z 15-162.

20 mg quantities of the ground samples were suspended in methanol. The wires were coated using 5 µl quantities of these suspensions, containing ca. 100 µg of dry material. Each sample was analyzed in triplicate. In this technique the pyrolyzate is fed into the ion source of the mass spectrometer. Scanning takes place continuously for about 15 s. The resulting spectra are summed to yield one signal averaged pyrolysis-mass spectrum per sample. The reproducibility of the technique is known to be sufficient as to find characteristic differences between samples (Meuzelaar and Kistemaker, 1973; Windig *et al.*, 1979).

Table 1. Samples used in this study (Data after Mackenzie et al., 1980).

Sample location	Sample code	Maximum depth (m)
Colombotte	COL	500
Creveney	CRE	500
G6-2.2	2.2	600
G6-5.6	5.6	600
Jouy-aux-Arches	JOU	700
Semecourt	SEM	700
Der	DER	1285
Cesarville	CES	2070
Grandville	GRA	2100
Coupvray	COUP	2100
Nangis	NAN	2130
Belou	BEL	2207
Montmirail	MON	2445
Courgivaux	COUR	2460

Curie-point pyrolysis-gas chromatography-mass spectrometry

Py-GC-MS was carried out using a pyrolysis reactor similar to the one described by Meuzelaar *et al.* (1975), modified for use at high temperatures (van de Meent *et al.*, 1980). Chromatographic separations were performed using the following conditions: column: glass capillary, coated with OV 101, 30 m, i.d. 0.3 mm; carrier gas: He, 1.6 ml /min; temp. progr.: from 30-280°C at 4°C/min; pyrolysis temp.: 610°C; pyrolysis time; 10 sec; mass spectrometer: Varian/MAT 311 A operated at 70eV; cycle time: 7 sec, m/z 20-400. Identification of the compounds was based on mass spectral data (Stenhagen *et al.* 1974) and gas chromatographic retention times (Zweig and Sherma, 1972; Svob and Deur-Siftar, 1974; Lee *et al.* 1979; Schröder, 1980).

Data processing

Comparison and interpretation of sets of pyrolysis-mass spectra by mere visual inspection is extremely impractical because of the large amount of data involved, viz. about 150 mass intensities per spectrum. The use of computerized data processing techniques can be very helpful in obtaining a detailed insight into the similarities and differences between the various samples. In this paper we make use of two of these techniques, viz. multivariate analysis and factor analysis. Only a brief outline of the methods will be given below; more information can be found in van Graas *et al.* (1980a,b). A mathematical description of factor analysis is given by for example Rummel (1970) or by Jöreskog *et al.* (1976).

In multi-variate analysis 40 mass intensities are used to characterize each spectrum. Selection of the 40 masses is based on the ratio between the variability of their intensities over the whole group of spectra and the reproducibility of their intensities in triplicate analyses (characteristicity). Using these intensities as coordinates the distance between each pair of spectra is calculated and serves as a quantitative measure of their dissimilarity. The distances between all spectra are grouped in a table (distance table) or represented in a 2-dimensional map (non-linear map). These calculations are carried out using a set of computer programs developed at the FOM-Institute for Atomic and Molecular Physics in Amsterdam (Eshuis *et al.* 1977).

The type of factor analysis we used (principal components analysis) looks for the principal directions of variation within the set of spectra. These directions are described by factors which are constructed from partial contributions from each mass. With this technique a large part (e.g. 90%) of the variance in the data set can be described by a limited number of factors. For each factor coefficients (factor loadings) give the degree of correlation between the factor and each mass. Each spectrum can be described as being composed of contributions from all factors with the "factor scores", the intensity of a factor in a spectrum. A possible correlation between factor scores and other properties of the series of samples can be an indication of the meaning of the factor. A chemical interpretation of the factor follows from the factor spectrum which reflects the extent to which the various masses contribute to the factor.

In our work computer programs from the *Statistical Package for the Social Sciences* (Nie *et al.*, 1975) were used. The construction of factor spectra was done by a program developed at the FOM-Institute for Atomic and Molecular Physics in Amsterdam (Windig *et al.* 1980).

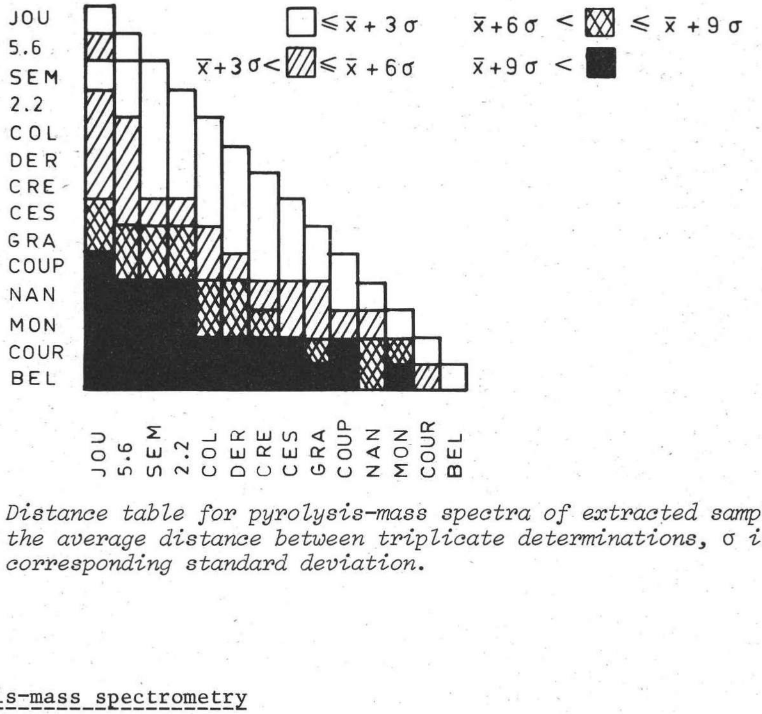


Fig. 1. Distance table for pyrolysis-mass spectra of extracted samples. $\bar{x}$ *is the average distance between triplicate determinations,* σ *is the corresponding standard deviation.*

RESULTS

Pyrolysis-mass spectrometry

Figures 1 and 2 show the distance table and the non-linear map of the extracted samples. The masses selected for the calculations are listed in Table 2. The distance table is presented in such a way that those samples which are closely related are grouped together. In this table a distance

Table 2. Masses selected for the construction of the distance table in fig. 1. Listed in order of decreasing characteristicity.

44-17-55-43-84-58-71-82-34-78-68-35-28-66-54-114-36-56-101-88-
94-31-57-48-100-70-118-30-83-96-69-122-97-60-42-72-111-85-52-50

between samples of less than $\bar{x} + 3\sigma$ (in which $\bar{x}$ is the average distance between the three spectra of a sample and σ the standard deviation) is considered to make them indistinguishable. According to the distance table we can discriminate groups of samples which partly overlap:

1 = JOU–SEM
2 = 5.6–SEM–2.2
3 = SEM–2.2–COL–DER–CRE
4 = COL–DER–CRE–CES
5 = DER–CRE–CES–GRA
6 = CRE–CES–GRA–COUP
7 = COUP–NAN
8 = MON
9 = COUR
10 = BEL

The non-linear map shows accordingly a gradual change from JOU to NAN, with BEL and COUR behaving as "outliers".

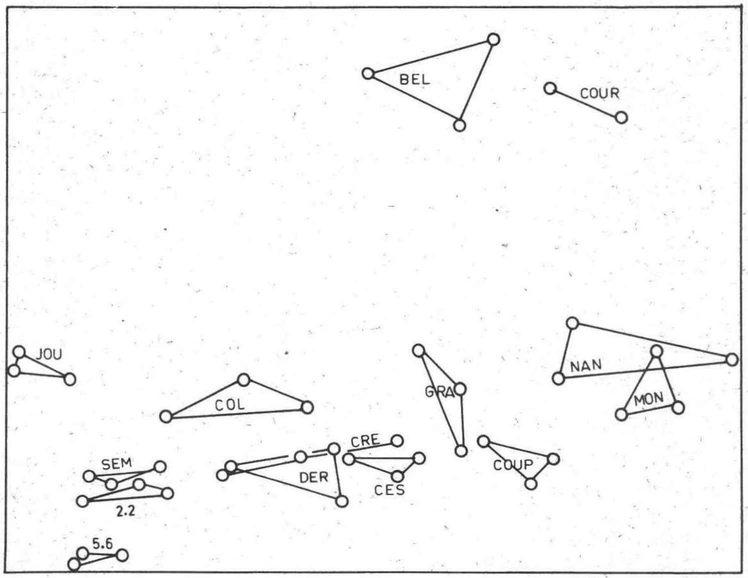


Fig. 2. Non-linear map for extracted samples based on the distance table from fig. 1.

The results of the factor analysis of the extracted samples are shown in Figs 3 through 6. Factor 1 and 2 describe respectively 43 and 25% of the total variance in the data set. The factor scores of the samples are plotted against their maximum burial depth. In the case of factor 1 this plot shows a tendency

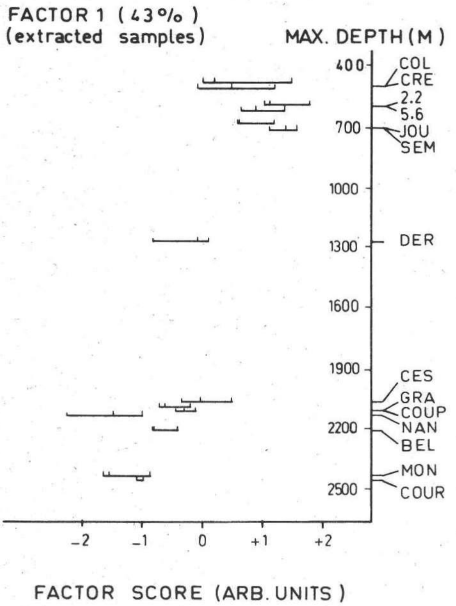


Fig. 3. Maximum burial depth of extracted samples vs factor score for factor 1.

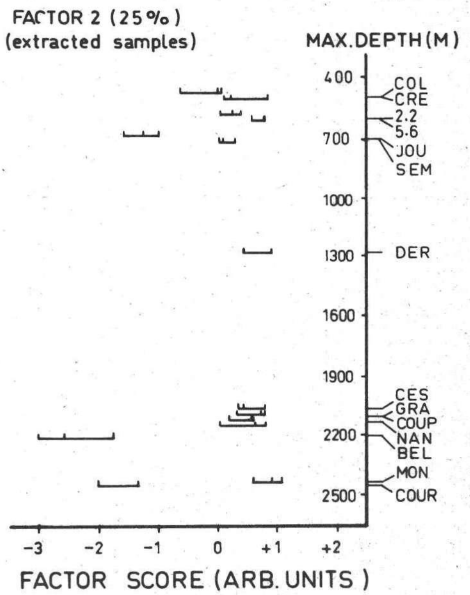


Fig. 5. Maximum burial depth of extracted samples vs factor score for factor 2.

for decreasing factor scores with increasing maximum burial depth (Fig. 3). The first factor can thus be related to the changes that occur in the samples during maturation. The negative part of the factor spectrum (Fig. 4) which characterizes the deep, more mature samples is dominated by masses that seem to be related to aliphatic hydrocarbons, whereas the positive part of the factor spectrum consists of masses that represent all kinds of other compounds.

A plot of the factor scores for factor 2 against the maximum burial depth of the samples (Fig. 5) shows that most samples behave more or less similarly with regard to this factor. The exceptions to this rule are JOU, BEL and COUR. Obviously, this factor represents another phenomenon than maturation; it is possibly related to differences in the original organic matter of the samples. The negative part of the factor spectrum (Fig. 6) is characteristic for the outliers and contains among others important contributions of masses that can tentatively be ascribed to several series of aromatic pyrolysis products as e.g. benzenes, phenols, indanes and/or benzofurans.

Factor analysis of the pyrolysis-mass spectral data of both the extracted and the unextracted samples yields for the first factor spectra and scores identical to those of the first factor of the extracted samples alone (see above). In the plot of the factor scores for factor 2 (Fig. 7) the extracted samples score in a similar way as shown in Fig. 5, with the same outliers BEL, COUR and JOU.

The unextracted samples behave differently. In immature samples extracted and unextracted samples have the same factor scores, but with increasing maturity the unextracted smaples show a tendency for higher positive scores than their extracted counterparts. This is most apparent for the samples CES, GRA, BEL and MON. The positive part of the factor spectrum (Fig. 8) describing the characteristics of the mature unextracted samples has major contributions of masses probably corresponding with aliphatic hydrocarbons.

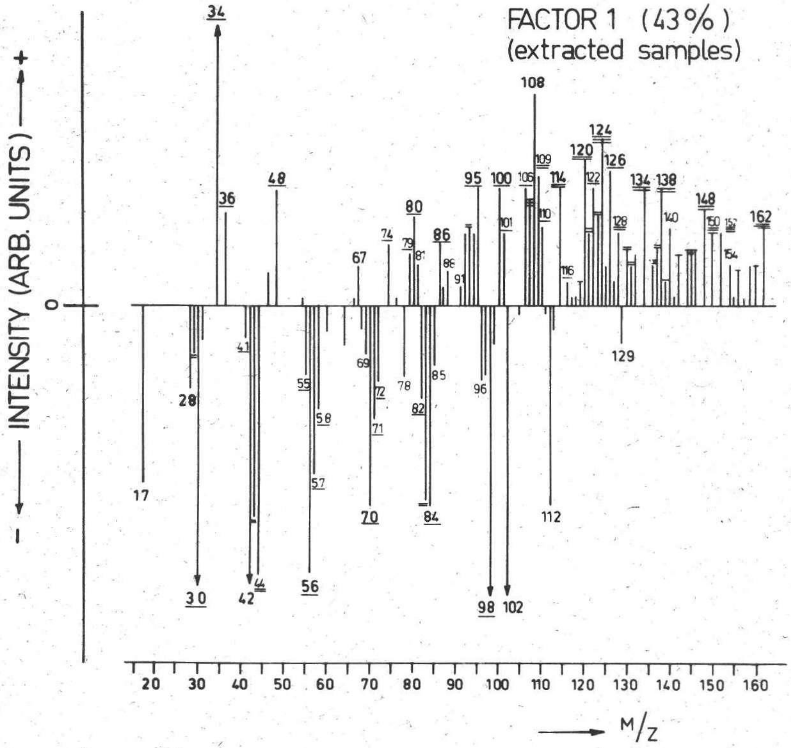


Fig. 4. Factor spectrum of factor 1 for extracted samples. Underlining of mass numbers indicates the amount of correlation between the mass and the factor. Triple underlined: correlation >0.9; double underlined: >0.8; single underlined: >0.6.

Pyrolysis-gas chromatography(-mass spectrometry)

In order to identify some of the pyrolysis products and to obtain a chemical interpretation of the differences and similarities observed in the pyrolysis-mass spectra, a selected number of samples were analysed with Py-GC and Py-GC-MS. The selected samples give a good representation of the changes that occur with increasing maximal burial depth, of the differences between outliers and "normal" samples and of the differences that are the result of extraction of the samples. Due to the similarity of the pyrolysis-gas chromatograms, Py-GC-MS analyses of three samples were sufficient to identify most of the important pyrolysis products. The Py-GC traces of SEM, MON and BEL are shown in Fig. 9. The identities of the numbered peaks are given in Table 3.

DISCUSSION

Differences between the samples as a result of maturation

In order to study the chemical changes occurring in the samples during maturation, as deduced from the factor analysis of the Py-MS data, the pyrolysis-gas chromatograms of the samples SEM, 5.6, DER, GRA and MON were compared. These pyrograms are all dominated by homologous series of n-alkenes and n-alkanes (Fig. 9a,b). Upon visual inspection there seems to

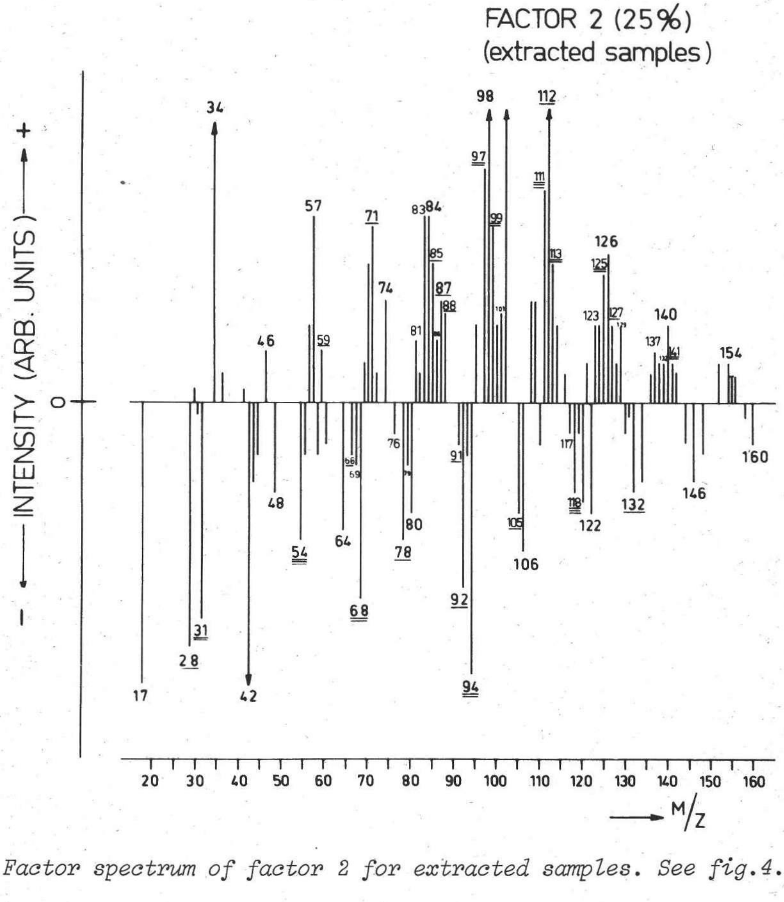


Fig. 6. Factor spectrum of factor 2 for extracted samples. See fig.4.

exist an increasing dominance of these series going from shallow (SEM, 5.6) to deep (MON, GRA) samples. This phenomenon is quantified by the ratio of the summed peak area of all n-alkanes and n-alkenes from n-decane up to and including n-hepta-dec-1-ene and the summed area of all other peaks in this range. A plot of these ratios (Fig. 10) indeed shows an increasing amount of n-alkenes and n-alkanes as compared to the other components of the pyrolyzate going from 5.6 to MON. The first factor from the factor analysis of the Py-MS data was also related to maximal burial depth. The important masses in the negative part of the factor spectrum (m/z 41, 42, 43, 44, 55, 56, 57, 58, 69, 70, 71, 72, 83, 84, 85, 98 and 112) are therefore most probably reflecting the presence of alkanes and alkenes of which the relative amounts in the pyrolyzate increase during the process of maturation.

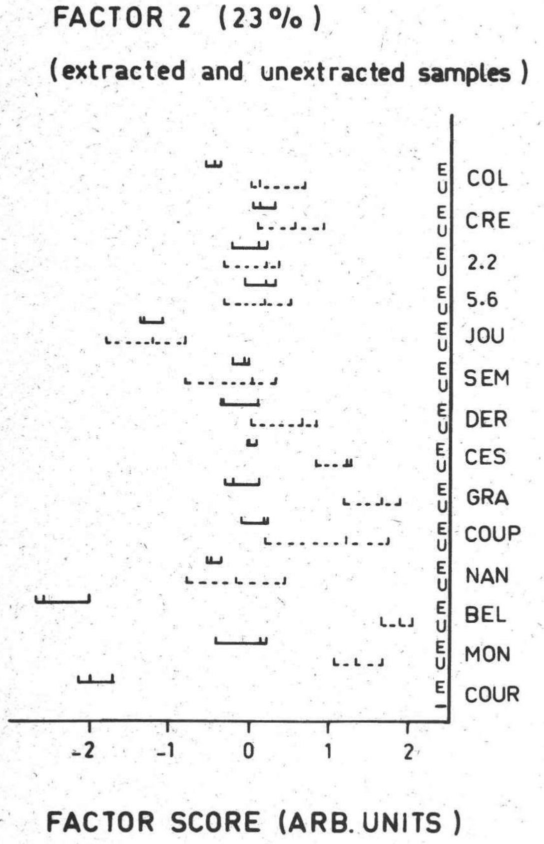


Fig. 7.
Factor score for factor 2 of both extracted (E) and unextracted (U) samples. For reasons of clarity the samples are listed according to their maximum burial depth order.

In a study of kerogens from the Paris Basin by IR spectroscopy Espitalié *et al.* (1973) also found indications for a slight relative increase of long chain ($(CH_2)_n$ with $n > 4$) aliphatic moieties in the deeper samples. The

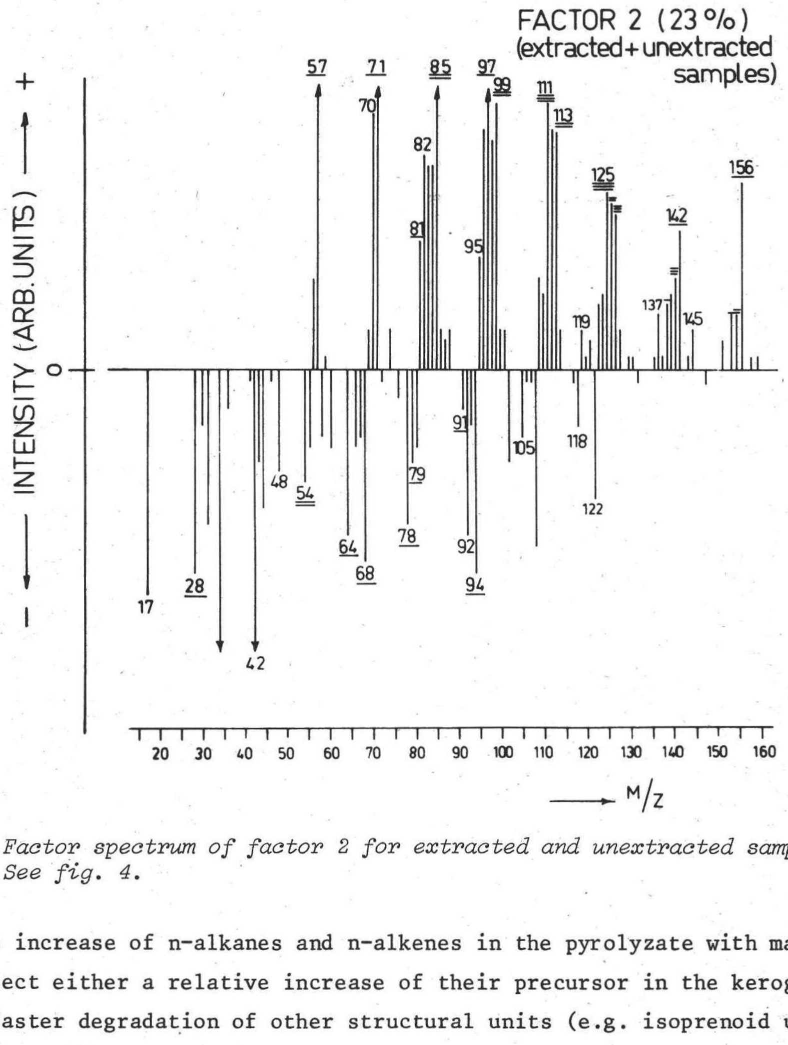


Fig. 8. Factor spectrum of factor 2 for extracted and unextracted samples. See fig. 4.

relative increase of n-alkanes and n-alkenes in the pyrolyzate with maturation may reflect either a relative increase of their precursor in the kerogen due to the faster degradation of other structural units (e.g. isoprenoid units) or the fact that a part of the organic matter other than n-alkane/n-alkene precursors becomes less amenable to pyrolysis. An example of the former explanation may be found in the very strong decrease of prist-1-ene with increasing maturation (Fig. 10).

Several authors (Ensminger, 1977; Huc, 1978; Mackenzie *et al.* 1980) observed an increase in the degree of maturation in shallow samples going from north to south. Ensminger and Huc suggested this trend to result from higher paleothermal gradients in the southern part of the basin. Mackenzie and coworkers noted that their results correspond with the maximum burial depths as they were measured by Goy (1979) who found values for the south-eastern part of the basin which are significantly higher than those which were originally

Table 3. Identification of the numbered compounds in fig. 9.

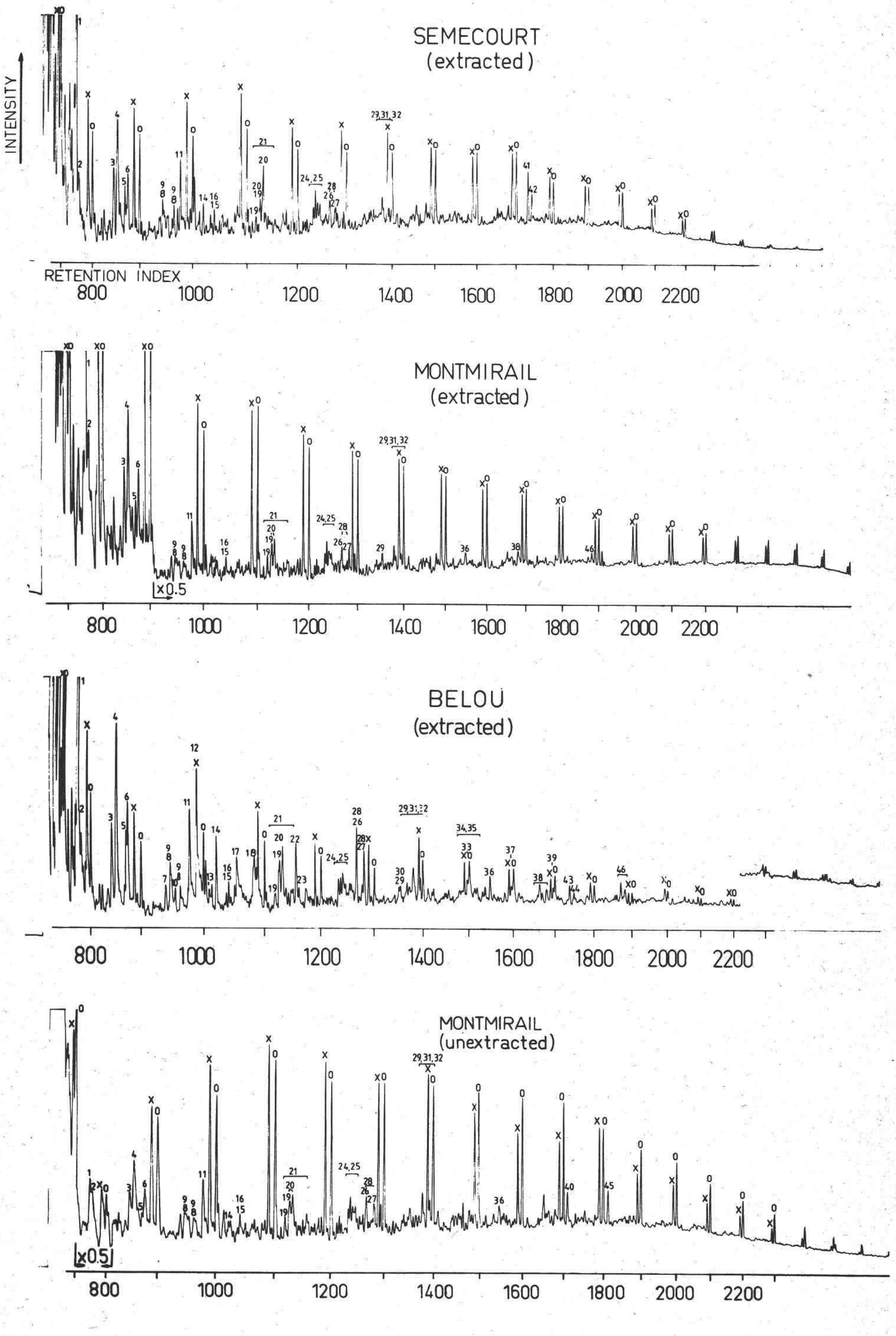
1. Toluene
2. Me-thiophene
3. Et-benzene + Et-thiophene
4. *m/p*-Xylene + Di-Me-thiophene
5. Styrene
6. *o*-Xylene
7. Benzaldehyde
8. C_3-benzene
9. C_3-thiophene
10. Benzonitrile
11. *m/p*-Me-styrene
12. Phenol
13. Indane
14. Indene
15. C_4-benzene
16. C_4-thiophene
17. *o*-Cresol
18. *m/p*-Cresol
19. Me-indane
20. Me-indene
21. C_5-benzene
22. Naphthalene
23. Benzothiophene
24. C_2-indene
25. C_6-benzene
26. 2-Me-naphthalene
27. 1-Me-naphthalene
28. Me-benzothiophene
29. C_3-indene
30. C_7-benzene
31. C_2-naphthalene
32. C_2-benzothiophene
33. Naphthol
34. C_3-naphthalene
35. C_3-benzothiophene
36. Fluorene
37. Benzophenone
38. Me-fluorene
39. 9-Fluorenone
40. Pristane
41. Prist-1-ene
42. Prist-2-ene
43. Phenanthrene
44. Anthracene
45. Phytane
46. Me-phenanthrene + Me-anthracene

Peaks marked with "X" or "O" are n-alken-1-enes and n-alkanes respectively.

used. These results, which mean an inversion of the maximum burial depth order for the shallow samples (COL—CRE—2.2-5.6—JOU—SEM) correspond better with our results too. In this case the factor scores for factor 1 (Fig. 3) show an even better trend with increasing maximum burial depth for the shallow samples.

Comparing the pyrograms of extracted and unextracted samples the results from the factor analysis (factor 2 figs 7 and 8) are well matched. In the case of a shallow sample (SEM) there is no difference between the two pyrograms. The pyrogram of a deep unextracted sample (MON) differs from its extracted counterpart in a higher amount of n-alkanes over n-C_{15} and in the presence of pristane and phytane which are not present in the extracted samples. These observations point to a generation of alkanes with increasing maturation and a vaporization of these extractable compounds during pyrolysis. According to the factor score plot (Fig. 7) the genesis of alkanes starts at a maturation stage comparable to that of DER and gradually increases. The exceptional behaviour of NAN in Py-MS -no difference between spectra of extracted and unextracted sample- cannot be explained. It should be emphasized that this same sample behaves somewhat peculiar in factor 1. However the Py-GC data did show a significantly higher amount of n-alkanes in the unextracted version.

Fig. 9. Pyrolysis-gas chromatograms of: a) SEM-extracted; b) MON-extracted; c) BEL-extracted; d) MON-unextracted. Identification of numbered compounds is given in Table 3.


SEMECOURT
(extracted)
INTENSITY
RETENTION INDEX
800
1000
1200
1400
1600
1800
2000
2200
29,31,32
21
24,25
MONTMIRAIL
(extracted)
x0.5
800
1000
1200
1400
1600
1800
2000
2200
BELOU
(extracted)
29,31,32
34,35
800
1000
1200
1400
1600
1800
2000
2200
MONTMIRAIL
(unextracted)
x0.5
800
1000
1200
1400
1600
1800
2000
2200

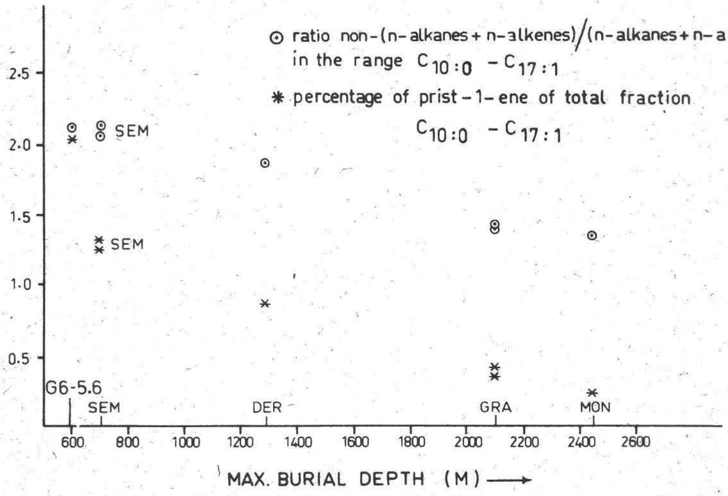


Fig. 10. Area of non-n-alkanes/enes divided by area of n-alkanes/enes in the range from n-decane to n-heptadec-1-ene, as measured in pyrolysis-gas chromatograms. The amount of prist-1-ene is expressed as percentage and calculated from its peak area relative to that of all peaks from n-decane to n-heptadec-1-ene.

The generation of pristane and phytane in the extract seems to be correlated with the observed decrease of prist-1-ene as a pyrolysis product during maturation (Figs 9 and 10). This phenomenon suggests that the precursor(s) of phytane and/or pristane during natural maturation yield(s) prist-1-ene upon analytical pyrolysis.

The absence of prist-1-ene in the pyrolyzate of the deeper samples and thus the absence of the natural precursor of pristane and phytane is in agreement with the mentioning by Tissot and Welte (1978) that the isoprenoid: n-alkane ratio decreases when the oil generation process continues. A better understanding of the observed phenomena requires a structural elucidation of the pristane and/or phytane precursor.

In conclusion we can state that the complementary analytical techniques of Py-MS and Py-GC(MS) provide a rather detailed insight into the stage of maturation in this series of samples and into some of the chemical transformations which occur in the insoluble organic matter during maturation.

Differences between the samples based on type of organic matter

Factor analysis (factor 2, Figs 5 and 6) shows clear differences between JOU, BEL, COUR and the other samples. The factor pyrogram characterizing these outliers contains masses possibly related to aromatic compounds. This observation is confirmed by the results from Py-GC and Py-GC-MS (Fig. 9). The pyrograms of BEL and JOU are much higher in the relative amount of alkylbenzenes, alkylphenols, alkylnaphthalenes, etc. In addition to this JOU was characterized by a substantial contribution of aromatic sulfur containing compounds such as alkylthiophenes and alkylbenzothiophenes in its pyrolyzate.

The relatively low amount of aliphatic structures in the pyrolyzate of BEL and COUR could indicate that these samples have generated more hydrocarbons than the other comparable samples. According to the factor score plot (Fig. 7) the genesis of alkanes starts at a maturation stage comparable to that of DER and gradually increases. This would mean that BEL has endured a substantially more severe diagenetic alteration than is suggested by its maximum burial depth. Moreover this explanation would be incompatible with the results obtained by correlating factor 1 with supposed maximum burial depths of the samples (Fig. 3) in which BEL and COUR behave "normal". Therefore we believe that the "outlying" character of BEL, COUR and JOU reflects either a different type of input material and/or different conditions during sedimentation.

ACKNOWLEDGEMENTS

One of us (G. van G.) gratefully acknowledges support by The Netherlands Foundation for Earth Science Research (AWON) with financial aid from The Netherlands Organization for the Advancement of Pure Research (ZWO). The Institute Français du Pétrole and the Organic Geochemistry Unit of the University of Bristol kindly put the samples at our disposal. Mr E.D. Tierie is thanked for technical assistance during the course of this investigation and Mrs A. Tom and B. Brandt for performing the Py-MS analyses.

REFERENCES

Bracewell J.M. and Robertson G.W. (1977) Pyrolysis studies on humus in freely drained Scottish soils. In *Analytical Pyrolysis* (eds. C.E.R. Jones and C.A. Cramers), pp. 167-178. Elsevier.

Durand B., Espitalié J., Nicaise G. and Combaz A. (1972) Etude de la matière organique insoluble (Kérogène) des argiles du Toarcien du Bassin de Paris. Première partie: Etude par les procédés optiques, analyse élémentaire, étude en microscopie et diffraction éléctroniques. *Rev. Inst. Fr. Pet.* 27, 865-884.

Ensminger A. (1977) Evolution de composés polycycliques sédimentaires. Thesis, Univ. of Strasbourg.

Eshuis W., Kistemaker P.G. and Meuzelaar H.L.C. (1977) Some numerical aspects of reproducibility and specificity. In *Analytical Pyrolysis* (Eds. C.E.R. Jones and C.A. Cramers), pp. 151-166. Elsevier.

Espitalié J., Durand B., Roussel J.C. and Souron C. (1973) Etude de la matière organique insoluble (kérogène) des argiles du Toarcien du Bassin de Paris.

Deuxième partie: Etudes en spectroscopie infrarouge, en analyse thermique différentielle et en analyse thermogravimétrique. *Rev. Inst. Fr. Pet.* 28, 37-66.

Goy G. (1979) Les "schistes carton" (Toarcien inférieur) du Bassin de Paris, en affleurements et en sondages. Thesis, Univ. Pierre et Marie Curie.

van Graas G., de Leeuw J.W. and Schenck P.A. (1980a) Characterisation of coals and sedimentary organic matter by Curie-point pyrolysis-mass spectrometry and pyrolysis-gas chromatography. *J. Anal. Appl. Pyrol.* 2, 265-276.

van Graas G., de Leeuw J.W. and Schenck P.A. (1980b) Analysis of coals of different rank by Curie-point pyrolysis-mass spectrometry and Curie-point pyrolysis-gas chromatography-mass spectrometry. In *Advances in Organic Geochemistry 1979* (eds. A.G. Douglas and J.R. Maxwell), pp. 485-494. Pergamon Press.

Huc A.Y. (1978) Geochimie organique des schistes bitumineux du Toarcien du Bassin de Paris. Thesis, Univ. of Strasbourg.

Jones C.E.R. and Vanderborgh N.E. (1979) Elucidation of geomatrices by laser pyrolysis-gas chromatography and pyrolysis-mass spectrometry. *J. Chromatogr.* 186, 831-841.

Jöreskog K.G. Klovan J.E. and Reyment R.A. (1976) *Geological Factor Analysis*, Elsevier.

Larter S.R. (1978) A geochemical study of kerogen and related materials. Ph.D. Thesis, Univ. of Newcastle upon Tyne.

Lee M.L., Vassilaros D.L., White C.M. and Novotny M. (1979) Retention indices for programmed-temperature capillary-column gas chromatography of polycyclic aromatic hydrocarbons. *Anal. Chem.* 51, 768-773.

Louis M.C. (1966) Etudes geochimique sur les "schistes cartons" du Toarcien du Bassin de Paris. In *Advances in Organic Geochemistry 1964* (eds G.D. Hobson and M.C. Louis), pp. 85-94. Pergamon Press.

Mackenzie A.S., Patience R.L., Maxwell J.R., Vandenbroucke M. and Durand B. (1980) Molecular parameters of maturation in the Toarcien shales, Paris Basin, France-I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta* 44, 1709-1721.

Maters W.L., van de Meent D., Schuyl P.J.W., de Leeuw J.W., Schenck P.A. and Meuzelaar H.L.C. (1977) Curie-point pyrolysis in organic geochemistry. In *Analytical Pyrolysis* (eds. C.E.R. Jones and C.A. Cramers), pp. 203-216. Elsevier.

van de Meent D., Brown S.C., Philp R.P. and Simoneit B.R.T. (1980) Pyrolysis-high resolution gas chromatography and pyrolysis-gas chromatography-mass spectrometry of kerogens and kerogen precursors. *Geochim. Cosmochim. Acta* 44, 999-1013.

Meuzelaar H.L.C. and Kistemaker P.G. (1973) A technique for fast and reproducible fingerprinting of bacteria by pyrolysis-mass spectrometry. *Anal. Chem.* 45, 587.

Meuzelaar H.L.C., Ficke H.G. and Den Harinck H.C. (1975) Fully automated pyrolysis gas-liquid chromatography. *J. Chromatogr. Sci.* 13, 12-17.

Meuzelaar H.L.C., Kistemaker P.G., Eshuis W. and Boerboom A.J.H. (1978) Automated pyrolysis-mass spectrometry; application to the differentiation of micro-organisms. In *Advances in Mass Spectrometry 7b* (ed. N.R. Daly), pp. 1452-1456. Heyden.

Nie N.H., Hull C.H., Jenkins J.G., Steinbrenner K. and Bent D.H. (1975) *Statistical Package for Social Sciences*, 2nd edn. McGraw-Hill.

Rummel R.J. (1970) *Applied Factor Analysis*. Northwestern Univ. Press.

Saiz-Jimenez C., Haider K. and Meuzelaar H.L.C. (1979) Comparisons of soil organic matter and its fractions by pyrolysis-mass spectrometry. *Geoderma* 22, 25-37.

Schröder H. (1980) Retention indices of hydrocarbons up to C14 for the stationary phase squalane. *J. High Resolut. Chromatogr. Chromatogr. Commun.* 3, 39.

Stenhagen E., Abramsson S. and McLafferty F.W. (eds) (1974) *Registry of Mass Spectral Data*. Wiley.

Svob V. and Deur-Siftar D. (1974) Kovats retention indices in the identification of alkylbenzene degradation products. *J. Chromatogr.* 91, 677-689.

Tissot B.P. and Welte D.H. (1978) *Petroleum Formation and Occurrence*, p. 174. Springer.

Tissot B., Califet-Debyser Y., Deroo G. and Oudin J.L. (1971) Origin and evolution of hydrocarbons in early Toarcian shales, Paris Basin, France. *Am. Assoc. Pet. Geol. Bull.* 55, 2177-2193.

Tissot B., Durand B., Espitalié J. and Combaz A. (1974) Influence of the nature and diagenesis of organic matter in formation of petroleum. *Am. Assoc. Pet. Geol. Bull.* 58, 499-506.

Windig W., Kistemaker P.G., Haverkamp J. and Meuzelaar H.L.C. (1979) The effects of sample preparation, pyrolysis and pyrolyzate transfer conditions on pyrolysis-mass spectra. *J. Anal. Appl. Pyrol.* 1, 39-52.

Windig W., Kistemaker P.G., Haverkamp J. and Meuzelaar H.L.C. (1980) Factor analysis of the influence of change in experimental conditions in pyrolysis-mass spectrometry. *J. Anal. Appl. Pyrol.* 2, 7-18.

Zweig G. and Sherma J. (eds) (1972) *Handbook of Chromatography*, Vol. 1. CRC press.

CHAPTER 9

EPILOGUE

Detailed investigations of the soluble and insoluble organic matter in two Italian Cretaceous black shale deposits (Chapters 2 and 3) make it possible to draw some conclusions with regard to the type of input material and the conditions at the time of sedimentation. Organic geochemical studies alone do not allow the construction of a complete and detailed model for the environment of sedimentation. For this purpose additional (geological) information is required. However, organic geochemical studies can be of help in determining whether or not certain models for the formation of black shale deposits (e.g. de Boer, 1982; Rossignol-Strick *et al.*, 1982) are feasible.

The results obtained on two sections from Italy examined in the course of this investigation indicate that in each case the formation of black shales is caused by a transition from oxic to anoxic conditions at the sediment-water interface which can lead to various degrees of anoxicity. Apart from this similarity in conditions the composition of the organic matter is determined mainly by local circumstances such as a high or a low productivity in the water column and the possible input of terrestrial material either by potamic or by eolian transport. Because of this major influence of local conditions on the sedimentation process one should not attempt to construct a uniform model for the origin of the Cretaceous black shale deposits (cf. Arthur, 1979).

Contrary to what might be expected from their paleolocation, the French sediments do not contain substantial amounts of terrestrially-derived organic material (Chapter 4). Their formation seems to have occurred under conditions similar to those in Italy. However, the degree of maturation is significantly higher in the French samples than in the Italian ones. An explanation of this phenomenon can only be given when additional geological information becomes available.

In the course of the black shale research many unknown compounds were encountered in the sediments. Some of them have been identified (Chapters 5 and 6). They are suggested to be potential marker molecules for certain organisms or to be indicative of a hitherto undescribed diagenetic pathway for steroids. Many more components of the extracts have remained unidentified (Appendix). A similar situation exists with regard to the pyrolytic studies of insoluble organic material. Many pyrolysis products can not be identified and in case of identified compounds it is often very hard or not possible to understand the meaning of the presence of these compounds. The pyrolysis data probably contain a wealth of information but at the moment only a limited part of these data can be adequately interpreted.

As a final conclusion one can say that - although organic geochemistry is a relatively young science and many of the processes that occur before, during and after sedimentation are far from completely understood - a combination of organic geochemistry and other fields of earth sciences can yield good results with regard to the reconstruction of the paleoenvironment of sedimentation.

REFERENCES

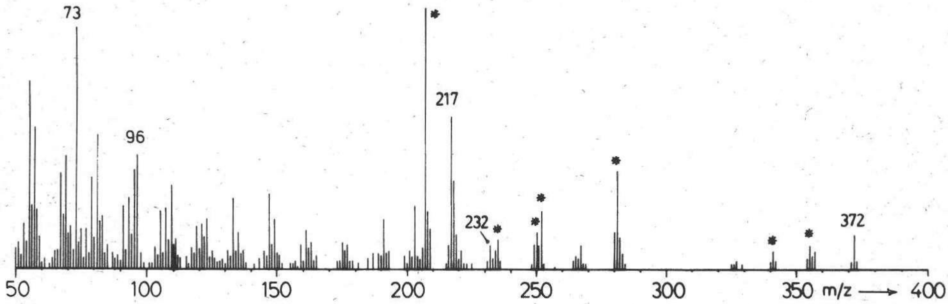
Arthur M.A. (1979) North Atlantic Cretaceous black shales: the record at site 398 and a brief comparison with other occurrences. In *Initial Reports of the Deep Sea Drilling Project*, vol. 47, part 2 (Sibuet J.C., Ryan W.B.F. *et al.* eds.), pp.719-751. U.S. Govt. Printing Office.

de Boer P.L. (1982) Cyclicity and the storage of organic matter in Middle Cretaceous pelagic sediments. In *Cyclic and Event Stratification* (Einsele G. and Seilacher A. eds.), pp.456-475. Springer.

Rossignol-Strick M., Nesteroff W., Olive P. and Vergnaud-Grazzini C. (1982) After the deluge: Mediterranean stagnation and sapropel formation. *Nature* 295, 105-110.

APPENDIX

During the GC-MS analyses of the extracts from Cretaceous black shales we encountered many unknown compounds. Some of these have been identified after synthesis of the proper reference compounds (Chapters 5 and 6). The mass spectra of several other unknown compounds, which may be of geochemical interest, are discussed in this appendix. The selection is mainly based on the quality of the spectra. In a number of cases a tentative identification is given. Other spectra, for which no structure is proposed, are nevertheless included because of their potential usefulness to other researchers.



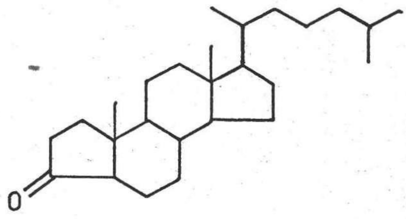
Peaks marked by an asterisk are due to instrument background.

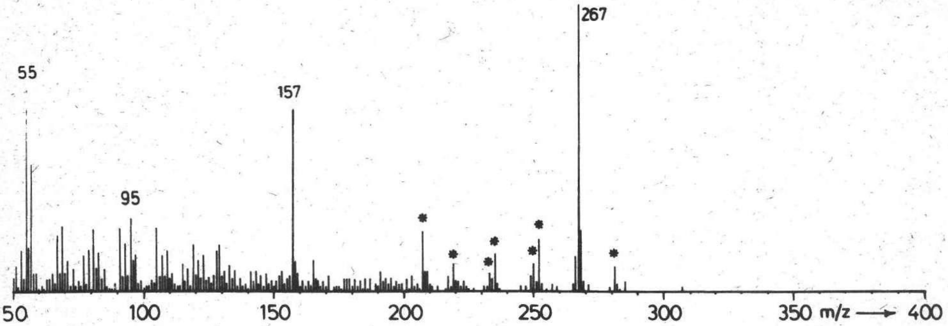
Occurrence

In the ketone fractions of Italian black shale samples. The spectrum shown above comes from sample 32, Livello Bonarelli (Chapter 3).

Remarks

The spectrum is indicative of an A-nor-steroid ketone. During the synthesis of the A-nor-steranes (Chapter 5) several A-nor-steroid ketones were obtained. The mass spectra of the synthetic compounds are very similar to the spectrum shown above. The retention time of the unknown compound suggests that it might be a 5α(H)- or a 5β(H)-A-nor-cholestan-3-one.





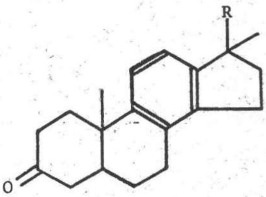
Peaks marked by an asterisk are due to instrument background.

Occurrence

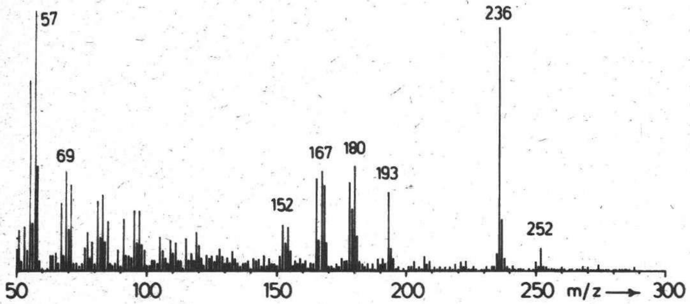
In the ketone fraction of several Italian black shales. The spectrum shown above comes from sample 9, Livello Bonarelli (Chapter 3).

Remarks

There are several compounds with identical mass spectra present in the ketone fractions investigated. The distribution of this series of compounds is similar to that often encountered in case of steroidal compounds. As the main fragment ions (m/z 157 and 267) are 14 mass units higher than those of ring-C aromatic steranes (m/z 143 and 253 respectively; Schaefle *et al.*, 1978) and there are no molecular ions detectable, we suggest the unknown compounds to be ring-C aromatic steroid ketones.



Schaefle J., Ludwig B., Albrecht P. and Ourisson G. (1978) Aromatic hydrocarbons from geological sources. VI. New aromatic steroid derivatives in sediments and crude oils. *Tetr. Lett.*, 4163-4166.

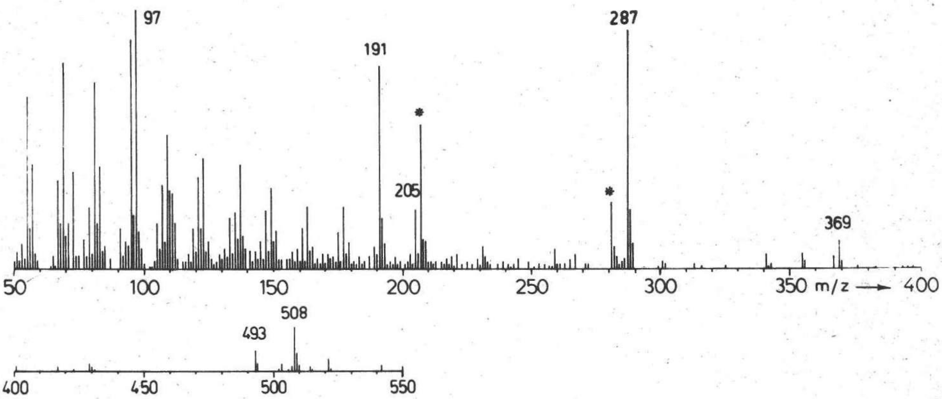


Occurrence

In the aromatic hydrocarbon fraction of sample 13, Livello Bonarelli (Chapter 3).

Remarks

Possibly a $C_{18}H_{20}$ compound. $M^{+\cdot} = 236$ (m/z 252 is a background peak).



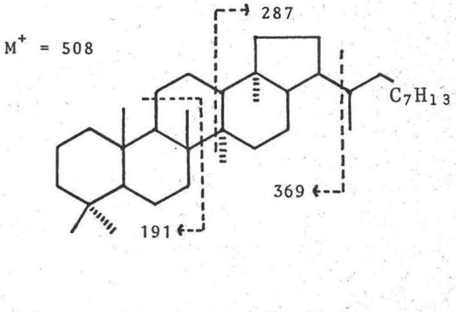
Peaks marked by an asterisk are due to instrument background.

Occurrence

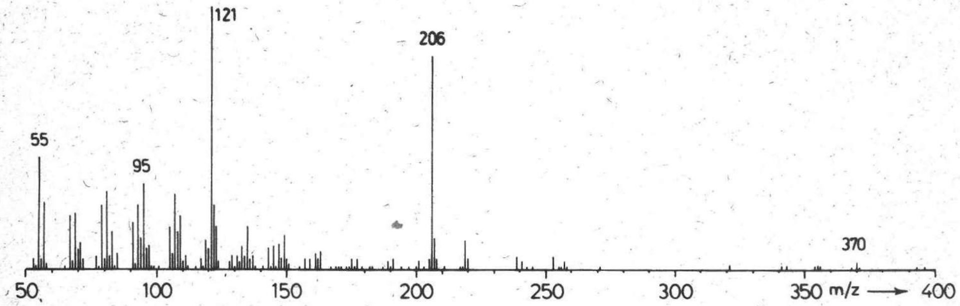
In the aromatic hydrocarbon fraction of sample 9, Livello Bonarelli (Chapter 3).

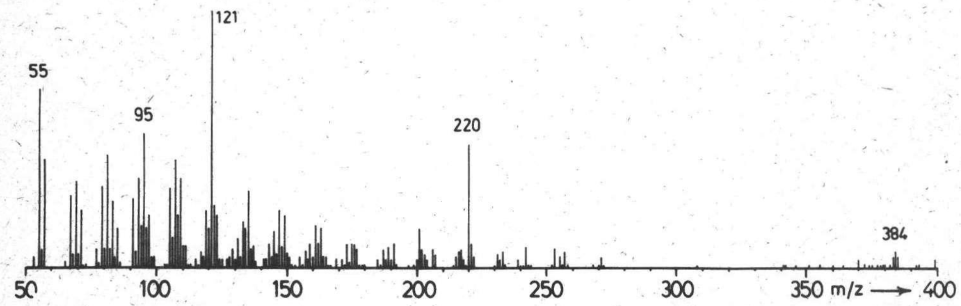
Remarks

The spectrum is indicative of an unsaturated extended hopane. The presence of m/z 369 (M^+- sidechain) indicates that the unsaturation is located in the sidechain (see scheme). The molecular ion (m/z 508) shows that we are dealing with a C_{37} compound. A homologue with intensive ions in the mass spectrum at m/z 191, 301 and 522 is also present in the sample. These compounds are probably related to the extended hopanes found by Rullkötter and Philp (1981) in Thornton bitumen.



Rullkötter J. and Philp R.P. (1981) Extended hopanes up to C_{40} in Thornton bitumen. *Nature* 292, 616-618.



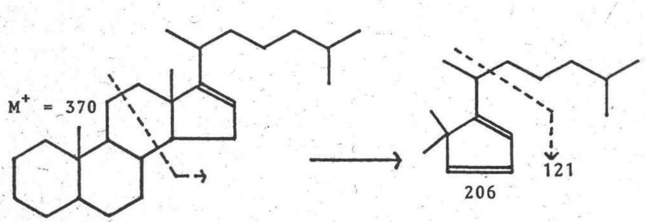


Occurrence

In the saturated hydrocarbon fraction of Italian black shales. The spectra shown above come from sample 39, Aqualagna series (Chapter 5).

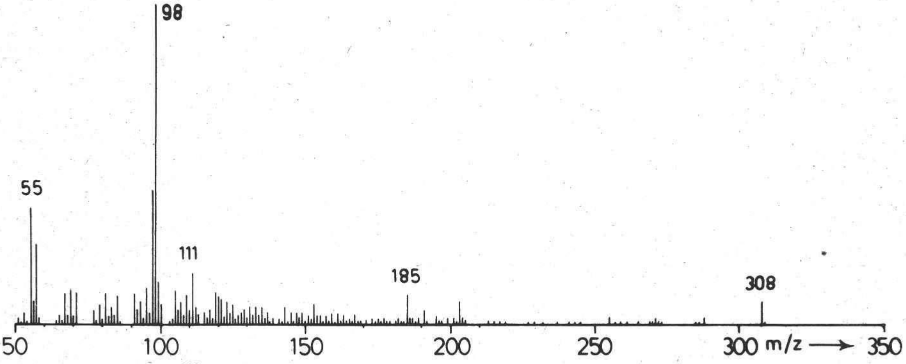
Remarks

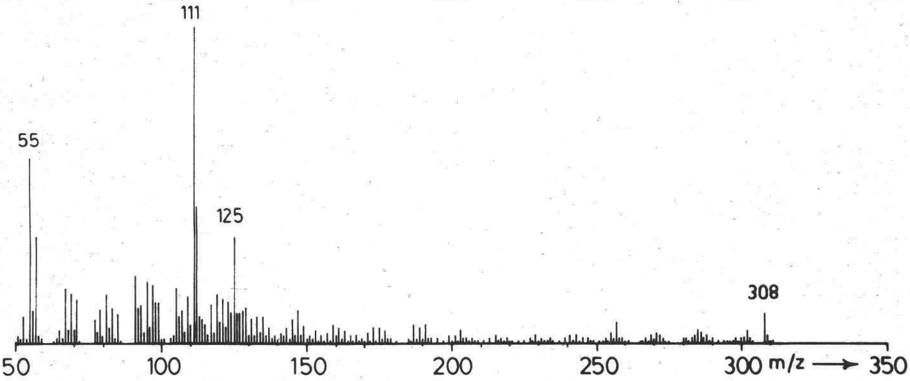
The samples contain a series of three compounds with related mass spectra. The third member, of which no pure mass spectrum could be obtained, is characterized by m/z 121, 234 and 398 as important peaks. The appearance of the spectra and the presence of many steroidal compounds in the same fractions suggest that we are dealing with sterenes. We propose the unknown spectra to be indicative of Δ16-sterenes. It is known that Δ16-androsten-3-ol has a main fragment ion at m/z 94, probably resulting from C-ring cleavage (Waller, 1972). The corresponding cleavage in a Δ16-C$_{27}$-sterene would produce a fragment with m/z 206 (see scheme below). Subsequent cleavage of the C-20/C-22 bond would yield a fragment at m/z 121. It is conceivable that the presence of Δ16-stere-



nes - should the tentative identification prove to be correct - is the result of a shift of the double bond from the sidechain (Δ22) to the D-ring. Δ16-sterenes are possibly intermediates in the formation of aromatic steroid hydrocarbons. A shift of the C-18 methyl group from C-13 to C-17 would move the double bond to ring C. Subsequent aromatization would yield the C-ring aromatic steroid hydrocarbons that have been identified by Albrecht and coworkers.

Waller G.R. ed. (1972) *Biochemical Applications of Mass Spectrometry*, pp.254-258. Wiley and Sons.
Albrecht P. Paper presented at the 10th International Meeting on Organic Geochemistry, Bergen, Norway (1981).





Occurrence

In the saturated hydrocarbon fraction of sample 9, Livello Bonarelli (Chapter 3).

Remarks

The two compounds appear to be structural isomers. The molecular ion and the main fragment ions are indicative of a C_{22} hydrocarbon with one double bond or ring structure.

SUMMARY

This thesis describes the organic geochemical investigations conducted in connection with a multidisciplinary research project on the origin of Cretaceous black shale deposits in Italy and France.

Chapter 1 gives a literature review of the research that has been carried out on Cretaceous black shales and of some models that are proposed to describe the formation of these deposits.

The detailed investigation of two black shale sections from an exposure near Moria, Italy, is described in Chapters 2 and 3. The insoluble organic matter is characterized microscopically and by Curie-point pyrolysis-mass spectrometry and Curie-point pyrolysis-gas chromatography-mass spectrometry. In the analysis of the soluble organic matter attention is mainly focussed on the saturated hydrocarbon fraction. The organic geochemical results lead to some conclusions concerning input material and environment of sedimentation. They can also be used to evaluate the validity of some models proposed for the origin of the black shale deposits.

Two samples from a related black shale deposit in France have also been investigated (Chapter 4). The composition of the organic matter is to a large extent similar to that in the Italian sediments. However, the French samples are different in that they are significantly more mature.

The extracts of the black shales contain many compounds that have not been described in the literature before. Two series of novel compounds - A-nor-steranes and de-A-steroid ketones - have been identified based on a comparison of their mass spectra with those of reference compounds synthesized for this purpose. A-nor-steranes (Chapter 5) are thought to be diagenetic products of 3-hydroxymethyl-A-nor-steranes that are present in certain types of sponges; they are therefore potential marker molecules for these organisms. The de-A-steroid ketones and de-A aromatic steranes, which were tentatively identified, (Chapter 6) are interpreted to be indicative of a novel diagenetic pathway of steroidal compounds.

Chapter 7 describes a theoretical approach to the use of isomerisation reactions of steranes in sediments as an indication of maturation. Using molecular mechanics the stabilities of molecules can be calculated and hence the composition of a mixture of isomers at thermodynamic equilibrium. It is also possible to predict the retention order of pairs of epimers based on the calculated preferential conformation of the molecules.

The application of Curie-point pyrolysis-mass spectrometry and Curie-point pyrolysis-gas chromatography-mass spectrometry to the characterization of insoluble organic material in sediments has been developed using several model series of samples. The results obtained on one of these - a suite of samples from the Toarcian of the Paris Basin - are included in this thesis (Chapter 8). Using computerized data processing techniques it is shown that the pyrolysis data are correlated with the degree of maturation of the sediments. The organic matter of some samples is different from the rest of the series as a result of differences in input material and/or environment of sedimentation.

SAMENVATTING

Dit proefschrift beschrijft het organisch geochemische gedeelte van een multidisciplinair onderzoek naar het ontstaan van afzettingen van zwarte schalies uit het Krijt, zoals deze voorkomen in Italië en Frankrijk.

Hoofdstuk 1 geeft een overzicht van het in de literatuur beschreven onderzoek aan de zwarte schalies uit het Krijt en van enkele modellen, die het ontstaan van deze afzettingen kunnen verklaren.

Het gedetailleerde onderzoek aan twee sekties met zwarte schalies uit een ontsluiting bij Moria in Italië staat beschreven in de hoofdstukken 2 en 3. Het onoplosbare organische materiaal is onderzocht met behulp van microscopie en met Curiepunt-pyrolyse/massaspektrometrie en Curiepunt-pyrolyse/gaschromatografie/massaspektrometrie. Bij de analyse van het oplosbare organische materiaal is de aandacht voornamelijk gevestigd geweest op de fraktie van de verzadigde koolwaterstoffen. Op basis van de organisch geochemische resultaten kunnen enkele conclusies met betrekking tot het oorspronkelijke organische materiaal en de afzettingsomstandigheden worden getrokken. Deze resultaten kunnen ook worden gebruikt om modellen, die het ontstaan van zwarte schalies beschrijven, op hun geldigheid te toetsen.

Er zijn tevens twee monsters uit een overeenkomstige afzetting van zwarte schalies in Frankrijk onderzocht (hoofdstuk 4). Het organische materiaal in deze sedimenten heeft een samenstelling die vergelijkbaar is met het materiaal in de Italiaanse sedimenten. Een belangrijk verschil is er met betrekking tot de diagenesegraad; deze is in de Franse monsters aanzienlijk hoger.

De extrakten van de zwarte schalies bevatten veel verbindingen, die nog niet eerder in de literatuur zijn beschreven. Door middel van het vergelijken van de massaspektra met die van - voor dit doel gesynthetiseerde - modelstoffen, hebben we twee series nieuwe verbindingen kunnen identificeren, namelijk A-nor-steranen en de-A-steroid ketonen. A-nor-steranen (hoofdstuk 5) zijn mogelijk langs diagenetische weg ontstaan uit 3-hydroxymethyl-A-nor-steranen, die in sommige typen sponzen voorkomen. Zij kunnen bruikbaar zijn als gidsmoleculen voor deze organismen. De-A-steroid ketonen en de-A aromatische steranen, waarvan een voorlopige identifikatie heeft plaatsgevonden, (hoofdstuk 6) zijn een aanwijzing voor het bestaan van een tot nog toe onbekende, diagenetische afbraak van steroiden.

Hoofdstuk 7 beschrijft de theoretische benadering van het gebruik van isomerisatiereakties van steranen bij het bepalen van de diagenesegraad van sedimenten. Met behulp van moleculaire mechanica kan de stabiliteit van moleculen worden berekend en kan vervolgens de samenstelling van mengsels van isomeren, die in thermodynamisch evenwicht verkeren, worden afgeleid. Het is ook mogelijk om de retentievolgorde van epimeren te voorspellen op basis van de berekende voorkeursconformatie van de moleculen.

De toepassing van Curiepunt-pyrolyse/massaspektrometrie en Curiepunt-pyrolyse/gaschromatografie/massaspektrometrie voor de karakterisering van onoplosbaar organisch materiaal in sedimenten is ontwikkeld met behulp van enkele modelseries. Eén daarvan - een serie monsters uit het Toarcien van het Bekken van Parijs - is bij wijze van illustratie in dit proefschrift opgenomen (hoofdstuk 8). Een belangrijk resultaat is, dat de pyrolysegegevens, o.a. via verwerking met behulp van een computer, gerelateerd kunnen worden aan de diagenesegraad van de monsters. Bovendien blijkt van enkele monsters het organische materiaal qua samenstelling af te wijken van dat in de andere, waarschijnlijk als gevolg van ander 'input' materiaal of van andere afzettingsomstandigheden.

CURRICULUM VITAE

Ger van Graas werd op 7 februari 1955 te Gouda geboren. Na het behalen van het diploma H.B.S.-B aan het St. Antonius College in zijn geboorteplaats begon hij in 1972 de studie aan de Afdeling der Scheikundige Technologie van de Technische Hogeschool te Delft. Het kandidaatsexamen (juni 1976) werd gevolgd door de afstudeerfase met als hoofdvak organische geochemie en als bijvakken massaspektrometrie, milieukunde, didaktiek van schei- en natuurkunde en een scriptie over het onderwerp 'Invloeden van chloorfluormethanen op klimaat en milieu'. Het afstudeeronderzoek (Toepassing van Curiepunt-pyrolyse technieken bij de analyse van organisch materiaal in oude sedimenten) verrichtte hij in de onderzoeksgroep Organische Geochemie (Vakgroep Algemene Scheikunde) bij prof. drs. P.A. Schenck en dr. J.W. de Leeuw. Na het behalen van het diploma ingenieur-chemicus (januari 1979) trad hij in dienst van de Nederlandse Organisatie voor Zuiver Wetenschappelijk onderzoek (ZWO) voor het verrichten van een door de Stichting Aardwetenschappelijk Onderzoek Nederland (AWON) gesteund onderzoek aan 'Zwarte afzettingen in het Midden-Krijt met betrekking tot anaerobe processen in de oceaan'.

STELLINGEN

1. De suggestie van Hussler *et al.*, dat C-ring aromatische steranen voornamelijk in een oxisch milieu worden gevormd, is te voorbarig.

   Hussler G., Chappe B., Wehrung P. and Albrecht P. *Nature* 294, 556-558 (1981)

2. De toepasbaarheid van de pristaan/fytaan verhouding als indicator voor de oxiciteit van het afzettingsmilieu wordt niet bevestigd door het gedrag van deze parameter in Italiaanse zwarte schalies.

   Didyk B.M., Simoneit B.R.T., Brassell S.C. and Eglinton G. *Nature* 272, 216-222(1978)
   Simoneit B.R.T., Brenner S., Peters K.E. and Kaplan I.R. *Geochim. Cosmochim. Acta* 45, 1581-1602(1981)

3. Bij de berekening van de meest stabiele struktuur van 1,4-dihydrobenzeen houden Lipkowitz *et al.* ten onrechte geen rekening met de mogelijkheid van een 'stoel' of een 'twist boat' conformatie.

   Lipkowitz K.B., Rabideau P.W., Raber D.J., Harder L.E., von R. Schleyer P., Kos A.J. and Kahn R.A. *J. Org. Chem.* 47, 1002-1005(1982).

4. De onduidelijkheid en verwarring, die bestaan met betrekking tot de struktuur van aromatische steranen, geven aan dat er op dit gebied nog veel gedetailleerd onderzoek nodig is, mede in verband met de mogelijke anthropogene herkomst van aromatische koolwaterstoffen.

   Schaefle J., Ludwig P., Albrecht P. and Ourisson G. *Tetr. Lett.*, 4163-4166(1978)
   P. Albrecht and J. Rullkötter. Papers presented at the 10th International Meeting on Organic Geochemistry, Bergen, Norway (1981).

5. De historische achtergrond van de geologie als beschrijvende wetenschap leidt nog regelmatig tot het optreden van onduidelijkheden met betrekking tot de exakte definities van sommige termen, zoals bijvoorbeeld in het geval 'zwarte schalie'.

   Howell J.V. *Glossary of Geology and Related Sciences* (Am. Geol. Inst., 1957).

6. Het afleiden van de samenstelling van het oorspronkelijk in het sediment afgezette, organische materiaal uit een driehoeksdiagram, dat de sterolsamenstelling weergeeft, gaat uit van een te grove vereenvoudiging van het zeer gecompliceerde gedrag van steroiden in sedimenten.

   Huang W.Y. and Meinschein W.G. *Geochim. Cosmochim. Acta* 43, 739-745(1979
   Dissanayake C.B., Senaratne A. and Gunatilaka A.A.L. *Org. Geochem.* 4, 19-26(1982).

7. Het aantreffen van relatief grote hoeveelheden hoog radioaktief materiaal op het KEMA terrein in Arnhem kan, onder andere, schade toebrengen aan de reputatie van het KEMA keurmerk.

8. Het succes van de herstrukturering van het laboratoriumonderwijs zal in hoge mate afhangen van de bereidheid van de docenten om hoge prioriteit te geven aan het verwerven van nieuwe vakkennis.

   Raamleerplannen opgesteld door de Voorbereidingscommissie Herstrukturering Laboratoriumonderwijs (VCLabo), 1981.

9. Het plan van ex-minister van Kemenade om afgestudeerden aan universiteiten in de toekomst allen de titel 'meester' te verlenen, moet worden gezien als een meesterplan om het aantal werkloze doctorandi te verminderen.

10. Het gebruik van kringlooppapier symboliseert een van de voornaamste doelstellingen van een proefschrift, namelijk het hergebruik van de erin beschreven resultaten bij andere onderzoeken.

11. Beter een beperkt computersysteem in bedrijf, dan een ideaal systeem in een beleidsnota.

Stellingen bij het proefschrift: "ORGANIC GEOCHEMISTRY OF CRETACEOUS BLACK SHALE DEPOSITS FROM ITALY AND FRANCE".

7 oktober 1982
Ger van Graas