



The influence of mineral matter on the separation of amorphous marine kerogens using density gradient centrifugation*

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Abstract—Three relatively immature amorphous marine kerogens were subjected to density gradient centrifugation (DGC). The density fractions obtained were analyzed by Curie-point pyrolysis in combination with gas chromatography (Py-GC) and with gas chromatography-mass spectrometry (Py-GC-MS). Despite the variations in density, no significant variations were observed in chemical compositions of the flash pyrolysates of the density fractions of each kerogen. The variations in density were due to varying amounts of inorganic matter, in particular pyrite, which remained after chemical demineralization procedures and was insufficiently removed during the sample processing. This was substantiated by the ash content of individual density fractions, which is linearly correlated to the densities of the kerogen density fractions. Further micronization and cryogenic treatment followed by a sink-float procedure of the Posidonia kerogen prior to DGC resulted in only a partial removal of the inorganic phase, as indicated by a shift of the average density towards lower densities. These results demonstrate the substantial effect of mineral matter, in particular pyrite, on the separation of amorphous marine kerogens into chemically distinct entities due to an intimate association of the organic and inorganic phase.

Key words—density gradient centrifugation, Posidonia Shale, kerogen, flash-pyrolysis, pyrite, micronization

INTRODUCTION

According to the “classical” neogenesis model, as proposed by Tissot and Welte (1984), kerogen is the result of a series of consecutive and random polymerization and condensation reactions of a very small fraction of the (bio)degradation products of biogenic polymers such as proteins and carbohydrates. The recognition of resistant biomacromolecules in algal cell walls and plant tissues has led to a reappraisal of the formation of kerogen (Tegelaar *et al.*, 1989). According to this new concept, kerogen can be considered as a mixture of, sometimes partially altered, highly resistant biomacromolecules. As a result of their different chemical natures (aliphatic, alicyclic, aromatic content), it may be assumed that biomacromolecules are characterized by different physical properties (e.g., density). Such differences have been successfully applied in density gradient centrifugation (DGC) experiments of heterogeneous coals, including cannel and boghead types, to obtain petrographically pure density fractions enriched in a

particular maceral (Joseph *et al.*, 1991; Crelling, 1994). Chemical characterization of individual macerals thus obtained has allowed the recognition of specific biological precursors contributing to the coal (Nip *et al.*, 1992; Hartgers *et al.*, 1994). Most marine kerogens (Types II and II-S), however, consist of amorphous, petrographically indistinguishable organic matter. Considering selectively preserved resistant biomacromolecules as a source and a part of) kerogen in marine sediments, DGC of amorphous kerogens could yield density fractions enriched in polymers derived from chemically distinct biomacromolecules. Senftle *et al.* (1987) and Kruger *et al.* (1993) have shown indeed that pyrolysates of density fractions from kerogens with a relatively low density are characterized by somewhat greater amounts of aliphatic compounds, and those of fractions with higher density by somewhat larger amounts of aromatic and phenolic compounds.

This study describes an attempt to separate three microscopically amorphous, marine kerogens by DGC. The fractions obtained were analyzed by Curie-point pyrolysis in order to examine in detail their chemical composition and to investigate relationships among distinct sources of organic matter.

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EXPERIMENTAL

Sample description

Three relatively immature, marine-derived kerogens were subjected to DGC. The Toarcian Posidonia Shale of southern Germany is a laminated black shale deposited in an epicontinental sea under exaerobic conditions (dysaerobic/anaerobic boundary at the sediment–water interface; Bottjer and Savrda, 1993). This black shale contains abundant fossils of the bivalves *Posidonia* (= *Bositra*) *radiata* and *Pseudomytiloides dubius* that are typically assigned to a benthic life habit. The Kimmeridge kerogen (Type II) was obtained from the Toarcian Upper Kimmeridge Clay Formation of southern England, which is described as a bituminous, microlaminated shale also deposited under exaerobic conditions (Miller, 1990). Bituminous marls of the Moroccan Tarfaya coastal basin are of Cretaceous age and were deposited in an open-shelf sea (Kuhnt *et al.*, 1990). Kerogens from this basin can be classified as Type II-S ($S_{org} > 0.04$; Eglinton *et al.*, 1992). Rock samples were crushed and powdered in a disc mill and extracted for 48 h in a Soxhlet apparatus using dichloromethane/methanol (7:1). Kerogens were concentrated according to standard procedures (Eglinton *et al.*, 1988) using HCl and HF to remove the greater part of the inorganic matter.

Density gradient centrifugation

A detailed description of the experimental set-up and of the principles of the density gradient technique is given by Dyrkacz and Horwitz (1982) and Dyrkacz and Bloomquist (1992a,b). The extracted and micronized samples were ultrasonically suspended in water and layered on top of an aqueous CsCl solution showing a density gradient ranging from 1.0 to 1.6 g·ml⁻¹. This suspension was centrifuged in a Beckmann J2-21M centrifuge using a JCF-Z zonal rotor which rotated at 17,500 rpm ($g_{max} = 30,500$) for one hour. After centrifugation the gradient was fractionated by pumping into a fraction collector, then filtered, weighed and dried. The kerogen density fractions were recovered by filtration through teflon filters for subsequent chemical analysis. The density and weight of each fraction of the kerogen samples were measured.

Prior to the second DGC experiment, an effort was made to obtain single component particles and to remove the residual mineral matter remaining after the acid demineralization procedure. First, the Posidonia kerogen sample was extracted exhaustively with dichloromethane/methanol (1:1) using ultrasonication to remove all extractable material. Thereafter, the kerogen was repeatedly cryogenically treated in liquid nitrogen and micronized in a fluid energy mill powered by dry nitrogen gas in order to obtain kerogen particles of micrometric size (1–10 µm; Crelling *et al.*, 1993). Subsequently, the kerogen was

subjected to a sink–float experiment. Approximately 2 g of the kerogen sample was suspended in an aqueous solution of CsCl with a density of 1.6 g·ml⁻¹ and then put into a vessel. After centrifugation the contents of the vessel were fractionated into a sink (density > 1.70 g·ml⁻¹) and a float (density range from 1 to 1.6 g·ml⁻¹). The float was subjected to DGC and the density and weight of each kerogen fraction obtained were measured.

Curie-point pyrolysis–gas chromatography (Py–GC) and Curie-point pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS)

Flash pyrolysis experiments were performed using a FOM-4LX Curie-point pyrolysis unit (Boon *et al.*, 1987) directly connected to the injector of a Hewlett Packard 5890 Series II gas chromatograph. Kerogen samples were pressed on flattened ferromagnetic wires (iron/nickel alloy; Curie-temperature 610°C) as described by Venema and Veurink (1985). The on-line flash pyrolysis experiments were performed by inductive heating of the wire, which was kept at its final temperature for 10 s using a high frequency generator (Fischer, model 9425). The gas chromatograph, equipped with a cryogenic unit, was programmed from 0°C (5 min) to 320°C (20 min) at a rate of 3°C/min. Separation of the pyrolysis products was achieved using a fused-silica capillary column (25 m × 0.32 mm) coated with CP Sil-5 (film thickness 0.45 µm). Helium was used as carrier gas. The compounds were detected either using an FID or by mass spectrometry using a VG-70S mass spectrometer (cycle time 1.8 s; resolution 1000; mass range 50–900; ionization energy 70 eV).

RESULTS AND DISCUSSION

Figure 1 shows the gas chromatograms of the flash pyrolysates of the Posidonia, Tarfaya and Kimmeridge kerogens. The flash pyrolysates are characterized by homologous series of *n*-alkanes and *n*-alk-1-enes, alkylated benzenes, -naphthalenes, -thiophenes and -benzo[*b*]thiophenes. The abundance of the organic sulphur compounds, i.e., alkylthiophenes and -benzo[*b*]thiophenes, is enhanced in the pyrolysate of the Tarfaya kerogen, consistent with its high sulphur content (Eglinton *et al.*, 1992).

These three kerogens were subjected to DGC. Figure 2 shows the density profiles of the three kerogens; the profiles are constructed from the weight and densities of the kerogen fractions obtained. Remarkable differences are observed between the density profiles of the three kerogen samples. The density range (1.1–1.6 g·ml⁻¹) of the fractions obtained from the Type II kerogens (Posidonia Shale and Kimmeridge Clay Formation) is much larger than that of the Type II-S Tarfaya kerogen density fractions (1.15–1.25 g·ml⁻¹). To investigate whether these variations in density are also reflected in variations in chemical composition, the starting kerogens

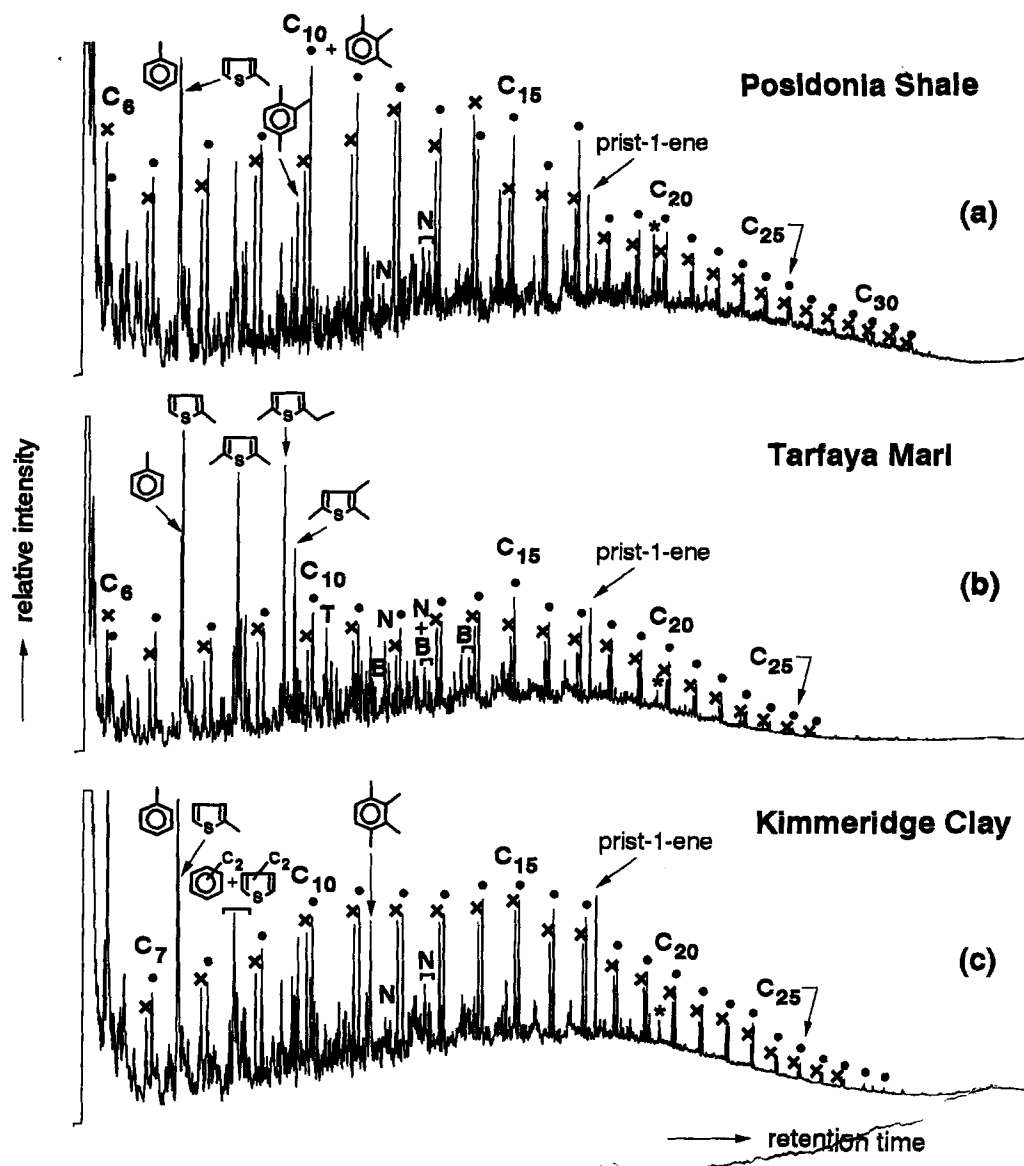


Fig. 1. Gas chromatograms of flash pyrolysates (Cu-temp. 610°C) of concentrated kerogens from (a) Posidonia Shale, (b) Tarfaya marl, and (c) Kimmeridge Clay Formation. Key: ● = *n*-alkanes; × = *n*-alk-1-enes; ★ = contamination; T = alkylthiophenes; N = alkyl-naphthalenes; B = alkylbenzo[b]thiophenes.

and selected density fractions (indicated by arrows in Fig. 2) of each kerogen sample were analyzed by flash pyrolysis-gas chromatography (Py-GC) and flash pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). The pyrolysates of the different density fractions of each kerogen were very similar to each other and to those derived from the original kerogen (Fig. 1).

Differences in density, therefore, are not reflected by distinct chemical properties. This discrepancy is probably due to the presence of various amounts of mineral matter in the different density fractions. This is illustrated by the ash contents of the density fractions of the Posidonia sample (Table 1). The ash

contents correlated nicely with the densities and this correlation could be expressed as a linear function (Fig. 3). The *y*-values of this function for *x* = 0 and *x* = 100 provided an estimate of the average density values of the organic and the inorganic phases: 1.08 and 2.78, respectively. The density calculated for the organic phase falls within the range of that of alginite (Kruge *et al.*, 1993), consistent with the predominantly aliphatic character of the pyrolysate of the Posidonia kerogen [Fig. 1(a)]. Thus, variations in density observed for the kerogen density fractions can be attributed mainly to different amounts of mineral matter in the density fractions. The separation of kerogen into its density fractions is obviously

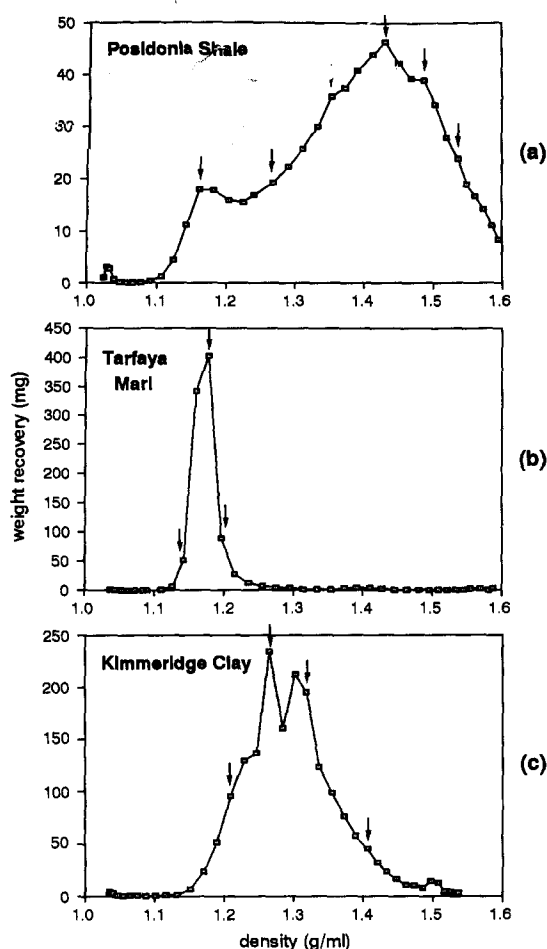


Fig. 2. Density profiles of concentrated kerogens of (a) Posidonia Shale, (b) Tarfaya marl, and (c) Kimmeridge Clay Formation. Arrows indicate density fractions analyzed by Py-GC and Py-GC-MS.

governed by the mineral matter present in these experiments.

In an attempt to remove the remaining mineral matter, the Posidonia kerogen was micronized even to smaller particles and subjected to a sink–float procedure prior to DGC. The Posidonia kerogen was selected because the density profile covers the largest range [Fig. 2(a)]. The floating fraction was subjected to DGC. The density profile is shown in Fig. 4. A significant shift towards lower densities is observed; the average density of the kerogen fractions decreased

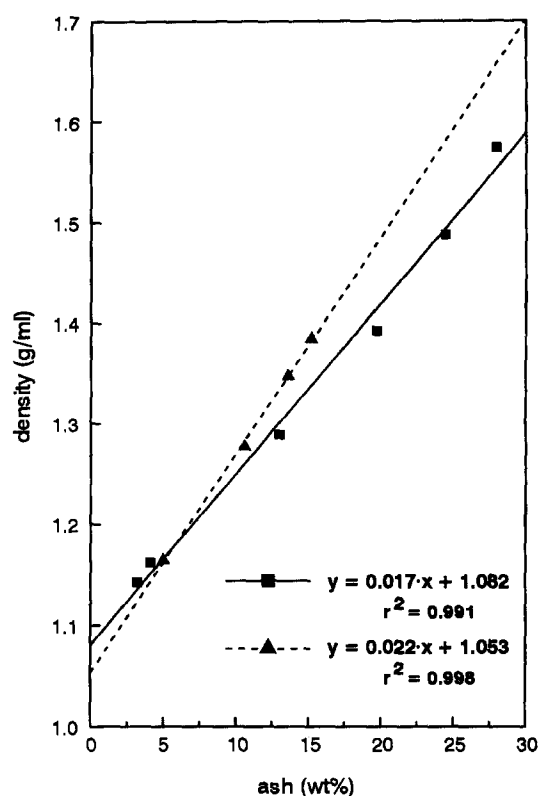


Fig. 3. Linear plot showing the correlation between the ash content (wt %) vs density ($\text{g} \cdot \text{ml}^{-1}$) of selected density fractions of Posidonia Shale kerogen from the first (squares) and second (triangles) density gradient centrifugation experiment.

from 1.45 to $1.30 \text{ g} \cdot \text{ml}^{-1}$ [cf. Fig. 2(a)]. It is noteworthy that the profiles of the density plots are similar before and after micronization. Again, the starting material (float) and selected density fractions (indicated in Fig. 4 by arrows) were analyzed by Py-GC and Py-GC-MS. Figure 5 shows the gas chromatograms of the flash pyrolysates of the float and of the selected kerogen density fractions. No significant differences between the pyrolysates are observed; minor peak ratio differences exist but the overall product distributions are very similar for all fractions. The large differences in density cannot be rationalized as a result of these subtle differences between the pyrolysates. Determination of the ash contents of the samples analyzed (Table 1) once again revealed a linear relationship between the ash contents and the densities (Fig. 3). A linear regression function provided an estimation of the densities of the organic and inorganic matter, 1.05 and $3.25 \text{ g} \cdot \text{ml}^{-1}$, respectively. These values are in the similar range as those calculated from the previous experiment and are still within the range expected for algal-derived kerogens (Kruege *et al.*, 1993).

Petrographic analyses of the floated Posidonia kerogen density fractions ranging from 1.10 to $1.16 \text{ g} \cdot \text{ml}^{-1}$ revealed that almost all organic material

Table 1. Results of ash analysis of density fractions obtained from kerogen of the Posidonia Shale

Before micronization		After micronization	
Density (g/ml)	Ash (%)	Density (g/ml)	Ash (%)
1.142	3.2	1.164	5.0
1.161	4.1	1.311	10.6
1.289	13.0	1.348	13.6
1.392	19.7	1.384	15.2
1.488	24.4		
1.574	27.9		

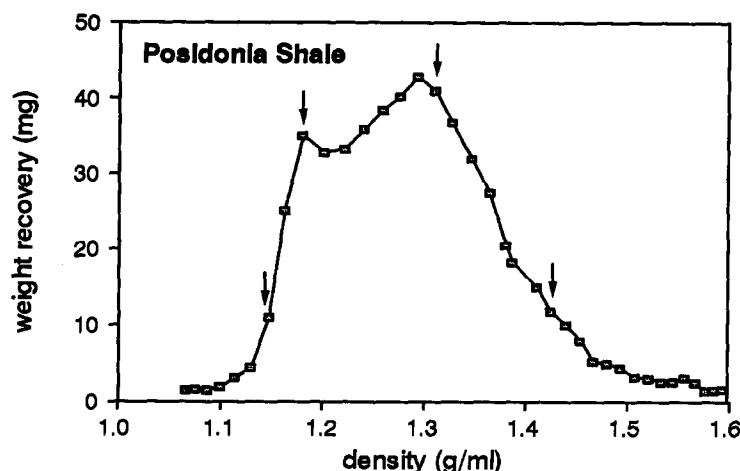


Fig. 4. Density profile of float obtained by sink-float procedure of micronized kerogen of the Posidonia Shale. Arrows indicate density fractions analyzed by Py-GC and Py-GC-MS.

in these fractions is alginite. Most of the particles were less than $10\ \mu\text{m}$ in size and were long and thin in shape, a shard-like texture. Little pyrite was observed. Kerogen fractions ranging from 1.20 to $1.40\ \text{g}\cdot\text{ml}^{-1}$ consisted predominantly of bright yellow fluorescing alginite shards and a weakly fluorescing brown matrix. Liberated single phase fragments of alginite were present as minor components. The amount of alginite decreased with increasing density. Most of the material with a density higher than $1.40\ \text{g}\cdot\text{ml}^{-1}$ occurs as weakly fluorescing amorphous kerogen particles, which were surprisingly large ($100\text{--}300\ \mu\text{m}$). Pyrite was ubiquitous and its amounts increased with increasing density. Although some pyrite is euhedral, most is framboidal. Since the calculated density of the inorganic phase (*ca* $3\ \text{g}\cdot\text{ml}^{-1}$) is lower than the density of pyrite ($5.02\ \text{g}\cdot\text{ml}^{-1}$) it must be assumed that clay minerals also contribute to the inorganic matter present in the density fractions. These clays must be intimately admixed with unrecognized components of the amorphous bodies.

The chemical and petrographical results demonstrate that DGC of these marine kerogens is severely hampered by the presence of residual inorganic matter. Because the original samples had been treated with HF and HCl and the presence of aluminum fluorides was possible, SEM/EDS analysis was conducted to detect aluminum and fluorine atoms. While some particles enriched in these two atoms were observed, they were very minor components of each sample and, therefore, not likely to cause significant density differences in particles. However, particle components composed of iron and sulphur were ubiquitous. These were clearly micron to sub-micron crystals of pyrite that were not liberated from the sample matrix in the sample processing. This pyrite was also more abundant in the higher density fractions. Quantitative analysis of the pyrite contents of

the isolated kerogens by incidental light microscopy showed that the Tarfaya kerogen contained the least amount of pyrite (approx. 1%), whereas the pyrite content of the Posidonia and Kimmeridge kerogens were approx. 20% and 7%, respectively. It should be noted that the Posidonia sample was repeatedly micronized, cryogenically treated and subjected to sink-float procedures in order to enhance the liberation of the organic phase. Surprisingly, the application of these methods and DGC have proven to be only partially effective in achieving the removal of pyrite, in spite of its relatively high density ($5.02\ \text{g}\cdot\text{ml}^{-1}$). It has been reported that the presence of inorganic matter also affects the maceral separation of heterogeneous coals (Dyrkacz and Horwitz, 1982). However, acid demineralization is generally adequate to obtain pure coal macerals of the demineralized coal sample by DGC. This observation is probably due to larger differences in physical properties of individual coal macerals as compared to distinct chemical entities in most marine amorphous kerogens and a more efficient liberation of the organic phase from the inorganic matrix upon demineralization and/or sink-float procedures. Petrographic analyses of the kerogen density fractions revealed an intimate association of amorphous, weakly fluorescing organic matter with the pyrite present. Pyrite typically occurs in the form of microcrystals coated with organic matter, when seen by scanning electron microscopy (Combaz, 1970). These multiphase particles obviously do not respond adequately to the micronizing procedure, yielding large fragments ($100\text{--}300\ \mu\text{m}$). As a result of this incomplete liberation of the organic matter from the pyrite present, the shape of the density profiles (Fig. 2) shows it to be governed by the height of the pyrite content in the kerogen samples. For example, the broad density profile of the pyrite-rich (approx. 20%) Kimmeridge kerogen represents a wide distribution of particles

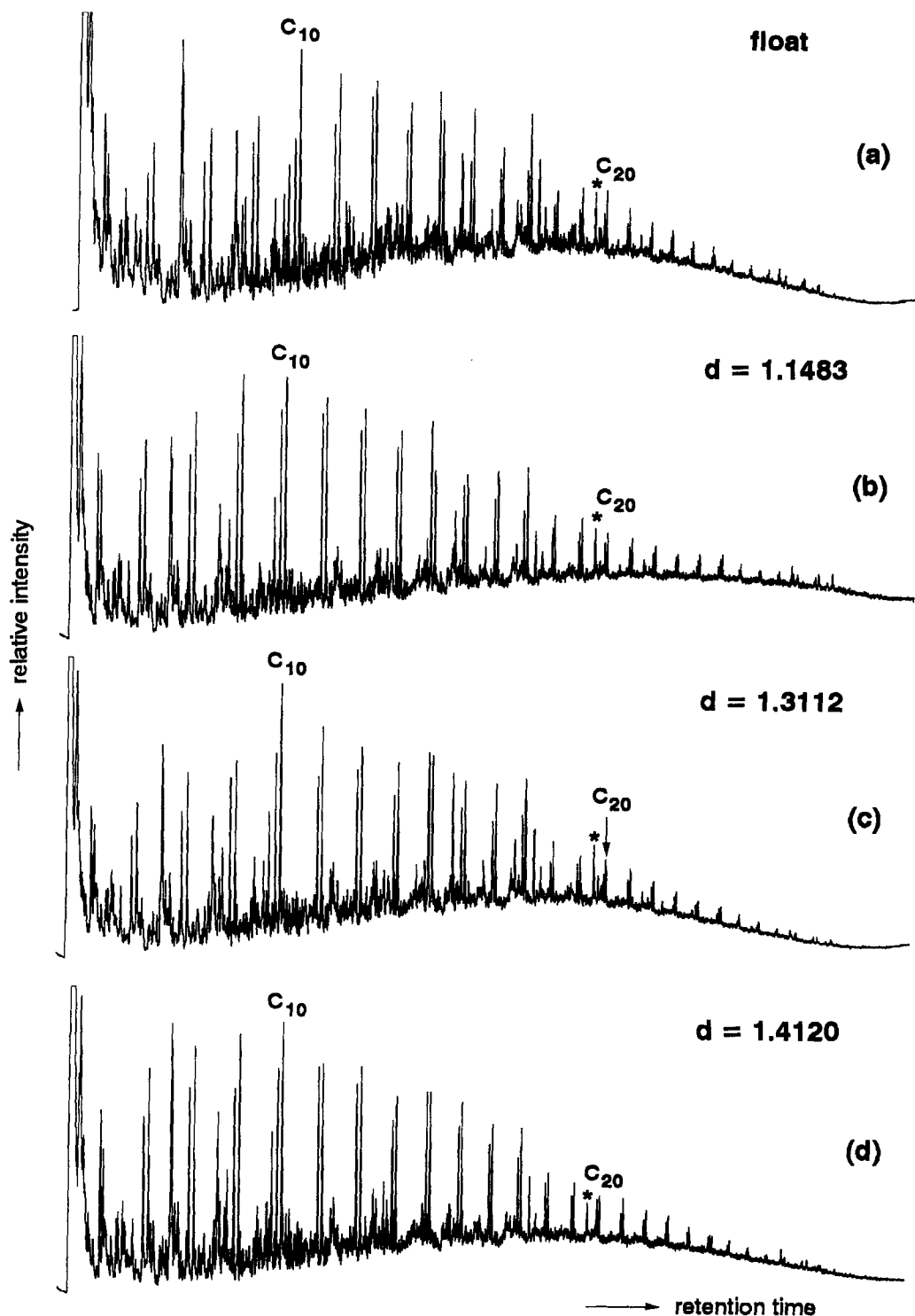


Fig. 5. Gas chromatograms of flash pyrolysates (Cu-temp. 610°C) of float and selected density fractions derived from the float of Posidonia Shale kerogen. Key: * = contamination.

containing different amounts of pyrite. In contrast, the narrow density profile of the Tarfaya isolated kerogen (Fig. 2) coincides with a very low pyrite

content (approx. 1%). This suggests that the organic matter in the Tarfaya sediment is very homogeneous in density since it cannot be separated by DGC even

though pyrite is virtually absent. Consequently, the organic matter in the Tarfaya kerogen is thought, in line with petrographic analyses, to be derived from one biogenic source, i.e., resistant algal biopolymers, which has become enriched in organo-sulphur moieties by reaction with reduced sulphur species (Sinninghe Damsté and de Leeuw, 1990; Sinninghe Damsté *et al.*, 1993).

A reconsideration of previous results brings to light other DGC studies of kerogens in which large variations in density also were not reflected by significant variations in the chemical compositions of their pyrolysates. The fact that Senftle *et al.* (1987) and Kruge *et al.* (1993) observed only minor differences between the pyrolysates of density fractions of a large density range from New Albany Shale, Green River Shale and Duwi kerogens is probably caused by varying contents of mineral matter in these fractions rather than by differences in type of organic matter. Our results show that a much more efficient removal of inorganic matter from a sediment sample is required before DGC experiments on isolated marine kerogens could be performed successfully. This requirement is hard to fulfil because of the strong interrelation between the inorganic matrix and the amorphous kerogen (which dominates the kerogen derived from most marine sediments), and the virtual impossibility of dissolving all inorganic matter without altering the organic matter simultaneously (Robinson, 1969). In this respect, application of a recently developed method to remove pyrite from kerogen by acidic chromous chloride reduction without altering the organic phase (Acholla and Orr, 1993) might result in an improved separation of kerogens into their petrographically and chemically distinguishable density fractions.

CONCLUSIONS

The density gradient centrifugation technique has been applied to three amorphous marine kerogens. SEM/EDS analysis revealed petrographically distinct macerals between fractions of low and high density. However, these microscopical observations were not accompanied by chemical differences as revealed by Curie-point pyrolysis. Apparently, the density distribution of the profiles was found to be governed by the amount of intimately associated pyrite, which could not be removed adequately during the DGC-procedures.

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REFERENCES

- Acholla F. V. and Orr W. L. (1993) Pyrite removal from kerogen without altering organic matter: the chromous chloride method. *Energy Fuels* **7**, 406–410.
- Boon J. J., Pouwels A. D. and Eijkel G. B. (1987) Pyrolysis high-resolution gas chromatography-mass spectrometry studies on beech wood: capillary high-resolution mass spectrometry of a beech lignin fraction. *Biochem. Soc. Trans.* **15**, 170–174.
- Bottjer D. J. and Savrda C. E. (1993) Oxygen-related mudrock biofacies. In *Sedimentary Review/1* (Edited by Wright V. P.), pp. 92–102. Blackwell Scientific Publications, Oxford.
- Combaz A. (1970) Microsphérules muriformes dans les roches mères du pétrole, hypothèse sur leur origine. *C. R. Acad. Sci. (Paris), Sér. D* **270**, 2240–2243.
- Crelling J. C. (1994) Targeting single coal macerals with density gradient centrifugation experiments. In *Preprints of Papers—Division Fuel Chemistry* Vol. 39, pp. 13–17. Am. Chem. Soc., Washington, DC.
- Crelling J. C., Thomas M. and Marsh H. (1993) The release of nitrogen and sulphur during the combustion of chars derived from lithotypes and maceral concentrates. *Fuel* **72**, 349–357.
- Dyrkacz G. R. and Horwitz E. P. (1982) Separation of coal macerals. *Fuel* **61**, 3–12.
- Dyrkacz G. R. and Bloomquist C. A. A. (1992a) Use of continuous flow centrifugation techniques for coal maceral separation. I. Fundamentals. *Energy Fuels* **6**, 357–374.
- Dyrkacz G. R. and Bloomquist C. A. A. (1992b) Use of continuous flow centrifugation techniques for coal maceral separation. II. Multiple density fractionations of coals. *Energy Fuels* **6**, 374–386.
- Eglinton T. I., Philp R. P. and Rowland S. J. (1988) Flash pyrolysis of artificially matured kerogens from the Kimmeridge Clay, U.K. *Org. Geochem.* **12**, 33–41.
- Eglinton T. I., Sinninghe Damsté J. S., Pool W., de Leeuw J. W., Eijkel G. and Boon J. J. (1992) Organic sulphur in macromolecular sedimentary organic matter. II. Analysis of distributions of sulphur-containing pyrolysis products using multivariate techniques. *Geochim. Cosmochim. Acta* **56**, 1545–1560.
- Hartgers W. A., Sinninghe Damsté J. S., de Leeuw J. W., Ling Y. and Dyrkacz G. R. (1994) Molecular characterization of flash pyrolysates of two Carboniferous coals and their constituting maceral fractions. *Energy Fuels* **8**, 1055–1067.
- Joseph J. T., Fisher R. B., Masin C. A., Dyrkacz G. R., Bloomquist C. A. and Winans R. E. (1991) Coal maceral chemistry. I. Liquefaction behavior. *Energy Fuels* **5**, 724–729.
- Krue M. A., Stankiewicz B. A. and Crelling J. C. (1993) Aspects of the organic geochemistry and petrology of kerogen and coal macerals. In *Organic Geochemistry—Poster Sessions from the 16th Int. Meeting on Org. Gechem., Stavanger 1993* (Edited by Øygard K.), pp. 140–144. Falch Hurtigtrykk, Oslo.
- Kuhnt W., Herbin J. P., Thürow J. and Wiedmann J. (1990) Distribution of Cenomanian–Turonian organic facies in the western Mediterranean and along the adjacent Atlantic margin. In *Deposition of Organic Facies* (Edited by Huc A. Y.), Vol. 30, pp. 133–160. AAPG Studies in Geology, Tulsa, Oklahoma.
- Miller R. G. (1990) A Paleocyanographic approach to the Kimmeridge clay formation. In *Deposition of Organic Facies* (Edited by Huc A. Y.), Vol. 30, pp. 13–26. AAPG Studies in Geology, Tulsa, Oklahoma.
- Nip M., de Leeuw J. W. and Crelling J. C. (1992) Chemical structure of bituminous coal and its constituting maceral fractions as revealed by flash pyrolysis. *Energy Fuels* **6**, 125–136.

- Robinson W. E. (1969) Isolation procedures for kerogens and associated soluble organic materials. In *Organic Geochemistry: Methods and Results* (Edited by Eglinton G. and Murphy M. T. J.), Ch. 6, pp. 181–195. Springer, Heidelberg.
- Senftle J. T., Yordy K. L., Barron L. S. and Crelling J. C. (1987) Analysis of mixed kerogens from upper Devonian Albany Shale. I. Evaluation of kerogen components derived from density separation. Presented at 1987 *Eastern Oil Shale Symposium* Lexington, Kentucky, 18–20 November, 1987, Technical Paper, pp. 155–167.
- Sinninghe Damsté J. S. and de Leeuw J. W. (1990) Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: state of the art and future research. In *Advances in Organic Geochemistry* 1989 (Edited by Durand B. and Behar F.). *Org. Geochem.* **16**, 1077–1101.
- Sinninghe Damsté J. S., de las Heras F. X. C., van Bergen P. F. and de Leeuw J. W. (1993) Characterization of Tertiary Catalan lacustrine oil shales: discovery of extremely organic sulphur-rich Type I kerogens. *Geochim. Cosmochim. Acta* **57**, 389–415.
- Tegelaar E. W., de Leeuw J. W., Derenne S. and Largeau C. (1989) A reappraisal of kerogen formation. *Geochim. Cosmochim. Acta* **53**, 3103–3106.
- Tissot B. P. and Welte D. H. (1984) *Petroleum Formation and Occurrence*. 2nd edn, Springer, Heidelberg.
- Venema A. and Veurink J. (1985) A method for solvent free application of polymers and inorganic materials to ferromagnetic wires used for pyrolysis-capillary gas chromatography methods. *J. Anal. Appl. Pyrolysis* **7**, 207–213.