

## Ninth EAOG Newsletter

### 1. Newsletter Secretary

Spring has arrived in Stavanger, with the tulips in full bloom, blossom on the fruit trees and redundancies in the oil industry. In Statoil, the only people to get sacked so far are the entire board of directors, who were recently dismissed by the Government (in their role as owners of the company). It remains to be seen what the new board decides to do, but no-one can count on the good life continuing as before. We are also approaching the end of our own internal reorganisation process, so no doubt I will soon get a new department name and a new manager. There aren't a lot of geochemists in the world, and if we lose too many we may have to apply for inclusion on the endangered species list.

This newsletter carries on the format from previous issues, with some thoughtful - even poetic - words from our Chairman, plus the Secretary's minutes of the last board meeting. There are also contributions from you the readers, this time from the NPD on the oil and rock standards for geochemical analyses, plus brief information on the new edition of the Norwegian Industry Guide to Organic Geochemical Analyses (which uses extensively results from the standards described by the NPD). Finally, there are two EAOG travel award reports written by the beneficiaries. So hopefully something for everybody. It's not as funny as usual though.

Richard Patience

### 2. From the Chairman

The 18th International Meeting on Organic Geochemistry (IMOG), held in Maastricht way back in September 1997, is but a faded memory (I come from a long line of poet-geochemists). Indeed, the publication of the proceedings from that meeting (*Organic Geochemistry* **29**, No. 1-3 and 5-7), towards the end of 1998, marked the end of a long and sometimes arduous road that began in earnest at San Sebastian (September, 1995) where the rudiments of what was to come in 2 years time were outlined to the assembled masses. It is clear that, all in all, the IMOG cycle typically lasts about 3 years. How difficult is the task of running these meetings? Is it only coincidental that almost all previous organisers (the male ones, at least) are either bald or grey(ing)? I certainly fit the mould. Having said this, there appears to be no shortage of volunteers who are willing to take on the challenge, and venues for the next three meetings are already set – 1999 Istanbul (Turkey); 2001 Nancy (France); 2003 Krakow (Poland).

The 19th International Meeting is almost upon us. Only 4-5 months to go before EAOG members from all over the globe congregate where the continents meet – Asia and Europe, that is – in the ancient and beautiful city of Istanbul! I know Prof. Namik Yalcin and his team are working hard, and have been for quite some time, making sure that the conference will be a success. The scientific programme is rich and varied, and the response to the Call for Papers was extremely strong. Add to that the rich and varied cultural history of Turkey, and we have an excellent conference in the making.

A personal regret is that numerous colleagues from the oil business will not be able to attend the meeting this time. Some have lost their jobs, and those still in work may find attendance

difficult because of budgetary constraints. I think it is fitting that we extend our best wishes to these organic geochemists, many of whom have taken a direct personal involvement in the staging and funding of IMOG over the years.

In closing, may I remind you that the EAOG Newsletter is there for you to express your opinions and exchange ideas on matters concerning organic geochemistry. The Schenck Award is there for you to nominate young scientists whose extraordinary talents should be acknowledged, and the Travel Award is there to help young scientists get experience working in other laboratories. What's more, the Board is working hard on your behalf; read the Secretary's Minutes – its true!

I very much look forward to seeing you in Istanbul!

Brian Horsfield

### **3. Secretary's report**

#### **Minutes of the EAOG Board Meeting; Hotel am Marschertor, Aachen, 7th March 1999**

Board members attending the meeting were Douglas, Hetenyi, Horsfield, Nederlof, Patience, Rowland and Rullkötter. Neither Telnaes nor Grimalt could attend because of family reasons.

##### Item 1: Welcome

The chairman, Brian Horsfield, opened the meeting at 9:00 a.m. on Saturday, 7th March 1999 and expressed a warm welcome to the other six Board members attending the meeting.

##### Item 2: Minutes of Istanbul Board Meeting

The minutes had been circulated and published as part of the EAOG Newsletter with no objections, and were thus taken to be approved.

##### Item 3: International Meeting on Organic Geochemistry 2001

Two proposals had been submitted for the 19th International Meeting on Organic Geochemistry 2001, both from France. Both proposals were of high quality and sufficiently detailed so that the Board could arrive at a decision. The main criteria for the evaluation were the budget plan, the structure of the meeting, the location, facilities and the experience of the proponents in organising previous meetings. The Board felt it was a shame that a decision had to be made between two such valuable proposals and thanked the authors of both submissions for the efforts they had put into their proposals. After long and intense discussions and consideration of all the material provided, the Board unanimously voted to have the 2001 meeting in Nancy. Patrick Landais will be invited to present more details of his plan at the Board meeting and General Assembly in Istanbul.

The Board also decided to provide a template which future proponents should use for their budget plans so that comparison of costs will be facilitated. Peter Nederlof will prepare a draft version, and after consent of the other Board members the template will be sent to the

organisers and proponents of future meetings (starting with 2001). The template will also have to be used for the financial budget report after the meeting.

#### Item 4: International Meeting on Organic Geochemistry 2003

A fairly advanced proposal had been received from Maciej Kotarba and Artur Stankiewicz for the 2003 meeting to be held in Krakow (Poland). The Copenhagen organic geochemistry group which had been approached earlier and expressed an interest in hosting the meeting, had indicated before the Board meeting in Aachen that they would prefer to withdraw if there was another option open to the EAOG. Thus, the Board discussed the Polish proposal using the same criteria as for the 2001 proposals and, due to its quality, unanimously decided to hold the 2003 international meeting in Krakow.

#### Item 5: Financial Report (Nederlof)

Although the membership fees have increased over the past years, they are not sufficient to fully support the organisation. Some additional income is from interest (mainly travel fund), but the main income of EAOG are still 'donations' of profits made by the meeting organisers. The donations show large fluctuations over the years, however. Main spendings are for the awards and the Board meetings. These Board meeting costs have increased since the oil companies are less willing to cover the travel expenses of Board members on their payroll, but recent costs appear to level out at about 6,000 Euro/2 years. The total assets of EAOG have fluctuated around 75,000 Euro in recent years, indicating an overall healthy situation. The Board registered that sponsoring of meetings by the oil industry will be low as long as the oil prices are as low as at present (i.e. March 1999). This may cause problems for meetings organisers, but the Board refrained from making a decision, for the present, on financially supporting the international meetings directly. The situation in the oil industry may also have an effect on the number of attendants at the meetings and will certainly affect the potential profit of the meetings and, thus, the income of EAOG from profit donations. Possibilities of indirectly supporting the international meetings were discussed but no decision was made. The Board will observe the financial developments and discuss this item again at the next meeting.

Elsevier has offered to organise future meetings through their conference department. The Board decided to invite Ms. Penny Moon of Elsevier to present details to the Board at the regular meeting in Istanbul. The Chairman will contact her to arrange this. Although Elsevier would cover any losses, the sponsoring situation and the consequences for EAOG income are unclear and will have to be discussed.

Horsfield presented the final budget report of the International Meeting on Organic Geochemistry 1997 in Maastricht. Due to the very favourable sponsoring situation, the meeting made a profit and donated 24,000 DM to EAOG. Also, 25,000 DM (included in non-member fees) were transferred to Elsevier for new members. The Board congratulated Brian Horsfield on the success of his meeting.

#### Item 6: Journal Report (Douglas)/Cooperation with Elsevier

Douglas distributed a written report on the journal situation. The impact factor of *Organic Geochemistry* has risen slightly to 1.510. The copy flow in 1999 is, so far, fairly regular. Issue 30/1 was despatched from the printer on February 8. Issues 30/2 and /3 had to be combined due to the small number of manuscripts ready for printing (despatched on March 3). Of the 109 manuscripts submitted in 1998, 39 have been accepted, 30 were rejected and 40 are still in the review process. There is a list of suggested special issues, but only some of them are in a

status that will probably materialise in 1999. The Istanbul proceedings will, most likely, be published by Yalcin, Inan and others as editors.

Three associate editors (Hower, Kohnen, Patience) resigned, two new ones were elected (Bishop, Snape). Douglas asked for suggestions for further associate editors by e-mail (with details of their fields of experience).

The length of notes (4 printed pages) will be more strictly reinforced. Because of the change of the journal format, new and more specific guidelines for preparation of notes will be included in the instructions for authors.

Elsevier agreed to a wager proposed by chief editors. Elsevier has agreed to a production time for manuscripts of not more than 14 weeks. Otherwise they will offer 10 free subscriptions for one year to needy groups (already happened once).

The problems in co-operation with Elsevier have recently grown to a serious level. They included proof reading of title pages, production schedule of proceedings and membership information (see below). The Board expresses strong concern about this development and will critically observe this in the near future, before alternative publishers will be considered.

#### Item 7: Board membership

In 1999, the terms of Grimalt, Hetenyi, Nederlof, Patience and Rullkötter will end, only Patience will be allowed to stand for re-election. At this meeting, the Board unanimously decided to further reduce the number of board members from eight to seven (plus Douglas as co-opted member). Because there has been little response to the call for candidates so far, the Board decided to extend the deadline to May 15, 1999.

The Board furthermore nominated the following candidates for membership: Richard Patience (re-election), Sylvie Derenne, Ger van Graas, Walter Michaelis. The Secretary will approach the candidates and will ask for CV and election statements. A Chairman-elect will have to be nominated at the next Board meeting in Istanbul.

#### Item 8: World Affiliations

In order to bring organic geochemically oriented societies closer together, Horsfield had contacted the chairmen of other organisations. Michael Lewan (OG Division of Geochemical Society), Luis Trinidad (ALAGO) were very enthusiastic regarding co-operation, while Ken Andersen (Geochemistry Division of ACS) did not see much freedom beyond the already existing links to ACS, but was open for further discussion. Individuals who responded to the suggestion of closer co-operation on the OG mail server, expressed a positive view as long as no additional formal meetings and other bureaucracy were generated. The chairmen of the corresponding African and Australian societies would like to be informed about further steps and to participate in the discussions.

For any near-future actions, the Board made the following suggestions:

- \* A joint "Best OG Paper Award" should be co-ordinated.
- \* Following his request, Mike Lewan will receive flyers of the Istanbul meeting for distribution among Geochemical Society members.
- \* Telnaes will contact the webmasters of the other societies for additional and more specific (meetings) links. The Secretary will inform Telnaes.

\* A decision on reduced registration fees at meetings was postponed due to the problem associated with the link of the EAOG members to the journal *Organic Geochemistry*.

On this occasion, the Board again discussed the option of changing the name of EAOG from 'European' to 'International'. The views were split. While some saw a better identification of the overseas members with the organisation if the name was changed, others itemised problems of scientific and Board meetings locations and Board membership. The new Board should discuss this again after the forthcoming elections.

#### Item 9: EAOG membership (Rowland)

Rowland presented an overview of the membership distribution by countries, but complained that he still has not received information from Elsevier on new members from the Maastricht meeting (about 300) and their fate in the society after the first year when the membership fee and journal subscription included in the registration fees ran out. According to an earlier agreement, Elsevier is supposed to provide membership information every three months. The last information was for May 1998 and did not include new members. Furthermore, despite many requests, information is still not provided in electronic form but on paper printout which has to be read and converted with much unnecessary effort. The Board decided that Archie Douglas will arrange a meeting with Henn (Elsevier), the persons responsible for membership lists within Elsevier, and Rowland to solve this problem. Applications of new members will in future go directly to Elsevier. An application form will also be put on the Web. Fees printed in the Journal will also be shown in Euro.

#### Item 10: Newsletter (Patience)

The newsletters, so far, have received reasonable approval according to feedback to Patience (which was overwhelmingly, but not 100%, positive). The next newsletter (i.e. this one - ed.) will appear as soon as possible after the minutes of the Aachen Board meeting are ready for distribution.

#### Item 11: Awards

Grimalt (in absentia) sent a document showing that three travel awards were granted in 1998, one application is presently under evaluation, one had to be rejected for formal reasons. Some additional inquiries were received by e-mail. Grimalt will send the travel report of Maria Hamor-Vido to Patience for inclusion in the newsletter. Reports due by Grossi, Werne, Nadalig and Yu will be claimed (reports by Grossi and Werne are included here - ed.).

No formal nomination was received for the Schenck Award 1999, but there were some requests for information.

As there was no other business, the Chairman closed the meeting at 3:25 p.m.

Jürgen Rullkötter, Secretary

## **4. Norwegian Geochemical Standards**

The Norwegian Geochemical Standards (NGS) project was financed by Norsk Hydro Produksjon AS, Saga Petroleum ASA, Statoil, and the Norwegian Petroleum Directorate. Three standard samples have been established, two for shales and one for crude oil. They are

primarily aimed at the petroleum industry and at research institutions performing geochemical projects within exploration and reservoir exploitation. The samples are now ready for use within these fields.

The reference values for the NGS samples are based on analyses carried out according to the Norwegian Industry Guide to Organic Geochemical Analyses, third edition (NIGOGA) (Patience et al. 1993).

### ***Sample descriptions***

Newsletters with sample documentation are available. These detail the origin of the samples, all procedures related to sampling, homogenisation, storage, and results from the first inter-laboratory calibration of the samples. In brief, the samples have the following characteristics:

#### **THE NORWEGIAN GEOCHEMICAL STANDARD SVALBARD ROCK – 1 (NGS SR-1)**

About 400 kg of the Svalbard Rock was collected from the southern side of Teistberget hill, Eastern Spitsbergen, Svalbard. The Svalbard Rock was taken from a horizon with relatively low Total Organic Carbon content in the Anisian, Middle Triassic Botneheia Formation. The sample has a mean vitrinite reflectance of 0.41 per cent Rm, a mean TOC content of 2.17 weight per cent and a mean extractable organic matter content of 4800 mg/kg rock. The sample has been homogenised and subsequently split into 1480 aliquots of 500 ml each. The aliquots are stored at -20°C at the NPD. We believe that enough sample material has been collected for the SR-1 sample to last for about 20 years.

#### **THE NORWEGIAN GEOCHEMICAL STANDARD JET ROCK – 1 (NGS JR-1)**

Nearly 200 kg of the Jet Rock was collected from the Port Mulgrave area, Yorkshire, NE England. The Jet Rock is an organic-rich black shale. It is classified as a member of the Toarcian age Whitby Mudstone Formation. The sample has a mean vitrinite reflectance of 0.47 per cent Rm, a mean TOC content of 12.4 weight per cent, and a mean extractable organic matter content of 16000 mg/kg rock. The sample has been homogenised and subsequently split into 980 aliquots of 300 ml each. The aliquots are stored at -20°C at the NPD. We believe that enough sample material has been collected for the JR-1 sample to last for about 10 years.

#### **THE NORWEGIAN GEOCHEMICAL STANDARD NORTH SEA OIL - 1 (NGS NSO-1)**

Around 1000 litres of crude oil was collected from the Oseberg field located in block 30/9 in the Norwegian part of the North Sea. The sample has been homogenised and tapped into ninety 12.5-litre aluminium flasks and ten 10-litre polyethylene flasks. The oil has a mean API gravity of 32.9°, a mean C15+ fraction of 77 per cent of the total crude, and a mean asphaltene content of 1.9 per cent. All flasks are stored at -20°C at the NPD. Aliquots are prepared in 300 ml aluminium containers intended for organic geochemical and stable isotopes analyses, and in 250 ml polyethylene flasks intended for trace metal and radiogenic isotope analyses. We believe that enough sample material has been collected for the NSO-1 sample to last for at least 20 years.

### ***Who can apply for samples?***

The NGS samples are aimed primarily at the petroleum industry and research institutions performing geochemical projects within exploration and reservoir exploitation on the Norwegian continental shelf. Petroleum geochemistry projects that are not directly related to

the Norwegian shelf may also be granted samples based on evaluation of the purely geochemical aspects of the application.

It is likely that the samples will be useful for analyses performed for environmental projects. Aliquots of the samples are allocated for possible usage in basic research, as well as for the development of new procedures, instrumentation etc.

#### ***Application requirements***

Anyone who receives the standard samples may be required to submit data from their routine analyses of the samples to the NPD for future refinement of the standards' calibration. The format for the data reporting is presently being evaluated. The latest information about data reporting routines may be found on the NPD's internet web site <http://www.npd.no>

The NPD Sample Release Committee evaluates all sample applications. The application should contain the applicant's name, postal address, telephone and fax number, e-mail address, and the name of a contact person. The normal analytical activity of the applicant must be stated (e.g. service laboratory for the oil industry, university laboratory working with environmental/geochemical problems, etc). It must also include a statement about the type of usage the NGS samples are intended for (e.g. quality control of TOC screening of drill cuttings, reference samples for comparison of different pyrolysis techniques, etc.).

#### ***Address for sample application:***

The Norwegian Petroleum Directorate  
Attn.: The Sample Release Committee  
P.O. Box 600  
4001 Stavanger, Norway  
Telephone: +47 51 87 60 00  
Fax: +47 51 55 15 71

#### ***Mailbox and WWW***

All parties involved in the use of NGS and NIGOGA are encouraged to share their experiences, suggestions, questions, etc. regarding NGS and NIGOGA with the NPD. This information will be used for future development of both the NGS samples and the NIGOGA. Please contact Trond Brekke at the address or fax number above, or e-mail to [Geochem@npd.no](mailto:Geochem@npd.no).

The latest news about the NGS samples is found on the NPD web site, [www.npd.no](http://www.npd.no).

#### ***References***

Patience, R. L. (Statoil), Pedersen, V.B. (Saga Petroleum), Hanesand, T. (Norsk Hydro), Weiss, H. M. (SINTEF Petroleum Research, former IKU Petroleum Research), Feriday, I. (Geolab Nor), and Nyland, B. (Norwegian Petroleum Directorate), The Norwegian Industry Guide to Organic Geochemical Analyses, Third Edition (1993)

Trond Brekke, NPD

## **5. The Norwegian Industry Guide to Geochemical Analyses (NIGOGA)**

The 3rd edition is currently very close to being completely revised, and the Guide committee hopes to get the fourth edition (NIGOGA 4) published on the World Wide Web within about two months. The geochemical community will be informed about the contents of the Guide and the way to access it once the document is on the Web. However, it is built around the new standards described above, and is more result-orientated than method-driven, compared to the 3rd edition.

Hermann Weiss, IKU, on behalf of the Guide Committee

## **6. Travel award reports**

### **i) Josef P. Werne**

In early 1998 I received an EAOG Student Travel Grant to go to the Netherlands Institute for Sea Research (NIOZ) and work in the lab of Dr. Jaap Sinninghe Damsté. I spent three months in his lab, learning methods and applying them to the sediments of the Cariaco Basin. This report is a brief summary of results from that study, which is still ongoing.

The first aspect of the study was to look for carotenoids, such as isorenieratene, in an attempt to document changes in the thickness of the anoxic water column in the Cariaco Basin over the last 12 thousand years. Our efforts produced no quantifiable amounts of any biomarkers indicative of photic zone anoxia, and we must conclude that the oxic/anoxic interface in the Cariaco Basin has not impinged on the photic zone over the time interval under study, the last 12 thousand years.

Second, we proposed to use Raney-Ni desulphurisation to analyse the organic sulphur-bound fraction of organic matter in sediments from the Cariaco Basin. Initial results from this aspect of the study show significant changes in the relative proportions of different sulphur-bound compounds released, indicating changes in either primary production in the surface waters, microbial reworking at the chemocline and/or in the sediments, or both. Desulphurised fractions are dominated by phytane, with significant contributions from highly branched isoprenoids, lycopane, unidentified triterpanes, and b-carotane. We are currently in the process of combining results from study of the organic sulphur in the Cariaco Basin with studies of inorganic sulphur species (performed by Tim Lyons at the University of Missouri-Columbia, USA), and intend to present this work at the IMOG meeting in Istanbul in September, 1999. An abstract is available upon request.

Third, we proposed to analyse kerogen-bound organic matter through pyrolysis-GCMS. An initial survey of kerogen-bound organic matter has been performed, and some differences in the composition of this OM have been identified. The kerogen-bound OM has substantial contributions from pristene, alkyl benzenes, alkyl thiophenes, isoprenoid alkenes, and isoprenoid algaenans.

Finally, an analysis of organic sulphur compounds in the extractable apolar fraction of the OM in the Cariaco Basin yielded results with significant implications for early diagenetic incorporation of sulphur into organic matter. A precursor-product relationship was identified, and we were able to calculate the kinetics of this sulphurisation reaction, involving an unidentified triterpenoid. Results of this aspect of the study have been submitted to *Geochimica et Cosmochimica Acta*, and are accepted pending revisions. We are currently

working with Dr. Philippe Schaeffer to identify the compounds involved in the sulphurisation reaction. A copy of the submitted manuscript is available upon request.

I am extremely grateful to EAOG for their generous support that made this research possible.

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ii) Vincent Grossi  
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#### a) Aims of the project

The main goal of this French-Dutch collaboration was to study the impact of some oxidative processes (photo-oxidation, auto-oxidation) on the fate of marine photosynthesized organic matter. More precisely, we tried to find out whether photo- and auto-oxidation of phytoplanktonic lipids can induce the formation of oxygen cross-linked macromolecular structures. This assumption was based on the work performed on marine humic substances by Harvey *et al.* (1983) and Kieber *et al.* (1997), on the recent recognition of ether-bond containing geomacromolecules in marine sediments (e.g. Koopmans *et al.*, 1997) and on recent results related to oxidation of lipids obtained at the LOB.

Another part of my post-doctoral work performed at the NIOZ was the study of the potential competition occurring between sulphurisation processes and anaerobic biodegradation of some lipids (phytol and derivatives) in Recent anoxic marine sediments. This work had been submitted for the 18th International Meeting on Organic Geochemistry in Maastricht, The Netherlands (September 1997).

#### b) Effects of reactive oxygen species ( $\text{HO}^*$ , $\text{HOO}^*$ , $\text{1O}_2$ ) on organic substrates: formation of oxygen cross-linked macromolecules?

##### Autoxidation of pure substrates

Pure substrates (1-octadecene, phytol acetate and oleic acid) were allowed to react either with a mixture of  $\text{H}_2\text{O}_2$ /Peroxidase (a producer of hydroxyl radicals) or with the Fenton reagent (a producer of hydroxyl and hydroperoxyl radicals made of  $\text{H}_2\text{O}_2$  and Mohr's salt). We failed to observe any oxidation of the pure substrates when treated with the former reagent whereas classical oxidation products of the starting molecules (see of instance Porter, 1986; Hancock *et al.*, 1989; Rontani and Aubert, 1994) were observed when stirred (48h) with the Fenton reagent. In this latter case, the yields were low probably due to the hydrophobic property of

the organics and no dimer, trimer or higher molecular weight compound was detected by GC, GC/MS or PyGC/MS, although a high oven temperature program was used.

### Sensitised photooxidation of lipid

#### Pure substrates

The pure substrates used for the autoxidation experiments (see above) were also photodegraded in sea water in the presence of hematoporphyrin (a producer of singlet oxygen). Dark controls were carried out in parallel. Classical photoproducts of the starting substrates were observed after a few days of irradiation (see for instance Rontani *et al.*, 1995; Rontani, 1998) but no condensation products were detected during the analysis of the total extracts by GC, GC/MS and PyGC/MS.

#### Phytoplanktonic lipids

A further experiment was performed by irradiating senescent cells of the diatom *Phaeodactylum tricornutum* in sterile sea water. During this experiment, we focused on the light-dependent degradation of the chlorophyll phytyl chain and of unsaturated fatty acids. It was shown previously that the photodegradation of the phytyl chain and of phytoplanktonic fatty acids involves mainly singlet oxygen. In killed phytoplanktonic cells, the photodegradation of esterified phytol leads mainly (>90%) to the production of two photoproducts quantifiable (after alkaline hydrolysis) in the form of an isoprenoid C18 ketone and an isoprenoid methylene diol (Rontani *et al.*, 1995), while the photodegradation of unsaturated fatty acids afford isomeric allylic hydroperoxides which can be reduced to the corresponding hydroxyacids or cleaved to  $\omega$ -oxocarboxylic acids (Rontani, 1998).

#### *Chlorophyll phytyl chain*

At the end of the irradiation period (15 days representing an exposure to 27.6 Ein.m<sup>-2</sup>), the sum [phytol photoproducts + intact phytol] has decreased from 1.15 to 0.24 micromole/l, while no change was observed in dark controls where the original phytol was quantitatively recovered. Phytol photoproducts have been demonstrated to be photochemically stable; thus secondary photochemical processes cannot be responsible of such a decrease in the amount of isoprenoid compounds. This surprising loss of phytyl chain was attributed to the formation of unidentified photoproducts. These compounds could be the results of photooxidative cross-linking of (intact and/or photooxidised) phytyl chain with itself and/or with other phytoplanktonic lipids such as unsaturated fatty acids. We therefore search for macromolecular structures in different organic fractions (see below).

#### *Unsaturated fatty acids*

The major unsaturated fatty acids present in *P. tricornutum* were C16:1, C18:2, C18:2 and C20:5. The mono-unsaturated fatty acids were present as D9 and D11 isomers as determined by DMDS derivatisation. After 15 days of irradiation, all these unsaturated fatty acids were photodegraded to a certain extent, depending on their unsaturation pattern, whereas no degradation occurred in the dark controls. Logically, the photodegradation rate of the unsaturated fatty acids quickly increases with their degree of unsaturation. The polyunsaturated fatty acids were completely removed while 40 to 60% of the mono-unsaturated fatty acids were degraded. Several isomeric allylic mono-hydroxy hexadecenoic and octadecenoic acids were detected and identified by GC/MS (following classical derivatisations). These compounds (which represent almost quantitatively the amount of mono-unsaturated acids that disappeared) arise from the addition of singlet oxygen on the ethylenic carbons of the C16:1 and C18:1 acids respectively. Four groups of hydroxyacids,

corresponding to the oxidation of D9 and D11 hexadecenoic and octadecenoic acids, were detected. Hydroxyacids which could have been formed during the photo-oxidation of polyunsaturated fatty acids were not detected in the acid fraction of the photo-oxidised extracts. On the other hand, *w*-oxocarboxylic acids and *a,w*-diacids ranging from C7 to C12 were detected in very low amounts. These compounds can arise from the cleavage of photoproducts of mono- as well as poly-unsaturated fatty acids. Although some steps of the analytical procedure (e.g. evaporation under nitrogen) could have induced a loss of these short chain compounds, it seems unlikely that all the poly-unsaturated fatty acids were degraded to smaller units that were not detected. We rather believe that (a part of) unsaturated fatty acids can also be incorporated into a macromolecular structure (via photocondensation processes) by oxygen bonds. This hypothesis was supported by the fact that the acidic fraction of the total extract as well as the residue after extraction were significantly bigger in the photo-oxidised samples than in dark controls. Thus, we searched for potential aliphatic macromolecular structures in these different fractions.

#### *Search for macromolecular structures*

Different analytical treatments were used to try to detect macromolecular structures in the photooxidised cells of *P. tricornutum*. The acidic lipid extract was treated with HI/NaSMe in order to cleave selectively C-O bonds and labelled the position of the oxygen on the carbon skeleton with a methylthio group. This treatment induced the formation of different methylthio-acids. Part of these methylthio-acids corresponded to the substitution of the hydroxy group by a methylthio group in the monohydroxy-acids formed by photo-oxidation. Nevertheless, the quantity of methylthio-acids formed during the treatment was significantly lower than the quantity of hydroxy-acids present in the photo-oxidised samples. This was in contradiction with the eventual presence of oxygen cross-linked fatty acids in the acidic fraction. Moreover, HI reacted with double bonds and induced the formation of methylthio-acids with a methylthio group at the position of the double bond. Finally, we detect small amounts of iodo-acids which resulted from an uncompleted substitution of the iodine by SMe groups. A model experiment was performed by treating a D9 C18:1 fatty acid with HI/NaSMe. It appeared that 25% of the starting compound was converted to the corresponding iodo-acid after HI treatment. The products formed after derivatisation with NaSMe were 9-SMe C18 acid and 10-SMe C18 acid. HI/NaSMe treatment also induced a *cis-trans* isomerisation; indeed, we started with pure *cis* oleic acid and we ended with a mixture of *cis* and *trans* isomers (100/30). We also observed significant losses (30%) of the starting substrate.

The acidic lipid extracts of the photo-oxidized cells was also directly analysed by PyGC/MS. We failed to observe a clear signal coming from polymeric aliphatic material. The only differences observed between the photo-oxidized cells and the blank were induced by the breakdown of simple photoproducts (hydroxyacids) present in the photodegraded cells.

The residues obtained after extraction of the lipids of the photo-oxidized cells and of the blank were also investigated. Following saponification, these residues were treated with trifluoric acid in order to exclude any remaining sugar and protein. PyGC/MS analysis of the final residues showed differences between the photooxidised and the blank samples. This differences could be attributed to remaining sugars and/or proteins and/or lipids in the residue of the photo-oxidised cells although the GC trace appeared very complex. Therefore, a second TFA treatment was performed which induced the disappearance of the previous residue. This demonstrated that no non-hydrolysable polymer was present in the residue analysed; this also

indicated that if photocross-linking of all kind of organics can occur in senescent phytoplanktonic cells, the eventual solubility of the polymerised material formed can induced its loss during some analytical procedures.

### Conclusions

Although many attempts were performed to try to determine whether abiotic oxidative processes can induce the cross-linking of lipids in the marine environment, no clear evidence of such a process could be obtained during these experiments. Nevertheless, different indications let us believe that such a phenomenon is presently occurring to a certain extent in senescent phytoplankton. Several analytical problems have to be solved before clear conclusions can be drawn. First of all, one has to find out in which fraction (dissolved, particulate, neutral, acidic, non-hydrolysable, etc.) the eventual oxygen cross-linked macromolecules could end up. This probably depends on the environmental conditions and on the reactivity towards reactive oxygen species of the different organics involved. On the other hand, if these hypothetical macromolecules are extractable by solvents, one has to find a way to distinguish the C-O bonds corresponding to hydroxy and/or hydroperoxy groups (coming classical oxidation) from the C-O bonds corresponding to ether and/or peroxy cross-links before the transformation of these "polymers" into sub-units can be investigated. The labelling of the hydroxy groups with SOCl<sub>2</sub> could constitute a solution to this problem. Hydrogenation of eventual double bonds present in the oxygen cross-linked monomers is another analytical step to be considered whereas chemical degradation treatments have to be used with caution since several side reactions can appear.

### c) Sulphurisation and biodegradation of phytol and its derivatives in Recent anoxic sediments

This work was presented (oral session) at the 18th International Meeting on Organic Geochemistry in Maastricht, The Netherlands (September 1997). The experiments performed and the results obtained have been discussed in a recent paper of Organic Geochemistry (Grossi *et al.*, 1998).

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