

## Study of the role of the mineral matrix in sedimentary organic matter preservation (Cenomanian black shale, Central Italy)

V. Salmon	Laboratoire de Sédimentologie, Ecole des Mines de Paris, 77205 Fontainebleau Cedex, France
S. Derenne	UMR CNRS 7573, Laboratoire de Chimie Bioorganique et Organique Physique, Ecole Nationale Supérieure de Chimie de Paris, 75231 Paris Cedex 05, France
E. Lallier-Vergès	UMR 6531 CNRS, Laboratoire de Géologie de la Matière Organique, Université d'Orléans, 45067 Orléans Cedex, France
C. Largeau	UMR CNRS 7573, Laboratoire de Chimie Bioorganique et Organique Physique, Ecole Nationale Supérieure de Chimie de Paris, 75231 Paris Cedex 05, France
B. Beaudoin	Laboratoire de Sédimentologie, Ecole des Mines de Paris, 77205 Fontainebleau Cedex, France

Understanding the mechanism(s) which led to sedimentary organic matter (OM) preservation is essential for oil exploration and for the reconstruction of palaeoenvironments and palaeoclimates, as well. In addition to the first model of OM preservation, the degradation-recondensation pathway as defined by Tissot and Welte (1984), two mechanisms have been extensively studied in the last few years and are now well understood, namely the selective preservation and the natural sulphuration pathways. Recently, a new mechanism has been proposed, involving a protective role by minerals: the so-called sorptive protection pathway. Mayer (1994) showed that in sediments from coastal shelves (where most of the OM is preserved in marine environment), outside from zones receiving a large amount of OM, a correlation can be derived between the organic content and the mineral surface area, corresponding to a monomolecular covering of the mineral surface, which was termed monolayer equivalent, or ME. Considering that most of the surface area is composed of pores less than 8 nm width, and that more than 90% of the OM cannot be physically separated from the mineral matrix, this author proposed that the OM is concentrated in these pores, the size of which excludes the hydrolytic enzymes and allows condensation reactions to take place although the latter reactions are characterized by low rates.

Up to now, studies on this fourth OM preservation pathway have only been carried out on Recent sediments (see review in Hedges and Keil, 1995). However, a recent study on a Cenomanian black shale

(90 Ma) suggested an important role for the mineral phase in OM preservation. Indeed, this study, mainly based on pyrolysis, indicated that the analysed kerogen was formed by condensation of lipidic moieties showing a very low degree of degradation, and that no substantial diagenetic alteration took place in the resulting kerogen, associated with its mineral matrix, till the present time.

The aims of the present study are (i) to confirm the hypothesis of a protective role for the mineral phase by morphological observations and (ii) to test whether this phase still plays a protective role for the kerogen, once formed, by comparing pyrolysates of the freshly isolated kerogen and of the same isolated kerogen after one and two years of storage. The pyrolysate of the kerogen isolated from the ground rock and stored for two years was also analysed.

### Microscopic observations

When observed with transmitted natural light and under UV excitation, thin sections showed that this black shale is composed of stacked organo-clayey and carbonate microlayers (*c.* 100  $\mu\text{m}$  in thickness). Scanning electron microscopy (SEM) coupled with X-ray measurements (pin-point analysis and elemental mapping) revealed that, at this scale, OM and clay signals cannot be separated. A transmission electron microscopy (TEM) study performed on ultra-thin sections of embedded rocks showed that, at a nanoscopic scale, the OM constitutes a network of organic nanolayers (*c.* 100 nm thick) lined by clay

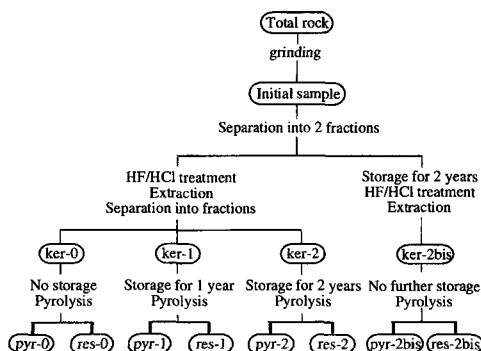


FIG. 1. Procedure.

particles. In the case of OM adsorption onto clay particles, such particles were expected to be coated by a very thin layer of OM (only a few nm). These observations suggest that a steric protection by clay minerals within a mille feuille-type structure was more likely involved in OM preservation, for this black shale, than mere adsorption.

### Pyrolytic study

Following the above observations on an intimate association between OM and clay minerals, we subsequently examined the possible role of the mineral matrix in OM stability. To this end, the kerogen isolated via elimination of minerals by the classical HF/HCl treatment was studied just after isolation, and after storage for one and two years, at room temperature, in the dark. The pyrolysates of the fresh kerogen and of the kerogens stored for 1 and 2 years are termed pyr-0, pyr-1 and pyr-2, respectively. In the same way, the kerogen, isolated after 2 years of storage of the ground rock under the same conditions as above, was studied immediately after HF/HCl treatment and its pyrolysate (pyr-2bis) compared to the above ones (procedure described in Fig. 1).

Comparison of pyr-0 to pyr-1 and pyr-2 revealed, along with storage duration, (i) an increase in the amount of volatile products, (ii) a shortening of the *n*-alkyl chains of the released products, (iii) a rapid disappearance, in less than one year, of the C<sub>40</sub> pyrolysis products based on a lycopane skeleton and (iv) a sharp decrease, within 2 years, of pyrolysate constituents with short isoprenic chain and hopanoids.

The appearance in FTIR spectra of bands at 1210 and 1150 cm<sup>-1</sup> corresponding to C-O bonds, as well as a significant increase of the oxygen index (from 9 to 30 mg CO<sub>2</sub>/g TOC) are consistent with an alteration via oxidative processes upon kerogen storage.

The whole set of these data points to the occurrence of a physicochemical alteration of the kerogen chemical structure after isolation from the mineral matrix. Indeed, the shortening of the released products in pyr-1 and pyr-2 and the appearance of new oxygenated functions, with the duration of kerogen storage, strongly suggest the occurrence of an oxidative process including the building of an increasing amount of linkage within the geomacromolecule, thus shortening the truly linear portion of long alkyl chains.

If we now compare the pyrolysate of the kerogen isolated from the ground rock stored for 2 years (pyr-2bis) with pyr-0 and pyr-2, the distributions of the main series of pyr-2bis are shown to be intermediate between the ones of pyr-0 and pyr-2, which indicates an intermediate degree of degradation. It thus appears that during 2 years of storage, the OM of the ground rock underwent some alteration, but that the extent of the latter was not as important as that undergone after the same storage duration by the isolated kerogen. This observation is consistent with our mille feuille protection model deduced from TEM observations, since after grinding the OM shall be partly exposed to air but also still partly protected within the mineral matrix. Hence an intermediate degradation between the crude rock and the isolated kerogen.

### Conclusions

This study, combining microscopic and pyrolytic approaches, provided, for the first time on a kerogen, direct indications for a major role of the protection by minerals in kerogen formation and for the determinant role played by minerals in OM accumulation in this black shale. Indeed, firstly the OM was physically protected by the clays, maybe by adsorption on the mineral phase but more probably by steric protection (according to the mille feuille model we propose, with alternation of OM and clay nanobeds). The OM could thus be partly preserved from early diagenetic degradation. Moreover, clays are known for their catalytic properties (Degens and Ittekkot, 1984) and condensation reactions of the associated OM leading to kerogen formation were likely favoured by this mineral phase. Finally, even once formed, such a kerogen was still protected by the mineral matrix as evidenced by the pyrolytic studies. This last result indicates that ancient OM is sensitive to physico-chemical alterations, once isolated from its mineral matrix.

Due to this unexpected instability, it appears that it is necessary to exercise caution in order to avoid misinterpretation in kerogen structures and derived interpretations, when isolated samples are analysed.