

# Alteration of organic matter during chertification of a Cenomanian black shale (Umbria-Marche Basin, 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 CNRS 6531, 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

A number of black shales, generally comprising clayey/siliceous intercalations were deposited in many locations at (or near to) the Cenomanian/Turonian boundary. One of the best-known and most extensively studied Cenomanian/Turonian black shale deposits is the "Bonarelli" horizon spanning a large area in the Umbria-Marche Apennines of Central Italy. Recently, the occurrence of 40, relatively thin (from less than 1 cm to 15 cm), black levels was reported below the Bonarelli horizon (Beaudoin *et al.*, 1996). These black levels occur in the uppermost 20 m of the section and their deposition spanned about 2.5 million years. Moreover, their periodicity corresponds to multiples of 20 ky. Such black levels were observed and correlated over the entire Umbria-Marche Basin and considered as precursors of the Bonarelli horizon (Beaudoin *et al.*, 1996). They are either homogeneous (laminated clayey layers, cherty layers) or heterogeneous (superimposition of both layers or laminated clayey layers comprising black chert nodules).

## Aims and methods

Our work is focused on a heterogeneous level comprising a clayey layer overlaid by a cherty one. This clayey layer was previously examined by microscopic, spectroscopic and pyrolytic methods (Salmon *et al.*, 1997 and this volume). This study pointed to a major role for clay minerals in OM preservation and in subsequent stability of the kerogen via steric protection provided by a mille feuille-type structure. The clayey layer and the cherty

one exhibit very different organic contents (total organic carbon, TOC of 13.5 and 0.5%, respectively). This sharp lowering indicates that a dramatic loss of OM took place during chertification process. The aims of the present study were therefore (i) to determine the nature and the extent of degradation of the chert OM and (ii) to tentatively identify a relationship between petrographical and geochemical characteristics and the chertification process.

To this end, microscopic and pyrolytic studies were performed on this cherty sample and the results compared with those derived from the underlying clayey layer.

## Petrographic results

The cherty layer is composed of a black part (just above the laminated clayey layer) and of a grey part (above the black one). Observations of thin sections of the chert sample under transmitted natural light revealed dark laminations in the lower, i.e. black part, of the cherty layer. Considering the occurrence of a laminated clayey layer below the chert, these laminations shall correspond to residual laminations of silicified clays. Such an interpretation is fully consistent with the occurrence of black chert nodules within one of the clayey level of the series. As a result, we will consider that the studied heterogeneous level initially corresponded to a homogeneous clayey level, a part of which underwent chertification. Hence, the same source organisms and initial chemical structure for the OM were assumed for both layers.

Observations of the isolated OM under natural light and UV excitation show that it is dominated by amorphous OM comprising opaque particles (accounting for 45% of total OM) and small sized (c. 0.1  $\mu\text{m}$  width) brown ones (20%). A rather high amount (c. 25%) of wood debris, exhibiting various oxidation stages and some shaped organic remains of marine origin (5%) are also observed. When compared with the clay OM, the chert OM presents a more degraded appearance and seems to have undergone a more severe alteration.

Examination of polished sections under natural light and SEM of the cherty layer revealed a very specific distribution: one part of the OM is disseminated within the mineral matrix, whereas the other part is located within microcracks (c. 10  $\mu\text{m}$  width). It is likely that the disseminated OM present in the chert matrix brown merely corresponds to AOM, microfossils and blade-shaped higher plant debris. On the contrary, the opaque mature organic aggregates observed in palynofacies preparation are thought to be specific of the OM filling the microcracks. This OM was deposited as a fluid or semi-fluid phase and can be considered as thermal cracking products of the kerogen from the underlying clays, which underwent some maturation, that filled the chert cracks. This implicates that chertification occurred after microbial diagenesis but largely before catagenesis (cracks already formed to take in catagenesis products).

### Chemical results

Upon pyrolysis at 400°C, only a relatively low weight loss (20% of initial OM) was observed for the kerogen isolated from the cherty layer. Moreover, this loss chiefly corresponds to the release of  $\text{SO}_2$ . As a result, the medium volatility pyrolysis products only account for a few percents of the unheated chert OM whereas they represent 15 wt.% of the clay OM thus pointing to important differences in the chemical structure of both materials. This is corroborated by the sulphur content (Sorg/C = 0.5 in the chert whereas it is much lower, 0.02, in the clayey layer). High Sorg contents in kerogens are usually associated with the natural sulphuration pathway (Sinninghe Damsté *et al.*, 1989). Kerogens formed *via* this pathway are characterized by an important production of organo-sulphur compounds (OSC) upon pyrolysis. Indeed, upon pyrolysis of the clayey layer OM, OSC (alkyl thiophenes, alkyl benzothiophenes) are generated in low amounts. In sharp contrast, no OSC were detected in the pyrolysate of the chert OM. This lack of OSC,

along with the important release of  $\text{SO}_2$  and spectroscopic features revealed by FTIR indicate that the sulphur-containing moieties that occurred in the starting clayey OM were selectively enriched during chertification. However, these moieties underwent marked alteration associated with oxidation processes.

GC/MS analysis of the pyrolysate of the cherty OM reveals a predominance of *n*-alkane/*n*-alk-1-ene doublets from  $\text{C}_{13}$  to  $\text{C}_{32}$ , the occurrence of hopanoids and of long chain fatty acids up to  $\text{C}_{28}$ . The shaped organic constituents observed in palynofacies are likely derived from selectively preserved resistant biomacromolecules. Since such macromolecules are known to exhibit a highly aliphatic character (Largeau *et al.*, 1986), the shaped remains may be partly responsible for the alkane/alkene doublets in the chert OM pyrolysate. In previous studies, we examined (i) the chemical structure of unaltered OM isolated from the underlying clayey sample and (ii) the changes in chemical structure underwent by such OM upon storage once separated from the mineral matrix. Comparison with the present results confirmed that chertification was associated with extensive OM alteration, as was hypothesized from palynofacies observations.

### Conclusion

In conclusion, this study on the OM of a cherty layer showed that chertification occurred at the interface between the black shale and the carbonate beds and that chert formation is an early process and was completed long before catagenesis. It also indicates that chertification was associated with a drastic elimination of the bulk of the initially present OM, along with a selective enrichment of some highly resistant constituents. Nevertheless, the latter constituents underwent pronounced oxidative alteration upon chertification, as revealed for example by the nature of sulphur-containing moieties.

### References

- Beaudoin, B., M'Ban, E. P., Montanari, A. and Pinault, M. (1996) *Comptes Rendus Acad. Sci. Paris* **323 II** a, 689–96.
- Largeau, C., Derenne, S., Casadevall, E., Kadouri, A. and Sellier N. (1986) In *Advances in Organic Geochemistry 1985*, eds D. Leythaeuser and J. Rullkötter, *Org. Geochem.* **10**, pp. 1023–32. Pergamon Press, Oxford.
- Salmon, V., Derenne, S., Lallier-Vergès, E., Largeau, C. and Beaudoin, B. (1998) this volume.