Information on source organisms and early degradation through complete analysis of acid moieties in surficial marine sediments in areas close to main river mouthes (Lena, Changjiang)

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The soluble fraction of Recent marine sediments has been extensively studied to derive information on the nature of source organisms, the relative contribution of terrestrial and marine inputs and the diagenetic changes underwent by lipids. Among the examined lipids, acids are often used since some of these compounds are specific of a type of microorganism. In sediments, acids can occur as extractible compounds, termed free acids or be covalently linked to the insoluble macromolecular network and are then termed bound acids. The release of such bound acids requires the use of chemical treatments such as hydrolyses. In almost all previous studies, only the acids released by a classical saponification using KOH were examined. More recently, saponification with KOH and a phase transfer catalyst (PTC) was shown to improve the release of OH⁻labile fatty acids from soils and kerogens (Amblès et al., 1993). The OH⁻-labile acids released by both saponifications corresponds to ester-linked moieties. However, some linkages, including amide and ether functions, are not cleaved upon saponification. In fact, it was observed that acid hydrolysis on previously saponified sediments can afford large amounts of acids, termed H⁺-labile acids (Goossens et al., 1989). It was also noted that some acids cannot be released by strong acid or base hydrolyses but these tightly bound acids can only be released upon pyrolysis (Kawamura and Ishiwatari, 1984; Largeau et al., 1986).

Aims and methods

The various acid fractions mentioned above should reflect differences in the mode of occurrence of acid moieties in kerogens. Separate analyses of these different types of acids should thus provide further information on the source organisms and on

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> degradation intensity upon early diagenesis. However, no study involving all the above different treatments has been carried out so far on a given sediment. In the present study, surficial sediments from two contrasted environments were successively submitted to the above treatments. A first set of three sediments was collected in an arctic area, close to the Lena River delta and in adjacent areas in Laptev Sea. The other two surficial sediments came from the Changjiang estuary and offshore in East China Sea.

Results and conclusions

Five acid fractions (free, OH^- -labile, $OH^-(PTC)$ labile, H^+ -labile and tightly bound) were thus obtained in substantial amounts from each sediment. In fact, the classical procedure which only involves the first two treatments would have released at most one-third of the total acids. Whatever the sample, the $OH^-(PTC)$ -labile fraction always predominates and the tightly bound acids are the less abundant ones. The total amount of acids decreases seaward.

The different acid fractions and the DMDS adducts of the unsaturated fatty acids were examined by GC/ MS so as to determine their nature and distribution. Comparison of the composition of the successive fractions obtained for a given sediment indicates that these fractions correspond to distinct pools. This result was expected for the fractions released by base or acid treatment since different types of chemical bonds are thus cleaved. However, it also appears that the two saponifications also yield different pools of acids and that the effect of the phase transfer catalyst is not a simple increase in recovery efficiency.

Information on source organisms can be derived from the nature of the acids present in each fraction. It thus appears that autochtonous organic matter derived from microalgae (including diatoms) was a major contributor to acid moieties in all the samples. The extent of early diagenetic alterations undergone by such moieties decreases from the free fraction to the OH^- -labile and $OH^-(PTC)$ -labile ones, the tightly bound acids being the less altered.

Bacterial inputs were rather low in all the samples. Bacterial populations were characterized by a relatively low diversity. Sulphate-reducing bacteria were likely implicated.

Terrestrial contribution to acid moieties appears to be very minor in the Lena delta and bay and in the Changjiang estuary. This low contribution, which was a priori rather unexpected in areas close to the mouth of such main rivers likely reflects the combination of two features : (i) a high primary productivity, stimulated by a large influx of nutrients from the river hence a dilution of terrestrial materials and (ii) riverine terrestrial organic matter was recently shown to be characterized by a high level of alteration and to mainly correspond to altered soil organic matter ; accordingly, terrestrial acids should be extensively degraded when reaching river mouth (Jaffé *et al.*, 1996).

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