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Detection of nitrogen stable forms in marine sediments by high resolution magic angle spinning (HRMAS) ^{1}H nuclear magnetic resonance (NMR).

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Nitrogen occurring in sedimentary organic matter (SOM) mainly derives from living organisms. Proteins and peptides, the most abundant nitrogen containing substances in SOM, have been traditionally considered as part of the labile fraction in the environment. On the other hand, recent studies have shown that proteinaceous material can resist microbial degradation in sedimentary environments and consequently a portion of the nitrogen is incorporated into biologically refractory organic material and removed from the active nitrogen pool (Knicker *et al*, 1996, Pantoja and Lee, 1999; Nguyen and Harvey, 2001; Knicker and Hatcher, 1997, 2001; Zang *et al*, 2001).

Different mechanisms have been discussed for understanding this preservation:

- Organo-mineral associations (Keil *et al*., 1994).
- Degradation-recondensation mechanisms leading to the formation of resistant kerogens by random condensation and polymerization of low molecular weight compounds arising from degraded naturally occurring macromolecules (Tissot and Welte, 1984; Patience *et al*., 1992)
- Encapsulation and protection from bacterial hydrolysis of proteins within the SOM macromolecular matrix (Knicker and Hatcher, 1997; Nguyen and Harvey, 2001).

- Protection of proteins during phytoplankton degradation in oceanic systems by covalent binding to macromolecular OM (Kirchman *et al*., 1989)

In the present study, we used one-dimensional HR-MAS NMR and two-dimensional HR-MAS ^{1}H-^{1}H total correlation spectroscopy (TOCSY) NMR experiments to study the structural characteristics of recent marine-coastal sediments sampled at the Southwest Atlantic coast of Spain.

HR-MAS techniques were applied to materials swollen in d_6-dimethyl sulfoxide (DMSO-d_6), which enhanced their molecular mobility. In addition, the magic angle spinning removes or minimizes effects of chemical shift anisotropy, dipole-dipole interactions and magnetic susceptibility line broadening (Keifer et al., 1996; Millis et al., 1997; Stark et al., 2000; Fang et al., 2001). Data obtained under these conditions allows a substantial improvement in functional group assignment capabilities.

We detected in most of the analyzed marine sediments samples cross-peaks, that may be assignable to protons directly linked to peptidic bonds and aromatic structures according to chemical shift computer assignment programs (Chemview). These signals are weak, but its presence, even in the sodium hypochlorite treated sample, is a clear sign of the stability of these Nitrogen-bearing structures.

Since other hypothetical assignments are also possible, further NMR experiments are still necessary for a better undertanding of the nature of recalcitrant peptide-like material in SOM.

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