Occurrence of lipids in crossed-lamellar layers of molluscan shells

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Mollusk shells, which present a variety of acellular CaCO3 structures, have long been recognized as composite materials: organic macromolecules are associated with the mineral phases at sub-micrometric scales. Previous studies on soluble matrices extracted from the shells were focused on proteins and sugars [1], and many investigations were centered at shells presenting an inner aragonite nacreous layer and an outer prismatic layer. However, this rather simple nacro-prismatic model does not reflect the variety and complexity usually found in mollusks: among them, the most commonly found yet least documented would be aragonite crossed-lamellar structure [2].

Herein, we report occurrence of diverse lipidic compounds extracted from aragonite crossed-lamellar shell layers of five species: one bivalve and four gastropods. SEM observations were carried out, as well as Tapping AFM to map the localization of organic compounds at sub-micrometric scales. FTIR analyses were performed to characterize molecular groups, and TLC was used to separate lipidic extracts with respect to polarity.

Whereas the observed structures are strongly similar among the wide array of taxa, differences in protein contents have already been found [1]. Our results suggest that lipidic contents are quite alike, and in relative high amount. They mostly consist of very apolar compounds such as waxes, some molecules close to triglycerides, as well as a few sterol esters and other unidentified common bands. Our results show that the lipid compounds of crossed-lamellar structures differ from lipids extracted from nacreous and prismatic layers [3], and from corals [4]. What is their role in biologically driven mineralization processes? Very little is known on their importance regarding the formation of the shell. Moreover, their behaviour during diagenetic processes cannot be neglected, as their response, as insoluble and polar compounds, will strongly differ from soluble proteins or sugars behaviour.

[1] Dauphin & Denis (2000) *Comparative Biochemistry & Physiology* A**126**, 367–377. [2] Boggild (1930) *D. Kgl. Danske Vidensk. Selsk. Skr. naturvidensk. og mathem.* **2**, **2**, 231–326. [3] Farre & Dauphin (2009) *Comparative Biochemistry & Physiology* B**152**, 103–109. [4] Farre & Dauphin (in press) *Zoology*.

$\delta^{13}C$ signatures of carbon pools and fluxes in a Holocene *Sphagnum* peat bog (Czech Republic)

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Peatlands cover only 3 % of Earth's land area, but store as much as 30 % of the entire amount of terrestrial soil carbon. This amount corresponds to one half of carbon that is present in Earth's atmosphere as CO_2. The decomposition of organic matter in peatlands is slowed by waterlogged conditions. Microbial activities and solubilities of dissolved gases are strongly temperature-dependent. In the era of global warming, thinning of peat deposits and elevated emissions of greenhouse gases (CO_2 and methane) might accelerate further temperature increases. Determination of carbon isotope ratios ($\delta^{13}C$) is one tool to obtain insights into mass transfers in bog ecosystems. Here we focus on C isotope systematics accompanying changes of C pool sizes and C input/output fluxes in an 8-meter deep peat bog in the Czech Republic, Central Europe. The bog, Velke Darko, started to accumulate organic matter 11 thousand years ago. Based on pollen analysis and ^{14}C dates, peat accumulation has never been interrupted.

Carbon isotope data have been obtained for living *Sphagnum*, solid peat substrate, dissolved organic carbon (DOC), and emitted gaseous products of terminal C mineralization (CO_2 and CH_4). $\delta^{13}C$ values of 18 grab samples of *Sphagnum* collected throughout the bog surface were systematically lower than $\delta^{13}C$ values of solid substrate along a vertical peat profile (means of 27. 2 and 25.8 per mil, respectively). We interpret this downcore positive $\delta^{13}C$ shift as a result of degradation of organic molecules. Sedges and spruce bark found as an admixture in the peat had lower $\delta^{13}C$ values than *Sphagnum* (-30.5, -29.0 and 26.3 per mil, respectively). Downcore, $\delta^{13}C$ of sedges, which may form 10 % of substrate mass, increased, similar to $\delta^{13}C$ of *Sphagnum* residuum. $\delta^{13}C$ of DOC in runoff formed a sinusoidal curve, with a minimum in July (-28.6 per mil), and a maximum in September (-27.2 per mil). $\delta^{13}C$ of emanating methane and CO_2 under day-time, mid-summer conditions were -40 and -14 per mil, respectively. These data will be needed for the contruction of a C isotope mass balance for the peat bog.