

Oxide charge and electric-double layer control on phospholipid adsorption and self-assembly at oxide surfaces

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We have used bulk adsorption isotherms and atomic force microscopy to examine the interactions of cell membrane-forming phospholipids on oxide surfaces, at pH 7.2. Vesicle adsorption and bilayer self-assembly of dipalmitoyl-phosphocholine (DPPC) increases as oxide point of zero charge (PZC) increases, from quartz to rutile to corundum. The results are interpreted in terms of an interfacial model with contributions from electrostatic and van der Waals for adsorption. Incredibly, the effects of surface charge and diffuse layer counter-charge are observed even at distances as large as nanometers away from the surface, suggesting a “thickening” of the diffuse layer due to physical exclusion of solution from the vicinity of the oxide surface by the sheer bulk of the DPPC bilayer. The model is verified by changing ionic strength with NaCl and by adding Ca²⁺ to the solution, which affect diffuse layer thickness. Thus, crystal chemistry and interfacial solvation, which ultimately control PZC, and interfacial electrostatic and vdW forces control cell membrane-mineral interactions even at long distances. These results indicate the significance of the Stumm and Schindler legacy in modern biogeochemistry. Our study has implications for pre-biotic evolution of cell membranes, development of oxide-supported lipid bilayers for biosensors, and for making orthopedic implants more biocompatible.

Belemnite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ record of the Lusitanian Basin Pliensbachian carbonate series (Portugal)

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The hemipelagic series of the Pliensbachian-lowermost Toarcian section of Peniche (Portugal), comprising approximately 110m, shows a diverse set of geochemical occurrences of great importance for the palaeoceanographical interpretation of the referred time span. In the present study, after determination of sample alteration using geochemical proxies (Fe, Mg and Sr), $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were determined in 109 belemnite rostra samples.

From the $\delta^{18}\text{O}$ record and the palaeotemperature calculations (following [1]), is possible to infer that the lowermost Pliensbachian is characterized by a noticeable cooling-salinity increase trend followed by a phase of warming-salinity decrease towards the upper Margaritatus Zone. Afterwards, a cooling tendency is observed until the middle Spinatum Zone. The uppermost Spinatum-extreme base of Polymorphum (Toarcian) Zones show an important warming phase, also observed in oxygen isotopic data from brachiopods [2].

Two striking features are associated to the $\delta^{13}\text{C}$ record. The first concerns the overall tendency of increasing $\delta^{13}\text{C}$ towards the upper Margaritatus Zone where several organic rich intervals are recorded. The second is the negative excursion that ends at the base of Polymorphum Zone.

Several of these geochemical events are also recognized in other European basins (e.g. [3, 4]). Taking in account the privileged palaeogeographic position of the Lusitanian Basin, between the Atlantic and Tethyan sectors, the present study has important implications in future environmental interpretations.

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- [1] Anderson & Arthur (1983) *SEPM Short Course* **10**, 1-151.
[2] Suan *et al.* (2008) *Paleoceanography* **23**, PA1202. [3] Rosales *et al.* (2006) *Terra Nova* **18**, 233-240. [4] Littler *et al.* (2008) *Geophysical Research Abs.* **10**, EGU2008-A-03736.