Structural diversity and fate of intact polar lipids in marine sediments

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Drilling into marine sediments has revealed the presence of a vast microbial ecosystem buried deeply below the seafloor. The magnitude of this largely unexplored habitat has been estimated to about 56–303 Pg of cellular carbon, representing 55-85% of total prokaryotes in marine sediments or 10-30% of total biomass on Earth [1, 2]. Recently, we provided an independent estimate based on intact polar membrane lipid (IPL) analysis of a globally distributed sample set of 90 Pg of cellular carbon that is consistent with previous cell-based estimates [3]. A variety of bacterial and eukaryotal phospholipids were detected in surface sediments from the Peru Margin, whereas deeply buried sediments were dominated by archaeal lipids with various polar head groups and core lipid structures [3]. This apparent dominance of archaeal IPLs in the deep biosphere has raised questions about lipid stability and possible selective preservation [4].

We explored the effect of varying stabilities of both cells and lipids on sedimentary pool sizes through box-modeling. Our results show that (*i*) constant supply of freshly synthesized lipid is necessary to explain the observed IPL profile, and (*ii*) lipid input rates decrease with burial depth, possibly as result of increasing recalcitrance of organic substrates and decreasing enzymatic degradation activity. A detailed comparison of ring distributions in intact and non-intact (=fossil) tetraether lipids in sediments covering a wide range of environments revealed a distinct pattern, e.g. the average number of rings is higher in fossil lipids with a mean value of 2.9, whereas the intact archael lipids contain 2.4 rings on average. This suggests that the live sedimentary archaeal population contributes a structurally distinct lipid distribution than the fossil pool. On geological timescales, this sedimentary new production of archaeal lipids may affect applications of GDGT core lipids as paleotemperature proxy with the extent depending on the cumulative flux of lipids from benthic archaea.

[1] Whitman *et al*. (1998) *Proc. Natl. Acad. Sci. USA* **95**, 6578-6583. [2] Parkes *et al*. (2000) *Hydrogeol. J.* **8**, 11-28. [3] Lipp *et al*. (2008) *Nature* **454**, 991-994. [4] Pearson. (2008) *Nature* **454**, 952-953.

Reactive iron in the northern Gulf of Alaska

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Coastal waters in the northern Gulf of Alaska (GoA) are considered iron-rich and nitrate-poor, in contrast to the nitrate-rich, iron poor HNLC waters of the central GoA. The degree of mixing between these two regimes through advection and mesoscale eddies is essential to the high productivity observed in the GoA. As part of a study on iron delivery to the central GoA via mesoscale eddies, extensive work was completed to characterize the coastal endmember. In coastal surface waters between Yakutat, AK and south of the Kenai Peninsula, AK, dissolved iron concentrations were low and fairly constant, ranging from 0.5 – 4 nM. Conversely, potentially bioavailable leachable particulate iron was much higher and more variable, ranging from over 1 μM in the lower salinity northeastern GoA to less then 5 nM in the higher salinity northwestern GoA. During a transect from near Seward, AK out into the gulf (along the GAK line), leachable particulate iron in surface waters decreased from 28 nM nearshore to 1 nM in offshore waters; dissolved iron decreased from 4 nM to <0.05 nM. Leachable particulate iron values were consistently at least an order of magnitude higher than dissolved values. The system's ability to solubilize this large concentration of labile particulate iron is overwhelmed by the massive input of glacier-derived iron. Nevertheless, leachable particulate iron remains available for exchange to the dissolved phase and maintains a constant (~ 1 – 2 nM) source of dissolved iron to phytoplankton in the coastal GoA.