EARLY DIAGENESIS OF AMINO ACIDS IN SEDIMENTS ACROSS THE NE ATLANTIC SLOPE

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Amino acids, constituents of proteins, are generally transported through the water column by large, rapidly sinking aggregates. During this transport, nitrogen-rich compounds like amino acids are degraded faster than nitrogen-poor compounds (e.g. lipids). Therefore, the contribution of amino acids to bulk organic matter decreases with ageing of the organic matter, and hence with increasing depth in the water column. Moreover, shifts occur in amino acid distributions due to differences in nutritional value, adsorption capacity, resistance against degradation, etc.

A study on total hydrolysable amino acids (THAA) in sediment trap samples and in sediments across the Goban Spur continental slope (NE Atlantic) demonstrated that amino acids can be used to assess the diagenetic state of organic matter in the sediments. The very low contribution of THAA to bulk organic matter as well as the rather constant amino acid distributions in bulk sediments indicated that organic matter was already substantially degraded prior to incorporation into the sediments. A diagenetic model was applied to measured THAA and total organic carbon concentration profiles in the sediments to study their input, mixing and degradation. Amino acids were degraded faster than total organic carbon at the upper slope only, confirming the relatively refractory character of the organic matter in the sediments at the lower slope. The difference in diagenetic state of the organic matter across the slope became clear by studying size fractions of the sediment top layer. Shifts in amino acid distributions indicated that the organic matter in the finest fraction (<0.5 µm) was more labile than that in coarser fractions at the upper slope and than any size fraction at the lower slope. The contribution of fine particles increased with depth across the slope suggesting they were eroded from the upper slope and accumulated at the lower slope. From this down-slope transport in combination with the continuous degradation of organic matter attached to the fine particles it was concluded that the organic matter degradability decreased from the upper slope to the deep-sea.

Across the slope of the Faeroe-Shetland Channel (FSC) in the NE Atlantic, down-slope particle transport by repetitive cycles of erosion-deposition was far more important for the delivery of organic matter to deep-sea sediments than vertical settling from the euphotic layer of the ocean. An end-member model based on total nitrogen (TN) and THAA concentrations as well as on amino acid distributions in suspended matter (SM) samples from the water column, sediment trap samples and surface sediments demonstrated that near-bottom SM comprised ~80% of fine particles that were resuspended from the sediment surface. The vertical flux from the upper water column contributed only to ~20%. The contribution of amino acid-N to TN in suspended matter increased with water depth and supported the model results that organic matter in near-bottom water was not derived from the euphotic layer. The enrichment in aspartic acid in near-bottom SM and sediments at the upper slope as well as in sediment trap samples at the lower slope suggested that carbonaceous particles were eroded from the upper slope and transported down in near-bottom SM layers. The mid-slope maximum of fine particles in the surface sediment, the elevated inventories of 234Th as well as the high contribution of amino acid-N to TN evidenced that young and amino acid-rich organic matter was transported down-slope and preferentially settled at mid-slope depth.

Part of the amino acids that are degraded by bacteria in the water column and in the sediments are used for synthesis of new biomass. Amino acid enantiomers were used to identify the contribution of bacterially derived amino acids to THAA in the sediments. Amino acids in proteins are generally composed of L-amino acids, which can a-biotically racemize to D-amino acids, the mirror image of the L-enantiomer, on time scales of a few hundred thousands to millions of years. Bacteria, however, are among the few organisms that can produce D-amino acids for peptidoglycan, the main constituents of their cell walls.

Across the Goban Spur, the contribution of D-amino acids by racemization was almost negligible which pointed at a bacterially source for D-amino acids. D-amino acids were likely not associated with whole bacterial cells, since the contribution of amino acids from whole cells would exceed measured THAA concentrations in the sediments by a factor 5. Amino acids from bacterial cell wall remnants could account for ~10% of THAA in the sediment surface and for more than one third of THAA in the deeper sediments. A diagenetic model was applied to THAA concentration profiles lowered for bacterially derived amino acids. First-order degradation rate constants of THAA were 2-10 times higher than rate constants calculated from original profiles, clearly indicating that studying THAA degradation without taking into account the synthesis of amino acids by bacteria in the sediments is unreliable.

An end-member model based on D-amino acids in suspended matter from the water column, sediment trap samples and surface sediments demonstrated that the erosion-deposition mechanism that was responsible for the down-slope transport of THAA across the FSC was

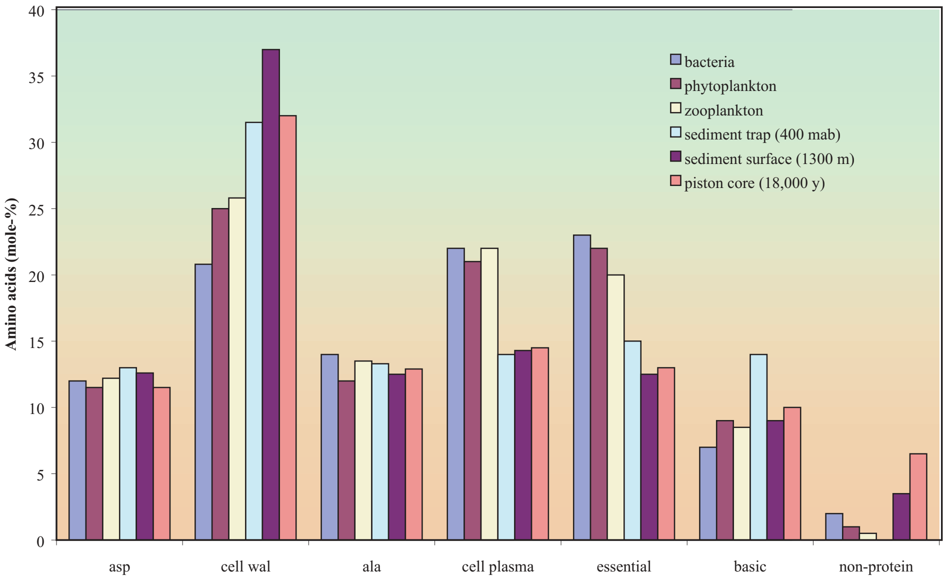

Figure X Mole-percentages of amino acid classes as measured by HPLC in samples from labile and refractory organic matter end-members. The figure demonstrates that amino acids become enriched during diagenesis in relatively refractory organic matter pools as bacterial cell walls and depleted in relatively labile organic matter pools as bacterial cell plasma. ASP denotes aspartic acid; CELL WALL denotes glycine, serine and threonine; ALA denotes alanine; CELL PLASMA denotes glutanmic acid, tyrosine and phenylalanine; ESSENTIAL denotes methionine, valine, iso-leucine and leucine; BASIC denotes lysine, arginine and histidine; NON-PROTEIN denotes b-alanine and g-aminobutyric acid.

also responsible for the distribution of amino acid enantiomers. D-amino acids in near-bottom water layers appeared not to be derived from the euphotic layer but from fine particles resuspended from the sediment surface. On average, approximately 5% of the D-amino acid concentration in the sediments could be accounted for by a-biotic racemization. Inventories of D and L-amino acids showed that there was a pronounced mid-slope accumulation of both enantiomers in the upper 5 cm of the sediments relative to the other stations. The ratio of D/L-amino acids in the upper sediments, obtained from the inventories, decreased with depth across the slope and indicated that the contribution of (newly synthesized) whole cells may increase down-slope. It was concluded that bacterial growth on fine, labile organic matter-rich particles transported down-slope in near-bottom water layers resulted in a mid-slope accumulation of D-amino acids in refractory bacterial cell wall material. With increasing depth in the sediments these amino acids are preserved as cell wall remnants and contributed at least 24% to THAA in the deeper sediments.

An important implication of the bacterial synthesis of amino acids is that degradable amino acids are transformed into labile cell plasma and relatively refractory bacterial cell walls. This conversion into cell wall material may enlarge the proportion of amino acids from primary production that survives early diagenesis, and could be the first step in the long-term burial of amino acids in marine sediments.