The Molecular-Level Diagenetic Clock of Sinking Marine Organic Matter

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The marine biological carbon pump is driven by sinking particulate organic matter. Sinking speed and remineralization rate determine flux attenuation in the mesopelagic. Since the fate of all marine organic matter is either complete remineralization or transformation to stable products, diagenetic modifications impact CO_2 sequestration time from the atmosphere. To investigate particle transformation at the molecular level, we characterize the organic matter (OM) fraction of sinking particles from dominant biogeochemical environments using ultrahigh-resolution mass spectrometry. We find distinct, inverse associations in molecular-level nitrogen content and degree of transformation (i.e., "stability") of OM across a productivity gradient from coastal upwelling to oligotrophic conditions (**Figure 1**). Nitrogen enrichment and low stability were observed at the coastal upwelling site and persisted to depths >400 m. Further, carbon flux is strongly correlated with the relative abundance of stable OM ("Island of Stability" formulae) across productivity regimes and depth (**Figure 2**). This suggests emergent patterns in epi- and mesopelagic diagenesis, highlighting that the molecular composition of sinking OM exiting the euphotic zone varies more across regions than as a function of depth. This is attributed to highly variable sinking rates and the microbial diagenetic histories within the euphotic zone. The stability–flux relationship is considered a "diagenetic clock" relative to OM formation where the relative abundance of Island of Stability molecular formulae describes the degree of departure from the OM molecular-level composition at formation. This ubiquitous trajectory of the diagenetic clock underpins a global ocean molecular signature of sinking OM.

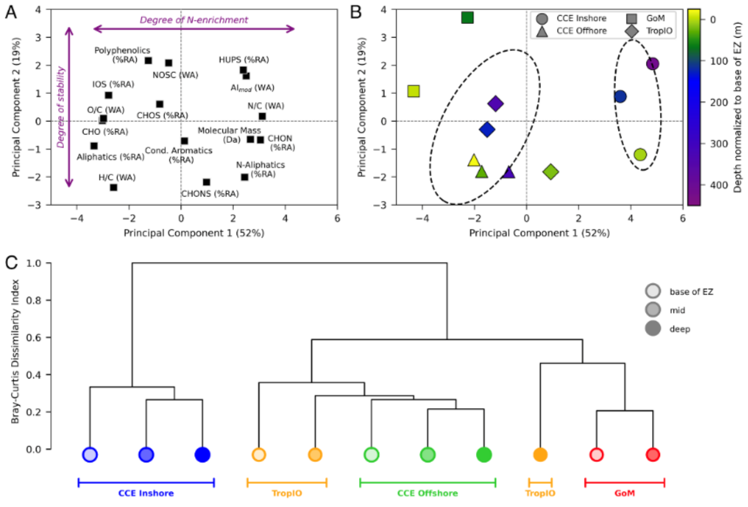

Figure 1. N-enrichment and stability gradients drive molecular-level characterization of sinking WEOM. **A.)** PCA biplot of OM properties from FT-ICR MS compound class assignments separates samples based on degree of N-enrichment (PC1) and degree of stability (PC2). **B.)** Presents each samples in the PCA space with the shape indicating the region, the color indicates depth normalized to the base of the euphotic zone and the dashed ovals bound oligotrophic versus upwelling samples. **C.)** Dendrogram showing the BCDI of the molecular formulae highlighting separation by site and depth.

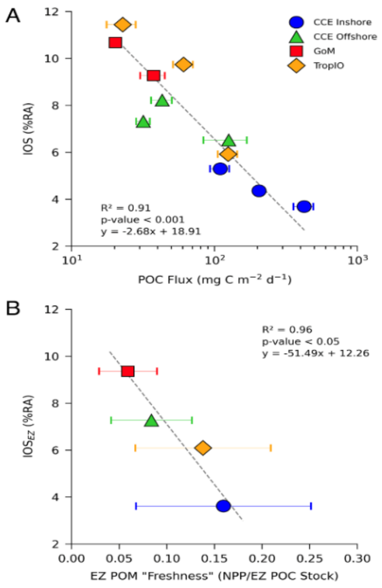

Figure 2.A.) Strong correlation between island of stability (IOS) formulae and POC flux. **B.)** The IOS at the base of the euphotic zone shows a strong correlation to freshness of particulate organic matter as diagenesis begins in this zone.

Facilities and instrumentation used: Geochemistry program, ICR program 21T FT-ICR MS.

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