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Methylation index of Overly Branched tetraether lipids (MOB): a proxy for deep ocean (de)oxygenation?

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Branched glycerol dialkyl glycerol tetraethers (brGDGTs) with lower (sparsely branched; SB-) and higher (overly branched; OB-) numbers of methylated branches relative to the "regular" brGDGTs (B-GDGTs) are abundant in anoxic waters in the Black Sea. Observed changes in abundances and numbers of methylated branches of the entire series OB-GDGTs, B-GDGTs, and SB-GDGTs relative to dissolved oxygen (DO) levels in anoxic waters suggest that these compounds can potentially track changes in oceanic DO levels through time. To explore this, we determine the entire brGDGT series in surface or near surface sediments (n = 24) from sites with different DO distributions in marine waters and sediments, extending the limited core-top collection of these lipids. We propose a modified methylation index based on only OB-GDGTs, called MOB, to avoid the potential impacts of terrestrial-derived B-GDGTs. Interestingly, MOB values in our extended core-top collection are strongly related to changes in bottom-water DO concentrations rather than the site-specific minimum DO values (i.e. usually within mid-depth OMZs). This suggests that sedimentary lipids are likely derived from heterotrophic bacteria living at the sediment-water boundary in sediments while lipids produced within mid-depth OMZs are not effectively exported to deep oceans. Analysis of MOB values in ancient sediments in the EEP region show a gradual decline in bottom water DO, correlating with the progressive increase in global export productivity, organic carbon burial, and elevated level of deep-water nutrient contents since the middle Miocene. These findings highlight the potential of MOB as a tool for reconstructing past oceanic (de)oxygenation events.