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Microbes That Utilize Kerogen: Degradation of Ancient, Refractory Organic Matter During Black Shale Weathering

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Degradation and remineralization of ancient organic matter held within sedimentary rocks is a key component of the global carbon cycle, instrumental in maintaining concentrations of atmospheric CO_2 and O_2 on geologic time scales, yet the processes involved in weathering of black shales remain only vaguely understood. Organic matter is lost from sedimentary rocks during weathering. Detailed geochemical analyses reveal that accompanying this loss are minor alterations in kerogen composition and structure, namely addition of carbonyl carbon and, at certain shale exposures, preferential loss of aliphatic carbon (Petsch et al., 2000a, b). By and large, however, kerogen weathering is relatively non-selective.

Relict organic matter derived from ancient sedimentary rocks has been detected in modern soils and sediments (Eglinton et al., 1997; Petsch et al., 2000b). The persistence of organic materials in the aerobic and biologically active environments of the earth's surface indicates that there is a strong kinetic control on organic matter weathering. Erosion rate and transport rate strongly effect the time afforded for organic matter remineralization before reburial in anoxic sediments where oxidation rates are suppressed; however, the ultimate controls lie in organic matter degradation and remineralization reactions. Because biological processes generally exhibit altered reaction rates and/or reaction pathways compared with purely abiotic reactions, and because earth surface environments are replete with micro-organisms, microbial activity may play a strong role in controlling ancient organic matter remineralization. Carbon oxidation during shale weathering represents a large potential energy source. However, most organic matter in ancient sedimentary rocks is complex, macromolecular and inert compared with other carbon sources; close synthetic analogs in composition are polymers such as polyethylene. Furthermore, porewaters in shale weathering profiles can potentially be very acidic due to sulfide mineral oxidation. Thus not only must organisms living within shale weathering profiles be acid-tolerant, but at least some must be capable of utilizing high molecular weight, insoluble, complex organic matter.

Weathering profiles developed on the organic matter-rich New Albany Shale exposed in central Kentucky, USA, were sampled to investigate the abundance and activity of microbial communities living in this weathered shale. Fluorescent *in-situ* hybridizations of environmental samples with group-specific probes confirmed the presence of predominantly bacteria and archaea within the weathering profile. Enrichment cultures incubated with sterilized shale in organic carbon-free mineral salts medium were developed from environmental samples, and revealed very abundant bacterial and archaeal populations after fluorescent *in-situ* hybridizations were performed (10^7 - 10^8 cells per gram dry weight shale). These data suggest that some fraction of the microbial consortia derives energy from the indigenous organic matter in sedimentary rocks. Preliminary experiments support our inference that some of these organisms may utilize dissolve organic carbon [DOC] released from organic carbon-rich unweathered shale; DOC analyses of short-term incubations indicate substantially lower DOC contents in the media from inoculated incubations compared with sterile controls. Fluorescent microscopy of sterilized polished shale surfaces to which enrichment culture innocula were added reveal an intimate association between organic matter clasts within the rock and colonies of adhered micro-organisms. Attachment of cells at or near organic matter clasts may indicate that these micro-organisms may play an active role in solubilizing and/or metabolizing solid phase macromolecular shale organic matter via the local production of metabolites. Ongoing research addresses whether microbial consortia increase the release rate of organic carbon from the rocks (compared with sterile controls) and how efficiently these consortia remineralize shale organic matter. Fatty acid methyl esters derived from bacterial cell membrane phospholipids are used to further refine classification of the micro-organisms found in both environmental samples and enrichment cultures; ^{14}C analysis of these phospholipid-derived fatty acids is used to unambiguously establish that ancient organic matter provides the sole organic carbon source for these organisms. DNA extraction, purification and sequence analysis are used to help establish phylogenetic affinities between these organic matter-degrading organisms and known bacterial and archaeal groups. The result of this study is to form a description of a microbial community capable of degrading ancient sedimentary organic matter so that a more complete understanding can be developed about the release and remineralization of organic matter from ancient sedimentary rocks and the importance of this process within the global carbon and oxygen cycles.

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