Discovery of organic acids in deep marine environments from ODP pore waters

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Pore waters collected from three ODP expeditions in the Pacific contain organic acids. These data are the first known occurrence of organic acids in deep oceanic environments. This finding is significant for the following reasons: 1) the presence of organic acids requires the existence of a more complex organic presursor; 2) the presence of organic acids impacts the acid-base chemistry of pore-water systems, and 3) organic acids represent a pathway for transferring reduced carbon from sedimentary solids to solution. The formation of organic acids can occur biochemically, chemically, and thermally; any of these processes requires a complex organic precursor. The organic acid assemblages found in the pore fluids from the three Pacific expeditions differ by tectonic setting. The abundance and diversity of the organic acids present in these different tectonic settings are most likely related to the source of the complex organic precursor and geochemical setting.

Organic acids are found in pore waters from near-shore sediments and land-based sections, but until recently, geochemists had not documented the existence of organic acids in pore waters from the deep marine realm. Organic acids were documented in anoxic pore waters from Holocene near shore sediments [*Parkes and Taylor,* 1983] and in hydrothermally altered sediments from the actively rifting Guayamas Basin [*Martins,* 1990]. In the last five years, the pervasive nature of organic acids in the deep marine realm was documented in a variety of tectonic settings (see table). Organic acid assemblages from forearc, backarc, and midplate settings are different. Pore waters squeezed from unconsolidated serpentine from Mariana forearc seamounts (Leg 125) have formate in excess of acetate, with the rare occurrence of malonate and propionate; the total abundance of organic acids in the diverse assemblage from the Mariana serpentine seamount is only comparable to the total abundance of organic acids from midplate guyots (Leg 144). The pore waters squeezed from pelagic sediments and basal clays on midplate guyots have the lowest diversity of organic acids, but the highest concentrations of acetate and malonate of all ODP locations investigated. In contrast, pore waters from Mariana and Bonin forearc sediments contain no organic acids. The organic acid assemblage in the Tonga forearc sediments (Leg 135) may not be representative of normal forearc sediments because serpentine was dredged from nearby areas. Backarc (Leg 135) organic acid assemblages appear to be dominated by propionate, with substantial formate and the rare occurrence of acetate. Controls on the abundance and diversity of organic acids in the assemblages from the deep marine environment appear to be related to the tectonic and geochemical setting and the nature of the complex organic precursor.

References:
Parkes, R.J., and J. Taylor, Analysis of volatile fatty acids by ion—exclusion chromatography, with special reference to marine pore water, *Mar. Biol., 77,* 113-118, 1983.
Martins, C.S., Generation of short chain organic acid anions in hydrothermally altered sediments of the Guayamas Basin, Gulf of California, *Appl. Geochem., 6,* 71-76, 1990.

Comparison of organic acid assemblages from different tectonic settings

(Data from Haggerty and Fisher [1992, 1994, and 1995])

ODP Leg	Tectonic setting	Material squeezed for pore waters	Malonate range (median) in μM	Formate range (median) in μM	Acetate range (median) in μM	Propionate range (median) in μM
125	Mariana Forearc Seamount	Unconsolidated serpentine	0-22 (0)	0-2272 (102)	0-208 (51)	0-68 (0)
125	Mariana Forearc	Diatom-radiolarian silty clay and vitric silty clay	0	0	0	0
125	Bonin Forearc	Nannofossil marls and chalks with volcanic detritus	0	0	0	0
135	Tonga Forearc	Clayey nannofossil ooze with vitric sand and vitric silt turbidites	0	0-29 (7)	0-10 (0)	0-25 (14)
135	Tonga Backarc	Clayey nannofossil ooze with beds of volcanic sand and silt	0	0-31 (7)	0-53 (0)	0-71 (16)
144	Midplate Guyots	Nannofossil-foraminifer ooze and foraminifer ooze	0	0	0-4051 (597)	0
144	Midplate Guyots	Basal clays	0-359 (252)	0	815-3453 (2966)	0