Abiotic formation of halocarbons during early diagenetic processes

H. F. SCHÖLER

Institute of Environmental Geochemistry,
University of Heidelberg,
INF 236, D-69120 Heidelberg/ Germany
(schoeler@ugc.uni-heidelberg.de)

Naturally produced organohalogens (NPO) in soil originate from biotic and abiotic transformations induced by decay of organic material and contact with the mineral phase of the soil. The variety and extent of NPO in soil is enormous - from volatile to involatile, from unpolar to polar compounds. The reaction processes are far from being comprehensively understood. This overview tries to spot abiotic milestones and to partly unveil the complexity of soil processes forming NPO.

Up to date halogenating enzymes such as chloroperoxidase seemed to be necessary for NPO production (Öberg and Grön, 1998). However, there is growing evidence of abiotic reaction schemes such as halide addition to vinylic ketons and ring cleavage of epoxides which lead to polar organohalogens.

A further novel reaction scheme, producing monohalogenated alkanes and alkenes, was presented by Keppler et al., 2000, 2002), starting from dihydroxylated aromatic substances, as model compounds for humic acid structures, and Fe^{3+} in the presence of halides leading to alkyl halides and Fe^{2+} while breaking down the aromatic ring (Pracht et al., 2001).

In addition, evidence arose that elemental chlorine is present in distinct soil compartments which reacts unspecifically with organic soil matter producing polyhalogenated volatile and polar compounds (e.g. chloroform and chlorinated acetic acids) - typical disinfection by-products (Fahimi et al., 2002). Suspected reaction partners for inorganic chloride are enzymes and/or OH-radicals (Keppler et al., 2001).

References

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Seasonal and spatial controls of $^{230}Th/^{231}Pa$ ratios in the Arabian Sea

J. C. SCHOLTEN[1], J. FIETZKE[1], A. MANGINI[2], P. STOFFERS[1] AND V. ITTEKKOT[3]

[1]Institute for Geoscience University Kiel, D-24118 Kiel (js@gpi.uni-kiel.de)
[2]Heidelberger Akademie der Wissenschaften, D-69120 Heidelberg (Augusto.Mangini@iup.uni-heidelberg.de)
[3]V. Ittekkot, Centre of Tropical Marine Ecology, D-28359 Bremen (ittekkot@zmt.uni-bremen.de)

The natural radionuclides of the uranium-thorium decay chains (e. g. ^{230}Th $T_{\frac{1}{2}}$ = 75.6 ky); ^{231}Pa $T_{\frac{1}{2}}$ = 32.5 ky) have a wide field of applications in oceanographic investigations such as: determination of sedimentation rates, lateral sediment transport and particle cycling in the water column. Due to the different particle reactivity, i. e. residence time (τ) of ^{230}Th (τ = 20 - 40 years) relative to ^{231}Pa (τ = 100 - 200 years) $^{230}Th/^{231}Pa$ ratios determined in sediments are believed to depend on the particle flux and thus may be used as a tracer for paleoproductivity in the geological past. In cases like the Atlantic where both water mass and radionuclide residence times are in the same order of magnitude, $^{230}Th/^{231}Pa$ ratios may also reflect changes in deep-water formation. Detailed investigations of removal processes indicate, however, more complex mechanisms such as particle type and remineralisation in the water column to control $^{230}Th/^{231}Pa$ ratios.

In the frame of the German contribution to the Joint Global Ocean Flux Study (JGOFS) the distribution of ^{230}Th and ^{231}Pa were studied in the water column, sediment traps (WAST, CAST, EAST), and surface sediments in the Arabian Sea in order to investigate the response of radionuclide fluxes to the seasonal and the spatial variability of the Arabian Sea environment. In the sediment traps investigated no relation between ^{230}Th and ^{231}Pa and the type of particles dominating the vertical particle flux was observed. Seasonal changes in the $^{230}Th/^{231}Pa$ ratios in the sediment traps were up to a factor 3, and at various locations in the Arabian Sea analogous differences were also observed in recently deposited phytodetritus (fluff) when compared to the underlying sediments. These differences are attributed to monsoon-intermonsoon changes in the hydrography of the western Arabian Sea which is dominated by the interplay of open ocean versus ocean margin upwelling. At location WAST average $^{230}Th/^{231}Pa$ ratios of sinking particles systematically increase with water depth from 6,6 ± 0,9 at 500m to 9,6 ± 0,9 in 3007m and further on to 10,7 ± 1,0 in 4029m water depth; and interaction of sinking particles with the suspended ones ($^{230}Th/^{231}Pa$ = 9-10 between 500m and 3000m water depth) is believed to be the cause. This suggests that the $^{230}Th/^{231}Pa$ ratios preserved in the sediments of the Arabian Sea reflect deep water-scavenging rather than represent a signal of bioproductivity in the euphotic zone.