

Carbon and hydrogen isotope fractionation during biodegradation of monoaromatic hydrocarbons

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Carbon and hydrogen isotope fractionation was determined for the biodegradation of benzene, toluene and xylenes by various reference cultures. Using the slope derived from hydrogen vs. carbon isotope signatures (Λ), specific biodegradation pathways could be distinguished.

Λ -values of < 9 were observed for the aerobic di- and monohydroxylation of the benzene ring [1, 2]. The highest Λ -values were estimated for the aerobic methyl monohydroxylation of toluene ($\Lambda > 50$) [2,3]. Significant differences in Λ -values were determined for the anaerobic degradation of benzene: Λ -values < 20 are characteristic for nitrate-reducing consortia, and Λ -values > 20 for sulfate-reducing and methanogenic consortia [1,4]. Those variations suggest that more than a single mechanism exists for the activation of benzene under anoxic conditions. Λ -values for anaerobic toluene degradation initiated by the enzyme benzylsuccinate synthase ranged from $\Lambda = 4$ for a phototrophic strain, $\Lambda = 11 - 15$ for nitrate reducing strains to $\Lambda > 20$ for sulfate and iron reducing strains [2,5]. Similar trends were observed for the anaerobic degradation of xylenes initiated by the benzylsuccinate synthase. The different Λ -values obtained for the anaerobic degradation of toluene and xylenes might be caused by (i) slightly different reaction mechanisms of benzylsuccinate synthase isoenzymes, or (ii) by the degree of quantum tunneling.

Our results show that the combined carbon and hydrogen isotope fractionation approach has great potential to elucidate biodegradation pathways of monoaromatic hydrocarbons in microcosm [1-5] and field studies [6].

- [1] Fischer *et al.* (2008) *Environ. Sci. Technol.* **42**, 4356-4363.
[2] Vogt *et al.* (2008) *Environ. Sci. Technol.* **42**, 7793-7800.
[3] Mancini *et al.* (2006) *Environ. Sci. Technol.* **40**, 7675-7681. [4] Mancini *et al.* (2008) *Environ. Sci. Technol.* **42**, 8290-8296. [5] Tobler *et al.* (2008) *Environ. Sci. Technol.* **42**, 7786-7792. [6] Fischer *et al.* (2007) *Environ. Sci. Technol.* **41**, 3689-3696.

From field to lab: Glass dissolution rates and sub-micron topography

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Mineral dissolution rates derived from field data are notoriously lower than rates measured in lab experiments. Here, we systematically compare dissolution rates of volcanic glass (obsidian) in a natural environment and in the lab. Samples of crushed sand-grain-sized obsidian mimicking an artificial sediment were exposed to natural weathering conditions for 5.5 and 16 months. We imbedded samples in regolith profiles and water wells of marine terraces at Santa Cruz coast [1]. Rate calculations based on surface-normal retreat data measured with an interferometer [2] show a range of three orders of magnitude for samples from the regolith profiles and the water wells. The sample imbedded in the regolith profile shows a strong increase in rate during the second weathering period. Lab experiments with polished glass samples (initial roughness $R_q < 10$ nm) were performed to map etch pit distribution and size variation. Rate data show a significant anisotropy of surface reactivity for areas in the mm^2 range.

- [1] White *et al.* (2008) *Geochimica et Cosmochimica Acta* **72**, 36-68. [2] Lüttge, Bolton & Lasaga (1999) *American Journal of Science* **299**, 652-678.