

Indirect evidence for the presence of secondary phosphorus in continental fine aerosol

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The role of the atmosphere in the biogeochemical cycle of phosphorus is generally associated with the emission of soil dust, sea-salt particles, bioaerosols and industrial aerosols. Quite independently, a reduced gaseous phosphorus compound (phosphine, PH₃) was measured over various sources such as marshes and sewage plants [1] and also in the global troposphere. Given that phosphine is a reactive gas that rapidly yields low-volatility phosphoric acid in the atmosphere [2], secondary aerosol formation can be an important sink that has never been considered in the global phosphorus cycle. In our study we present mass size-distribution measurements of phosphorus in aerosol samples collected at two locations in Hungary. The bimodal size distribution of phosphorus indicated two distinct formation mechanisms in the fine and coarse modes. As expected, the mass concentration of phosphorus was dominated by the coarse particles (aerodynamic diameter >1 μm), the contribution of fine mode phosphorus was in the range of 10–27 % (median 19 %) of the total. The contribution of biomass burning to the fine mode phosphorus was inferred from measured K concentrations and P/K ratios reported for biomass smoke [3]. It was found that biomass burning accounted for only a small fraction of fine mode phosphorus, the rest of which likely formed as secondary aerosol component from gaseous phosphine. Secondary aerosol phosphorus can be even more important in providing this essential nutrient for remote ecosystems since it is associated with fine aerosol particles which have longer residence time and thus are more prone to long-range atmospheric transport than coarse primary particles.

[1] Dévai *et al.* (1988) *Nature* **333**, 343–345. [2] Frank & Rippen (1987) *Lebensmitteltechnik* **7-8**, 409–411. [3] Echalar *et al.* (1995) *Geophysical Research Letters* **22**, 3039–3042.

Enhanced calcite dissolution in the presence of aerobic methanotrophic bacteria

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Aquatic microbial aerobic methane oxidation (MOx) causes the production of carbon dioxide, leading to decrease of liquid phase pH. Therefore, MOx activity impacts the carbonate system, potentially favouring dissolution of calcium carbonates. In addition, carbonate dissolution has recently also been attributed to microbially produced organic polymers. To date, the impact of metabolic products from MOx on carbonates has been poorly constrained. To discriminate between different mechanisms acting on carbonate stability, calcite dissolution experiments were conducted with (1) prospering cells (2) starving cells, and (3) dead cells of the methanotrophic bacterium *Methylosinus trichosporium*, as well as abiotic controls, under brackish conditions (salinity 10) near calcite saturation (saturation state (Ω) 2.22 to 1.76). Abiotic controls showed no calcite dissolution during the experiment. In contrast, dissolved calcium and total alkalinity markedly increased in experiments containing *M. trichosporium* cells, indicative for calcite dissolution. After initial system equilibration, calcite dissolution, ranging from 29.6 to 14.9 μmol l⁻¹ d⁻¹ between treatments, was observed. While concentrations of transparent exopolymer particles concentrations declined considerably over time in the presence of prospering and starving cells, concentrations increased in experiments with dead cells. Scanning electron microscopy of calcite crystals revealed surface corrosion after exposure to prospering, starving, and dead *M. trichosporium* cells. The results of this study demonstrate a strong potential impact of MOx bacteria on calcite stability, clearly facilitating calcite dissolution. In addition to CO₂ production by methanotrophically active cells and starving cells, we suggest that the release of acidic and/or calcium-chelating organic carbon compounds also facilitated enhanced calcite dissolution.