

From sea to lake, the geochemical history of Lake Champlain, North America

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The Lake Champlain region (NY and VT) experienced a transition from freshwater to marine to freshwater deposition as a consequence of post-glacial sea level rise and isostasy. Here we focus on the marine stage known as the Champlain Sea as it developed into the modern freshwater Lake Champlain approximately 9 kyr ago. The marine-lake transition offers the unique constraint of two well-established endmember environments that include modern marine conditions (with sulfate of known concentration and isotopic composition) and a large (1100 km²) freshwater lake. These transitions yielded juxtapositions of chemical conditions that could favor biological hotspots associated with sulfate reduction and methanogenesis. Collectively, these gradients provide an ideal opportunity to define and refine geochemical proxies for marine and nonmarine conditions, including the complications *and* novel chemical fingerprints of secondary overprints associated with dramatic variations in depositional conditions.

Several lines of evidence support the transition from marine to freshwater deposition. Coupled with changes in physical properties and microfossil abundances are pronounced geochemical contrasts, including a shift from a carbonate-rich marine stage to a carbonate-lean lacustrine stage and a prominent maximum in pyrite concentration at the depositional contact. The chemical record within the environmental switch has the potential for an interesting biogeochemical interface between methane charged lake sediment ([CH₄] upwards of 1.5 mM) overlying marine porewater sulfate. We continue to explore the signals of redox sensitive metals (e.g. Mo and Fe) coupled with provenance indicators (Al/Ti) to fully develop and refine geochemical indices of marine/nonmarine deposition.

Spectro-microscopy of carbonaceous particulates

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Combining multiple spectro-microscopic techniques can provide detailed information on morphology, elemental analysis, and chemical bonding. We combine complementary spectro-microscopic techniques such as scanning transmission X-ray microscopy, capable of performing near edge X-ray fine structure micro-spectroscopy, (STXM/NEXAFS), and computer controlled scanning electron microscopy coupled with an energy dispersive X-ray analyzer (CCSEM/EDX). Results are presented on the chemical analysis of individual atmospheric aerosol particles collected at urban and rural sampling sites during the Mexico City MILAGRO 2006 field study. Physical and chemical transformations of particles aged in the outflow from Mexico City were investigated. Our results show that as the aerosol plume evolves from the city center, the organic mass per particle increases and the fraction of carbon-carbon double bonds, associated mostly with elemental carbon, decreases. At the city center the most prevalent aerosol types had substantial inorganic phases containing S, N, O and K and were coated with organic material. As the aerosols travelled further from the city center, the fraction of homogeneously mixed organic particles increased. These observations demonstrate the unique evolution of physicochemical mixing state and organic bonding in individual particles as they age in a photochemically active environment.

These complementary methods also provide chemical speciation on metals in sub-micron particles and serve as a further example of the strength of combining multiple micro-spectroscopic methods when examining environmental samples.

[1] Moffet *et al.* (2009) *Atmos. Chem. Phys. Discuss.* **9**, 16993–17033. [2] Moffet *et al.* (2008) *Environ. Sci. Technol.* **42**, 7091–709.