Biosynthesis of sterols and wax esters by *Euglena* of acid mine drainage biofilms: Implications for eukaryotic evolution and the early Earth

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Acid mine drainage (AMD) environments are potential analogs for Earth's primordial environment. We studied biofilms of an AMD system (pH 2.0-3.5) in western Indiana, USA. Biofilms, either floating or attached to the bottom of the AMD flow channel, are formed by the acidophilic, microeukaryote *Euglena mutabilis*. Lipid analysis of benthic and floating biofilms revealed the dominance of photosynthetic organisms, *Euglena mutabilis*, as indicated by the detection of abundant phytadiene, phytol, phytanol, polyunsaturated *n*-alkenes, polyunsaturated fatty acids, short-chain (C_{25-32}) wax esters (WE), ergosterol, and tocopherols. The WE were probably synthesized in mitochondria under anaerobic conditions, whereas the sterols (ergosterol and ergosta-7,22-dien-3β-ol) were likely synthesized in the cytosol in the presence of molecular oxygen by the acidophilic, photosynthetic microeukaryotes *Euglena*. The dual aerobic and anaerobic biosynthetic pathways may be the biochemical relics of the anaerobic past of the Earth. Given that the oxygenation of the oceans is a relatively recent event (i.e., ~580 Ma ago), ca 1 billion years after eukaryotes arose, the conserved compartmentalization of *Euglena* biosynthetic machinery may have allowed early eukaryotes to survive and diversify early on Earth, when the oceans were anoxic and sulfidic, and despite their evolution, they preserved this physiology. Wax esters and their diagenetic products (short-chain *n*-alkanes and alkanoic acids) may be the molecular biosignatures of these organisms in the geologic record.

Unconstrained fluxes to the ocean: Calcium isotopes in dust-producing regions

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Though mineral dust can be an important input to the ocean over geologic time scales, little is known about its Ca isotopic composition (delta44/40Ca). This study measures the Ca isotopic composition of sediments from an active dust source in the western U.S. (Black Rock Desert, NV). We present geochemical, mineralogical, and isotopic data from 22 sediments collected from the upper 0.5 cm of the playa. Isotope data for sequential water & 0.5 N HCl leaches and leached residues are presented. Lithium metaborate fusions of bulk sediments reveal Ca concentrations between 0.28 and 40 wt.% (median: 6.8 wt.%), an 80% enrichment relative to upper continental crust. XRD data indicates calcite concentrations of 2–32%, with most samples containing 7–14%. Water leaches generally sample <1% of total Ca, while acid leaches sample >60%. Water leaches are, on average, +0.33±0.16‰ (1SD) heavier than acid leaches; the degree of fractionation varies ($\Delta_{w\text{-}a}$ = ~0-0.6‰) and appears to depend only on the fraction of Ca in the acid-soluble fraction. Acid leaches are, on average, -0.45±0.07‰ (bulk Earth scale), similar to the delta44/40Ca of modern nannofossil ooze (-0.4‰) and modern rivers (-0.41±0.08‰; Tipper *et al*., 2010).

Dust-derived Ca is an important mass flux to constrain. Assuming a modern mineral dust flux of ~10^3 Tg/yr to the global ocean (e.g., Duce and Tindale, 1991) and a calcite concentration <10%, the inferred Ca mass flux to the ocean is <100 Tg/a. This flux is comparable to the mass flux of Ca delivered by rivers to the modern ocean (~550 Tg/yr). The implication of this work is that the "mobile" fraction of playa-derived dust (water- & acid-soluble pools) is not fractionated relative to riverine input to the ocean. If, however, the acid-soluble fraction is not readily released into the water column, the water-soluble fraction (which can be significantly heavier) is the appropriate flux to consider when discussing atmospheric inputs of Ca to the ocean. During transport, calcite dissolution can be inhibited by high pHs (>8) generated when soluble Na-carbonates dissolve in aerosols. Such pHs are seen in modern systems close to dust sources (e.g., the Mediterranean), where the bulk of dust is deposited.