## Oxygenic photosynthesis 3 billion years ago

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Prior to the evolution of oxygenic photosynthesis, life on Earth was dominantly anaerobic with an estimated activity level of 1000 times less than today[1]. With the evolution of biological oxygen producers, oxygen became available to fuel aerobic metabolisms, increasing the abundance and activity of the biosphere and changing the dominant modes of metabolism. The first long-term oxygenation of the atmosphere took place around 2.3 billion years ago (Ga) during the Great Oxidation Event (GOE)[2] and oxygenic photosynthesis must have evolved by this time. Geochemical proxies, however, suggest transient atmospheric oxygenation dating back to 2.6-2.7 Ga[3,4,5], while molecular clocks indicate the possible evolution of oxygenic phototrophs as early as the Mesoarchean[6].

We examined the distribution of Cr isotopes and redoxsensitive metals in the approximately 3 billion year old Nsuze paleosol and in the near-contemporaneous Ijzermyn iron formation from the Pongola Supergroup, South Africa. These measurements reveal atmospheric oxygen concentrations of some  $10^{-4}$  of present day levels. This mid-Archean oxygenation of Earth's atmosphere implies that oxygenic photosynthesis evolved at least 3 billion years ago, more than 600 million years before the GOE. Despite possible fluctuations in oxygen levels, oxygenic phototrophs have likely fueled Earth's aerobic biosphere since at least 3.0 Ga.

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## Geochemical changes in wet dune slacks: natural or anthropic driven?

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Lagoa da Sancha (LS) and Poço do Barbaroxa de Baixo (BB), located in the Portuguese SW coast, are smaller than  $0.4 \text{km}^2$  wet dune slacks including shallow (<1m) open-water bodies, which occasionally dry out in summer. Both environments are part of a Natural Reserve since 2000. BB is a blind depression, whereas LS collects inputs from a  $35 \text{km}^2$  watershed. Bottom sediments are CaCO<sub>3</sub>-free organic muds, LS materials being peculiar in comparison to BB due to hyperacidity, lower organic and higher heavy metals contents.

Field surveys conducted since 2002 show that BB is an oligohaline to freshwater (0.2 -3.8%) and slightly acidic to slightly alcaline (pH 5.9-7.6) environment, with DO of 3-7mg/l and low values of Eh (environments near reducing conditions: -110 to +150mV). The water chemistry shows that BB has medium to high mineralization (0.060 meq/l).

In the late 1980's, LS shared similar environmental parameters: salinity (2.5-5‰, exceptionally up to 12‰ due to overwash or evaporation), dissolved oxygen (3-12mg/l) and pH (6.0-8.0). It hosted diverse macrobenthos, ictyo and avifaunas. However, surveys performed after 2001, show a drastic change in this system, with almost complete elimination of those organims. Although LS waters remain mainly subsatured to satured (DO 2.8-9.5mg/l), all the other parameters are substantially different. The LS hydrossome became strongly oxidant (Eh:+315 to +546mV), acidic (pH: 2.7 to 3.8), the salinity dropping to 0-4.3%. Also, it shows lower mineralization (0.026 meq/l), but the heavy metals content is up to 3 orders of magnitude higher than in BB (17mg/l Fe, 1.8mg/l Mn, 3.4ug/l Cu, 57ug/l Co, 83ug/l Ni, 18ug/l Cu). Such values resemble the composition of waters associated with acid mine drainage or metalliferous leaching.

Until present the extreme changes at LS have been interpreted as related to sulphide oxidation, a meteorologicaldriven hardly reversible consequence of prolonged bottom exposure during dry years. However, the recent discovery of an illegal industrial waste disposal proximal to LS opens a new hypothesis for that dramatic change related to anthropic contamination conveyed through groundwater circulation.