

Evidence for the O₂ and CO₂ rich Archean atmosphere

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In the oxygenated world, the CO₂ and O₂ contents of the atmosphere and oceans are regulated at steady-state levels by the balance between the forward and backward reactions of: CO₂ + H₂O = CH₂O + O₂. Today, ~100% of the CH₂O formed on land and ~99.7% of the CH₂O formed in the oceans by oxygenic photosynthesis are recycled back to CO₂ in <10 yrs by aerobic oxidation. Burial of the ~0.3% of marine organic matter as kerogen in sediments has been responsible for the long-term (>1,000 yrs) production of O₂ in the atmosphere and oceans. Oxidation of the kerogen during soil formation has been the main pathway for the long-term consumption of O₂.

In the anaerobic world, such as the one postulated by many for the Archean, organic synthesis is carried out by anoxygenic photosynthesis (e.g., CO₂ + 2H₂ → CH₂O + H₂O). Fresh organic matter decomposes by fermentation (e.g., CH₂O → CO + H₂ and 3CH₂O → 2CO + CH₄ + H₂O, c.f., Hoeler et al., 2001), but kerogen is not decomposed. In such a world, the atmospheric CO₂ is continuously converted to reduced C compounds (CH₂O, CO, CH₄ and C) and not completely recycled back to CO₂. Thus, the atmospheric CO₂ continuously decreases, even with continuous supplies of CO₂ by volcanic gas and weathering of carbonates, and disappears in <~100 Ma since the emergence of photoautotrophs, creating an icy, dead planet (Ohmoto and Lasaga, 2001). However, the abundances of carbonates and organic C-rich shales, and their δ¹³C values, in Archean sedimentary rocks are essentially the same as those in younger ones (Ohmoto, 2004), suggesting that since ~3.8 Ga, the atmosphere and oceans have remained O₂- and CO₂ rich and the modern-styled redox cycle of C has operated.

Black shales with high pyrite contents, which positively correlate with organic C contents, and sulfate-rich sediments are not uncommon in Archean rocks (Ohmoto, 2004). δ³⁴S values of the pyrites and sulfates show large variations, from -20 to +35‰ and from +2 to +27‰, respectively (Ohmoto, 1992, 2004; Kiyokawa et al., in prep.). The common δ¹⁵N values for kerogen in Archean shales (0 to +15‰) are essentially the same as those in Phanerozoic ones (Yamaguchi, 2004; Kerrich et al., 2006). These data suggest that since >3.5 Ga, the oceans have been rich in SO₄²⁻ and NO₃⁻. Researchers have interpreted the isotopic records of S, Fe, Mo and Cr in sedimentary rocks based on anoxic Archean atmosphere models. However, we can better explain these isotopic data, as well as the Pb isotope data and the variations in the Fe^{III}-, Mo-, Ce, and U contents, of Archean rocks with the model of a fully-oxygenated Archean world. The isotopic variations in the 2.7-2.5 Ga Hamersley sediments can be explained by combinations of biological-, diagenetic- and hydrothermal processes in a nearly-closed euxinic basin, which episodically hosted matalliferous brine pools and/or opened to the O₂-, S-, Mo- and U rich oceans.

Many researchers have cited the presence of AIF-S (or MIF-S) and detrital grains of uraninite and pyrite in some Archean-aged sedimentary rocks as strong evidence for an anoxic Archean atmosphere. But such arguments are invalid, as AIF-S and these detrital minerals have also been found in much younger-aged materials (Ohmoto, 2004; Watanabe et al., Goldschmidt 2012).

Trace element composition of size-fractionated particulates in the North Atlantic U.S. GEOTRACES section

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Sinking (>51µm) and suspended (<51µm) marine particulates were collected via *in situ* filtration during the US GEOTRACES North Atlantic Zonal Transect cruises on the *R/V Knorr* in 2010 and 2011. Total and acetic acid-leachable compositional profiles for key trace elements and isotopes (TEIs—Fe, Al, Zn, Mn, Cd, Cu) and other TEIs of interest (Co, Ti, Ba, V, Ni, Mo) are presented, allowing a first look at particulate composition for a full ocean transect, in sixteen-point depth resolution.

This transect explores a diverse array of sites—the Saharan African and North American continental margins, a mid-ocean ridge hydrothermal plume, several benthic boundary layers, as well as open-ocean sites—which significantly expands our knowledge of the highly-variable and dynamic marine particulate world. Common behaviors are observed for several groups of elements, highlighting differences between lithogenic and biogenic particulate pools, and the dynamics that exchange material between different size-fractions. Acetic acid-leachable particulate data furthermore provides constraints on exchangeable and/or bioavailable elemental pools, and also explores the behaviors of redox-sensitive metals in oxygen minimum zones, benthic boundary layers, and in surface waters. Combination of this dataset with other, forthcoming GEOTRACES results (e.g. ²³⁴Th export, dissolved TEI parameters) will be an exciting product of the worldwide GEOTRACES program.