

Abiotic syntheses of organic matter and Fe-oxides in submarine hydrothermal plumes in a deep ocean ~3.45 Ga ago

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The evolutions of life and O₂ on the early Earth have long been debated among astrobiologists. Some have suggested that the life did not evolve until ~2.7 Ga, and that the organic matter (OM) in pre-2.7 Ga sedimentary rocks represent OM synthesized abiotically via Fischer-Tropsch-type reactions in submarine hydrothermal environments. The current paradigm for atmospheric evolution is that the atmosphere remained anoxic until ~2.5 Ga because of the presence of MIF-S signatures in pre-2.5 Ga sedimentary rocks. However, some researchers have suggested that the oxygenated atmosphere and the diverse biosphere, including anaerobic and aerobic microbes, have existed since at least ~3.5 Ga. Based largely on nano-scale investigations of the physical and chemical characteristics of OM and Fe-oxides in the Marble Bar Chert/Jasper (MBC) from Western Australia, here we suggest that abiotic hydrothermal synthesis of OM was important and that the diverse biosphere existed in the ~3.5 Ga oceans.

Our investigations of the MBC, utilizing state-of-the-art analytical instruments for nanomaterial sciences (e.g., HRTEM, STEM, EELS, TALOS), have recognized intimate associations of sub-nano- to nano-sized (<0.5 nm – 100 nm) particles of Fe-oxides (FeNP) and organic matter (OM) in the every sample we have examined. Two modes of FeNP-OM associations were recognized. In the first mode, FeNP occurs abundantly both inside and outside of what appear to be “fossils of aerobic Fe-oxidizing microbes” . This mode of FeNP-OM association typically occurs as microbial mats in chert beds formed by low-T hydrothermal fluids (see Watanabe et al., this session).

In the second mode, FeNP and OM occur as a ~30-50 nm-sized aggregate, which is comprised of a spherical- or tear-shaped Fe-rich core (~10-20 nm size) made of FeNP (hematite ± magnetite) with minor OM; the core is surrounded by a ~5 nm-thick ring of OM and then by a ~10-20 nm-thick outer zone comprised of mixtures of sub-nano-sized particles of Fe-oxides and OM. Such aggregates are typically coagulated to form larger clusters of Fe-oxides and OM. Considering the various geochemical data (e.g., Eu anomalies) of the jasper beds that host the FeNP-OM association, we interpret that the Fe-oxides and OM were synthesized abiotically during the mixing in hydrothermal plumes of high-T hydrothermal fluids and ocean bottom water. The abiotic reactions created colloidal Fe²⁺-bearing proteins by utilizing CO₂ from the seawater and Fe²⁺ from the high-T hydrothermal fluids; the colloids were subsequently transformed into mixtures of sub-nano-sized particles of Fe-free OM and hematite (some to magnetite) through further reactions with seawater O₂ and hydrothermal Fe²⁺. These chemical reactions are basically the same as those that produced the OM and Fe-oxides by aerobic Fe-oxidizing bacteria. The main difference is that one is promoted by biochemistry, while the other is promoted by heat.

The abiotic production of OM in the Archean oceans would have been much more important than today because the atmospheric pCO₂ was 100 PAL, the pO₂ was already ~1 PAL, and submarine hydrothermal activity was more extensive than today. The abiotically produced OM would have been more digestible to heterotrophic organisms and more reactive to chemical reactions than the OM produced by autotrophic organisms because of the absence of cell-wall lipids. Therefore, microbial activity would have flourished more during the Archean compared to later times. Thermochemical sulfate reduction by the reactive OM (rich in Fe-bearing proteins) would have generated MIF-S signatures. Decreasing submarine hydrothermal

activity and decreasing atmospheric $p\text{CO}_2$ due to the increasing continental crust size since ~ 2.5 Ga would have decreased the productions of reactive OM and the MIF-S signatures. The disappearance of MIF-S at ~ 2.5 Ga does not indicate a change from an anoxic to oxic atmosphere.

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