

## 6.6.14

### Lightning associated with hot-spot island arc volcanoes and the localized synthesis of prebiotic compounds on the primitive Earth

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Many geoscientists today doubt that the primitive atmosphere had the highly reducing composition similar to that simulated by Miller in his classic 1953 spark discharge experiment. Even though reducing conditions may not have existed on a global scale on the early Earth, localized high concentrations of reduced gases may have existed around volcanic eruptions, especially in hot-spot island-arc systems which may have been common on the early Earth. Whether reducing volcanic gases would have been dominant in these systems would depend on the oxidation state of the early mantle. Although results suggest that the mantle has had its current oxidation state for the last 3.6 to 3.9 Ga, the oxidation state prior to this is not known and could have been more reducing than today.

The localized release of reduced gases by volcanic eruptions on the early Earth has appealing prebiotic chemistry implications. The gases would likely have been immediately exposed to intense localized volcanic lightning, which is commonly associated with volcanic eruptions today and has been suggested to exceed the amount of atmospheric lightning associated with thunderstorms. Lightning around volcanic eruptions could have been one of the most effective ways that nitrogen fixation took place on the early Earth. In present day volcanic gas mixtures, NO is the main product, but with reducing hydrogen, methane and nitrogen mixtures, HCN, acetylene and other prebiotic reagents would have been produced. It is interesting to note that in the original studies by Miller, a spark discharge apparatus was designed that generated a hot water mist that could be considered similar to a water vapor-rich volcanic eruption into a reducing atmosphere. Experiments with this apparatus produced similar distributions and quantities of amino acids and other organic compounds as those produced in Miller's original spark discharge. Thus, in localized volcanic plumes, the essential reagents may have been produced and involved in the prebiotic synthesis of organic molecules such as amino acids. Island arc systems may have been particularly important in localized Strecker-type syntheses because the reagents could have locally rained out into tidal areas where evaporation or periodic freezing could have concentrated them.

## 6.6.15

### Using genomes to speculate on early microbial evolution & environments

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We formed trees based on the presence & absence of families of genes observed in 86 prokaryotic genomes. There are features of these trees that are not congruent with typical rRNA trees. Our results imply the last common ancestor (LCA) of the Archaea was not a methanogen, leaving sulfur and iron reduction as the most geochemically plausible metabolisms for the base of the archaeal crown group [1]. Prior to the evolution of methanogenesis, atmospheric sulfur deposition likely fueled sulfur-reduction, consuming atmospheric H<sub>2</sub>. The sulfur isotopic composition of Archean minerals provides ample evidence for sulfur deposition on the early Earth [2]. For the most part, the same microbes that can reduce sulfur, can also reduce iron. Given the insolubility of ferric iron, iron reduction may have been most prevalent in ancient sediments, providing a mechanism for carbon remineralization prior to the evolution of methanogens. Work is proceeding to investigate if HCN from the early atmosphere played a role as a mediator of the evolution of metabolisms helping shape their genomic content.

Our investigations also map metabolisms onto the tree of life as a step toward predicting geochemical signatures of ancient nodes of the tree. The most parsimonious explanation for the distribution of carbon fixation pathways predicts that the C isotopic fractionation exhibited by the ancestor of the Bacteria and the ancestor of the Archaea was low, if they were autotrophic cells [3].

We have utilized microbial genome sequences to predict that the LCA had relatively high requirements for Fe, Zn and Mn, with low Co, Cu, Mo, W, and Ni requirements. Trace metal requirements indicated by modern microbial genomes demonstrates that cellular metal requirements vary with phylogeny, metabolism, O<sub>2</sub> tolerance, & growth temperature. These "metallomes" can be superimposed on the tree to consider the evolution of trace metal usage. The metallome of the LCA indicated by extrapolation is much different than that indicated by the inferred origins of individual enzymes through time, suggesting that gene transfer has been important in shaping the genetic composition of extant organisms.

#### References

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