## **Gast Lecture**

## Chemical and biological evolution of the early Earth:

## A minority report

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A currently popular model for the chemical evolution of the atmosphere and its connection to the evolution of life on early Earth postulates the following scenarios: (1) methanogenic microbes were the primary producers in the oceans until cyanobacteria appeared  $\sim 2.7$  Ga ago; (2) the atmosphere was rich in CH<sub>4</sub> but poor in O<sub>2</sub>, and the oceans were rich in  $Fe^{2+}$  but poor in  $SO_4^{2-}$  and  $O_2$  until the Great Oxidation Event (G.O.E.) ~2.3 Ga ago raised the  $pO_2$  from <0.01% to  $\sim15\%$  PAL (present atmospheric level); (3) the  $pO_2$  gradually rose to ~50% PAL, and the oceans became rich in  $SO_4^{2-}$  and biogenic H<sub>2</sub>S but poor in Fe<sup>2+</sup> during the period between ~2.0 - ~0.6 Ga; and (4) the second (or third?) major oxidation event occurred ~0.6 Ga, creating the modern oxygenated world and causing the appearance of metazoans (e.g., Canfield 1998; Anbar and Knoll, 2002; Holland, 2002; Kasting, 2002). The mass independent fractionation of sulfur isotopes (MIF), discovered by Farquhar et al. (2000) in Archean rocks, has been hailed by many researchers as the best evidence to support the above model. However, serious discrepancies exist between the MIF characteristics of natural samples and those of photochemical experimental products. The presence of MIF in geologic samples younger than ~2.3 Ga also poses a serious problem for the model that links the MIF to the atmospheric  $pO_2$  level.

Our research group has conducted extensive investigations on the geological, mineralogical, and geochemical characteristics of Archean and Paleoproterozoic sequences in parts of Australia, South Africa, Finland, Canada, and USA. From comparisons of the various characteristics in stratigraphic sections of these districts, we recognize frequent fluctuations in the redox structure of oceans in local and regional scales, but not in global scale, since ~3.5 Ga. Similarities in petrochemical characteristics between pre- and post-2.3 Ga shales (e.g., relative abundances and distributions of black- and greyshales, concentrations and morphology of organic matter and sulfide minerals,  $\delta^{13}$ C,  $\delta^{34}$ S, and  $\delta^{15}$ N values, and trace element ratios) are difficult to explain if the global redox cycles of C, S, N, Mo, Fe, and other elements significantly differed between pre- and post-2.3 Ga periods. Without an effective mechanism to recycle kerogen in sedimentary rocks to CO<sub>2</sub> during weathering, the CO<sub>2</sub> and global carbonate reservoirs would have been completely converted to reduced C, and life on Earth would have become extinct in less than ~1 billion years since the first appearance of organisms. If the pre-2.3 Ga world was anoxic, what was the kerogen recycling mechanism?

Many Algoma-type BIFs formed in deep oceans. If the Archean oceans were anoxic, why do they possess essentially the same mineralogical and geochemical characteristics of deep submarine hydrothermal deposits of Phanerozoic age (e.g., abundant hematite; positive Eu and negative Ce anomalies)?

We also recognize that many lines of "evidence" for the popular evolution model are either "not true" or "ambiguous": (i) the loss or retention of Fe in paleosols; (ii) the formation of "detrital"- vs. "groundwater"-type U deposits; (iii) the age distribution of banded iron formations (BIFs); and (iv) the distinction in  $\delta^{15}$ N values between early- and late-Archean kerogens. For example, contrary to popular belief, uraninite dissolves as fast in anoxic water as in oxic water. Therefore, the survival detrital grains of uraninite in some modern and ancient sediments should not be related the atmospheric  $pO_2$ level. The U content of organic-poor groundwater is primarily controlled by the availability of U in the aquifer rocks, not by the DO content; thus, the formation of groundwater-type U deposits may not be related to the atmospheric  $pO_2$ .

A popular mechanism for creating an anoxic atmosphere on early Earth postulates high fluxes of reducing volcanic gas; but there is no supportive evidence, such as low  $Fe^{3+}/Fe^{2+}$  ratios in Archean igneous rocks. Furthermore, this theory has failed to provide satisfactory explanations as to why it took more than ~300 million years to raise the atmospheric  $pO_2$  from <0.01% to ~15% PAL since the emergence of cyanobacteria; why the  $pO_2$  gradually rose to ~50% PAL during the following ~1.5 billion-year period; and why the  $pO_2$  jumped to ~1 PAL ~600 Ma ago and basically remained constant ever since.

All the available geochemical data on Archean and Proterozoic rocks are, however, consistent with the Dimroth-Ohmoto-Lasaga model that postulates the following scenarios: (a) major anaerobic and aerobic organisms (methanogens, sulfate-reducers, cyanobacteria, and possibly eukarya) appeared at least 3.5 Ga ago (possibly before 3.8 Ga); (b) an oxygenated world was established within ~10 Ma of the appearance of cyanobacteria; and (c) the  $pO_2$  and oceanic  $SO_4^{2-}$  levels have been maintained within ±50% of the present values by the coupling of two major negative feedback mechanisms: the responses to a change in  $pO_2$  of (i) the burial flux of organic C and (ii) the oxidation flux of soil kerogen.

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