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**J.F. Keating: EVOLUTION OF THE ATMOSPHERE**

The Earth's atmosphere must be of secondary origin; that is, it was outgassed from the interior rather than captured from the solar nebula. The evidence for this is the strong fractionation of rare gases (Ne, Ar, Kr, Xe) relative to solar abundances. These gases could not have been lost over time by escape to space or by chemical interactions with the crust; hence, their concentrations would be much higher today if the atmosphere were originally derived from nebular materials. If the Earth's crust has always been close to its present oxidation state, as seems likely, the "excess volatiles" that were outgassed would have consisted primarily of H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub>, with smaller amounts of CO, H<sub>2</sub>, SO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>S. The composition of such an atmosphere might be described as weakly reducing.

The climate of the Archean Earth would have been influenced by the fact that solar luminosity was approximately 25-30 percent lower than it is today. Since liquid water existed on the Earth's surface, the early atmosphere must have contained some infrared absorbing "greenhouse" gases in addition to those present today to compensate for the low solar flux. The most likely scenario involves greatly enhanced levels, perhaps 100-1000 the PAL (Present Atmospheric Level) of CO<sub>2</sub>. There are additional reasons to believe CO<sub>2</sub> levels were higher in the past, involving differences in the carbonate-silicate geochemical cycle. Because of increased volcanic and tectonic activity the weathering of calcium silicate (CO<sub>2</sub>+CaSiO<sub>3</sub> → CaCO<sub>3</sub>+SiO<sub>2</sub>) would have been slower, while the reverse reaction, which occurs during metamorphism, would have been faster.

The O<sub>2</sub> content of the prebiotic atmosphere can be estimated by balancing sources and sinks of H<sub>2</sub>. The governing equation may be written as:

$$\Phi_{\text{esc}}(\text{H}) + 4 \times R(\text{H}_2\text{CO}) = \Phi_{\text{out}}(\text{H}) + 2 \times R(\text{H}_2\text{O}_2)$$

where  $\Phi_{\text{esc}}(\text{H})$  is the rate at which hydrogen escapes to space,  $\Phi_{\text{out}}(\text{H})$  is the volcanic flux of reduced gases, and  $R(\text{H}_2\text{CO})$  and  $R(\text{H}_2\text{O}_2)$  are the rainout rates of formaldehyde and hydrogen peroxide, respectively. The rainout terms become important at CO<sub>2</sub> levels much higher than those of today. Model calculations yield H<sub>2</sub> mixing ratios on the order of 10<sup>-4</sup> to 10<sup>-3</sup> and extremely low surface O<sub>2</sub> mixing ratios (≈10<sup>-12</sup>.)

The effect of life on the atmosphere was probably small until the evolution and subsequent widespread distribution of bacterial photosynthesis. With bacterial photosynthesis H<sub>2</sub> levels would have been lowered and atmospheric CH<sub>4</sub> levels would have risen as a result of the activities of methanogens. Distribution of methanogens on a global scale may be recorded by the wide spread in  $\delta^{13}\text{C}$  values in the organic material in sediments around

2.8 billion years ago.

Evidence in the geological record for oxygenic photosynthesis dates from at least 2.5 billion years ago, the time at which the Hamersley iron formations of Western Australia were deposited. However, the oxygen-producing photosynthetic process of bacteria may have originated much earlier. The effect of oxygenic photosynthesis on the atmosphere depends upon the relative rates of supply of reduced and oxidized materials to the atmosphere, surface ocean, and deep ocean. The surface ocean and atmosphere may have switched from reducing to oxidizing about 2.4 billion years ago, based on evidence from detrital uraninites, fluvial deposits (redbeds), and paleosols. The deep ocean apparently remained anaerobic until approximately 1.7 billion years ago, at which time the banded iron formations disappeared. The interpretation of the geologic record is clouded by the possible importance of atmospheric oxidants other than  $O_2$ , specifically  $H_2O_2$ .

Atmospheric  $O_2$  levels must have reached some relatively high, stable value ( $10^{-3}$ – $10^{-2}$  PAL) by about 1.4 billion years ago, the time at which eukaryotes first appeared. The origin of metazoa, some 600 million years to 1.0 billion years ago, presumably required still higher  $O_2$  levels ( $10^{-2}$ – $10^{-1}$  PAL? – see Schopf, chapter 13). The emergence of land life during the late Silurian (480 million years ago) indicates that  $O_2$  levels probably exceeded  $10^{-1}$  PAL, the amount required to generate an effective ozone screen against solar ultraviolet radiation. These are all lower limits on atmospheric  $O_2$ . Oxygen concentrations may have been much higher than this, perhaps reaching the present level as early as 1.7 billion years ago. In this case the appearance of shelled organisms at the beginning of the Cambrian and the emergence of land life during the Silurian would be completely unrelated to changes in atmospheric oxygen, contrary to suggestions by Cloud (1972) and Berkner and Marshall (1964). Further analysis of the geologic record is needed to more accurately estimate the history of atmospheric oxygen.

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