Algae and Oxygen in Earth's Ancient Atmosphere

T.-M. Han and B. Runnegar report (*1*) finding eukaryotic microfossils, tentatively identified as *Grypania*, in the 2.1-billion-year-old Negaunee iron formation in northern Michigan. They suggest that free oxygen (O_2) was a significant component of the atmosphere between 2.0 and 2.5 billion years ago on the basis of the metabolic requirements of these organisms. This argument does not account for the possibility (*2*) that ocean surface waters might have been locally enriched in photosynthetically derived O_2, while the atmosphere itself remained free of O_2. Present rates of marine photosynthesis and of diffusive loss of O_2 through the ocean-atmosphere interface suggest that dissolved O_2 concentrations could have been up to eight times higher than the 0.01 present atmospheric level that is needed to sustain *Grypania* (*2*). The existence of an atmosphere free of O_2 before about 2.0 billion years ago would be consistent with several other types of geologic evidence cited in (*3*).

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Response: In a recent book (*1*), Kasting has used a modern value for C of 1 g m^{-2} day^{-1} (1.2×10^{-5} g m^{-2} s^{-1}) for the "primary production by phytoplankton in regions of high productivity" as an estimate of the O_2-producing capacity of optimal regions of the Archean and early Proterozoic oceans. All of the O_2 resulting from this production (10^{-6} mol m^{-2} s^{-1}) was assumed to have been involved in outgassing by diffusion through the stagnant film at the ocean surface. Kasting estimated (*1*) (by dividing the assumed rate of O_2 production by a calculated transport velocity of 5×10^{-5} m s^{-1} across a 40 μm-thick unstirred boundary layer) that productive parts of the surface ocean could have retained as much as 2×10^{-5} mol of O_2 per liter (0.08 PAL O_2), where PAL represents the present atmospheric level, in disequilbrium with an anoxic atmosphere containing as little as 10^{-14} PAL O_2. These "oxygen oases" might therefore have provided localized habitats for early eukaryotes before the origin of an O_2-rich atmosphere.

Kasting's model of a diffusion-limited rate of escape for O_2 from the ocean surface would work if the primary production beneath the oases were as high as that found in modern areas of upwelling (C, 0.5 to 10 g m^{-2} day^{-1}) and if all of the O_2 stayed close to where it was produced. The model would not work if the Archean O_2 oases were less productive than the modern net euphotic zone (average production of C equals about 0.1 g m^{-2} day^{-1}) (*2*) or if the O_2 were transported away from the oases by currents. In either of these cases, the O_2 tension in an oasis would have fallen below 0.005 PAL and thus would have been insufficient to support aerobic respiration (*3*).

In modern oceans, upwelling water masses provide the nutrients to support areas of high productivity. The slow upward circulation (about 10^{-5} m s^{-1}) translates into surface currents with velocities of tens of centimeters per second (*4*). As these surface currents are four orders of magnitude faster than the O_2 transport across the unstirred boundary layer, it seems likely that the Archean O_2-rich waters would have been rapidly dispersed from areas of high productivity. In other words, the area of the air-sea interface available for the diffusive export of O_2 was probably much larger than assumed in Kasting's model (which also neglects the extra area that results from sea surface roughness).

R. F. Keeling and S. R. Shertz (*2*) have used a sensitive measure of the ratio in air of O_2 to N_2 to estimate the seasonal fluxes of O_2 across the air-sea interface. In the Southern Hemisphere alone, about 8×10^{14} mol of O_2 flows into the atmosphere during spring and summer, and a similar amount returns to the oceans in autumn and winter. This is equivalent to an average one-way flux of O_2 some 4 mol m^{-2} $year^{-1}$ (about 2.5×10^{-7} mol m^{-2} s^{-1}) or about one-fourth the production rate of Kasting's proposed oases. So, if surface currents in the Archean and early Proterozoic oceans merely increased the effective area available for air-sea exchange by diluting O_2-containing waters, all the O_2 produced in seasonal phytoplankton blooms could have been outgassed.

Kasting (*1*) is correct that oxidized chemical precipitates (for example, banded iron formations) do not necessarily provide evidence of an O_2-rich atmosphere. However, the same argument should not be applied to the remains of megascopic eukaryotes such as *Grypania spiralis* because those organisms required that an O_2 tension of 0.01 to 0.1 PAL be maintained during their lifetimes (weeks to months). Kasting's proposed oases might have existed as transient phenomena beneath an anoxic atmosphere, but it is unlikely that they could have been stable for longer than hours or days given the factors that would have tended to dissipate them (episodic O_2 production, fast surface currents, high winds, and rough seas). Therefore, the discovery of *Grypania* in 2.1-billion-year-old rocks (*5*) is an indication that the atmosphere as well as the surface ocean contained at least 10^{-2} PAL of O_2 (*3*, *6*).

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Laser-Enhanced NMR Spectroscopy: Theoretical Considerations

W. S. Warren *et al.* (*1*) report that the proton magnetic resonance spectra of chiral molecules are modified slightly by circularly polarized laser light. While it is not unexpected that circularly polarized radiation can influence chiral molecules (*2*), the large magnitude of the reported results is surprising. From conservation of parity, and under the conditions of the experiment, the relevant energy shifts per randomly oriented molecule show several simple relations (Table 1). The chemical shielding of a chiral molecule in right circularly polarized light must be the same as its enantiomer in left circularly polarized light. However, the splitting of nuclear magnetic resonance

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