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*).

James F. Kasting
Department of Geosciences, Pennsylvania State University, University Park, PA 16802

REFERENCES

1. T.-M. Han and B Runnegar, *Science* **257**, 232 (1992).
2. J. F. Kasting, in *The Proterozoic Biosphere: A Multidisciplinary Study*, J. W. Schopf and C. Klein, Eds. (Cambridge Univ. Press, Cambridge, United Kingdom, 1992), pp. 1185–1187
3. J. C. G Walker *et al.*, in *Earth's Earliest Biosphere: Its Origin and Evolution*, J. W. Schopf, Ed (Princeton Univ. Press, Princeton, NJ, 1983), pp 260–290.

23 July 1992, accepted 5 October 1992

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*).

B. Runnegar
Department of Earth and Space Sciences, University of California, Los Angeles, CA 90024–1567

REFERENCES

1. J F Kasting, in *The Proterozoic Biosphere A Multidisciplinary Study*, J W Schopf and C Klein, Eds (Cambridge Univ Press, Cambridge, United Kingdom, 1992), pp 1185–1187.
2. R. F Keeling and S R Shertz, *Nature* **358**, 723 (1992).
3. B Runnegar, *Palaeogeogr Palaeoclimatol. Palaeoecol.* **97**, 97 (1991).
4. R S. Smith, in *Coastal Upwelling*, F A. Richards, Ed (American Geophysical Union, Washington, DC, 1981), pp 107–118
5. T M Han and B Runnegar, *Science* **257**, 232 (1992)
6. R Riding, *Nature* **359**, 13 (1992)

28 September 1992, accepted 5 October 1992

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

Table 1. Energy shifts per randomly oriented molecule. The external magnetic field is **B**, the nuclear magnetic moment is μ_N, and σ_0 is the scalar chemical shielding in the absence of light. The light is characterized by intensity I_0 and is assumed to be parallel to **B**. The constants (a, b, b_0) are characteristic of the molecule in the linear light shift regime (*3*).

Handedness	Light polarization	
	Right	Left
(+)	$(\sigma_0 + aI_0) B \mu_N + I_0 (b_0 + b B) \mu_N$	$(\sigma_0 + aI_0) B \mu_N + I_0 (b_0 - b B) \mu_N$
(−)	$(\sigma_0 + aI_0) B \mu_N - I_0 (b_0 + b B) \mu_N$	$(\sigma_0 + aI_0) B \mu_N - I_0 (b_0 - b B) \mu_N$

(NMR) lines in left circular polarization will not necessarily equal that for right circular polarization because of the zero magnetic field term, b_0I_0.

Direct calculation using the standard Hamiltonian descriptive of the interaction between radiation and matter in a magnetic field shows that for light intensities of 10 W cm^{-2} the nonchiral chemical shift in the NMR spectrum should yield a value of aI_0 on the order of 10^{-15} σ_0. The chiral chemical shift, bI_0, is on the order of 10^{-18} σ_0; for a magnetic field of 10^4 gauss, this intensity-dependent shift corresponds to about 10^{-15} Hz. The zero magnetic field shift (b_0I_0) is about 10^{-10} Hz.

In conclusion, the ordinary manifestation of chirality on light-perturbed chemical shifts is too small to be observed. Shining laser light on a racemic mixture and seeing a single NMR line split into two lines would provide a convincing experimental result. Our calculations predict that it will not occur.

Robert A. Harris
Ignacio Tinoco, Jr.
Department of Chemistry,
University of California,
Berkeley, CA 94720

REFERENCES AND NOTES

1. W. S. Warren, S. Mayr, D. Goswami, A. P. West, Jr., *Science* **255**, 1683 (1992)
2. M. W. Evans, *J. Phys Chem.* **95**, 2256 (1991)
3. C. Cohen-Tannoudji *et al.*, *Atom Photon Interactions* (Wiley, New York, 1992), pp. 206–209

4. We acknowledge that part of the material presented in this response was influenced by a letter from M. W. Evans. R.A.H thanks W S. Warren for a helpful discussion Supported by NSF and American Chemical Society–Petroleum Research Foundation grants to R.A.H. and NIH and Department of Energy grants to I.T

15 July 1992; accepted 15 October 1992

Response: We are pleased to see that our recent paper (*1*) has attracted the attention of theorists. As noted in that paper, the laser-enhanced NMR effect we reported could be useful if the magnitude of the effect can be increased, and additional theory is welcome.

Our predictions of the size of the expected effect are much larger than those of Harris and Tinoco. Their calculations assume that the only terms in the field-matter Hamiltonian that can contribute significantly to a resonance frequency shift are those that are proportional to the laser intensity (the square of the field amplitude, ε^2). This assumption seems too restrictive. At least one reasonable mechanism [an off-resonance electric field inducing polarization, $P(\omega) = \alpha(\omega)\varepsilon(\omega)$ (where P is the polarization, ω is the frequency, and α is the molecular polarizability), which in turn acts like a direct current magnetic dipole (*1*)] is proportional to ε. This effect thus has nonvanishing consequences in first-order perturbation theory. In atomic systems, such as a hydrogen atom, the contributions can be calculated quite accurately and would give resonance frequency shifts of several hertz at reasonable bond distances for our laser intensity (*1*). A related derivation based on

$$P(\omega) = -N\beta(\omega)d\mathbf{B}(t)/dt$$

(where N is the number of molecules, β is the chiral response parameter, **B** is the magnetic field, and t is time) would give differences for different enantiomers. In this case the effect is smaller, but still first order, and many orders of magnitude larger than that predicted by Harris and Tinoco.

In molecular liquids, other complications must be considered. For example, molecules in solution experience rotational reorientation (as manifested by fluorescence depolarization, for example). However, picosecond laser measurements by many researchers have shown that typical fluorescence depolarization times for medium-sized molecules in solution are on the order of 5 ps; fluorescence lifetimes for the molecules we are examining are probably several hundred picoseconds or less, and the quantum yield is probably high. Thus we would still expect residual polarization on the order of at least 1% of the maximum figure we would calculate for atomic systems.

Since the publication of our paper (*1*), we have improved the resolution and accuracy of our shift measurements. Off-resonant irradiation with reasonable laser powers (1 to 3 W cm^{-2}) produces shifts that cannot be dismissed as simple thermal effects. For example, if we leave the laser on continuously, the center frequencies of the peaks change as polarized light, which is held at the same intensity, is shifted from left to right circularly; shifts on the order of ± 0.2 Hz in chiral molecules such as *p*-methoxyphenyliminocamphor are observed. These shifts are largest for resonances near the chromophoric group and somewhat different for the two enantiomers. Unfortunately, these shifts are still too small to be useful, and one disadvantage of a dominant mechanism proportional to $\boldsymbol{\varepsilon}$ is that increasing the laser power scales up heating effects (proportional to ε^2) faster than it scales up the desired shifts.

Before submitting our paper (*1*), we attempted several experiments on the racemic mixture. However, with shifts smaller than the linewidth, we did not expect to see significant broadening in the racemate. We agree with Harris and Tinoco that increasing the magnitude of the effect to force a splitting between resonances would be an important test of the practical value of this technique, and we are happy to accept this challenge.

Warren S. Warren
S. Mayr
D. Goswami
A. P. West, Jr.
Department of Chemistry,
Princeton University,
Princeton, NJ 08544

REFERENCES

1. W. S. Warren, S. Mayr, D. Goswami, A P West, Jr., *Science* **255**, 1683 (1992)

7 October 1992; accepted 15 October 1992