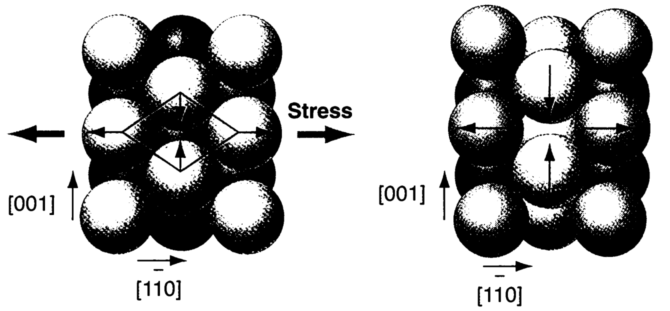
Poisson's ratios were unknown and even thought to be impossible (*3*). Since then, foams with ν as small as −0.8 have been produced by changing the shape of the cells (*4*). These foams expand laterally when stretched. Isotropic negative Poisson's ratio materials easily undergo volume changes but resist shape changes and may thus be viewed as the opposite of rubbery materials, or "antirubbers" (*5*).



Directions parallel to stress (singular)

Directions perpendicular to stress

Stretching a cubic crystal with negative Poisson's ratio. [001] refers to the direction along a cubic principal axis. [011] and [1̄10] are directions at a 45° angle from a cubic principal axis.

To achieve a negative Poisson's ratio, one must have noncentral forces or an unfolding mode of deformation (*6*, *7*). Milton has presented hierarchical laminates (*8*) that approach the isotropic lower limit $\nu \approx -1$ and called such materials "dilational" because they easily change volume. These laminates have a chevron structure with multiple length scales. Alderson and Evans have made microporous ultrahigh molecular weight polyethylene (*9*) with a negative Poisson's ratio by sintering and extrusion and called it "auxetic."

Anisotropic materials have properties that depend on direction. This extra freedom makes it easier to attain unusual or extreme behavior. For example, arsenic, antimony, and bismuth (*10*) are highly anisotropic in single-crystal form; Poisson's ratios calculated for these materials are negative in some directions (bottom panel in the first figure). A crystalline form of silicon dioxide, α-cristobalite (*11*), exhibits Poisson's ratios of +0.08 to −0.5, depending on direction. Many cubic metals when deformed in an oblique direction with respect to the cubic axes exhibit a negative Poisson's ratio (see the second figure) (*12*).

Anisotropy can give rise to curious effects. Remarkably, it is possible for Poisson's ratio to be negative in one direction and highly positive in another direction, so that the material becomes denser when stretched (*13*). Baughman *et al.* now show that the surprising combination of incompressibility and negative Poisson's ratio in a cubic material is also possible (*2*). These characteristics are incompatible in an isotropic material. Baughman *et al.* predict negative Poisson's ratios for several extreme forms of matter, such as ultradense matter (10^4 to 10^{11} g/cm^3) in neutron star crusts and white dwarf star cores. These "star crystals" are thought to have a body-centered cubic structure, similar to the structure of some metals. However, extreme matter is not held together by the same forces as metals. The particles in extreme matter interact by a Yukawa potential in which the usual 1/r Coulomb dependence decays exponentially. This can be due to charge screening. In contrast, bonding in metals can be approximated as a balance between the attraction between atom cores and repulsion from an electron gas. Similar counterintuitive behavior is also predicted in ultralow density (10^{-15} g/cm^3) plasma "crystals" of trapped ions and in colloidal crystals of particles in a liquid matrix. Plasma crystals were actually observed to have a negative Poisson's ratio (*2*).

Understanding of these unexpected properties of dense matter may help in understanding reaction rates and "star quakes" in dense stars. Tuning of the Poisson's ratio in low-density cubic plasmas could be useful in sensors or in photonic light valves. Besides providing an intriguing glimpse into the strange properties of some unusual materials, Baughman *et al.*'s results may therefore be of importance both in fundamental studies and for applications.

CREDIT: ADAPTED FROM (*12*)

References

1. S. P. Timoshenko and J. N. Goodier, *Theory of Elasticity* (McGraw-Hill, New York, ed. 3, 1970).
2. R. H. Baughman *et al.*, *Science* **288**, 2018 (2000).
3. F. P. Beer and E. R. Johnston, *Mechanics of Materials* (McGraw-Hill, New York, ed. 1, 1981, ed. 2, 1992).
4. R. S. Lakes, *Science* **235**, 1038 (1987).
5. J. Glieck, *New York Times*, 14 April 1987, Science Times, p. 21.
6. R. S. Lakes, *J. Mater. Sci.* **26**, 2287 (1991).
7. L. L. Rothenburg, A. A. Berlin, R. J. Bathurst, *Nature* **354**, 470 (1991).
8. G. Milton, *J. Mech. Phys. Solids* **40**, 1105 (1992).
9. K. L. Alderson and K. E. Evans, *Polymer* **33**, 4435 (1992).
10. D. J. Gunton and G. A. Saunders, *J. Mater. Sci.* **7**, 1061 (1972).
11. A. Y. Haeri, D. J. Weidner, J. B. Parise, *Science* **257**, 650 (1992).
12. R. H. Baughman, J. M. Shacklette, A. A. Zakhidov, S. Stafström, *Nature* **392**, 362 (1998).
13. R. H. Baughman and D. S. Galvao, *Nature* **365**, 735 (1993).

PERSPECTIVES: OCEANOGRAPHY

Tracer from the Sky

Michael L. Bender

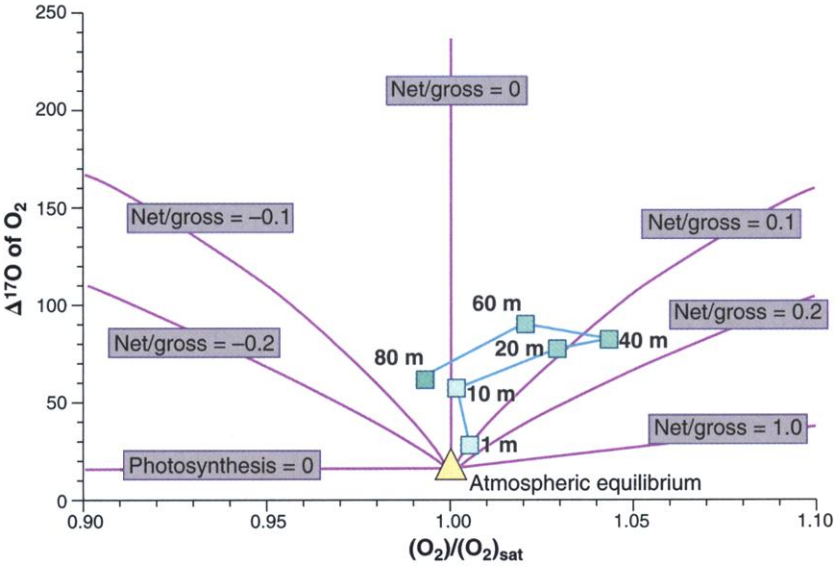
The stable isotope abundance ratios of light elements such as hydrogen, carbon, and oxygen often vary slightly in materials at Earth's surface. These variations result from subtle differences in the chemical or physical behavior of atoms of the same element but different masses and can provide important information about geological, biological, climatic, and hydrological processes. On page 2028 of this issue, Luz and Barkan (*1*) exploit one such isotopic variation to determine the gross rate of photosynthesis in seawater.

The rate of marine photosynthesis is of great importance, because the process establishes the basis of the food chain, supports vertical carbon fluxes that induce nearly all chemical variability in the oceans, and affects climate by influencing the CO_2 concentration of surface seawater and, therefore, the concentration of CO_2 in air. It is difficult to measure from environmental properties because it does not directly induce substantial chemical changes (these are a manifestation of net production or photosynthesis in excess of respiration). It is also difficult to measure in vitro, because capturing an ecosystem "in a bottle" may change its characteristics and does not provide a means of adequately covering the oceans.

The work of Luz and Barkan is based on the anomalous isotope composition of O_2 in air, perhaps the smallest and most obscure isotope abundance variation discovered to date. Oxygen has three stable isotopes, ^{16}O (99.76%), ^{17}O (0.04%), and ^{18}O (0.20%). Isotope abundance variations generally depend on mass, and variations in $\delta^{17}O$ (the difference in parts per thousand in $^{17}O/^{16}O$ ratios between a sample and a standard) (*2*) are normally 0.5 (actually 0.52) times as large as those in $\delta^{18}O$. But the $\delta^{17}O$ of O_2 in air is about 0.2 per mil (‰) less than 0.52

The author is in the Department of Geosciences, Princeton University, Princeton, NJ 08540, USA. E-mail: bender@princeton.edu

times $\delta^{18}O$ (*3*). This anomaly results from an isotopic exchange reaction in the stratosphere between O_2 and CO_2 (*3–5*), which transfers ^{16}O to O_2 and ^{17}O and ^{18}O to CO_2. The latter process occurs with an $^{17}O/^{18}O$ transfer rate of 1/1 rather than 0.52/1. It is this anomalous "mass-independent" transfer that causes $\delta^{17}O$ of O_2 to be lower than expected.



Tracers for net and gross production. Open triangle: ^{17}O and $[O_2]/[O_2]_{sat}$ values for seawater at equilibrium with air. Purple lines: Coevolution of ^{17}O and $[O_2]/[O_2]_{sat}$ for photosynthesis and respiration in a closed system. Coevolution lines are plotted for net/gross production > 0 [photosynthesis (*P*) > respiration (*R*)] and < 0 ($P < R$). Data points are for the euphotic zone of the Atlantic Ocean near Bermuda on 7 July 1998 (*1*). The ratio of net/gross O_2 production, which can be read from this diagram, is ~0.05 in the mixed layer (top 10 m) and 0.1 in the upper part of the euphotic zone (depth of 20 to 60 m). The sample at 80 m is net heterotrophic ($[O_2]/[O_2]_{sat} < 1$; therefore, $P < R$) but still carries the isotopic signature of photosynthesis (that is, ^{17}O is greater than the atmospheric equilibrium value).

Photosynthesis and respiration are the only other processes on Earth besides this stratospheric isotopic exchange reaction that produce or consume O_2 and thereby substantially influence its isotopic composition. Photosynthesis adds O_2 with the isotopic composition of the source water, adding normally fractionated O_2 and thus diminishing the ^{17}O anomaly. Respiration fractionates in the normal, mass-dependent manner, consuming ambient (anomalous) O_2 and thus accelerating the change toward normal composition.

These insights form the basis of Luz and Barkan's methodology for measuring the gross primary productivity of seawater (*1*). By combining oxygen isotope measurements in the euphotic zone of the oceans (the top 100 m at Bermuda) with measurements of biological O_2 supersaturation and of water mixing and gas exchange rates, they are able to constrain net and gross production rates in seawater. A plot of $\Delta^{17}O$ versus biological O_2 supersaturation illustrates their approach (see the figure). Here, $\Delta^{17}O$, in units of per meg (1000 per meg equals 1‰), is the mass-independent anomaly and is defined as $1000 (\delta^{17}O - 0.52 \times \delta^{18}O)$. Air O_2 is chosen as the standard for logistic reasons, despite its anomalous character. By definition, $\delta^{17}O = \delta^{18}O = \Delta^{17}O = 0$ for air O_2.

Seawater at equilibrium with air has $[O_2]/[O_2]_{sat} = 1$, and $\Delta^{17}O = +16$ per meg. $[O_2]_{sat}$ is the saturation concentration in O_2 in seawater. ($\Delta^{17}O$ is slightly positive because of a small solubility fractionation between air O_2 and dissolved O_2). As photosynthesis adds O_2, $\Delta^{17}O$ rises toward +0.25‰, the value at which the mass-independent anomaly becomes zero (*1*). Net production, which is the difference between photosynthesis and respiration rates, causes $[O_2]/[O_2]_{sat}$ to rise for systems in which the photosynthesis rate exceeds the respiration rate and to decrease for systems in which the photosynthesis rate is lower than the respiration rate. For a given ratio of net/gross production, $\Delta^{17}O$ and $[O_2]/[O_2]_{sat}$ values thus coevolve away from atmospheric equilibrium (see the figure). By measuring these two properties of a water sample, one can deduce the ratio of net/gross production, which is a fundamental property of marine ecosystems.

The amount by which $\Delta^{17}O$ departs from atmospheric equilibrium and the change in biological O_2 saturation depend not only on the rate of photosynthesis and respiration but also on the time that has elapsed since the water was reset, by gas exchange, to atmospheric equilibrium. If one knows the history of a water sample or the rate of gas exchange in the oceanic mixed layer, one can calculate absolute rates of photosynthesis, respiration, and net productivity, the basic rate processes of an ecosystem. Luz and Barkan (*1*) validate this methodology with measurements from the Sea of Galilee. They show that gross O_2 production values, calculated from $\Delta^{17}O$ measurements and estimates of gas exchange rates, agree very well with rates determined by bottle incubations (*6*).

Luz and Barkan also present data for $\Delta^{17}O$ and biological O_2 supersaturation in upper ocean waters near Bermuda. Their results show the seasonal cycle of biological production inferred in earlier work (*7*). Gross production in the surface mixed layer (the top 10 m) is fairly rapid throughout the year. Gross production decreases with depth in the euphotic zone. However, the $\Delta^{17}O$ signature of gross production persists longer and therefore rises to a maximum in the slowly mixing, density-stratified waters below the mixed layer, where gas exchange is absent (see the figure).

These coupled measurements of $\Delta^{17}O$ and biological O_2 supersaturation complement standard techniques for ocean biogeochemistry studies. Bottle incubation measurements remain essential, because they allow instantaneous rate measurements that can be related to simultaneously measured biological properties. Incubation measurements also do not need to be interpreted in the context of water mixing and gas exchange rates. $\Delta^{17}O$ studies are free of artifacts associated with bottle incubation experiments and record biological rates over the weeks to months preceding sampling Collecting samples requires only a modest effort at sea. $\Delta^{17}O$ and $[O_2]$ measurements constrain net/gross production and the rate of photosythesis over longer time scales and larger spatial scales than is possible with other techniques. The $\Delta^{17}O$ method will see service in a variety of aquatic ecosystems, including lakes, rivers, estuaries, and coastal areas as well as the open sea.

References and Notes

1. B. Luz and E. Barkan, *Science* **288**, 2028 (2000).
2. $\delta^{17}O = [(^{17}O/^{16}O)_{sample}/(^{17}O/^{16}O)_{ref} - 1] \times 1000$. $\delta^{18}O$ is defined analogously.
3. B. Luz, E. Barkan, M. L. Bender, M. H. Thiemens, K. A. Boering, *Nature* **400**, 547 (1999).
4. M. H. Thiemens, T. Jackson, E. C. Zipf, P. W. Erdman, C. van Egmond, *Science* **270**, 969 (1995); M. H. Thiemens, T. L. Jackson, C. A. M. Brenninkmeyer, *Geophys. Res. Lett.* **22**, 255 (1995).
5. Y. L. Yung, A. Y. T. Lee, F. W. Irion, W. B. DeMore, J. Wen, *J. Geophys. Res.* **102**, 10857 (1997).
6. In these bottle experiments, water is labeled with $H_2{}^{18}O$ and incubated. Gross production is calculated from the rate at which the isotopic label is transferred from water to dissolved O_2.
7. W. J. Jenkins and J. Goldman, *J. Mar. Res.* **43**, 465 (1985).