

Guiding light. (Top) A hollow capillary refracts light at all angles of incidence. There is no angle at which light can be trapped in the hollow core, so capillaries cannot guide light under any circumstances. (Middle) A hollow-core photonic crystal fiber with an appropriately formed cladding (see scanning electron micrograph on the right) can guide light at angles of incidence where a photonic band gap operates (left), but otherwise refracts like a hollow-core capillary. (Bottom) A solid-core photonic crystal fiber (see scanning electron micrograph on the right) refracts light at steep angles of incidence on the core-cladding boundary (left). When the angle is shallow enough, light is trapped in the core and guided along the fiber.

materials in the early 1990s, driven largely by a remarkable possibility of these materials: the formation of photonic band gaps, light frequency ranges that cannot exist within the material, much like the electronic band gap in semiconductors.

It was predicted in 1995 (2) that a band gap in a photonic crystal fiber—if one could only be made—would enable light to be guided down a larger air hole embedded in the array. Light cannot normally be guided down an air hole (for example, a hollow glass capillary, see the second figure, top panel) because conventional guiding required cladding material with a lower refractive index than the core, and none lower than that of air exists. By surrounding the air hole with a photonic crystal, however, frequency ranges corresponding to the band gap of the crystal would be trapped within, and guided along, the air core (see the second figure, middle panel).

Such an air-core fiber enables new possibilities in optical telecommunications by overcoming some of the problems associated with the silica core that currently limit the performance of optical fibers. The air-guide concept has been verified experimentally (3), and efforts to design and make such structures continue (4, 5). Air-core fibers are already useful in scientific applications, but optical losses due mainly to structural imperfections (4) currently limit large-scale commercial applications.

photonic crystal fibers provides a massive advantage over those early structures (8).

Solid-core photonic crystal fibers, because of the two-dimensional nature of their cladding material, have some characteristics very different from conventional fibers. This has some advantages: It makes it practical to make a fiber with a very large core

A light-guiding core can also be formed (1) by creating a local region of higher refractive index, for example, by embedding a solid silica cane within the photonic microstructure. This fiber (see the second figure, bottom panel) guides light by a mechanism analogous to total internal reflection, in that the guiding is confined in a region which has a higher refractive index than its surroundings. Reported optical losses in these fibers are relatively low (6) and continue to fall. These fibers have much in common with microstructured fibers developed in the earliest days of fiber optics (7), but the new insight afforded by designing them as pho-

size, which can carry more optical power than its conventional counterpart. They can have a very large refractive index contrast, enabling spectacular nonlinear effects such as the generation of a broadband supercontinuum (9) that has led to a new generation of high-precision measurements in optical frequency metrology (10). Photonic crystal fibers also permit access to guided light in a way not possible in conventional optical fibers, providing new opportunities for fiber devices (11) and sensors.

Applications for photonic crystal fibers abound, and are presently being commercialized by a number of organizations. More exciting, the optics of these structures have not yet been fully explored, and the possibilities are limited only by the imagination. The renewed excitement in the field of optical fiber technology has led to a sea-change in our perception of what optical fibers can do.

References and Notes

1. J. C. Knight, T. A. Birks, P. St. J. Russell, D. M. Atkin, *Opt. Lett.* **21**, 1547 (1996).
2. T. A. Birks *et al.*, *Electron. Lett.* **31**, 1941 (1995).
3. R. F. Cregan *et al.*, *Science* **285**, 1537 (1999).
4. D. C. Allan *et al.*, in *Photonic Crystals and Light Localization in the 21st Century*, C. Soukoulis, Ed. (Kluwer, Dordrecht, Netherlands, 2001), pp. 305–320.
5. J. Broeng, S. E. Barkou, T. Sondergaard, A. Bjarklev, *Opt. Lett.* **25**, 96 (2000).
6. K. Suzuki *et al.*, *Opt. Express* **9**, 676 (2001).
7. P. Kaiser, H. W. Astle, *Bell Syst. Tech. J.* **53**, 1021 (1974).
8. The early fibers contained air-silica microstructures but did not consist of a two-dimensional pattern of air holes. Much of the optical physics was different but there are similarities in the fabrication procedure.
9. J. K. Ranka, R. S. Windeler, A. J. Stenz, *Opt. Lett.* **25**, 25 (2000).
10. R. Holzwarth *et al.*, *Phys. Rev. Lett.* **85**, 2264 (2000).
11. B. J. Eggleton *et al.*, *Opt. Express* **9**, 698 (2001).

PERSPECTIVES: PALEOCLIMATE

Corals, Chemistry, and Climate

Daniel P. Schrag and Braddock K. Linsley

To most people, coral reefs are symbols of the extreme biodiversity of the undersea world. But to many geochemists, corals hold the key to understanding the recent temperature history of the tropical oceans. Certain coral species grow like trees, putting down layers of their skeletons every year, and can live for 300 years or more. By examining the chemistry of the coral skeleton, geochemists have been able to reconstruct the

temperature history of the tropical oceans spanning the last several centuries, providing a better understanding of climate oscillations such as El Niño. The Sr/Ca ratio of corals has received particular attention, with claims of precision better than 0.5°C (1).

Such records are not without controversy. A coral skeleton is made of an inorganic mineral, aragonite (a form of calcium carbonate), but it is precipitated through a biological process that is not well understood. Furthermore, many corals used for paleotemperature reconstructions have algal symbionts that may affect the chemistry of the skeleton. This uncertainty has led some to question the reliability of these temperature reconstructions (2).

D. P. Schrag is at the Laboratory for Geochemical Oceanography, Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA. E-mail: schrag@eps.harvard.edu B. K. Linsley is in the Department of Earth and Atmospheric Sciences, State University of New York, Albany, NY 12222, USA. E-mail: blinsley@albany.edu

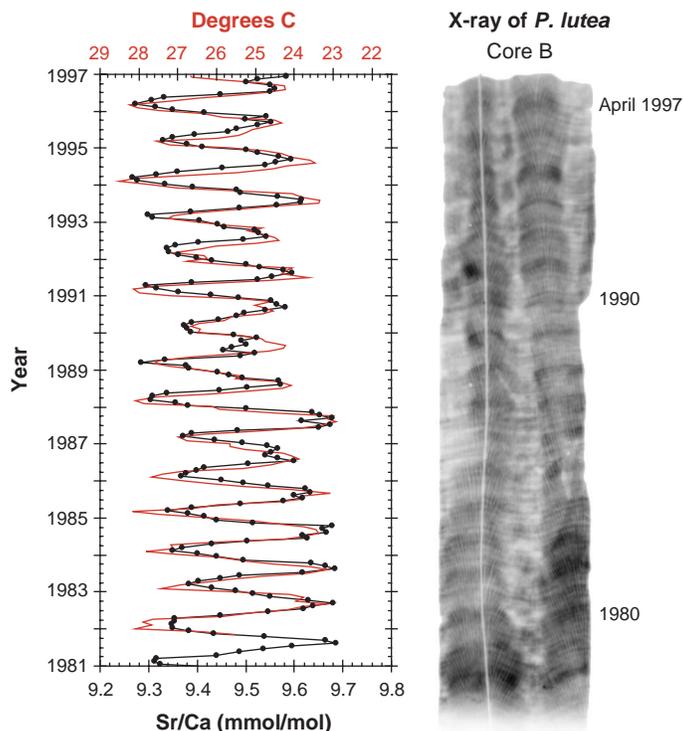
On page 331 of this issue, Cohen *et al.* (3) report further data that amplify these concerns. They have studied the incorporation of Sr into a species of coral, *Astrangia poculata*, that has both symbiont-bearing and non-symbiont-bearing forms and can grow far outside of the tropics. With an ion microprobe with 20- μm resolution, they analyzed spatial (and presumed temporal) variations in skeletal Sr/Ca ratios from the living tip of a coral calyx to a depth of 2.7 mm (about 4 years of growth) in two specimens, one with symbionts and one without, collected at the same place and time from Woods Hole, Massachusetts.

The authors conclude that algal symbionts living in the coral tissue have a marked effect on the degree to which Sr substitutes for Ca in the coral aragonite lattice. The Sr/Ca ratio of the non-symbiont-bearing form is higher and appears to reflect local sea surface temperatures (SSTs), similar to that of inorganic aragonite precipitated under known equilibrium conditions in a laboratory. The Sr/Ca ratio of the symbiont-bearing form does not resemble the SST record and appears to reflect changes in photosynthetic activity.

These results complement earlier work (4) that showed a similar phenomenon in a symbiont-bearing species between aragonite precipitated in the daytime and aragonite precipitated at night when photosynthetic activity had ceased. On the basis of these results, Cohen *et al.* argue that up to 65% of the Sr/Ca variability in a coral with algal symbionts is related to symbiont activity and does not reflect SST. They question the validity of most work on tropical paleotemperatures based on Sr/Ca ratios in corals, because most of these studies have analyzed species of the genus *Porites*, which has algal symbionts. They suggest that non-symbiont-bearing corals might provide more reliable SST reconstructions.

The work of Cohen *et al.* raises the specter of an old and continuing struggle in the field of paleoceanography—between those who want to use geochemical proxies (imperfect as they are) to answer questions about the history of the oceans and climate, and those who want to first understand completely the causes of the geochemical signals in biologically precipitated minerals. In the extreme, both views

are ridiculous. If we had never tried to use the geochemistry of shells to study the history of the oceans, we would know little about how climate has varied through Earth's history. But we cannot be completely confident in our reconstructions of past climates if we do not understand all the factors that may contribute to the chemical signals we measure.



A strong correlation. (Left) Comparison of monthly sea surface temperature (red) for the grid including Rarotonga (1° by 1° ; centered at 22°S , 160°W) and Sr/Ca measurements (black) analyzed at 1 mm intervals in a coral core (right) from a colony of *P. lutea* from Rarotonga.

The fundamental problem is that geochemists have tended to treat the shells of organisms as if they were inorganic minerals, controlled simply by the laws of thermodynamics. In a pioneering study of the Sr/Ca thermometer, Beck *et al.* (1) asserted that the relationship between temperature and Sr/Ca ratios in the coral was due to the temperature dependence of the partitioning coefficient between aragonite and seawater. Because the strontium concentration of seawater does not vary widely, they argued that the Sr/Ca ratio depends on temperature alone.

Most workers now appreciate that the mechanism of Sr/Ca incorporation into calcium carbonate skeletons and shells is not so simple. In coccolithophores, a calcareous algae and the dominant producer of calcium carbonate in the oceans, the Sr/Ca ratio of the shell depends on the growth rate of the algae (5). Similar effects have been observed in foraminifera, a calcareous zooplankton (6).

The temperature dependence of the Sr/Ca ratio in corals probably involves the substitution of strontium for calcium in the transport of ions across membranes to the sites of mineral nucleation and growth. Other processes may also play a role. Some calcareous organisms form their shells first within small vesicles as amorphous calcium carbonate, and then convert

this to aragonite or calcite at the site of shell formation (7). The amino acid sequences of glycoproteins, which are used by calcareous organisms as templates for their new shells, may also affect the shell chemistry (8).

Despite these concerns, the Sr/Ca thermometer in corals appears to work very well. Many studies have found a correlation between the Sr/Ca ratio and monthly SST of better than 0.8 (see the figure) (9, 10). At many sites, temporal variations in Sr/Ca ratio are reproducible between coral colonies, and they match instrumental records of climate variability at seasonal, interannual, and longer time scales. Many oceanographers find the correlation between Sr/Ca ratio and SST compelling enough to use it now, and are unwilling to wait until the detailed mechanisms of biomineralization are revealed.

But correlation is not causation. Cohen *et al.* probably go too far in suggesting that their study is applicable to all species of symbiont-bearing corals. Data from a coral living in Massachusetts in cold water with seasonal extremes in light intensity may not teach us much about the biomineralization of a coral living in warm water in the tropics. But it is a reminder that we still have much to learn.

References

1. J. W. Beck *et al.*, *Science* **257**, 644 (1992).
2. S. de Villiers, B. K. Nelson, A. R. Chivas, *Science* **269**, 1247 (1995).
3. A. L. Cohen *et al.*, *Science* **296**, 331 (2002).
4. A. L. Cohen, G. D. Layne, S. R. Hart, P. S. Lobel, *Paleoceanography* **16**, 20 (2001).
5. H. M. Stoll, D. P. Schrag, *Geochim. Geophys. Geosyst.* **1**, 1999GC000015 (2000).
6. D. W. Lea, T. A. Mashioita, H. J. Spero, *Geochim. Cosmochim. Acta* **63**, 2369 (1999).
7. S. Raz, S. Weiner, L. Addadi, *Adv. Mater.* **12**, 38 (2000).
8. Y. Levi, S. Albeck, A. Brack, S. Weiner, L. Addadi, *Chem. Eur. J.* **4**, 389 (1998).
9. C. Alibert, M. T. McCulloch, *Paleoceanography* **12**, 345 (1997).
10. B. K. Linsley, G. M. Wellington, D. P. Schrag, *Science* **290**, 1145 (2000).