such as cobalt. With this approach, arrays of magnetic nanodots with potential applications in data storage can be obtained (*13*).

Several other materials containing metallic units within potentially self-assembling polymer architectures are also being pursued. Star-shaped block copolymers with metal cores (**9**) have been prepared by controlled polymerization methods. These materials should exhibit rich and interesting supramolecular behavior (*14*). Block copolymers containing main chain and side chain nonmetallocene coordination complexes have been developed and are of similar interest (*15–17*).

Supramolecular self-assembly is not limited to metal-containing block copolymers. For example, Co polymers **10** form liquid crystalline phases in solution, whereas lamellar and irregular honeycomb-shaped morphologies have been identified in the solid state (*18*). Weak metal-metal interactions involving the heavy transition elements Cu, Ag, and Au have been used to guide the self-assembly of cyclic building blocks (**11**) into luminescent, superhelical fibers based on stacked structures (**12**) (*19*).

Metal-based polymers are emerging as interesting and useful materials. Further synthetic breakthroughs are still needed, but with the immense structural diversity and range of properties and intermolecular interactions made possible by the presence of metallic elements, supramolecular metallopolymers will be a particularly fruitful area of future research.

References

1. I. Manners, *Angew. Chem. Int. Ed. Engl.* **35**, 1602 (1996).
2. R. D. Archer, *Inorganic and Organometallic Polymers* (Wiley-VCH, Weinheim, 2001).
3. P. Nguyen, P. Gómez-Elipe, I. Manners, *Chem. Rev.* **99**, 1515 (1999).
4. D. J. Caruana, A. Heller, *J. Am. Chem. Soc.* **121**, 769 (1999).
5. R. Yoshida, T. Takahashi, T. Yamaguchi, H. Ichijo, *Adv. Mater.* **9**, 175 (1997).
6. R. P. Kingsborough, T. M. Swager, *Prog. Inorg. Chem.* **48**, 123 (1999).
7. D. A. Foucher, B. Z. Tang, I. Manners, *J. Am. Chem. Soc.* **114**, 6246 (1992).
8. M. J. MacLachlan *et al.*, *Science* **287**, 1460 (2000).
9. K. Kulbaba, I. Manners, *Macromol. Rapid. Commun.* **22**, 711 (2001).
10. L. I. Espada *et al.*, *Inorg. Organomet. Polym.* **10**, 169 (2000).
11. Y. Ni, R. Rulkens, I. Manners, *J. Am. Chem. Soc.* **118**, 4102 (1996).
12. J. Massey *et al.*, *J. Am. Chem. Soc.* **123**, 3147 (2001).
13. J. Y. Chang *et al.*, *Adv. Mater.* **13**, 1174 (2001).
14. C. L. Fraser, A. P. Smith, X. Wu, *J. Am. Chem. Soc.* **122**, 9026 (2000).
15. U. S. Schubert *et al.*, *J. Synth. Met.* **121**, 1249 (2001).
16. S. J. Hou, W. K. Chan, *Macromol. Rapid. Commun.* **20**, 440 (1999).
17. R. Tassoni, R. R. Schrock, *Chem. Mater.* **6**, 744 (1994).
18. W. Steffen *et al.*, *Chem. Eur. J.* **7**, 117 (2001).
19. M. Enomoto, A. Kishimura, T. Aida, *J. Am. Chem. Soc.* **123**, 5608 (2001).
20. J. A. Massey *et al.*, *J. Am. Chem. Soc.* **120**, 9533 (1998).
21. J. A. Massey, K. N. Power, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **122**, 11577 (2000).

PERSPECTIVES: ATOMIC CLOCKS

Raising the Standards

Patrick Gill

From the Global Positioning System to international timekeeping standards, accurate clocks play a fundamental role in science and technology. The higher the frequency of the oscillator used in the clock, the higher is the clock's accuracy. Quartz clocks operate at frequencies in the megahertz range, whereas atomic clocks are based on microwave absorptions in the gigahertz range. At the Sixth Symposium on Frequency Standards and Metrology, held from 9 to 14 September 2001 at the University of St. Andrews, Scotland, researchers presented tantalizing evidence for atomic clocks based on optical absorptions. These "optical clocks" offer even higher accuracies, providing a tool for better timekeeping and improved tests of the fundamental laws of physics.

The symposium opened with a review by N. Ramsey, regarded by many as father of modern frequency standards. In 1949, he developed the separated oscillatory field technique, in which an atomic absorption is probed by two pulses of radiation separated in time or space to give improved spectral resolution. This approach is still applied to both microwave and optical atomic frequency standards and underlies the atomic fountain (*1*).

In an atomic fountain, laser-cooled atoms are launched up a meter or so and fall back under gravity. In the process, they pass twice through a microwave probe region. Interference between the two time-separated probe fields allows the microwave absorption signal to be subdivided to provide higher resolution, achieving typical absorption features of ~1 Hz width. Cesium fountains of this kind are currently the most accurate clocks in the world. Some of these, together with slightly less accurate nonfountain clocks, comprise the international group of clocks that define Coordinated Universal Time (UTC), the official world time.

State-of-the-art fountains (A. Clairon, Laboratoire Primaire du Temps et des Fréquences, Paris) achieve clock frequency uncertainties of about 1 part in 10^{15} after averaging for a day or so but are eventually limited by small shifts in the center frequency of the absorption due to collisional perturbations between the cold atoms in the fountain. It should be possible to reduce this uncertainty to a few parts in 10^{16} for cesium and to 1 part in 10^{16} for cold rubidium fountains, which are affected much less by collisions.

For even faster clocks, we must go beyond microwave atomic clocks to optical clocks. A standard based on an absorption of much higher frequency (~10^{15} Hz in the optical, compared with ~10^{10} Hz in the microwave) but a similarly narrow experimental spectral width of ~1 Hz is much more monochromatic. The achievable frequency stability is proportional to the monochromaticity (or Q) of the absorption, so optical clocks promise better standards.

Direct optical analogs of the atomic fountain have not yet been demonstrated. Two groups have reported good progress (*2*, *3*) toward a neutral atom optical clock based on the weak Ca absorption at 657 nm, despite the relatively large natural linewidth of this absorption. Katori (University of Tokyo) (*4*) described the cooling of neutral Sr, which has a highly "forbidden" and hence very weak absorption at 671 nm with megahertz natural linewidth. Several groups plan to observe this high-Q transition in an optical fountain.

A high-Q optical frequency standard may also be achieved by probing a weak "forbidden" absorption in a single laser-cooled ion held in an electromagnetic trap. Experimental absorption linewidths for different trapped ion candidates discussed at the symposium include mercury (*5*), strontium (*6*, *7*), indium (*8*), and ytterbium (*9*, *10*). Most of these ions have "forbidden" absorptions with limiting natural linewidths between 0.1 and 3 Hz, offering Q values of ~10^{15}. Bergquist and co-workers (*5*) have achieved a linewidth of 6.7 Hz in Hg^+, not much above its natural width. Tamm *et al.* (*9*) have demonstrated a linewidth of 30 Hz for the 435-nm Yb^+ absorption. Other species have smaller natural linewidths but experiments have not yet reached these levels. In particular, the natural linewidth of the extremely weak Yb^+ 467-nm absorption is orders of magnitude below 1 Hz (*10*). In this case, the experimentally achievable linewidth will be limited not by the natural linewidth but by the probe laser linewidth.

The potential use of these high-stability optical absorptions as frequency standards

The author is at the National Physical Laboratory, Teddington TW11 0LW, UK. E-mail: patrick.gill@npl.co.uk

critically depends on our ability to compare, to high accuracy, their optical frequency values with the cesium microwave standard frequency. Until 2 years ago, complicated frequency chains of microwave sources and lasers were required to synthesize an optical frequency from the known microwave frequency. Since then, Haensch and co-workers (*11*, *12*), followed by Hall and co-workers (*13*), have pioneered a much easier method.

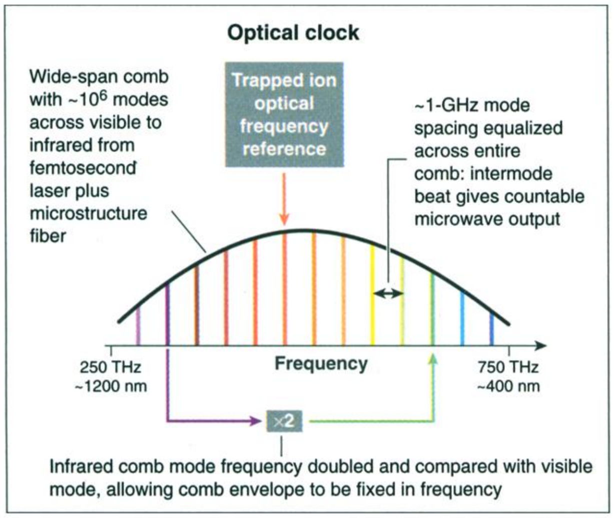
A train of femtosecond pulses from a self–mode-locked laser (corresponding to a small frequency comb extending a few percent on either side of the laser central wavelength) is launched into microstructured fiber in which air holes surround the fiber core. Considerable broadening occurs because of nonlinear interactions in the fiber, producing a broad comb from ~400 nm in the blue to ~1200 nm in the mid-infrared. By referencing the comb mode spacing to a high-accuracy microwave standard (ideally the cesium clock), one obtains an optical frequency ruler with equal frequency separations. By further ensuring that the complete comb is properly anchored relative to zero frequency, the comb can be used to measure any laser frequency within its bandwidth to the accuracy of the microwave standard.

Diddams and co-workers [National Institute of Standards and Technology (NIST)] have used this technique to measure the same optical frequency using two independent combs. They obtained agreement at the parts in 10^{17} level for averaging times of a few hundred seconds (*14*). Telle and co-workers [Physikalisch-Technische Bundesanstalt (PTB), Braunschweig] reported even better agreement for optical frequency ratio measurements, with uncertainties at the parts in 10^{19} level (*15*). Laboratories in Germany, USA, UK, and Japan have now used these combs to make absolute frequency measurements of cold atoms and ions and laser standards, with accuracies ranging between 1 in 10^{14} and 2 in 10^{12}. These accuracies are not yet as good as the comb comparison accuracies (*14*, *15*), largely due to limitations of the microwave or optical standards.

Diddams *et al.* recently demonstrated the first optical clock (see the figure) by referencing the comb to the Hg^+ optical absorption rather than to a microwave standard (*16*). A fractional frequency instability of 7×10^{-15} at 1 s has now been achieved, nearly an order of magnitude better than the best microwave standards. Thus, optical clocks are now a reality and capable of delivering a microwave output. This has important implications for the SI unit of time, which may be redefined in terms of an optical absorption at some stage over the next decade. Which ion, or atom, to choose remains an open question.

D. Wineland (NIST) suggested that ideas borrowed from quantum computing may improve trapped ion clocks. Entanglement of ions within a linear ion trap can reduce frequency instability to a limit inversely proportional to ion number N rather than $N^{1/2}$. This is more appropriate to microwave standards using strings of ions than to a trapped ion optical standard. He also suggested that separating the "logic" or cooling ion from the clock ion should allow simultaneous cooling and probing without interference and hence increased interrogation times.

S. Chu (Stanford University) presented the latest progress toward an improved measurement of α, the fine structure constant, using cold atom interferometry. This fundamental constant is a measure of the strength of the electromagnetic force holding atoms together and contributes to the magnitude of the absorption and emission frequencies of an atom. Agreement with the recommended value published by the international Committee on Data for Science and Technology (CODATA) was within 3.5 ppb. M. Kasevich (Yale University) highlighted the use of atom interferometers as sensors for rotation, acceleration, and gravity gradients, and their subsequent use in inertial guidance and navigation, and oil surveying. He showed that cold atom sensors provide nearly a factor of 100 increase in sensitivity for an atom interferometer gyro over a standard ring laser gyro used in commercial aerospace navigation. He noted that gravity-gradient–induced phase shifts will eventually be a limit on optical fountain clocks.



An optical clock. The optical clock comprises a narrow-linewidth laser locked to a cold trapped ion reference absorption, combined with the frequency comb from a femtosecond mode-locked laser, which is considerably expanded by nonlinear generation in a microstructure fiber. Clock outputs include about a million accurately known mode frequencies across the visible to infrared span and a microwave countable intermode beat.

With the rapid evolution and improvement of frequency standards and local oscillators, there is substantial interest in extending the limits of tests of fundamental physics. C. Salomon (Laboratoire Kastler Brossel, Paris) outlined experiments using the cold atom clock project scheduled for the international space station. In the microgravity environment, with projected clock accuracies of about 1 in 10^{16} over a few days, a range of tests on relativity [improved gravitational redshift and a search for time variation of α and for speed of light (*c*) anisotropy] are possible.

S. Schiller (University of Dusseldorf) and M. Tobar (University of Western Australia) described experiments to check for anisotropy of *c* using an infrared laser and microwave reference source, respectively. In the infrared case, the laser is frequency-locked to a resonance of a stable optical cavity. If *c* is anisotropic, the frequency of the laser will change as the cavity is rotated because the cavity resonance to which it is locked depends on *c*. These cavities have already improved our knowledge of the experimental limit to the test by a factor of three.

L. Maleki (Jet Propulsion Laboratory) took relativity tests even further with a proposal for a NASA triple-clock mission to the Sun. The clocks, based on different ions, would experience common nongravitational perturbations but differential gravitational perturbations. As the probe approached a few solar radii, there would be greater sensitivity to gravitational redshift and time variation of α.

The emergence of frequency standards with reproducibilities of 1 in 10^{15} and better promise unprecedented time transfer capabilities for Earth-based and deep-space network satellite navigation and substantially improved tests of physics. The major change since the Fifth Symposium in 1995 has been the arrival of an optical clockwork using femtosecond lasers, enabling rapid progress toward high-*Q* optical clock developments over the next few years. For the next decade, we can project clock capability on the order of 1 in 10^{18}, with major impacts in physics and metrology.

References and Notes

1. M. A. Kasevich, E. Riis, S. Chu, R. G. DeVoe, *Phys. Rev. Lett.* **63**, 612 (1989).
2. F Riehle *et al.*, *IEEE Trans. Instrum. Meas.* **48**, 613 (1999).
3. C. W. Oates, F. Bondu, R. W. Fox, L Hollberg, *Eur. Phys. J.* **D7**, 449 (1999).
4. H. Katori, T. Ido, M. K. Gonokami, *Atomic Phys.* **17**, 382 (2001).
5. R. J. Rafac *et al.*, *Phys. Rev. Lett.* **85**, 2462 (2000).
6. J. E. Barnard *et al.*, *Phys. Rev. Lett.* **82**, 3228 (1999).
7. G. P. Barwood *et al.*, *IEEE Trans. Instrum. Meas.* **50**, 543 (2001).
8. Th. Becker *et al.*, *Phys. Rev. A* **63**, 051802 (2001).
9. C. Tamm, D. Engelke, V. Buehner, *Phys. Rev A* **61**, 053405 (2000).
10. M. Roberts *et al.*, *Phys. Rev. A* **62**, 020501(R) (2000).
11. J. Reichert, R. Holzwarth, T. Udem, T. W. Haensch, *Opt. Commun.* **172**, 59 (1999).
12. R. Holzwarth *et al.*, *Phys. Rev. Lett.* **85**, 2264 (2000).
13. S. A. Diddams *et al.*, *Phys. Rev. Lett.* **84**, 5102 (2000).
14. S. A. Diddams, L. Hollberg, L.-S. Ma, L. Robertsson, *Opt. Lett*, in press.
15. J. Stenger, Ch. Tamm, N. Haverkamp, H. R. Telle, preprint available at http://xxx.lanl.gov/abs/physics/0108062.
16. S. A. Diddams *et al.*, *Science* **293**, 825 (2001).

17. The author would like to acknowledge the numerous other excellent papers presented at the symposium. It has been impossible to mention all these in this short article given here.

PERSPECTIVES: GEOLOGY

North American Devastation or Global Cataclysm?

Tim Flannery

Sixty-five million years ago (Ma), our planet was struck by a carbonaceous meteorite (*1*), a relic from the formation of the solar system. This errant piece of celestial real estate was around 10 km in diameter and was traveling at 90,000 km/hour, in a trajectory from the southeast. It struck the southern margin of North America, in what is now Yucatan but was then a shallow, tropical sea. The impact released as much energy as 100 million megatons of high explosives. The glancing blow, much like a chip shot in golf, sent a divot of debris straight into the heart of North America (*2*). It was far more devastating than a perpendicular collision would have been, releasing thousands of times more energy.

This scenario, developed over the past few decades, has led paleontologists to suspect that the extent of damage suffered by North America's ecology was unique. The continent's bountiful fossil deposits have indeed revealed extensive evidence of ecological devastation. The Gulf Coast was swept almost clean of life, and evidence of giant tsunamis exists. The dinosaurs perished, as did many smaller life forms, including most mammals. North America's forests were flattened, and four out of five plant species were driven to extinction (*3*).

It has been suggested that for decades or centuries after the impact, much of the continent resembled a vast muddy field devoid of live. Many of the life forms that eventually recolonized the land are thought to have come from refuges in the Arctic north—as distant as you can get from the impact point and still be in North America. Others came from other continents and perhaps from especially sheltered locations such as the lees of mountain ranges.

The author is in the South Australian Museum, Adelaide, 5000 Australia. E-mail: flannery.tim@saugov.sa.gov.au

The recovery of North America's ecology was slow. For thousands of years, much of the continent was little more than a field of ferns. The most dominant of the handful of species that reclaimed the wasteland belonged to the genus *Stenochlaena*, which includes the Malayan climbing fern so beloved of greenhouse owners (see the figure). The same fern covered the bared ground of Krakatoa after the 1883 eruption, where it remained dominant for decades (*4*) and formed thickets of such impenetrability that biologists examining the return of life to the island became lost in them.

Malayan climbing fern.

"Fern spikes"—extremely high abundances of fern spores preserved in sediments where evidence of other plants is scarce—are now widely recognized as evidence of catastrophic ecosystem disruption. They are characteristic of North American and far-eastern Eurasian sediments dating to just after the meteorite impact of 65 Ma. The fact that sediments of a similar age from the Southern Hemisphere did not show fern spikes has been regarded as prime evidence that the celestial chip shot uniquely devastated North America. Indeed, (rather limited) pollen and spore data indicated that southern forests suffered remarkably little extinction or disturbance at the time (*5*).

Zoogeographic studies have tended to support this view, indicating that the Southern Hemisphere may have acted as a refuge for certain groups, of ancient organisms, such as araucarian conifers and ratites (emus, ostrich, and rheas), which have predominantly southern distributions. Unfortunately, very little is known about the relevant part of the fossil record of much of the Southern Hemisphere. In places such as Australia and Antarctica, clear evidence of how the impact affected land animals has remained elusive. On the basis of the fossil record of these regions alone, it is not even clear whether the dinosaurs became extinct there at the time of the impact: The fossil record is so poor that we simply do not know.

On page 1700 of this issue, Vajda *et al.* (*6*) provide the first clear evidence for a fern spike from the Southern Hemisphere. It comes from the South Island of New Zealand, about as distant from the site of the impact as it is possible to be. The pollen from this remote location speak eloquently of ecological devastation on the same order as in North America.

Before the meteorite impact, the area around what is now Moody Creek, New Zealand, supported a swamp forest rich in ferns, southern conifers, and flowering plants. In contrast, above the layer marking the impact, fern spores dominate, making up around 90% of the pollen assemblage. Flowering plants, which would dominate forests worldwide a few million years later, vanish from the local record, and the conifers suffer a serious decline. The devastation does not seem to be quite as complete as it was in North America but is still awesome. It will probably force a rethinking of some zoogeographic theories and of the overall impact of the asteroid strike.

Vajda *et al.*'s evidence also reveals some curious longer term consequences of the impact. After the initial devastation, the New Zealand data reveal a pattern of long-term environmental disruption that may relate to a massive injection of CO_2 into the atmosphere. Rapid oscillation between warmth- and cool-loving species and the advance and retreat of tree ferns occurred for at least a million years after the impact, indicating that once CO_2 levels in the atmosphere are disturbed, they take quite a while to return to

CREDIT: CARIBBEAN GARDENS, WWW.NAPLESZOO.COM