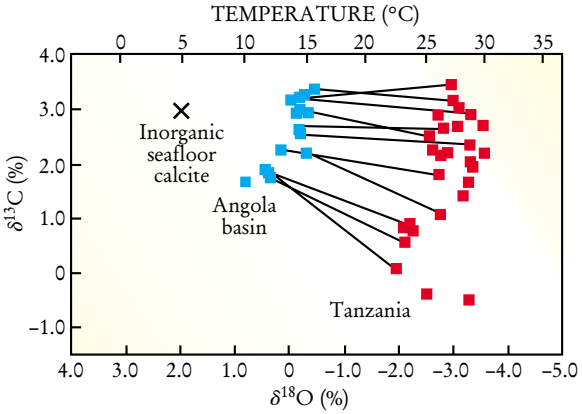

FIGURE 2. ISOTOPIC COMPOSITIONS of two different samples of fossil planktonic foraminifera shells suggest conflicting tropical sea surface temperatures 45 million years ago. The oxygen-18 excess, δ^{18}O, relative to a laboratory calcite standard, is plotted for various species against the carbon-13 excess, δ^{13}C. Common species are connected by lines. δ^{18}O serves as a paleothermometer. The well-preserved Tanzanian sample (red) suggests a sea about 15°C warmer than does the Angola basin sample (blue), which is compromised by posthumous recrystallization on the ocean floor. Variations within each sample reflect the different depths at which species floated. The recrystallization metamorphosis appears to converge on a point corresponding to inorganic calcite made entirely on the ocean floor. (Adapted from ref. 2.)

isotopic fractions of ^{18}O and ^{13}C are given as percentages in excess of the isotopic fractions in a convenient laboratory calcite standard—the so-called Vienna Pee Dee Belemnite standard. (The Pee Dee is a river in South Carolina.)

The ^{18}O excess, corrected for the absence of polar ice caps at the time, translates into the temperature at which the shells were formed. The more ^{18}O, the colder the water. Assuming that the range of temperatures in the pristine Tanzanian sample reflects the different depths at which the various floating species resided, the authors take the highest temperature—about 30°C—to have been the temperature at the surface. The traditional Angola basin sample in figure 2, presumably corrupted by evident recrystallization, suggests a much chillier surface temperature of about 16°C.

The ^{13}C range of the Tanzanian sample is another manifestation of the vertical range of the habitats of different species. The lines connecting the same species in the two samples shows the ^{13}C range shrunk to half its pristine width. The argument that both the oxygen and carbon isotopic changes are due to recrystallization is strikingly bolstered by the observation that the changes appear to be converging on the point in the figure that represents the expected isotopic composition of purely inorganic calcite precipitated at the seafloor.

Because the traditional Angola basin sample is about halfway between the pristine sample and the convergence point on this plot of carbon and oxygen isotopic fractions, the Pearson group concludes that roughly half the calcite in the fossil microshells of the traditional sample has been replaced, over the eons, by recrystallized material.

The paper concedes that the two samples may have been somewhat different from the start. Unlike the planktonic foraminifera of the Angola basin, those in the Tanzanian sample lived in shallower coastal waters. Nonetheless, the authors argue, the new results should help to free the discussion of global warming from the cool-tropics paradox that has bedeviled paleoclimatology. "For those parts of the late Cretaceous and Eocene epochs that we have sampled, tropical temperatures were at least as warm as they are today, and probably several degrees warmer."[2] If it were otherwise, we would have trouble believing any of the CO_2 greenhouse models.

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Can Polymeric Carbon-60 Be Magnetic?

A research team has polymerized carbon-60 at high pressures and temperatures and reported[1] that the product exhibits ferromagnetic properties at surprisingly high temperatures: near 500 K. Naturally, such an announcement elicits skepticism, because the constituent molecules have no magnetic moments and also because there have been premature claims of ferromagnetic behavior in other organic polymers.[2]

The experimenters—who hail from Russia, Sweden, Germany, and Brazil—were themselves duly cautious about this serendipitous result, discovered while they were looking for superconductivity. After spending two years ruling out spurious effects from possible impurities, the collaborators decided to publish. "They've made a reasonable argument for ferromagnetism," comments Joe D. Thompson of Los Alamos National Laboratory, "and produced compelling evidence that the material should be studied further."

If a recent experiment is confirmed, theorists will be challenged to explain the evidence for weak ferromagnetism in a compound made solely of carbon.

Further studies will be motivated by two factors. One is the intrinsic curiosity about what might cause magnetic behavior in a structure made solely of carbon, an atom that has no unpaired electrons.

The second factor is interest in possible applications. Considerable research is already focused on producing molecule-based magnets, fueled by the ease with which such magnets might be made and the ability to modulate their properties by synthetic chemistry techniques. Some researchers have looked for magnets that have no metallic atoms and that hence might be less dense. However, as team member Tatiana Makarova of the Ioffe Physico-Technical Institute in St. Petersburg, Russia, cautions, "the application of this material is only a dream. The samples are very expensive because we start with a costly commercial fullerene and use nearly the same technology as that for making artificial diamonds."

Magnetism was seen in a metal-free organic compound about ten years ago,[3] but it had a very low Curie temperature

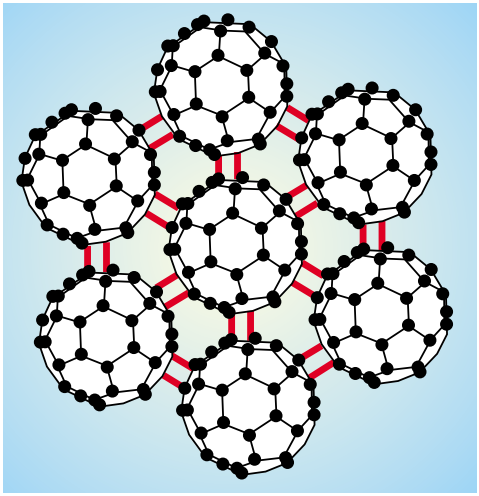

FIGURE 1. RHOMBOHEDRAL CARBON-60 consists of planes of soccer-ball shaped molecules arranged with hexagonal edges linked to one another by double bonds (red).

T_c (the temperature above which magnetization sharply drops). About the same time, a metal-free, fullerene-based molecule was found to exhibit weak ferromagnetism[4] with T_c = 16 K. In that material, C_{60} molecules are intercalated with strong organic donor molecules and receive electrons from them. The newly reported C_{60} material has attracted attention because it has a high T_c without doping.

Magnetic behavior in fullerenes involves electrons from an unfilled *p* band. That's rather new, compared with *d*- and *f*-band magnetism seen in conventional transition-metal and rare earth magnets.

The behavior of the newly discovered polymerized C_{60} is similar to that of the inorganic compound calcium hexaboride, which exhibits weak ferromagnetism and a high Curie temperature.[5] Both materials have surprisingly low concentrations of spins, which must somehow become strongly coupled. Also, both are close to a metal–insulator transition. Perhaps theorists will find a connecting thread.

Formed under pressure

The reported magnet is a polymerized form of C_{60} that consists of two-dimensional layers of the "buckyballs" in a highly oriented rhombohedral phase, as shown in figure 1. The polymer samples were formed under high pressure (6 GPa) and high temperatures (around 1000 K) by researchers at the Institute of High Pressure Physics in Troitsk, Russia. The sample properties were measured by experimenters from collaborating institutes: the University of Umeå in Sweden (where Makarova is now a visiting researcher); Ilmenau Technical University and Leipzig University, both in Germany; and the University of Campinas in Brazil. Although formed under extreme conditions, the materials are subsequently handled at normal pressures and temperatures.

The collaborators also looked at samples of similarly produced one-dimensional orthorhombic polymers and two-dimensional tetragonal polymers, but only the rhombohedral C_{60} manifested ferromagnetic behavior. The temperature dependence of the saturation magnetization, plotted in figure 2, suggests that T_c = 500 K. The magnetization has a hysteresis loop, with the remanent magnetization also plotted in figure 2. The rhombohedral C_{60} polymers are stable and have shown no degradation during the two years they've been studied.

All samples have the same T_c, Makarova reports. However, the saturation magnetization varied from sample to sample. Throughout preparation, the researchers were extremely careful to avoid impurities, reporting an upper limit of 22 parts per million for the concentration of impurities in their samples. That amount, they estimate, should contribute no more than a few percent of the magnetism they observe. Samples with higher impurity concentrations show smaller saturation magnetism, they say.

Possible mechanisms

The measurements indicate that, on average, only about one in a hundred C_{60} molecules has an unpaired electron in rhombohedral C_{60}. Any explanation of the magnetic behavior must explain how far-flung spins can become strongly coupled. But the spins may be concentrated in certain domains, and the experimenters report some evidence of a domain structure. In that case, any models of the magnetism must explain why the electrons remain unpaired when carbon atoms with unpaired spins have a strong propensity to form spin-pairing covalent bonds.

Makarova and her colleagues suggest that the material has defects, with one carbon sphere slightly rotated, disrupting the normal bonding between hexagon–hexagon edges of neighboring buckyballs. The resulting bonds might produce a conduction electron that could be the source of itinerant magnetism (so called because the electron is free to travel).

Alternatively, the researchers speculate, the mechanism may stem from self doping caused by destruction of the rhombohedral C_{60} structure: The magnetic phase appears at temperatures just below the stability limit for the fullerene cages, although Raman and x-ray analyses do not detect any presence of wrecked fullerenes.

If the magnetism does indeed stem from defects in the rhombohedral C_{60} structure, speculate theorists Marvin Cohen and Steven Louie of the University of California at Berkeley, the effect may not be unique to this material but might show up in other forms of carbon as well.

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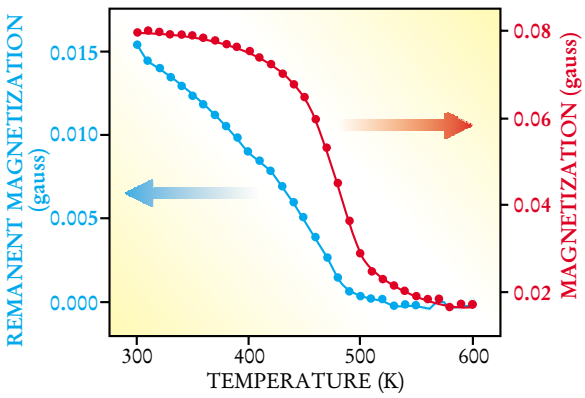

FIGURE 2. FALLOFF of magnetization for rhombohedral carbon-60 (red), measured at 0.2 tesla, indicates that the Curie temperature is around 500 K. Remanent magnetism (blue) is the magnetism at zero magnetic field determined from hysteresis curves. (Adapted from ref. 1.)

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