The different growth response of C₃ and C₄ species to elevated CO₂ concentrations has important consequences. Earth system models assume a positive relationship between C₃ plant growth and CO₂ concentration, an assumption that Reich et al.’s results challenge. As a result, Earth’s future carbon-sequestration potential could be far lower than predicted by these models, because most vegetation is C₄ dominated. Furthermore, agricultural production involving C₃ plants such as wheat, rice, and temperate pasture species might not increase with the rising CO₂ concentration. It is also likely that introduced plant species, many of which are C₄ plants, will increase in vigor and become an even greater problem than they are now. Finally, ecosystems in which C₃ and C₄ species grow together are likely to change as the competitive balance alters, with consequences for forage supply and its nutritional quality (5). Increased growth rates of C₃ species are even more likely in the future because of global warming; the efficiency of C₃ photosynthesis declines with increasing temperature, but this does not occur in C₄ plants, making them more competitive in warmer conditions (9).

Reich et al. were only able to make their discoveries because their experiment ran uninterrupted for two decades. This is extremely rare globally, showing that funding for long-term global-change experiments is a necessity. The experiment relied on a concerted effort to continually apply for funding, given the largely short-term nature of funding cycles. Because most funding agencies place a value on innovation and novelty, scientists are forced to come up with new reasons and new measurements to keep existing experiments running. The tenacity of Reich et al. and their ability to keep their experiment running has overturned existing theory and should lead to changes in how we think about and prepare for Earth’s future. Who knows how many processes remain undiscovered because of the unwillingness of funding agencies to support long-term experiments?  

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MATERIALS

On the quest for the strongest materials

Diamond nanoneedles have strength approaching the theoretical maximum

By Javier Llorca

The strength of a material is a measure of its ability to withstand a load without breaking. Scientists in search of the strongest materials have recently turned their attention to nanomaterials, which have few of the defects that typically reduce a material’s strength. On page 300 of this issue, Banerjee et al. (1) show that when nanoscale single-crystal diamond needles are elastically deformed, they fail at a maximum local tensile stress of ~89 to 98 GPa, which is very close to the theoretical limit for this material.

The maximum possible strength that a material can have in either tension or shear is controlled by the fracture of the interatomic bonds and is on the order of 10% of the elastic or shear moduli, respectively. However, it is difficult to achieve these strengths in practice because defects in the solid will lead to inelastic relaxation or brittle fracture well before the atomic bond can be stretched to the theoretical limit. Maximum elastic tensile strains supported by bulk solids are between 0.2 and 0.4%, whereas tensile strains of up to 4% have been measured in micrometer-size whiskers (2). Recent progress in nanomaterial synthesis and nanomechanical testing has opened the possibility of probing the strength of material systems that are practically free of defects (3). In parallel, atomistic simulations based on density-functional theory and molecular dynamics can predict accurately the fracture strength of perfect crystals and allow the influence of defects and free surfaces on this property to be explored.

Because the carbon-carbon bond is the strongest in nature, the search for the strongest material has focused on one-dimensional carbon nanotubes and two-dimensional graphene nanoscale objects (see the figure). Experimental results and ab initio calculations indicate that the elastic modulus of carbon nanotubes and graphene is ~1 TPa (4–6). The strengths measured in both types of nano-objects are thus very close to the theoretical limit (see the figure). By contrast, the reported tensile strength of bulk cubic diamond is much smaller (~10 GPa) (7). These differences in strength have been partially attributed to brittle fracture from defects during tensile deformation of bulk samples. Higher tensile strengths (up to 20 GPa) for diamond have been reported from Hertzian indentation tests (8), but these values must be treated with caution because of the uncertainties associated with the spherical indentation to determine the tensile strength. Regardless of the experimental technique, diamond fractures by cleavage along the (111) plane, which has the lowest fracture energy. The strengths reported by Banerjee et al. (which correspond to a tensile strain of ~9%) are very close to the theoretical limit for diamond and to the maximum strength values reported for carbon nanotubes and gra-
The authors applied these large elastic strains by bending the nanoneedles (see the image); fracture was not triggered at smaller strains because of the small volume of the nanoscale needles, the paucity of defects, and the smoothness of the surface, which was produced with careful reactive ion etching from a (111)-oriented diamond film produced by means of chemical vapor deposition. Fracture occurred through cleavage along (111) planes, and the strength measured was supported by combined density-functional and molecular-dynamics simulations at 300 K. The latter predicted a maximum critical strain of 13%, corresponding to a tensile strength of 130 GPa. These results open the possibility of modifying fundamental properties of diamond through elastic strain engineering (9). The properties of any crystalline material depend on the lattice parameters, which are dictated by the electronic structure. Large elastic deformations (around 10%) modify the electronic structure, leading to changes in electronic, magnetic, catalytic, and other properties that could be tuned as a function of the applied strain tensor. This concept has been used to enhance the drive current in complementary metal-oxide semiconductor technology by improving the electron and hole mobility through lattice strainning (10). Other applications include the transformation of paramagnetic materials into ferromagnetic ones (11) and the manipulation of mechanical coupling so as to increase catalytic activity (12).

However, the elastic strains applied to modify the properties in all these cases were much lower (below 5%) than those reported for carbon nanotubes, graphene, and diamond needles, which were closer to 10%. Changes in properties should increase with the elastic strain and, as postulated by Gilman (13), the electronic structure should be drastically modified near the critical bond-breaking strain, leading to unusual or singular chemical and physical properties. Thus, exploration of the effect of very large elastic strains on the properties of crystalline solids may lead to the discovery of new or unexpected behaviors. Many applications of elastic strain engineering require the elastic strains to be distributed over a substantial area or volume. This can be achieved by means of epitaxial growth (10) or severe plastic deformation (11) in the case of bulk materials. However, this task is more challenging in the case of nanoscale objects because it is difficult to maintain the mechanical continuity between these objects. For instance, the maximum strengths reported for carbon nanotube fibers, which are made up of bundles of nanotubes, are ~2.5 GPa, which is well below the values reported for single carbon nanotubes (see the figure) (14–15). Elastic straining techniques that can be applied to bulk materials, such as the elastic bending of nanoneedles in Banerjee et al., can potentially be extended to large surfaces and different materials. Thus, this strategy can be used to explore the effect of large elastic strains on chemical and physical properties of diamond and other solids.

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A nanoindenter tip bends a diamond nanoneedle.