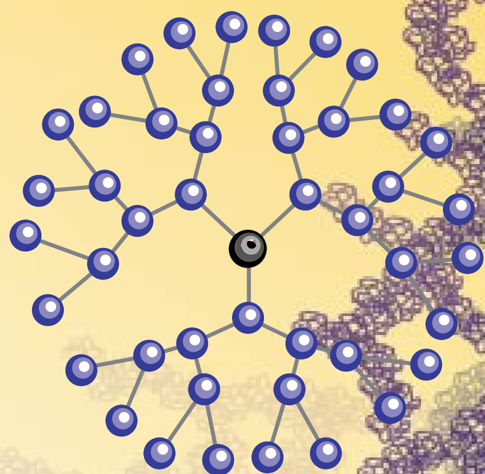
A Predictable Structure for Aerogels



A Livermore scientist needs a support system with virtually no mass for a project he is working on. He is certain to end up using an aerogel. No mass at all is an impossibility, but aerogels come pretty close. Researchers at Livermore have already synthesized a silica aerogel only twice as dense as air.

Sometimes called frozen smoke, aerogels are open-cell polymers with pores less than 50 nanometers in diameter. In a process known as sol-gel polymerization, simple molecules called monomers suspended in solution react with one another to form a sol, or collection, of colloidal clusters. The macromolecules become bonded and cross-linked, forming a nearly solid, transparent sol-gel. An aerogel is produced by carefully drying the sol-gel so that the fragile network does not collapse.

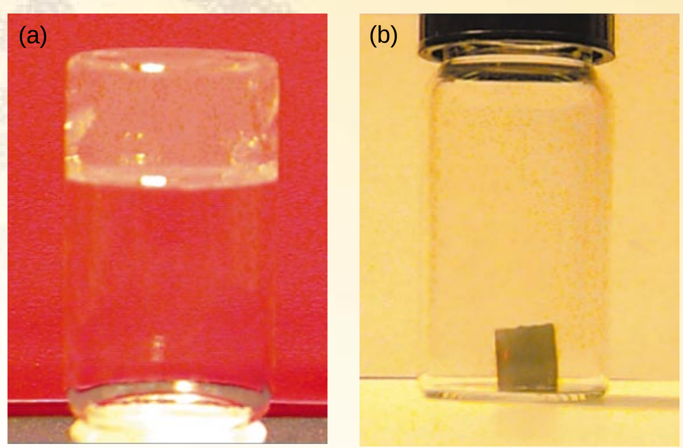
The complicated, cross-linked internal structure gives aerogels the highest internal surface area per gram of material of any known material. Aerogels also exhibit the best electrical, thermal, and sound insulation properties of any known solid.

For about the last 15 years, Livermore has been developing and improving aerogels for national security applications. Livermore scientists have also synthesized electrically conductive inorganic aerogels for use as supercapacitors and as a water purifier for extracting harmful contaminants from industrial waste or for desalinizing seawater. For a time, Livermore was involved with a NASA project in which an aerogel was to be installed in a satellite to collect particles of meteorites as they flew by.

Given aerogels' many sterling qualities, one would expect to find them in use everywhere. Indeed, there has been major industrial interest in aerogels. However, using them in everyday applications presents practical problems, specifically the cost of fabrication and processing. Several years ago, a Livermore team won an R&D 100 Award for developing a new fabrication method that was faster and cheaper. (See *S&TR*, December 1995, pp. 22–25.)

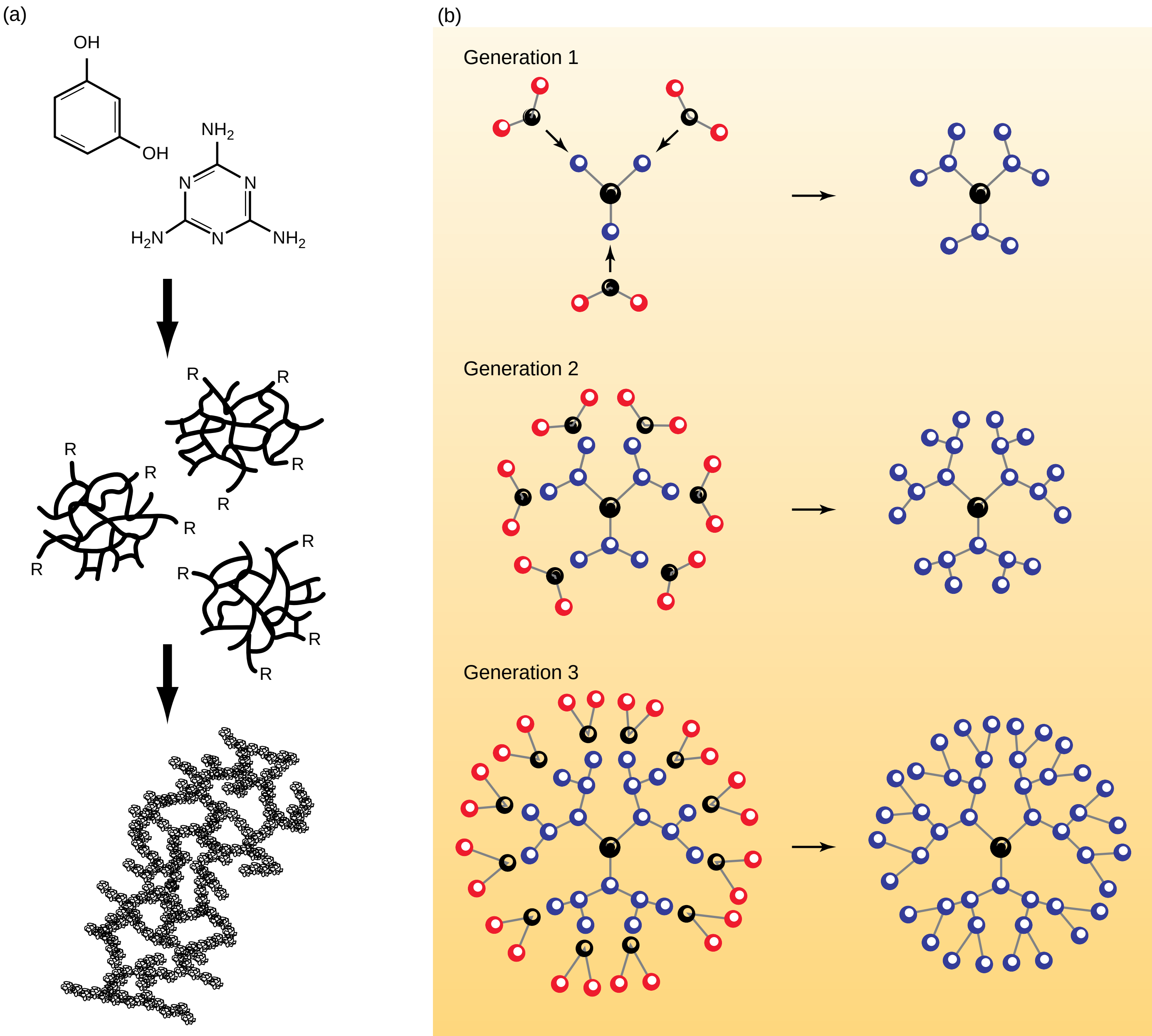
But another problem still stood in the way. Sol-gel polymerization is a bulk process with no way to control the size of the sols or the way they come together. The structure and density of the final aerogel are dictated to some extent by the conditions during polymerization such as temperature, pH, type of catalyst, and so on. But with current fabrication methods, the aerogel's structure cannot be controlled at the molecular level.

Chemist Glenn Fox is leading a project at Livermore that aims to bring more control to the design and synthesis of



A sol-gel polymer (a) in the sol-gel stage and (b) after it has been dried. This particular sol-gel polymer uses dendrimers and is called a dendrigel.

organic aerogels. “Laboratory programs would find many more uses for aerogels if only we could fabricate them to precise specifications,” Fox says. “They could be used as sensors for biological agents, in environmental remediation, as catalysts for chemical reactions, or in experiments on the National Ignition Facility. Aerogels have also been of interest for insulating appliances and homes and for a plethora of other uses. Nanostructured materials are attracting increased scientific and practical interest. But control of the material’s structure all the way down to the



(a) Traditional organic aerogels start out as either resorcinol or melamine combined with formaldehyde. There is no way to control how the cluster formation takes place, and the end result is a cross-linked polymer resembling a string of pearls. In (b), with dendredic polymers, the design and synthesis of reactive, multifunctional monomers can be tailored, with specific sites on the molecules activated for cross-linking. The formation and properties of the resulting gel can thus be carefully controlled.

molecular level is needed first.” Fox and a small team obtained funding from the Laboratory Directed Research and Development program to apply a relatively new polymerization method to this problem.

Starting with a Tree

Dendrimers are highly branched, treelike macromolecules that can be synthesized “generationally” to produce perfectly regular structures (*dendron* is the Greek word for tree). Conventional polymers are chains of differing lengths with a range of molecular weights and sizes, while dendrimers have a precise molecular size and weight. Large, multigenerational dendrimers tend to form tidy spherical shapes with a well-defined structure that makes them particularly strong.

Fox’s team has begun applying dendritic methodology to the creation of sol-gels and aerogels in the hope of achieving structural control. The Livermore team is one of the first to use dendritic technology in the organic sol-gel process.

Says Fox, “We are trying to understand and control the sol-gel polymerization process on a molecular level. Using dendrimers allows us to separate the clustering and gelling processes when an aerogel is being formed, something that has not been possible before. If we succeed, the payoff for Laboratory programs will be extremely important. We may be able to script the physical properties of the aerogel or build specific tags on molecules in a uniform way.”

Organic aerogels are currently formed by combining either resorcinol (1,3-dihydroxybenzene) or melamine (2,4,6-triaminotriazine) with formaldehyde. Fox’s team is synthesizing and experimenting with a whole collection of new starting materials that are being assembled into dendrimers. Some are based on resorcinol to take advantage of its well-documented reactive attributes. Another set of new dendrimer systems with rigid cores could give the resulting aerogel greater structural efficiency, improving the ease of processing and lowering the cost of aerogel production. Other experiments involve the synthesis of new organometallic materials and ways to evenly disperse metal ions in an organic aerogel.

These tailored dendritic monomers are being combined with preformed, dendritic, sol-gel clusters whose outer surface has been coated to react with the monomer. Two kinds of dendrimer precursors have been studied, amino-based and aromatic-based, each having different advantages. Amino-based dendrimers are available commercially and have been studied extensively. Reactants can be added relatively easily to their outer surfaces to “functionalize” them, prompting them to cross-link as desired. Benzyl ether dendrimers, on the other hand, are structurally similar to the colloidal sols of the resorcinol–formaldehyde mix. They are not commercially available but can be prepared readily in the laboratory.

Controlling the size and composition of the clusters formed during gelation as well as the type of cross-linking involved should give Fox’s team a new-found architectural control over aerogels. Analysis of the structures with infrared spectroscopy, nuclear magnetic resonance spectroscopy, and mass spectroscopy will provide a better understanding of how chemistry can affect the composition and structural efficiency of these nanostructured materials.

—Katie Walter

Key Words: aerogels, dendrimers, polymers.

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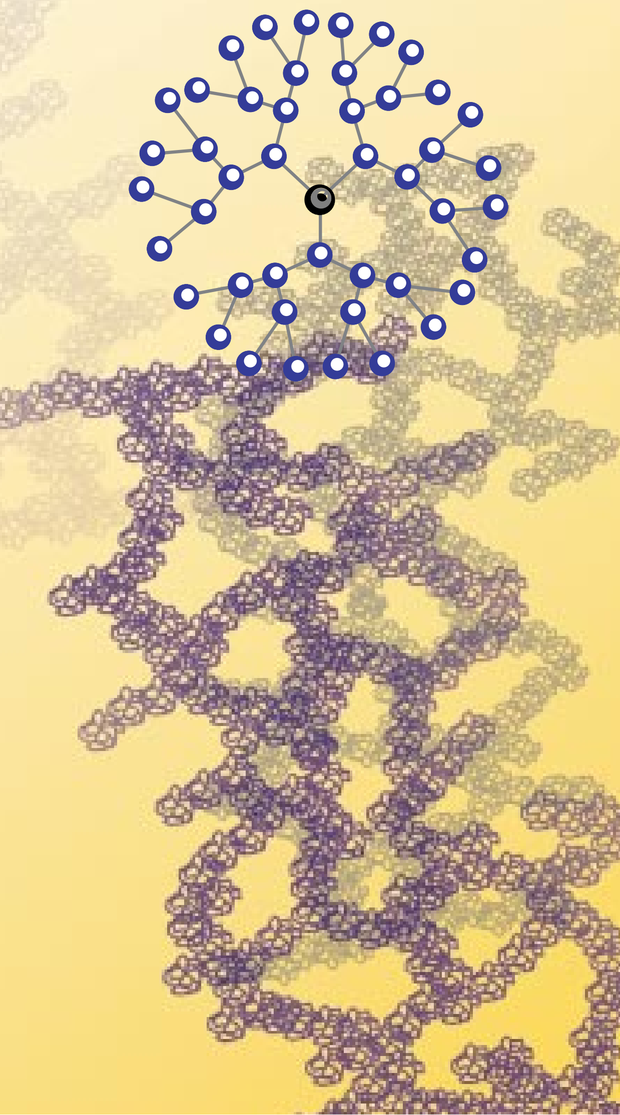


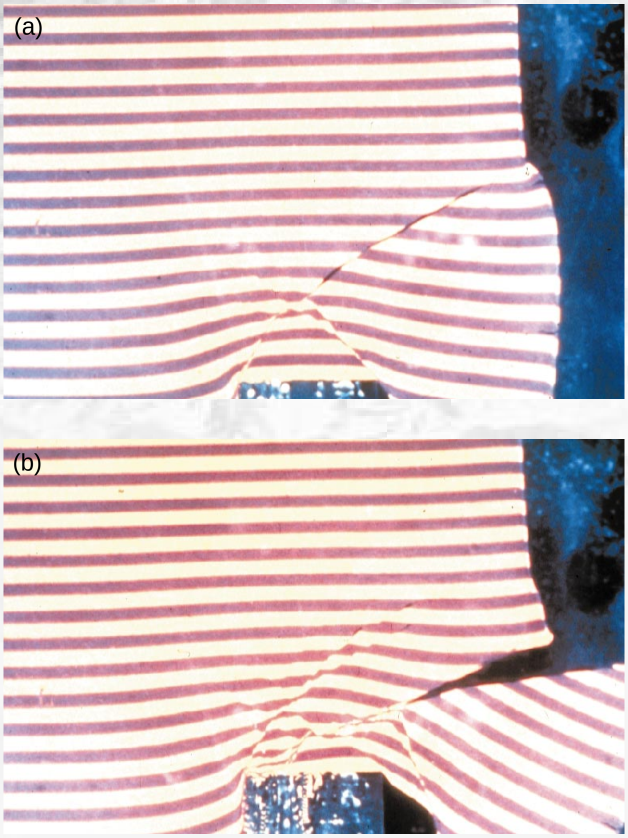
Tibet

Where Continents Collide

THE Himalayas get their height from India, and we aren't talking about genes. About 50 million years ago, the Indian subcontinent collided with Asia, and the two continents continue to converge at a rate of about 5 centimeters every year. The ongoing collision has been violent enough to push up the Himalayas, shove Southeast Asia further and further southeast, and perhaps most impressively, raise the Tibetan Plateau—a landmass as large as two-thirds of the lower 48 states—to an average elevation of 5,000 meters. Uplift of the Tibetan Plateau has been linked to intensification of the Asian monsoon and, by virtue of its erosion products, to gradual changes in seawater chemistry over long time periods. The Indo-Asian collision thus provides not only a natural laboratory for studying the mechanical response of Earth to plate tectonic forces but also an opportunity to explore the links between tectonics, climate, and ocean history.

Livermore geophysicists Rick Ryerson, Jerome van der Woerd, Bob Finkel, and Marc Caffee, along with collaborators from the University of California at Los Angeles and from Paris and Beijing, have been studying this terrestrial wrestling match for several years, making the first-ever measurements of long-term movement along large faults in northern Tibet. The Kunlun, Altyn Tagh, and Haiyuan faults are strike-slip faults that allow blocks of Earth's crust to slide past one another, often with disastrous consequences. All of these faults have experienced large earthquakes ranging in intensity from 7.5 to 8.7.

The function of the faults is a subject of considerable geophysical controversy. Faults may define major discontinuities in Earth's lithosphere (the outer 100 kilometers of the crust that define the plates in plate tectonics) and thus absorb a significant portion of the convergence between India and Asia. Or they may be shallow features that play a secondary role in a more fluid lithosphere. Some research indicates that the Kunlun and Altyn Tagh faults extend to the base of Earth's lithosphere, suggesting that they indeed define continental plates. A first step in deciding the faults' extent and function is to obtain accurate, long-term slip rates at enough sites along the faults to characterize their large-scale behavior.

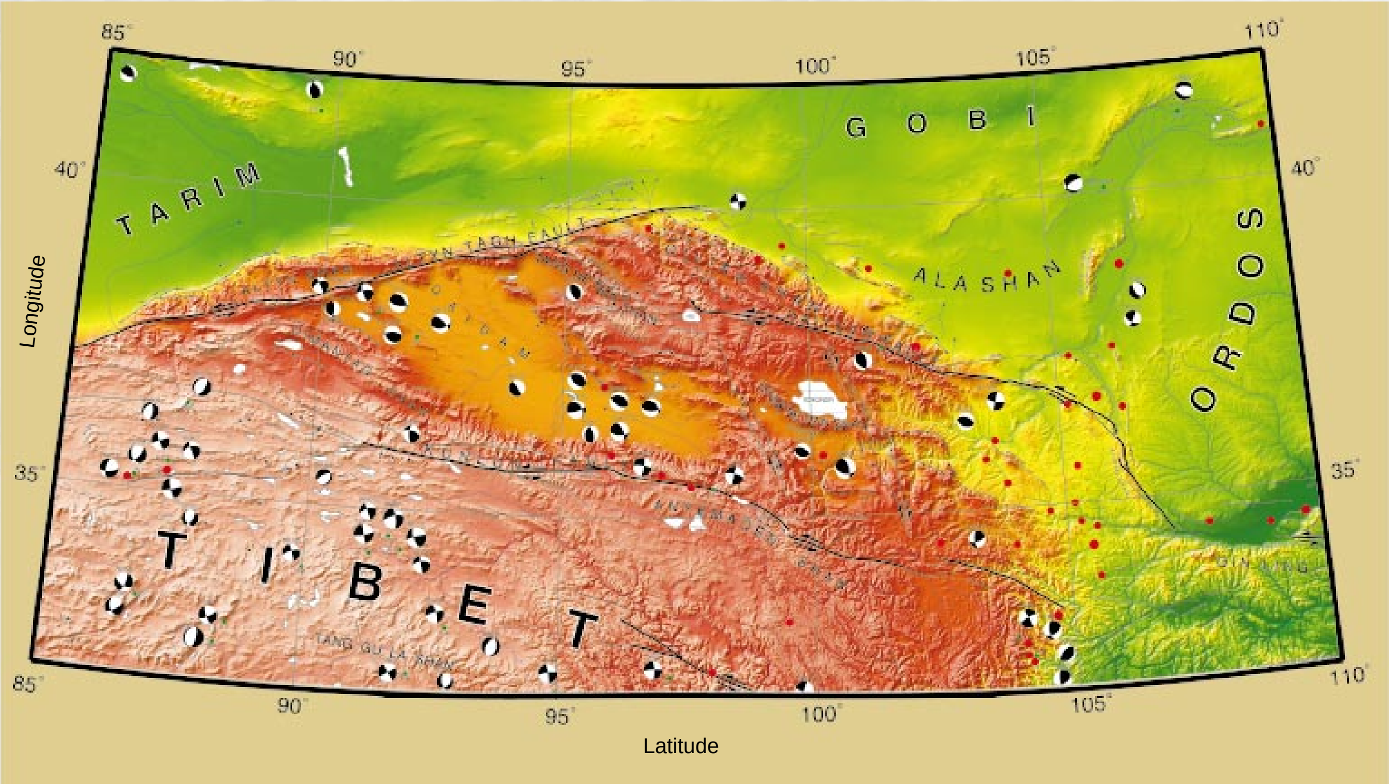


(a) In this plasticine model, the northward movement of a body representing India simulates the creation of faults that have allowed the southeastward displacement of the Southeast Asian landmass, among other features. (b) To accommodate the extrusion of Indochina, the South China Sea opened up to the east. Continued continental collision results in successively younger faults to the north. Paul Tapponnier and Gilles Peltzer of the Institut de Physique du Globe de Paris created this model. They collaborate regularly with Livermore scientists.

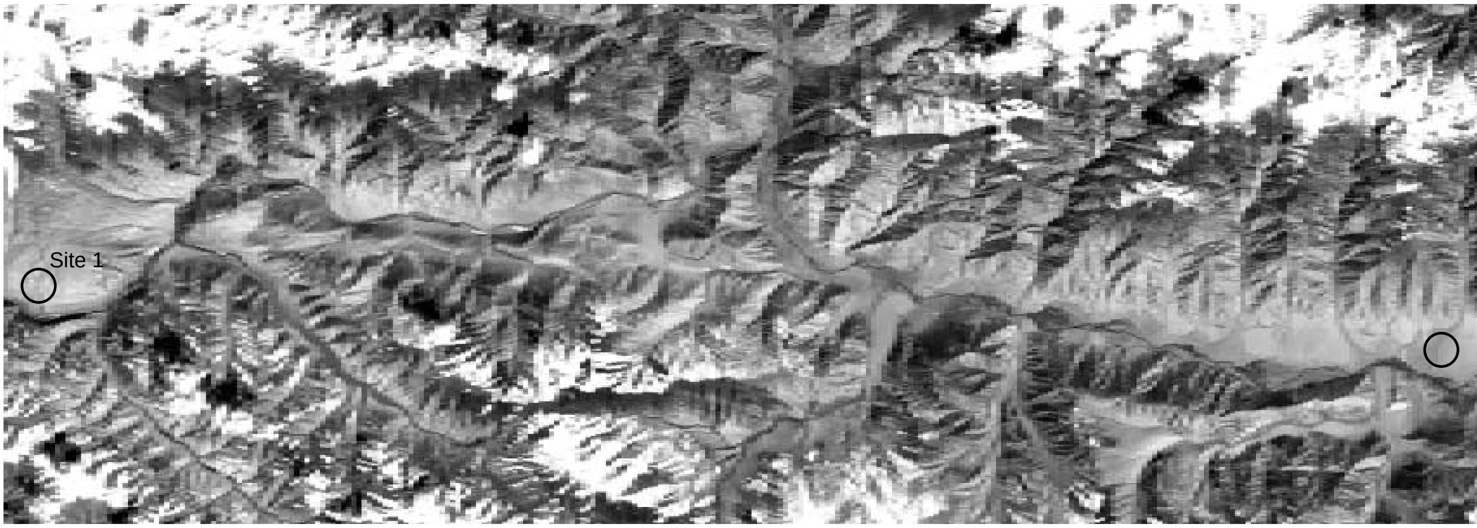
AMS and the Dating Game

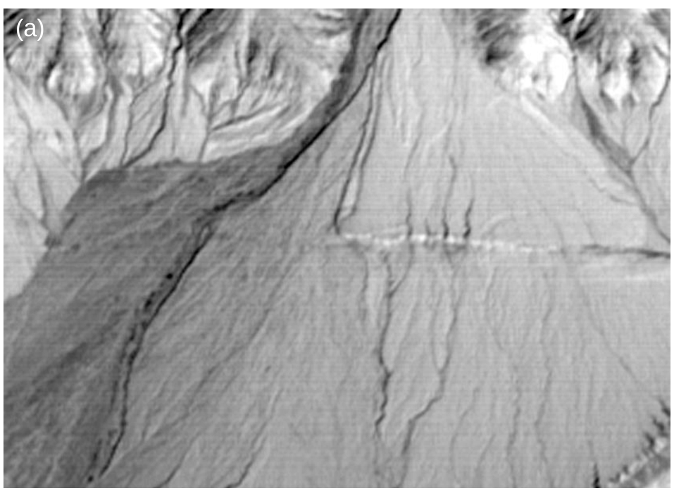
To derive rates of motion along faults, scientists first identify a site where lateral offset has occurred and then measure the offset and determine its age. Commercially available satellite imagery, with resolution to 10 meters, allowed the team to select regions where tectonic offsets are best preserved, such as abandoned stream beds and surfaces formed by glacial action. As shown in the figure on pp. 28–29, the team took measurements at several sites where the faults cross alluvial fans formed by melting glaciers. As a glacier shrinks, the stream running from it becomes narrower, leaving behind an older, wider streambed in a series of terraces. The boundaries between different terrace levels represent lateral offset markers.

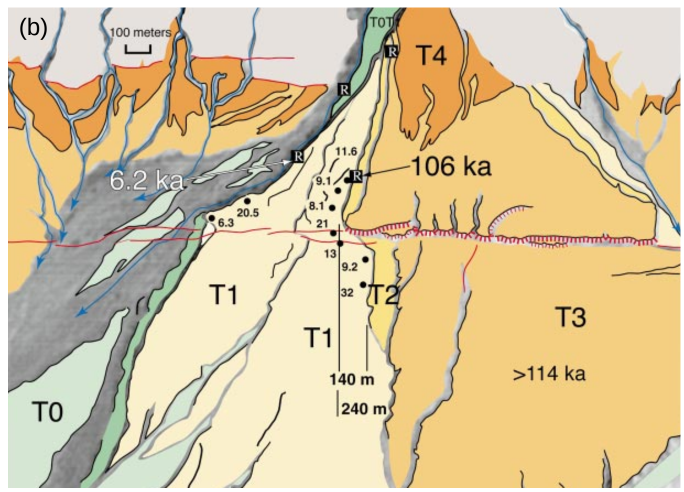
To determine the age of these surfaces and thus a slip rate, the team relied on experts from Livermore's Center for Accelerator Mass Spectrometry. Conventional mass spectrometry measures the concentrations of different isotopes of the same element. Accelerator mass spectrometry (AMS) does the same job but is much more sensitive than conventional mass spectrometry. The most common dating method is to measure carbon-14 relative to other carbon



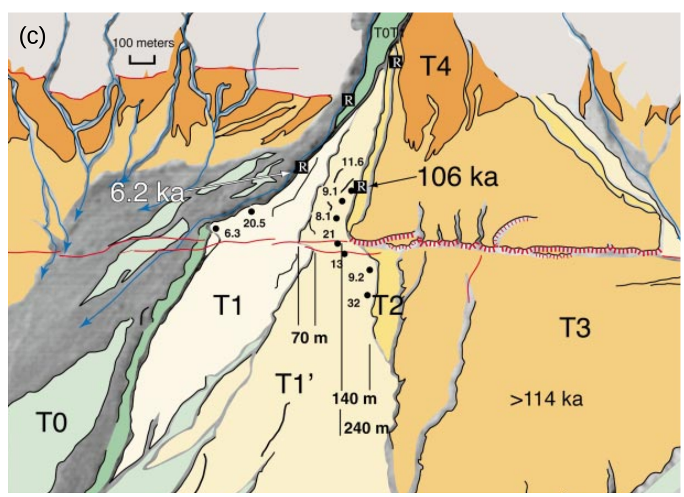
Map of Tibet showing the major faults and geopolitical boundaries for reference.

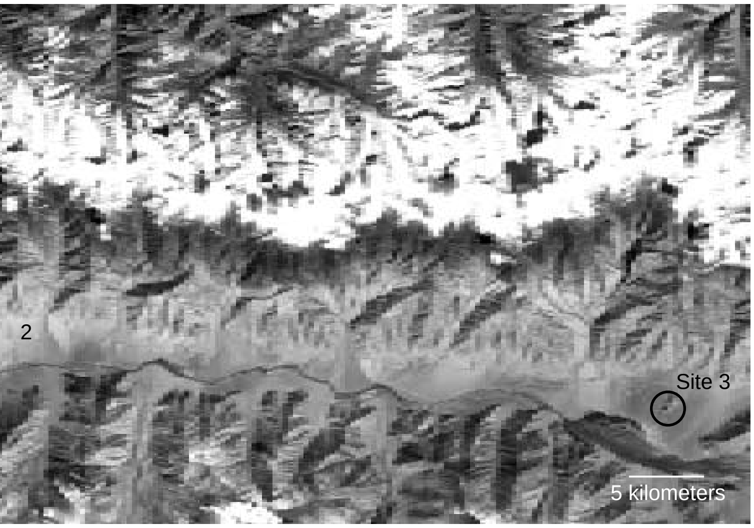






(a) Site 1 on the Altyn Tagh Fault. The fault is illuminated from the south and may be seen as a bright line running across the image. The active streambed is on the left and the older streambed terraces rise sequentially to the right. (b) and (c) Alternative interpretations of the evolution of the various terraces. (ka = 1,000 years)





Three sites studied along the Altyn Tagh Fault are shown. The fault is visible where it crosses several alluvial fans.

isotopes. AMS, for instance, can find one atom of carbon-14 in a quadrillion other carbon atoms, which means that extremely small samples can be studied.

However, in high, arid mountain ranges, fossil organic remains are often hard to find. Moreover, the ages of some surfaces may be too old to measure by carbon-14 methods. Therefore, for its first study, on the Kunlun Fault, the team compared slip rates obtained through radiocarbon dating with those obtained by measuring the cosmogenic nuclides beryllium-10 and aluminum-26 in quartz rock. Cosmogenic nuclides are produced through the interaction of surface samples with cosmic rays. Whereas carbon-14 levels fall over time, the levels of cosmogenic nuclides rise the longer a sample resides at Earth's surface. But the amounts they contain are still small. It has only been in the last 10 years, with advancements in such techniques as AMS, that measuring cosmogenic isotopes has been possible at all.

Under optimal conditions, samples taken from the surface will yield the true age of the surface. But a surface may also contain samples that were previously exposed to cosmic rays. Or rocks may simply roll downhill and contaminate a previously abandoned surface. Scientists must, therefore, collect many samples, both buried and from the surface, to account for all sources of contamination and derive a site's true age.

For the Kunlun studies, slip rates derived from beryllium-10 and aluminum-26 ages compared extremely well with those from radiocarbon dating.

What the Data Say

The figure at the bottom of p. 28, showing one alluvial fan along the Karakax Valley segment of the Altyn Tagh Fault, is an example of the many sites studied on both faults. The fault is clearly visible in part (a) of the figure as is lateral offset of terrace levels along the fault. Parts (b) and (c) show two interpretations of the evolution of this site.

Measurements at 10 sites along the Altyn Tagh Fault yielded slip rates as high as 3 centimeters per year in the west, decreasing to rates below 1 centimeter per year at the fault's eastern end. The rate decreases as lateral movement in the west is transformed into the vertical uplift that has created young mountains in northeastern Tibet. In contrast, using on measurements at six sites along a 600-kilometer length of the Kunlun Fault, the team found a uniform slip rate of about 12 millimeters per year over a time span of 40,000 years.

Comparison of the two faults suggests that the Kunlun Fault may be a more mature version of the Altyn Tagh. While the Altyn Tagh Fault is still in the process of propagating eastward, piling up new mountains along its bow, the Kunlun's movement appears to be fully transferred to other faults to the east. But Ryerson is quick to add, "We don't really understand yet what is happening at the eastern end of the Kunlun Fault."

These data indicate that the birth and growth of strike-slip faults has been moving north with time, suggesting that the northern portion of the Tibetan Plateau has been uplifted by successive episodes of eastward fault propagation coupled with the uplift of young mountain ranges. Sediments from the young mountain ranges accumulate in closed basins that are in turn uplifted by fault movement. Ironically, much of one of the greatest mountain ranges on Earth, the Tibetan Plateau, may have been built not of mountains but of basins.

The relatively high slip rates observed along the Altyn Tagh and Kunlun faults are consistent with the models showing that these faults play an important role in accommodating Indo-Asian convergence. Livermore's data indicate that the models representing the lithosphere as a fluid may be flawed.

The first stage of this work, assessing the slip rates on active faults in northern Tibet, is nearing completion. Barely begun, however, is the next stage—extrapolating these observations of active faulting back to the early history of the collision. Meanwhile, continents continue to collide in Tibet.

—Katie Walter

Key Words: accelerator mass spectrometry, cosmogenic isotopes, dating techniques, faults, plate tectonics, Tibet.

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