

## News Item

### Understanding Zeolite Structures

Not too many people – scientists or others – have had the experience of beating a Cray supercomputer to the solution of a mathematical problem. Joe Smith has. Smith – Joseph V. Smith, that is, a University of Chicago geochemist – recently solved the structure of a zeolite called boggsite. And in so doing, he's done more than just solve an intellectual puzzle; he's set off a massive race in the petrochemical industry to synthesize boggsite. The reason for the race is that zeolites are minerals whose chemical properties make them tremendously valuable as catalysts in the manufacture of gasoline and other substances.

Indeed interest ran high enough at Exxon that Smith went there last year to give a lecture on his work. When the talk was finished, John Newsam, Exxon chemist, brought Smith to his computer lab to show him a computer program developed there for puzzling out zeolite structures. The two scientists entered some of the raw data Smith had exploited to resolve the boggsite structure. Then they asked the Cray what structure might correspond to those data. In a few minutes the supercomputer produced a number of possible structures – but none of them matched the correct structure Smith had already deduced. Chalk one up for the human brain.

What makes this story even more intriguing is the quirkiness of Smith's methods. He doesn't, for the most part, work with high-powered modern mathematics. On the contrary, he uses concepts based on the geometric solids first discussed by the Greek philosophers Plato and Archimedes. "You might say that through our work, Plato and Archimedes have helped make millions of dollars for the petrochemical industry," says Smith, in the burr of his native Derbyshire in England.

One remarkable thing about Smith's way of working is that he reverses the usual order of things in science. Most science moves from the real to the ideal. That is, a set of observations of real phenomena is interpreted to yield an ideal structure or mechanism that is embodied in a theory. Smith, on the other hand, has used Platonic and Archimedean solids to describe many possible theoretical structures of materials like zeolites. In the end, some of these have turned out to be the structures of actual zeolites – many with great economic significance.

"What we've done over the last 30 years is look at various ways of inventing some of the infinite number of three-dimensional networks of tetrahedral atoms," says Smith. At first the purpose of this intellectual exercise was to see how various geometric constructions could fit together to make molecules. But, Smith adds, "it has turned out, of course, that some of the theoretical networks match the three-dimensional structures of both natural and synthetic zeolites."

Smith makes these comments in his domain in the Geophysics Building at the University of Chicago, a space dominated by models – his, Plato's and Archimedes'. Wiggly masses of red, blue, black, and yellow plastic tetrahedral

connectors that look like a child's jack's and lots of clear plastic tubing are scattered on bench tops, file cabinets, chairs, shelves, and inside glass-fronted cabinets. These represent the various ways that atoms of aluminum, silicon, and oxygen – the constituents of all zeolites – might conceivably fit together.

Smith's interest in zeolites goes back to the late 1950s, when he studied the zeolite called Linde A, an ion-exchange zeolite now used in phosphate-free detergents. "Linde A crystallizes quite easily, so we had the crystal structure and a nice model to look at," says Smith. But Linde A was just the starting point for an encyclopedic approach to zeolite structure, a project that is quite unusual in the world of today's science.

"There aren't many people in the world like Joe Smith who would take on an enormous project such as trying to systematically describe possible zeolite structures," comments John B. Higgins, a crystallographer and model builder at the Mobil Research and Development Corp.

That systematic bent was apparent early in Smith's career. Trained as a physicist and crystallographer at Cambridge University, Smith took an early interest in mineral structures. His first work as a young assistant professor at Penn State was on the mineral feldspar, an interest that eventually led to the two-volume opus *Feldspar Minerals*, still considered the definitive reference work on feldspar.

As Smith pondered the geometry of the molecular model he had developed for Linde A, he realized that the entire structure could be broken down into two geometric shapes: cubes and truncated octahedra. And such simple geometric shapes also appeared elsewhere. The mineral faujasite, another zeolite, was composed of hexagonal prisms connected to truncated octahedra. So, too, were Linde X and Linde Y, synthetic zeolites that differ chemically from faujasite but have the same three-dimensional structure.

For Smith, this geometry harked back to classical times. "What we have here are huge crystals assembled from geometric units first described by the ancient Greeks – the Platonic and Archimedean solids."

For those who have been away from geometry for a while, the Platonic solids are the five regular polyhedra whose faces are all the same. The simplest is the tetrahedron, made from four equilateral triangles. Then come the cube (6 squares), the octahedron (8 equilateral triangles), the dodecahedron (12 pentagons) and the icosahedron (20 equilateral triangles). The 13 Archimedean solids are those made from two regular shapes. The hexagonal prism, for example, is made of rectangles and triangles; the truncated octahedron contains hexagons and squares.

Smith's approach to inventing possible zeolite structures is to view them as an assemblage of a finite number of geometric building blocks, with the aluminum, silicon, and oxygen atoms sitting at the corners of these shapes. Assembling these simple solids is one way of creating a three-dimensional network. Another is to build a two-dimensional structure – a sheet of atoms – and connect the sheets to form the third dimension. The combination of these two approaches has been remarkably successful: explaining about half of all zeolite structures discovered so far.

Part of what Smith does is to play with known structures, rearranging them to produce new networks. For example, one common sheet arrangement consists of hexagons connected by squares, which, when linked together, produces pores made

of 12-membered rings. In the early 1980s Smith wondered what would happen if there were two squares between the hexagons. He built a model of this imagined material: a theoretical zeolite structure with pores composed of 18-membered rings.

In 1984 Smith published a paper outlining this theoretical concept. At just the same time Mark Davis, a chemical engineer at Virginia Polytechnic Institute at Blacksburg, was trying to synthesize a zeolite with large pores. Davis saw Smith's paper and eventually succeeded in creating a zeolite called VPI-5, which has precisely the structure Smith had predicted. "Joe's paper certainly was helpful in our thinking," Davis enthuses, adding "I'm a big fan of what he does." (The National Science Foundation is, in turn, a big fan of Davis's, having named him the first engineer to win the Waterman Award – for this same work.)

The focus on the rings in VPI-5 was by no means accidental, because these rings – and the channels they create – are directly related to the economic contribution of zeolites. All zeolites are microporous aluminosilicates in which each tetrahedral aluminum and silicon atom is bonded to four oxygen atoms, and each oxygen atom is bonded to two aluminum atoms, two silicon atoms, or one of each. In each of the 40 or so known zeolites, the atoms are arranged in interconnected regular polyhedra, forming channels of various sizes. Depending on the size of the channel, zeolites can act as molecular sieves, ion-exchange agents and, most critically, as catalysts.

Zeolites are unique in nature – and so useful in industry – because of the large amount of empty space that the channels create within the mineral. In their natural state, this empty space is filled with molecules of water. The water, however, can be driven off simply by heating. Zeolites are also filled with various loosely bound cations, such as sodium, potassium, and calcium. These can be washed out and replaced by ions such as magnesium, barium, strontium, and cesium; each zeolite-ion combination can be put to its own individual industrial uses.

Zeolites make good catalysts because protons can be detached easily from the silicon and aluminum framework, leaving behind many "active sites" that can react with various organic molecules. To pick the most significant economic example, in the zeolite ZSM-5 the active site reacts with a molecule of methanol to produce a carbonium ion, which reacts with another molecule of methanol to produce a two-carbon molecule. That molecule in turn reacts further to yield a three-carbon chain, and so on. In this way ZSM-5 converts methanol into the mixture of hydrocarbons known as gasoline – a reaction of billion-dollar significance.

For the chemists who study zeolites and try to develop new industrial applications for these materials, knowing the microporous structure – the size of the channels and the direction they take through the material – is paramount. That's because this structure can determine just what kind of reactions will occur within the zeolite. ZSM-5's pores, for instance, are just large enough so that when ethylene reacts with benzene, only monoethyl benzene diffuses out; any diethyl or triethyl benzenes remains trapped in the aluminosilicate cages.

And that's where the models that Joe Smith and a few other geochemists build have proved to be so valuable. "When we make a new zeolite, or when a new one is discovered in nature," Higgins says, "the thing we really want to know is what are the channels like. And that requires knowing the crystal structure. The problem is we can't grow crystals for most of these zeolites."

In most cases the best a crystallographer can do is to obtain what's called a powder diffraction pattern. The zeolite is crushed into a uniform powder, from which the crystallographer can obtain a crude X-ray diffraction pattern. That pattern offers rough structural information, but nothing as detailed as atomic positions or even channel size. Enter Smith and his models.

After Smith and his colleagues build a model of a theoretical network, they sit down with a ruler and compass and measure the bond lengths and angles. An energy minimization computer program optimizes these data and calculates a theoretical powder diffraction pattern for the hypothetical mineral. "We can then compare the calculated diffraction patterns in our data base with the diffraction pattern for a new zeolite," says Smith. "When we find a match, which isn't hard to do," he adds modestly, "we've solved the structure."

And that was just how things went last year in resolving the structure of boggsite, which had been discovered by amateur rock hounds in Washington State and then studied by Smith. "Without Joe Smith's models, this structure would not have been solved," Higgins notes, "and there wouldn't now be a massive effort throughout the chemical industry to try and synthesize this very interesting material."

As in the case of the other zeolites, commercial interest in boggsite is high because of its channel structure. Boggsite has channels of two different sizes — 5.5 Angstroms and 7 Angstroms — that intersect throughout the material, a structural combination that could give the material some interesting and useful catalytic activities. Smith's theoretical interest in the network that turned out to describe the structure of boggsite stemmed from the way the various geometric shapes fit together to form a network with channels made up of 10-membered rings and channels made of 12-membered rings.

Smith's successes have led others to turn to model building as a way of understanding zeolite structure and function. "This is really an important activity in industrial labs," according to Higgins.

One example of that activity is the computer program that Smith outfoxed at the Exxon Research and Engineering Company in Annandale, New Jersey. From crude crystallographic data, basic chemical bonding information, and a mineral's elemental composition, the program generates possible structures. "We can take this data and in the worst case generate 10 or 12 structures that the zeolite might have," program designer Newsam explains. Then the computer's possibilities are used to calculate theoretical powder diffraction patterns. "We've used this program successfully to solve some simpler zeolite structures," says Newsam.

More complex structures still lie outside the range of the computer's prowess. Yet Smith sees great value in the computerized end of this work. "They can generate many, many structures in a short amount of time," he says. "But there is something about the process of actually building these models by hand, an insight you gain by assembling a new structure from your mind that a computer program will always be lacking."

And fellow model builder Higgins notes: "This will always be an exercise that requires the human intellect. Particularly Joe Smith's."

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