

# THE DISCOVERY

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R O B E R T M. H A Z E N

Scientific discoveries are few and far between in most scientists' careers. Most scientific research proceeds at a halting pace. Data accumulate gradually by tedious, repetitive experiments and painstaking analysis. But 1988 at the Carnegie Institution of Washington's Geophysical Laboratory was a most unusual year. In January and February we identified three new superconductors, all of economic importance. During the summer months we found three new minerals, each with a beautiful, previously unknown atomic structure. But perhaps the most memorable discovery was saved for last.

The crucial experiment started routinely enough at about noon on Thursday, December 22. That morning I had played hooky with my wife, Margee. We arrived early at a blissfully deserted shopping mall to complete our Christmas chores. It was almost 11:00 A.M. when I drove up the winding, tree-lined driveway to the Geophysical Laboratory's hilltop site in northwest Washington, D.C. My research partner, Larry Finger, was waiting. We share the X-ray crystallography lab, where we study the atomic arrangements of interesting minerals and other crystals.

The concept of X-ray crystallography is simple. Shoot a focused beam of X rays at a crystal. Some of the X rays will scatter off planes of atoms in certain fixed directions, and by measuring the directions and intensities of those reflected X-ray beams, or "peaks," we can deduce the atom positions. In practice, X-ray crystallography requires fancy, expensive machines called X-ray diffractometers that orient crystals and collect data automatically. Our lab has four of the beasts, each with precisely machined

geared circles and jutting arms, each with its own distinctive personality.

Larry and I hoped to keep the diffractometers grinding away over the holidays studying a synthetic crystal of magnesium silicate, denoted  $\text{MgSiO}_3$ , because of the 1:1:3 ratio of its elements—magnesium, silicon, and oxygen. One form of magnesium silicate, the hard, usually dark mineral pyroxene, adopts one of the most common atomic structures in nature. In its transparent pale green variety it sometimes serves as a semiprecious gemstone. But we were exploring the atomic structure of a different form of  $\text{MgSiO}_3$ . As you squeeze pyroxene at above approximately 200,000 times room pressure, the atoms get uncomfortable and shuffle around to form a denser structure—ilmenite. Finally, at about 300,000 times atmospheric pressure, the  $\text{MgSiO}_3$  in its ilmenite form transforms again as the atoms shift into yet another arrangement, called the perovskite structure. Those “transformations” cause big increases in density, which account for some of the seismic blips deep in the earth. The earth is in effect an onion with thin layers of denser and denser stuff the deeper you go. Scientists believe that the ilmenite form of  $\text{MgSiO}_3$  contributes to one of those layers.

The crystal we were to study looked quite ordinary. It was a colorless, clear speck about 0.01 of an inch across. Japanese researcher Eiji Ito created the specimen in a giant high-pressure, high-temperature device used to synthesize diamonds and the like. Everything in that Japanese synthetic run was supposed to be  $\text{MgSiO}_3$ , ilmenite. But high pressure is tricky—you can never be sure what a million pounds of force at temperatures of thousands of degrees might do to magnesium and silicon.

Larry and I mounted the crystal on our new Rigaku diffractometer. The automated marvel did most of the work for us. We went off to lunch, and by 3:00 P.M. the Rigaku had located peaks and revealed the dimensions of the regular atomic lattice.

Something was clearly wrong. Crystals can be described in terms of regularly repeating boxlike units called unit cells, which stack together to form the crystal. The size and shape of the unit cell is a kind of crystallographic fingerprint. Magnesium silicate ilmenite should have unit-cell dimensions of about 4.72 by 4.72 by 13.5 angstroms (an angstrom

is a minute distance, just one ten-billionth of a meter), but our crystal was different. Its unit cell was 4.75 by 4.75 by 12.95 angstroms: close, but entirely different. For one thing, it was 4% denser—a huge difference when talking about the earth. We went over the possibilities. The similarity of the two unit cells was too close to be a coincidence—there was some relationship between ilmenite and our stuff. Could the Japanese scientists who first described the material have made a huge crystallographic boo-boo? Was it a typographical error in the original paper that described the ilmenite? No, others had confirmed the ilmenite numbers and density. We spent the next two hours trying to check out all the possibilities, looking at peak shapes and measuring intensities. I began to suspect the only remaining logical conclusion—we had discovered a new high-pressure variant of  $\text{MgSiO}_3$ , a new atomic structure. After all, our crystal was denser and its close dimensional relationship to the ilmenite phase was obvious. Larry started an overnight data collection that would allow us to refine the structure in the morning.

Larry had to leave at 5:30 P.M., but I stayed around the lab and resolved to talk to Rus Hemley, a lab colleague and mineral physicist who had done a lot of thinking about the high-pressure transformations of  $\text{MgSiO}_3$ . I gave him the facts. We had a crystal of  $\text{MgSiO}_3$  that was supposedly synthesized in the ilmenite stability range. The unit cell was very close to ilmenite's, but our phase was 4% too dense, with a slightly longer  $a$ -axis and a much shorter  $c$ -axis. It only took Rus a second to respond.

“Have you checked out the lithium-niobate structure?”

His question rang only the faintest of bells. As I mumbled something about not having had time to check that possibility he retrieved a full folder neatly labeled ilmenite/ $\text{LiNbO}_3$  and handed it to me. The dark green, well-worn file contained a dozen dog-eared reprints and preprints on the rare structure of lithium niobate as well as recently documented high-pressure transitions from the ilmenite structure to this  $\text{LiNbO}_3$  type. The density change was 4 percent. The  $a$ -axis got longer. The  $c$ -axis got much shorter. And in one of the preprints the authors (one of whom was

our lab's director, Charlie Prewitt) suggested that  $\text{MgSiO}_3$  in the ilmenite structure might transform to  $\text{MgSiO}_3$  in the lithium niobate structure at high pressure.

We had made a discovery of tremendous importance. Deep within the earth is a 100-kilometer-thick zone containing ilmenite-type  $\text{MgSiO}_3$ . Mineral physicists claim that at a depth of 670 kilometers ilmenite transforms to the much denser perovskite form. The trouble is that seismologists, who first identified the abrupt 670-kilometer discontinuity on the basis of reflected seismic waves, say the density change is all wrong—mineral physicists, they complain, see much too large a density change in their experiments. Now we had the solution to this conflict. Instead of transforming from ilmenite to perovskite all at once, the crystal undergoes an obvious structural transition from ilmenite to lithium niobate to perovskite, a much gentler change that takes place over a thicker layer.

Our work had taken on a new urgency. This was big news—the kind that makes a lead article in prestigious periodicals like *Science* or *Nature*. The familiar tingling feeling of being on the track of something big crept up.

I called Larry at his home and we agreed to meet early the next morning. I also reached Charlie Prewitt and told him of the discovery that matched his predictions. Home, finally, at 8:00 P.M., I remained in a thoroughly agitated and exhilarated state. Thank goodness the Christmas errands were out of the way. Margee and the kids listened patiently as I described the data and their significance. Then I phoned Lab colleague Dave Mao, who had first obtained the crystals from Japan and was supervising their distribution. He, too, was excited and immediately grasped the importance of the findings. I spent the evening plotting strategy, particularly the manuscript preparation that would have to begin immediately the next morning.

Sleep was a lost cause. I was up at 5:00 A.M. Margee suffered a largely sleepless night thanks to my incessant jostling, but she got up to cook a sustaining egg breakfast. We were extra-quiet so as not to disturb the

children (who had been sleeping poorly in anticipation of Christmas) and the dog (who, once aroused, would wake up the children). I sneaked out with a quick good-bye kiss and got to the lab before 6:00 A.M.

The diffractometer had completed its task, so I gave it another crystallographic chore and headed to my word processor. The prose flowed smoothly, for this was an elegant experiment with unambiguous results and profound conclusions. There was a sense of urgency in my writing, too, for the lab's Christmas party was to begin at 1:00 P.M., and after that there would be no hope of soliciting secretarial help. Larry also arrived early, as promised, and he went straight to work analyzing the diffractometer output. By 9:30 A.M. we were ready to refine the crystal structure. It was an easy task because previous authors had described the lithium niobate structure clearly. All we had to do was substitute magnesium for lithium and silicon for niobium in the computer description. And bingo—on the first try it refined to a disagreement between our model and our data of less than 10 percent, a good, low number indicating that we were clearly on the right track.

Two hours later we were still on the right track, but things weren't getting any better. We could locate atoms well enough, and all the presumed lithium niobate atom positions were properly occupied by atoms. The trouble was that the atoms didn't look exactly like silicon or magnesium. We assumed that our problems were all the result of twinning—a nasty habit crystals have of not being quite regular. Larry had just written a sophisticated computer program that analyzed for twinning, but it took time to run. The minutes ticked by: 11:45, 12:00, 12:20, 12:40. The Christmas party was approaching, and still no solution. Some of our models matched the data almost perfectly, but the atomic vibrations ended up being much too small, and sometimes even negative—an impossible result. What was going on?

We quit for a while to enjoy the traditional lab Christmas-party fare—a fresh roast-beef sandwich, garden salad, apple pie, and beer. Larry and I were the center of attention, surrounded by other scientists eager to hear the latest details of the find. Charlie Prewitt was beaming, having helped to predict the transition before its discovery. Drs. Liang-chen

Chen, Ming Sheng Peng, and Jinfu Shu, postdoctoral fellows from the People's Republic of China, kept their cameras busy as they took dozens of pictures of the party; Larry and I were asked to pose with each for commemorative portraits. It was quite a celebration, and after a couple of beers we really got into the swing of the celebrity status that any significant scientific advance affords. That we had not yet solved the structure was a minor fact, easily forgotten.

It remained only to tidy up details of the recalcitrant structure refinement. We headed back to the computer terminal and were working on another twin model when Dave Mao walked into the office and sat down. He had been following our work with keen interest all day and had obviously been doing a lot of thinking about the problem. You can never be sure what Dave is going to say, but his remarks are always well considered and deserving of respect. His question was devastating.

"Have you considered corundum?"

Do you know the feeling when you've done something incredibly silly or profoundly dumb and it just sort of slowly creeps up on you what an idiot you've been? Corundum's structure— $\text{Al}_2\text{O}_3$ —is closely related to that of ilmenite. The crystal structures are actually almost identical, because the atoms are arranged the same way. The unit cell of corundum is 4 percent smaller than ilmenite's. It has a longer *a*- and shorter *c*-axis. The only structural difference is that 2 aluminum atoms (with 13 electrons each) take the place of a magnesium and a silicon (with 12 and 14 electrons, respectively). Corundum is everywhere in our lab. We use it as a high-pressure calibrant, as an abrasive, and as an X-ray standard. And the Japanese use corundum to pack high-pressure experiments. There were a hundred ways that a tiny corundum crystal might have contaminated the capsule of  $\text{MgSiO}_3$ . We had been so intent on finding the magnesium silicate that we ignored the simple and obvious alternative. All that fuss over a piece of grit! What could we say or do?

I guess everyone reacts in his or her own way. Larry said nothing. He turned to the computer for reassurance, his jaw set, his expression unrevealing. Quickly he attacked the keyboard, magically transforming

silicon and magnesium into 2 aluminums. For that was all we really had to do. The refinement converged quickly and smoothly, a perfect agreement with the common corundum structure.

At first I refused to believe it. Surely the lithium niobate story was true. It seemed so right from an esthetic point of view. But at the same time I knew corundum was the answer. Scientists are taught to look for the unexpected but always to accept the simplest answer. And I could only laugh that we had, in our unthinking, delirious, greedy rush for science headlines, missed the most obvious and trivial reason for the anomalous data. Our crowning achievement of 1988 had turned to dust. Even worse, we had trumpeted our "discovery" to our colleagues, before all the data were in.

By 5:00 P.M. the Geophysical Laboratory was deserted. Larry had left for home, looking forward to a week in the Grand Cayman islands with his wife and daughter. He would soon forget the embarrassment. Dave Mao, Charlie Prewitt, and Rus Hemley had also left for their homes. They had said little upon hearing the revised news that we had "discovered" corundum. Perhaps they were chuckling inside, thinking that in a few months our folly would make for a funny story over a beer at some professional meeting. But they were also sensitive enough to know that the jokes should wait. I alone remained at the lab, determined to make one final test of that deceptive crystal. Chemical analysis would tell for sure if we had aluminum oxide or magnesium silicate. Of course, I knew the answer before it appeared on the microprobe output. I called home, gave Margee a brief synopsis of the day's depressing results, and headed home for the holidays.

I got home at 7:30 P.M., exhausted and discouraged. The street was quiet and the house dark. I trudged up the front steps and was fumbling for my front-door key when the mail slot popped open, and a small hand appeared, silhouetted in a rectangle of light.

"Dad's home!" Elizabeth called out.

Almost at once the door swung open, and Margee was there with a hug and a kiss. Ben yelled out "Hi!" from the TV room, and our dog,

## THE DISCOVERY

Yipko, ran her usual excited circles, alternately jumping on my leg and tugging at my shoelaces. They all seemed so happy to see me—they didn't care at all that I had failed.

And it struck me that in the whole scheme of things, it really hadn't been such a bad day after all. Science is a great way to spend a life, and there will doubtless be other good years with other exciting finds. But that is only part of life's equation.

It's not often that you make such an important discovery.