# A new mathematical approach to understanding zeolites

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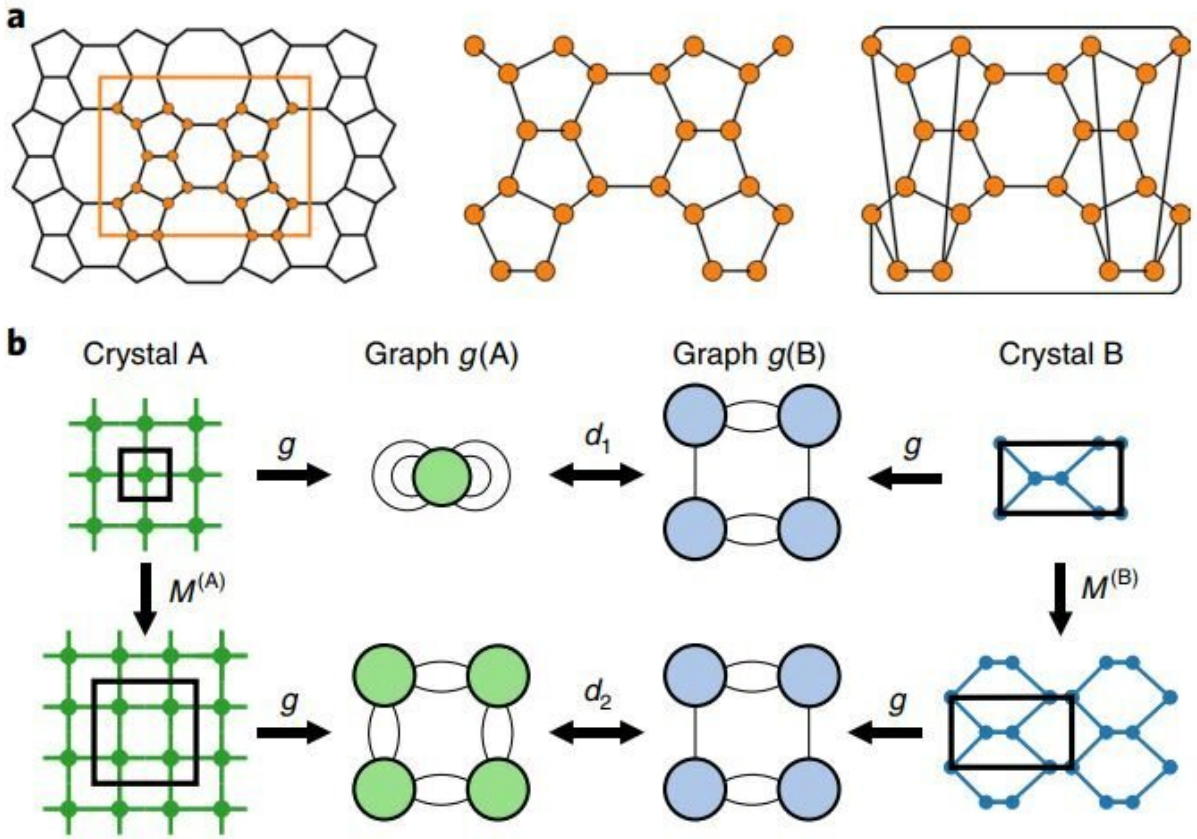


Graph and supercell matching. a, Representation of a zeolite using a graph (left). The unit cell graph (middle) is modified to satisfy periodic boundary conditions by looping bonds back into the unit cell (right). b, Graph distance between different hypothetical crystal structures. The distance d between the crystal graphs varies with the choice of the crystallographic unit cell. In the given example, the transformation matrices are M(A) = 2I and M(B) = I , with I the identity matrix. With the choice of an appropriate metric, d2≤d1. c,

Hypothetical A–B transformation. The bond-breaking step removes two extra edges from the M(A)A crystal graph to match the M(B)B crystal graph, and is followed by a diffusionless transformation at constant graph. Credit: *Nature Materials* (2019). DOI: 10.1038/s41563-019-0486-1

Zeolites are a class of natural or manufactured minerals with a sponge-like structure, riddled with tiny pores that make them useful as catalysts or ultrafine filters. But of the millions of zeolite compositions that are theoretically possible, so far only about 248 have ever been discovered or made. Now, research from MIT helps explain why only this small subset has been found, and could help scientists find or produce more zeolites with desired properties.

The new findings are being reported this week in the journal *Nature Materials*, in a paper by MIT graduate students Daniel Schwalbe-Koda and Zach Jensen, and professors Elsa Olivetti and Rafael Gomez-Bombarelli.

Previous attempts to figure out why only this small group of possible zeolite compositions has been identified, and to explain why certain types of zeolites can be transformed into specific other types, have failed to come up with a theory that matches the observed data. Now, the MIT team has developed a mathematical approach to describing the different molecular structures. The approach is based on graph theory, which can predict which pairs of zeolite types can be transformed from one to the other.

This could be an important step toward finding ways of making zeolites tailored for specific purposes. It could also lead to new pathways for production, since it predicts certain transformations that have not been previously observed. And, it suggests the possibility of producing

zeolites that have never been seen before, since some of the predicted pairings would lead to transformations into new types of zeolite structures.

## Interzeolite tranformations

Zeolites are widely used today in applications as varied as catalyzing the "cracking" of petroleum in refineries and absorbing odors as components in cat litterbox filler. Even more applications may become possible if researchers can create new types of zeolites, for example with pore sizes suited to specific types of filtration.

All kinds of zeolites are silicate minerals, similar in chemical composition to quartz. In fact, over geological timescales, they will all eventually turn into quartz—a much denser form of the mineral—explains Gomez-Bombarelli, who is the Toyota Assistant Professor in Materials Processing. But in the meantime, they are in a "metastable" form, which can sometimes be transformed into a different metastable form by applying heat or pressure or both. Some of these transformations are well-known and already used to produce desired zeolite varieties from more readily available natural forms.

Currently, many zeolites are produced by using chemical compounds known as OSDAs (organic structure-directing agents), which provide a kind of template for their crystallization. But Gomez-Bombarelli says that if instead they can be produced through the transformation of another, readily available form of zeolite, "that's really exciting. If we don't need to use OSDAs, then it's much cheaper [to produce the material].The organic material is pricey. Anything we can make to avoid the organics gets us closer to industrial-scale production."

Traditional chemical modeling of the structure of different zeolite compounds, researchers have found, provides no real clue to finding the

pairs of zeolites that can readily transform from one to the other. Compounds that appear structurally similar sometimes are not subject to such transformations, and other pairs that are quite dissimilar turn out to easily interchange. To guide their research, the team used an artificial intelligence system previously developed by the Olivetti group to "read" more than 70,000 research papers on zeolites and select those that specifically identify interzeolite transformations. They then studied those pairs in detail to try to identify common characteristics.

What they found was that a topological description based on graph theory, rather than traditional structural modeling, clearly identified the relevant pairings. These graph-based descriptions, based on the number and locations of chemical bonds in the solids rather than their actual physical arrangement, showed that all the known pairings had nearly identical graphs. No such identical graphs were found among pairs that were not subject to transformation.

The finding revealed a few previously unknown pairings, some of which turned out to match with preliminary laboratory observations that had not previously been identified as such, thus helping to validate the new model. The system also was successful at predicting which forms of zeolites can intergrow—forming combinations of two types that are interleaved like the fingers on two clasped hands. Such combinations are also commercially useful, for example for sequential catalysis steps using different zeolite materials.

## Ripe for further research

The new findings might also help explain why many of the theoretically possible zeolite formations don't seem to actually exist. Since some forms readily transform into others, it may be that some of them transform so quickly that they are never observed on their own. Screening using the graph-based approach may reveal some of these

unknown pairings and show why those short-lived forms are not seen.

Some zeolites, according to the graph model, "have no hypothetical partners with the same graph, so it doesn't make sense to try to transform them, but some have thousands of partners" and thus are ripe for further research, Gomez-Bombarelli says.

In principle, the new findings could lead to the development of a variety of new catalysts, tuned to the exact chemical reactions they are intended to promote. Gomez-Bombarelli says that almost any desired reaction could hypothetically find an appropriate zeolite material to promote it.

"Experimentalists are very excited to find a language to describe their transformations that is predictive," he says.

**More information:** Graph similarity drives zeolite diffusionless transformations and intergrowth, *Nature Materials* (2019). DOI: 10.1038/s41563-019-0486-1 , nature.com/articles/s41563-019-0486-1

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