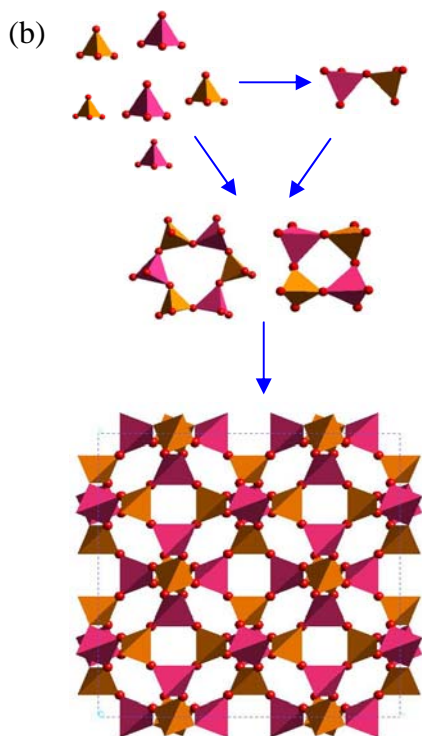




The Building Blocks of Crystals

The smallest building blocks of a crystal is the atom or molecule and these can combine in nature to form some of the most beautiful crystals, such as the snowflake. Just like lego, building blocks can be put together in a myriad ways to form crystalline materials of rich structural complexity and chemical diversity. One of the most important classes of inorganic crystalline materials are zeolites, the uses of which span from aesthetic jewellery, the washing powder that gets our clothes ‘whiter than white’ to environmental cleaning of nuclear waste. So far scientists have been able to tailor make zeolites by fine tuning synthesis processes, without having an atomic scale picture of why the building blocks form particular arrays or matrices. We try to rectify this by attempting to simulate zeolite growth using state of the art computer simulations.



Zeolites are 3D microporous crystals comprised of silica and alumina and are found naturally amongst sources of alkaline waters and volcanic rock [Fig. 1(a)]. Most natural zeolite materials are formed when volcanic ash settles in areas of alkalinity, such as rivers and lakes. Over thousands of years, chemical reactions of the volcanic ash and salt-water gradually result in zeolite formation. Synthetic zeolites are formed in much the same way, but without the volcano! Aluminium and silicon sources, such as alumina and silica, (acting as the volcanic ash) are dissolved in an alkaline oxide such as Li_2O (the makeshift lakes). As the geological timescale of a few hundred centuries is not possible in the laboratory, zeolite formation is greatly accelerated by hydrothermal treatment of the ingredients (high temperatures and pressures within a sealed vessel), in some circumstances taking less than a single hour.

At the atomic level, zeolites are built up of corner sharing silica (SiO_4) and alumina (AlO_4^-) tetrahedra organised to form a framework full of regular pores and channels [Fig. 1(b)]. The mechanism of zeolite growth follows the condensation of small monomeric and polymeric aluminosilicate species forming larger units and zeolite substructures, eventually forming the crystalline product [Fig. 1(b)]. The framework carries an extra negative charge for each alumina unit incorporated. This additional charge is balanced by the housing of a cation (usually single or doubly charged, group 1 or 2 elements of the periodic table) for each alumina unit within the pores and channels of zeolite framework.

Fig. 1: (a) An erupting volcano, a source of zeolite rocks (b) steps of zeolite growth. The arrows depict the direction of condensation, from monomeric species to the eventual formation of the crystalline product.

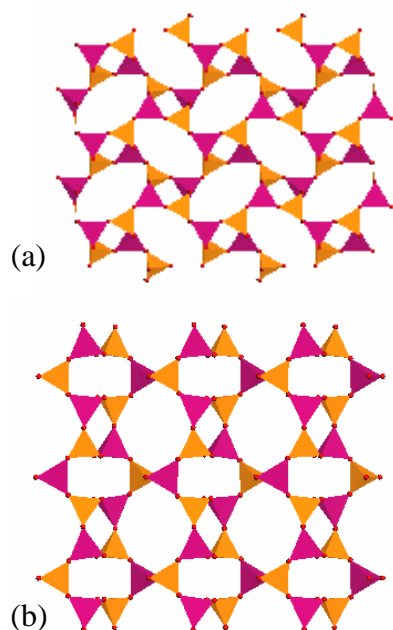


Fig. 2: Framework representations of (a) Li-A(BW) and (b) Na-J(BW)

The strictly ordered, shape selective porosity of zeolites is why they have such wide applications in industry. Zeolites are particularly prominent in (a) separation processes, as they act to remove molecules of a specific size and shape dependent on that of the specific zeolite pores, and (b) catalysis, owing to their catalytically active pore walls.

Since the first commercialisation of zeolites, scientists have focussed on tailoring zeolites to their specific needs by altering synthesis conditions, with significantly less focus on how or why specific phases form over others. The reason for this is that many different, and sometimes related, synthesis factors affect zeolite growth. A number of competing processes also cause fluctuations in the dynamics of the building process. Separating out and focussing on a single variable is therefore extremely difficult. One of the most fundamental and problematic issues is that there are conflicting reports on the nature and identity of the building blocks – the lego pieces. If we don't know what the critical pieces are, it is difficult to forecast how they might be put together.

So, how can computational methods investigate crystal growth in a way that experiment cannot? Using sophisticated computer simulation methods our work focuses on understanding how a single experimental parameter, cation type, influences the species present in the zeolite growth media and the reaction mechanisms of zeolitic fragments condensing on the crystal surface. In order to focus on this single variable, two zeolites were chosen, Li-A(BW) and Na-J(BW), which are synthesised from identical starting conditions, the cation oxide present being the only variable. Li_2O forms Li-A(BW) and Na_2O forms Na-J(BW), the cation present dictating the resulting framework structure [Fig. 2]. A study of Li-A(BW) and Na-J(BW) therefore affords insight into the structure directing effects of extra-framework cations Li^+ and Na^+ , independent of other structure directing agents.

Computer simulation of each phase involved in zeolite growth, the solution species and the bulk zeolite structures, serves as the first step on the road to understanding how these phases interact with one another during the growth process. The lowest energy geometries of the bulk structures of Li-A(BW) and Na-J(BW) were achieved with a relatively computationally cheap method, in which the energetics of the systems are described in terms of attractive and repulsive forces between the component ions. The final structures were obtained to within 3% of the experimental models. Uncertainty, however, surrounding the exact cation occupations within Na-J(BW) channels suggested by experiment prompted the synthesis of Na-J(BW) and re-determination of the cation occupations. Different still to the simulated model, more sophisticated dynamics simulations were performed to simulate the thermal response of the cations at room temperature (temperatures at which experimental structural data is recorded) and up to 400°C (synthesis temperatures). We found that the occupation of some cation sites fluctuate with temperature and hence the precise structure of Na-J(BW) is dependent on temperature fluctuations during synthesis. Now that we have understood the bulk structures, work is well underway to establish the solution species and zeolite surface structure using quantum mechanical methods. The final step will combine all components to simulate the mechanism of crystal growth, by application of advanced state-of-the-art simulation techniques.

