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The original paper was published at Macla,

Reference: M.A. Camblor, Macla, 2006, 6, 19-22

A digitalized version of the original paper will be made available at

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INTRODUCTION

The term *geoinspiration* was coined by Ruiz-Hitzky to simply denote the wealth of motivation that materials scientists can borrow from the mineral world. Any plausible synthetic strategy affording the preparation of new synthetic materials which, by its own characteristics or by the chemical pathway involved in its synthesis, resemble but do not match materials found in nature, would fit into that concept. The idea parallels that of *bioinspiration*, and intends to highlight the richness of materials and preparation routes that the synthetic scientist can get by studying, copying and modifying natural materials and processes. My purpose here is to show that over the last half a century zeolite scientists have successfully used a geoinspired approach, *avant la lettre*, to produce a vast range of new materials with a high impact in the industry and in every day life. While the importance of zeolites as industrial catalysts, adsorbents, active phases for industrial gas separation and purification and detergent builders is easily recognized, other applications closer to the man in the street may pass unnoticed. Two examples are the use of zeolites in double-glazing panels to keep windows clear and transparent and, for some more importantly, its use as active component in the self-cooling beer barrels recently introduced in the Spanish market.

While nature has “produced” 50 topologically different zeolites within a limited range of chemical compositions, synthetic geoinspired efforts have afforded to more than triple the number of available zeolitic topologies (161), while largely expanding the compositional range to cover not only aluminosilicates but also aluminophosphates, pure SiO₂ zeolites and many other compositions (containing Ge, Ga, B, Ti, V, Fe, ... in framework positions). The resulting materials may possess properties radically different from those presented by the natural zeolites, as is the case, for instance, of SiO₂ zeolites with strict hydrophobic properties and absolutely no cation exchange capacity. New structures, new compositions and hence, new physicochemical properties enlarge the range of applications of zeolites.

A BROADER DEFINITION OF ZEOLITES

A traditional definition of zeolites is that they are crystalline aluminotectosilicates with cavities, channels and windows of “molecular dimensions”. However, the successful geoinspiration we will deal with below have produced such an explosion of new compositions that has in fact broken this narrow definition. The Structure Commission (SC) of the International Zeolite Association (IZA) has been given the IUPAC authority to classify and name the different zeolitic topologies (see below), and the Commission has done so without restricting itself to aluminosilicate zeolites. This is, in our

opinion, a wise decision given that in occasions “zeolitic” topologies have been discovered first as aluminophosphates or SiO₂ and latter on as aluminosilicates. We can broaden the definition to materials that contain a framework of tetrahedral elements that share every vertex once and only once with four neighbours, and which have a density “significantly lower” than the corresponding “dense” phases. Thus, a pure SiO₂ or AlPO₄ material is a zeolite if is much less dense than quartz or berlinite, respectively.

The SC-IZA determines, on the basis of crystallographic reports, if a proposed structure is sound enough and new, and assigns a three letter code to its “topology” (see <http://www.iza-structure.org/databases/>). Topology, like that in Fig. 1, exclusively refers to the way in which the tetrahedra are interconnected, irrespective of its composition, symmetry or physicochemical properties. For instance, the SOD topology, first discovered in the aluminosilicate sodalite, actually exists also as pure silica, AlPO₄, zincosilicate, beryllsilicate, beryllarsenate, beryllgermanate, and many other compositional variants.

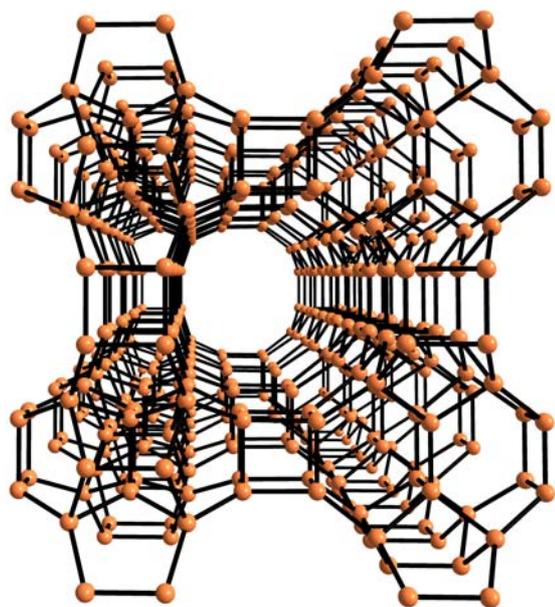


Figure 1.- The framework topology ISV, defining the connectivity of tetrahedra in the SiO₂ zeolite ITQ-7. One of the large pores is shown ($\approx 7\text{\AA}$ effective free diameter).

FROM NATURE TO THE LAB AND INDUSTRY

According to R.M. Barrer (1982), the natural formation of zeolites involves the following genetic types:

1. Crystals resulting from hydrothermal or hot-spring activity involving reaction between solutions and basaltic lava flows
2. Deposits formed from volcanic sediments in closed alkaline and saline lake-systems
3. Similar formations from open freshwater-lake or groundwater systems acting on volcanic sediments
4. Deposits formed from volcanic materials in alkaline soils
5. Deposits resulting from hydrothermal or low-temperature alteration of marine sediments
6. Formations which are the result of low-grade burial metamorphism

Thus, the most common conditions require hydrothermal reactions in which it is possible to identify several components as well as their roles (Table 1). Zeolite scientists have widely and systematically varied each component to produce a vast pool of materials with diverse structures, compositions and physicochemical properties in what it might be the best example of geoinspiration.

Table 1. Components in the hydrothermal crystallization of natural and synthetic zeolites

Role	Natural crystallization	Synthetic crystallization
Solvent	H ₂ O	H ₂ O HOCH ₂ CH ₂ OH and other alcohols H ₂ NCH ₂ CH ₂ NH ₂ and other amines Ionic Liquids none
T atoms	Si, Al (Be, Zn)	Si, Al, P, Ge, Ga, Ti, Be, V, Zn, Li,...
Counteranions	Ca, Na, K (Sr, Ba, Mg)	Na, K (Rb, Cs, Li) Organoammonium cations
Mineralizer	OH ⁻	OH ⁻ , F ⁻
Uncharged pore fillers	H ₂ O, small gases	H ₂ O, amines, organo-oxygenated compounds, small gases

The hydrothermal crystallization of zeolites in nature commonly occurs in a hydrothermal environment in the presence of alkali or alkali earth cations and a source of alumina and silica, predominantly in basic media. Water acts not only as a solvent but also as a pore filler, while the OH⁻ anion acts as a catalyst for the break and rebuilding of T-O-T bondings, allowing the transformation of a number of materials into zeolites.

Early studies on the synthesis of zeolites used similar conditions, including in some cases the use of volcanic glasses and high pressures, but more and more emphasis was put on using standard chemical reagents, affording a better reproducibility, at autogeneous pressure. At this stage, zeolites with low Si/Al ratios (1-3) with cavities and pores full of hydrated alkali cations were typically produced. Relevant from the applied point of view were zeolites X (FAU) and A (LTA), nearly fully saturated in Al, discovered by Milton at Union Carbide in the late fifties of the XX century (for a historical perspective of the early years of zeolite science see Flanigen, 1984). By just optimizing the synthesis conditions it was possible to increase the Si/Al ratio of some fully inorganic zeolites up to 5, thus improving their thermal and hydrothermal stability.

Interestingly, it was found that some zeolites that were easily prepared in the lab were scarcely, if ever, found in nature whilst the most common zeolites were very difficult to synthesize in the lab. A good example of the first case is zeolite A (LTA), which has no natural counterpart but is massively produced by the industry because of its use as a detergent builder. Another one is zeolite Y (FAU), of large technological importance as an active component of catalysts for gasoil cracking, and whose natural analog, faujasite, is relatively rare (although there is a recently discovered large bed at Jordan). A good example of the second case is clinoptilolite (HEU), which forms very large deposits with a high purity, but is very difficult to synthesize in the lab, with scarce reports which sometimes prove difficult to be reproduced.

This apparent paradox may be perhaps explained by first considering that nature can make use of a much longer reaction time than afforded by the industry or even the hardest working PhD candidate. Universities are unlikely to admit, and the government would probably not fund, a PhD thesis produced in a geological time scale. Clinoptilolite has Ca²⁺ as the main counteranion and this limits the maximum pH attainable to moderate values (say 9.5). Since OH⁻ is a catalyst for the reaction, a moderate pH value would imply a long crystallization time. By contrast, zeolite A is synthesized in Na form at very high pH values (typically above 12) and its industrial crystallization takes place in just 2-3 hours at temperatures around 80°C. As a second factor, zeolites may suffer transformations following the Ostwald rule and, thus, the most abundant natural zeolites may be those that are more stable or that were formed in relatively non-reactive environments. This is not the case in the lab or in industry, where we will favour fast reactions in highly reactive conditions and may be interested in isolating any metastable phase before a phase transformation occurs. For instance, zeolite A may rapidly transform into sodalite in the crystallizing medium, and this could also contribute to its scarcity (or so far non-existence) in nature.

GEOINSPIRED STRATEGIES

The next breakthrough in zeolite science was a very good example of the geoinspired strategies in the synthesis of zeolites. Knowing that the nature of counteranions has a clear influence on the zeolite formed and also knowing that they are finally occluded in pores and cavities, Barrer and Denny (1961) and Kerr and Kokotailo (1961) decided to substitute the small alkali cations, with their high charge density, by larger organic cations. The use of organic cations had two important effects: -a large increase in the attainable Si/Al ratios, determined by the large size of the cations and the limited intrazeolitic space. Even pure silica zeolites, containing Si-O⁻ and SiOH connectivity defects but no Al, could be obtained. -a significant structure direction effect that afforded the preparation of many zeolites with new topologies. The observation that certain zeolites could not be synthesized in the absence of a particular organic cation led to the concept of *template* in zeolite synthesis: the size and shape of the organic cation would determine the size and shape of the pore system in which it finally resides.

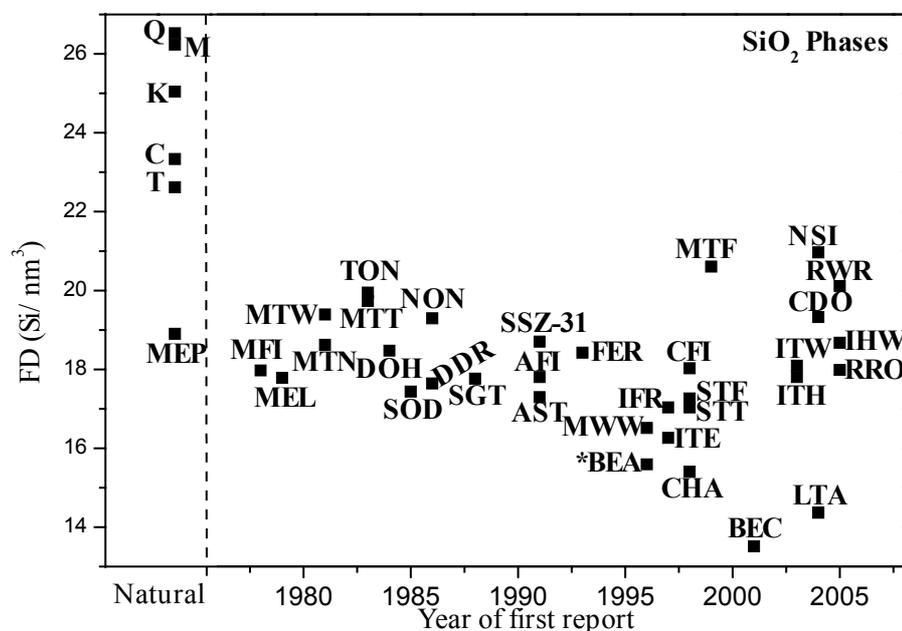
The template concept spurred scientist on the use of organic cations in zeolite synthesis and had a tremendous impact in zeolite science and technology. Many new structures were discovered and several of them had found use in important technological applications. However, the term template suggests a close geometric correspondence between host (zeolite) and guest (cation) and a large specificity between them that most frequently does not occur. This has led to the more frequent use of the term "Structure Directing Agent".

Another important strategy to obtain new zeolitic materials was the substitution of the Si and/or Al tetrahedral atoms (T atoms) by other elements. In some cases this simply led to the isomorphous substitution, some times affording materials with new interesting properties. For instance, the Ti-substituted zeolites are active and selective catalysts in the oxidation of a number of organic molecules using H₂O₂ or organic peroxides. But in certain cases the new T atom exerts some degree of structure-direction leading to new zeolitic structures. The synthesis of topologies containing "spiro-5" units using Zn is a good example. A particular case is constituted by the microporous AlPO₄ phases (Wilson, 1982), in which the Lowenstein rule (avoidance of AlOAl bridges) and the Al/P ratio of 1 leads to the strict alternation of Al and P and thus to topologies lacking windows with an odd number of tetrahedra. Many microporous AlPO₄ have been synthesized, sometimes displaying completely new topologies. The incorporation of other T atoms is also possible (Si, Mg, Co, Fe, Ga, Zn...).

An interesting geoinspired approach is represented by the use of fluoride as a mineralizer, substituting for OH⁻. In this case the synthesis may be carried out at circum-neutral pH, resulting in very high yields (Flanigen, 1978). The method is particularly well suited for the synthesis of pure silica phases, (Cambor et al., 1999) yielding after calcination a crystalline microporous SiO₂ material. Thus, there are seven crystalline SiO₂ phases found in nature, all of them being dense phases except for the rare mineral Melanophlogite (MEP), while there are now more than 30 synthetic microporous crystalline SiO₂ phases, with densities ranging from 50 to 80 % that of quartz (Fig. 2). For this burst of new SiO₂ phases, half of them reported within the last decade, it was necessary first to combine the use of fluoride and organic structure directing agents. But second it

was necessary to realize that the water/silica ratio in the synthesis mixture has also an important effect in directing the crystallization, with the empirical observation that the more concentrated the mixture the less dense the phase that crystallizes (what we call *the Villaescusa rule*, Cambor et al. 1999).

Figure 2. Pure SiO₂ crystalline phases represented as a function of framework density and year of discovery. The natural phases (quartz, Q, tridimite, T, cristobalite, C, moganite, M, stishovite, S, keatite, K and melanophlogite, MEP) are grouped together at the left.

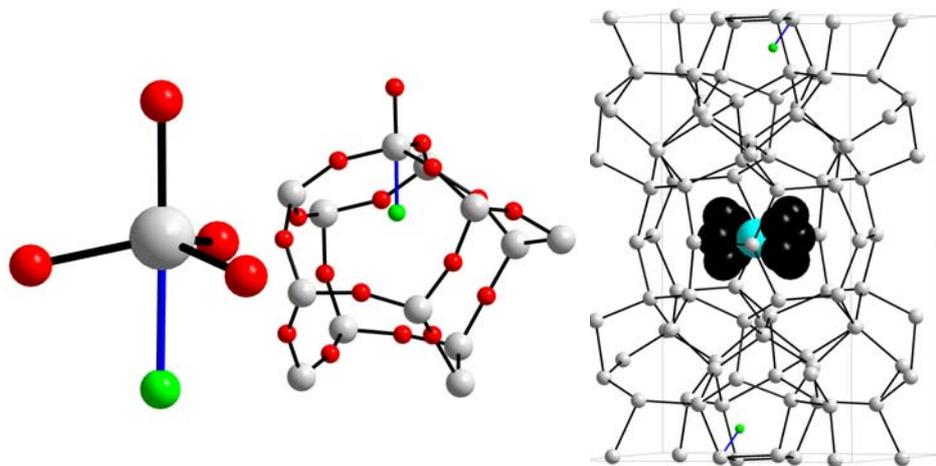


Of interest is also the fact that F⁻ ends up occluded into the final SiO₂ zeolite balancing the charge of the organic cation. Actually, F⁻ seems to have an structure-directing effect of its own, since it typically finally resides in small cavities of the zeolite, with a preference for cavities with some four member ring windows and a special preference for double four member rings, D4R. This type of cavity is relatively common in zeolites with low Si/Al ratios but was never observed in SiO₂

materials until the use of fluoride as a mineralizer (Caullet et al., 1991). It is also interesting that, with the exception of the D4R cavity, F⁻ has been shown to strongly interact with some of the Si atoms making the cavity. This may result in fivefold coordinated Si atoms (in SiO_{4/2}F⁻ units) or to a dynamic situation in which F jumps to coordinate with different Si atoms,

which thus change between 4 and 5 coordination (Koller et al. 1999). By calcining the as-made solids, both the organic cation and the fluoride anion are removed, leaving the microporous SiO₂ tetrahedral zeolite (Villaescusa et al. 1998).

Figure 3. A pentacoordinated [SiO_{4/2}F]⁻ unit (left), which forms part of a small cavity (centre) of nonasil (NON, right) and balances the positive charge of a [Co^{III}(η⁵-C₅H₅)₂]⁺ structure-directing agent (van de Goor et al., 1995). Grey Si, red O, green F, black C, blue N.



An interesting example of the combined structure-directing effects of a rigid organic SDA (a trimethylimidazolium) and of fluoride is the synthesis of pure silica ITQ-12 (ITW, Barrett et al. 2003). This material has D4R cavities, containing F⁻, and slit-shaped cages in which the rigid flat aromatic organic cation nicely fits (Yang et al. 2004). After removal of the guests the material shows a large selectivity for the adsorption of propene in propene/propane mixtures. The pure SiO₂ composition avoids pore blockage by acid-catalysed polymerisation, while adsorption is not distorted by the presence of humidity. The selectivity is virtually infinite at 80°C, allowing for a separation process cheaper and more environmentally friendly than the current cryogenic distillation (Olson et al. 2004).

CONCLUSIONS

We intended to show that geoinspired strategies, based on the study and systematic modification of natural processes, may yield a huge wealth of interesting materials, not to speak about the amusement of the chemistry involved. We now wonder what would happen if similar approaches and efforts were extensively applied to other minerals.

ACKNOWLEDGEMENTS

Financial support by the Spanish CICYT (projects BTE2003-05757-C02-02 and MAT2003-06003-C02-01) is gratefully acknowledged. The author wishes to thank Prof. Ruiz-Hitzky for stimulating discussions on his *geoinspiration* concept. Thanks are also due to P. Aranda, L.A. Villaescusa and C.M. Zicovich-Wilson.

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