

1 Nature's Porous Materials: From Beautiful to Practical

Porous materials are materials that contain voids, channels, holes, or basically pores. This type of material has always attracted a lot of attention as the presence of pores means that the material possesses an internal surface area of interest for all type of applications (see Chapter 2). Nowadays, many porous materials are made in the laboratory and can even be produced on a large industrial scale (see Chapters 3 and 4). However, many porous materials are naturally occurring and were first produced in “Nature’s laboratory” without any human influence. In fact, mankind has often based the preparation procedures of synthetically porous materials on processes that occur in nature.

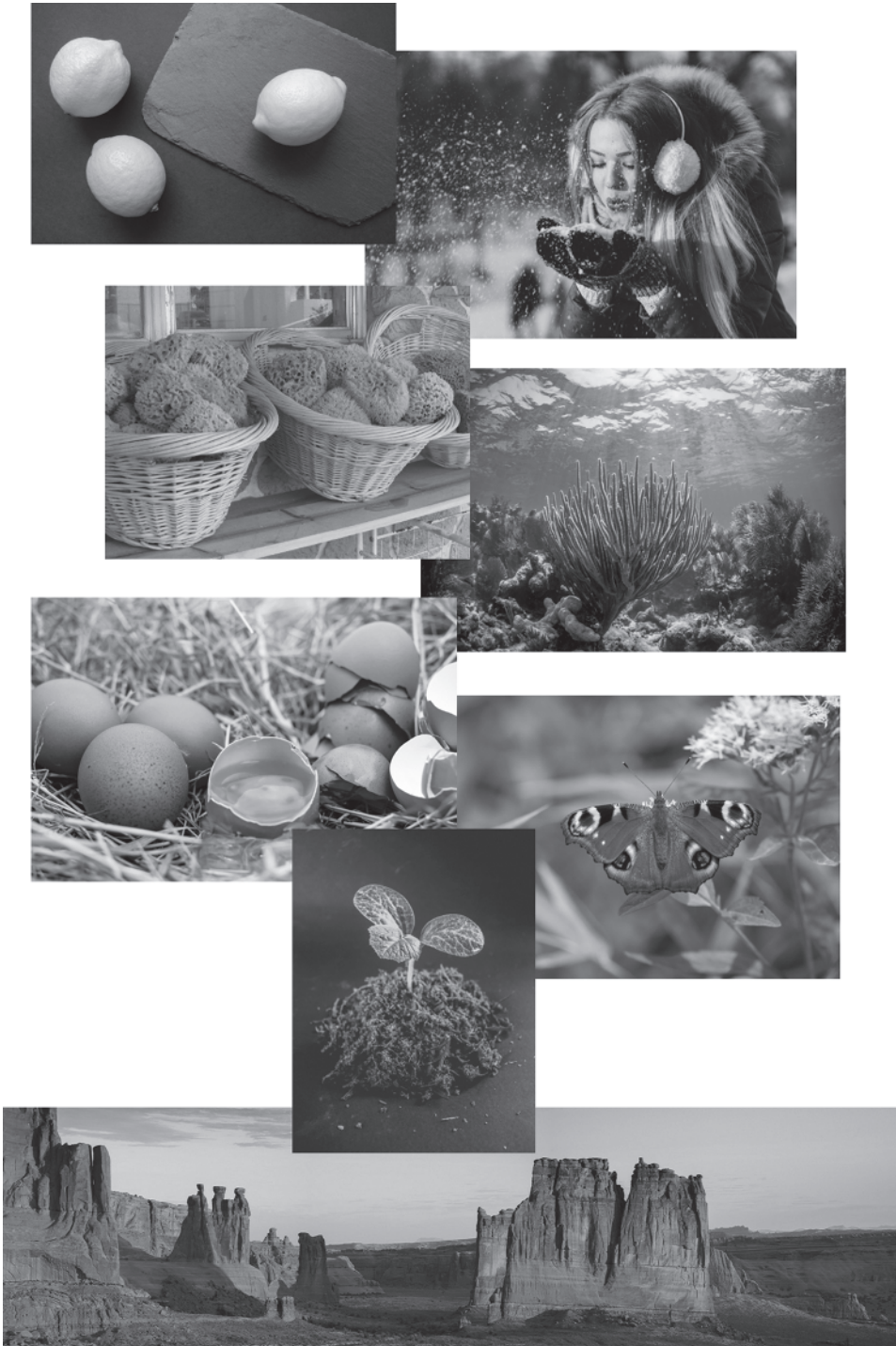
Nature has found a way to produce beautiful and practical porous materials and they can be very diverse: tissue or bones in the human body and animals, rocks, fruit, and so on. A general overview with some examples is presented in Figure 1.1. Besides that, mankind has found its own way to introduce porosity in many materials as some examples clearly demonstrate (Figure 1.2). Ceramics, bricks, and clothing are a few items that were developed very early.

This chapter describes a few carefully selected naturally occurring porous materials. It aims to give the reader a taste of what is available in nature. These materials are also the foundation for development of synthetic porous materials that are more elaborately described in Chapters 3–9 of this book. Silicas and zeolites are also materials that were originally found in nature before a synthetic procedure was discovered to produce them. They will not be covered in this chapter, as they are described in depth in Chapters 3 and 4.

1.1 Living Porosity

1.1.1 Butterflies

Porous materials can be found in animal and human bodies. The bones and lungs of humans are famous examples of ingenious porous structures. In particular, the bones of a human skeleton are very robust, despite their high porosity, as they must support and protect our body and vital organs, respectively. Animals can also create porous structures of very diverse and beautiful shapes. For example, sponges are multicellular organisms that have an entire body containing pores. The wings of butterflies are not only colorful and useful to fly, but they are also porous (Figure 1.3). The cuticle on the scales of these butterflies’ wings is composed of nano- and microscale,

**Figure 1.1**

Examples of naturally occurring porous materials: lemons, snowflakes, sea sponges, coral reef, egg shells, butterfly wings (European peacock butterfly), soil, and sandstones. Source: All photographs are public domain.



Figure 1.2
Synthetic porous materials, all made by mankind: Concrete road, paper, fabric of clothes, chalk, ceramics, cake, bread, pottery, bricks, and artificial sponges for cleaning. Source: All photographs are public domain.

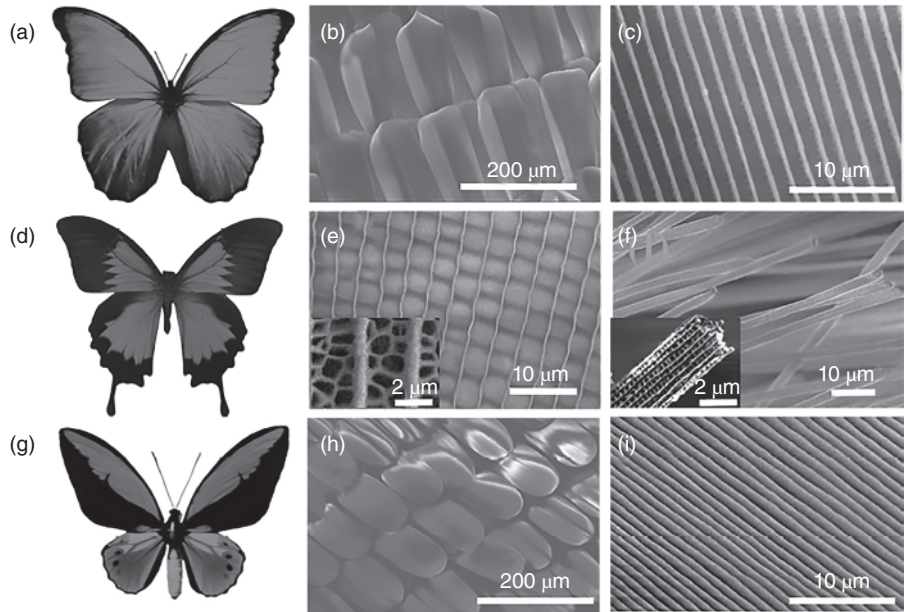


Figure 1.3

(a) Optical image of *M. menelaus*; (b,c) Scanning Electron Microscope (SEM) image of the nanostructure of the wing under different magnification. (d) Optical image of *P. u. telegonus*; (e) SEM image of the nanostructure of the blue region; the insert in (e) is the high magnification of SEM image; (f) SEM image of the nanostructure of the fiber region; and, the insert in (f) is the high magnification of SEM image. (g) Optical image of *O. c. lydius*; (h,i) the SEM image of the nanostructure of the wing according to different magnification. Source: Reproduced with permission. Taken from Ref. [1], open access: <https://creativecommons.org/licenses/by/4.0/>.

transparent, chitin-and-air layered structures. Rather than absorb and reflect certain light wavelengths as pigments and dyes do, these multiscale structures cause light that hits the surface of the wing to diffract and interfere. Cross ribs that protrude from the sides of ridges on the wing scale diffract incoming light waves, causing the waves to spread as they travel through spaces between the structures. The diffracted light waves then interfere with each other so that certain color wavelengths cancel out (destructive interference) while others are intensified and reflected (constructive interference). The varying heights of the wing scale ridges appear to affect the interference such that the reflected colors are uniform when viewed from a wide range of angles.

1.1.2 Algae

Single-celled diatoms can also produce porous structures, however, on a very different scale. Diatoms are microalgae that can be abundantly found in, for example, oceans all around the world. They are part of the phytoplankton family and contribute a staggering 20% of total oxygen produced on our planet every year. They are very unique and useful small creatures and, moreover, they produce a porous cell wall or protective shell called a frustule [2]. The frustule consists of two overlapping structures with identical shapes but slightly different in size. They are called the thecae or valve, and a girdle band or expansion joint holds the two thecae together.

The frustule is entirely made from silica, with a very well-defined structure and unique for every diatom species. It is estimated that approximately 200 000 separate

species exist with very different frustules [3]. The dimensions of the frustules can be very different depending on the species. Pore sizes range from 3 nm up to a few hundred nm [4].

A few examples of different species are presented in Figures 1.4–1.6. These figures clearly show the different morphologies, but also diverse types of porosity. These frustules do not only have beautiful porous structures, they can also be used practically.

These algae can be produced on a large industrial scale as they possess a very fast growth rate and only need a limited amount of space. Moreover, they use carbon for

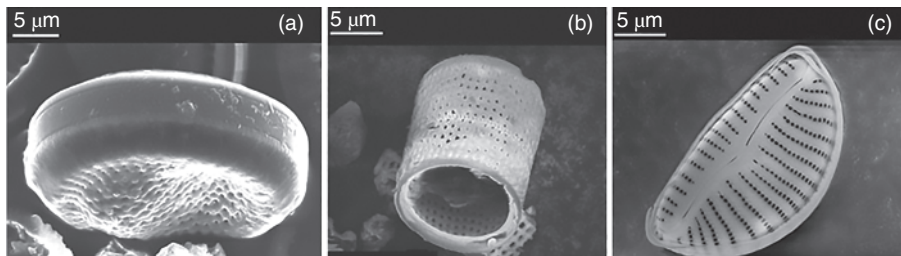


Figure 1.4

SEM images of purified diatom frustules of *Coscinodiscus* sp. (a), *Melosira* sp. (b) and *Navicula* sp. (c). Scale bar = 5 μm. Source: Reproduced with permission of John Wiley & Sons, Ltd. Taken from Ref. [4c]

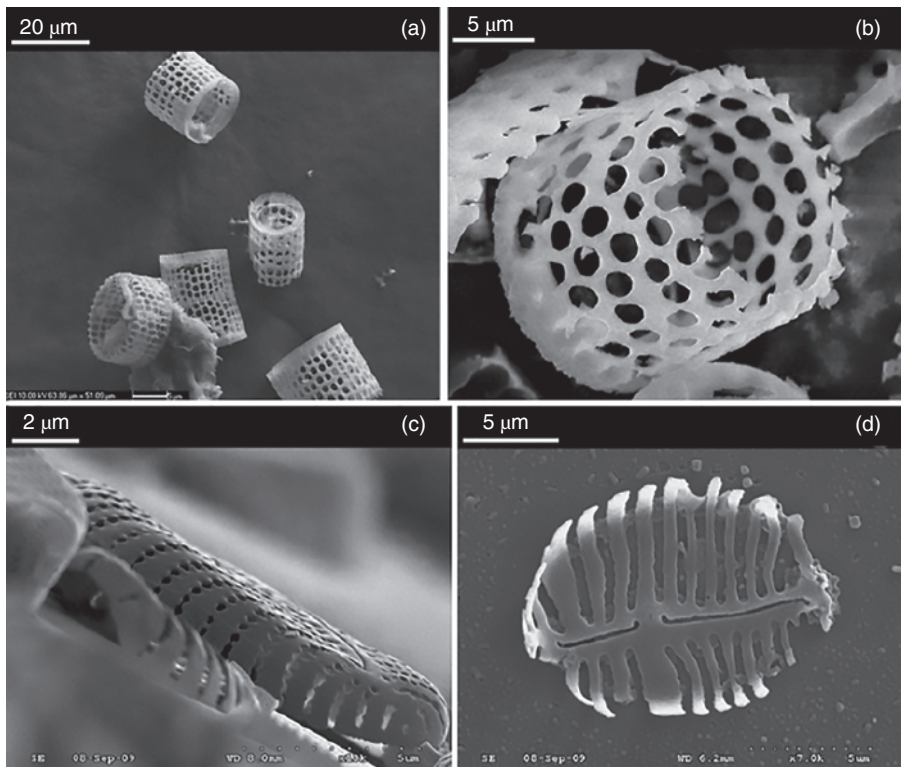


Figure 1.5

SEM images of diatom frustules after 1% HF treatment: (a) and (b) *Melosira* after 2 and 3 h, respectively; (c) and (d) *Navicula* after 1 and 2 h, respectively. Source: Reproduced with permission of Springer Nature. Taken from Ref. [4c].

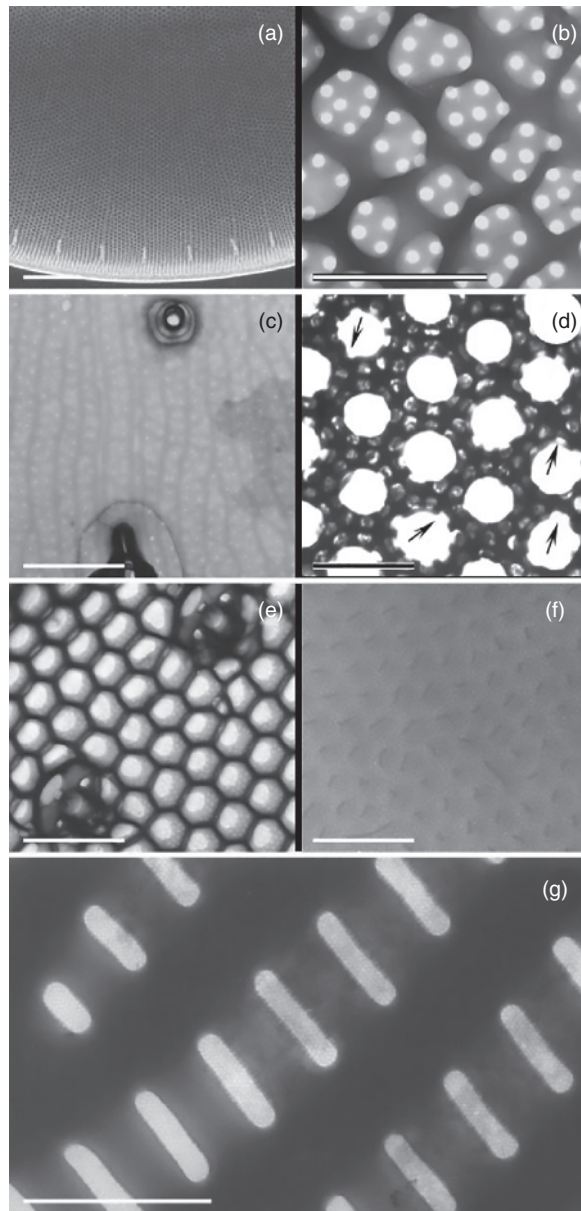


Figure 1.6

Electron micrographs of the pore structures of different diatom species: (a) *Lauderia borealis*; (b) *Odontella sinensis*; (c) *Thalassiosira weissflogii*; (d) *Coscinodiscus granii*; (e) *Navicula salinarum*; (f) *Nitzschia sigma*; (g) *Stauroneis constricta*. Scale bar = 5 μm (a) and 0.1 μm (b–g). Source: Reproduced with permission of the RSC. Taken from Ref. [4b].

photosynthesis, which also makes them very interesting. It is believed that diatoms for these reasons are a very promising alternative biomass resource to produce biofuels. Additionally, they present a new source of porous silica with very defined pore sizes and distinct morphologies. The silica source can be further used as support for all kinds of applications (Chapter 5).

As an example, here we show how we extracted the silica from algae and used it as a photocatalyst for air purification [5]. Diatom frustules were extracted from a sample containing a cultivation of *Thalassiosira pseudonana* in its salt water medium. After an initial washing procedure to remove the majority of the salts, an acid treatment was used to remove any remaining carbonates and partially digest the organic matter. After washing away the acid, calcination in air at 550 °C was used to completely free the frustules of organic components. The resulting pure silica sheets are shown in Figure 1.7.

It can be clearly seen that these silica sheets contain very uniform pores. We then deposited titania nanoparticles onto these frustule sheets. The results are shown in Figure 1.8.

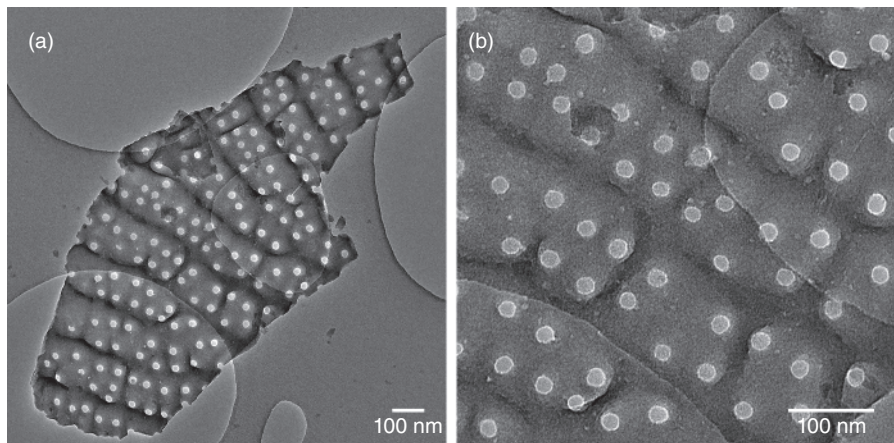


Figure 1.7

Silica extracted as diatom frustules from the algae species *Thalassiosira pseudonana*. Source: Reproduced with permission of Elsevier. Taken from Ref. [5].

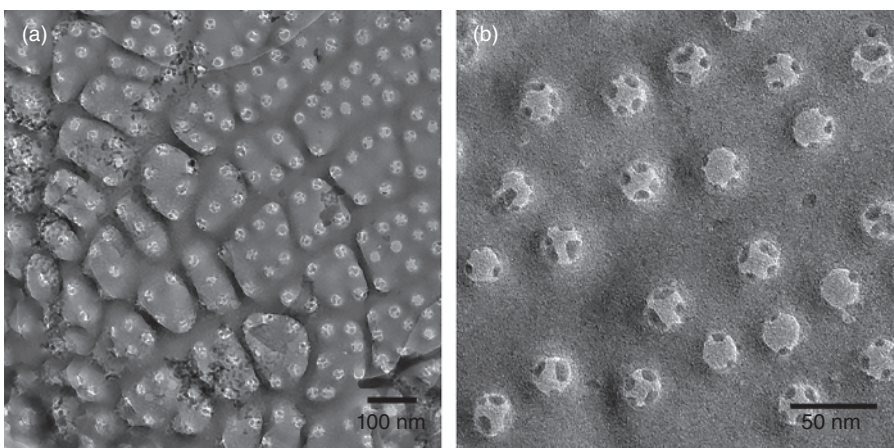


Figure 1.8

TEM images of the optimized titanium functionalized frustules, showing an overview of the nanoparticles (a) and a detail of the nanoparticles contained inside the pores. Source: Reproduced with permission of Elsevier. Taken from Ref. [5] with permission.

It is remarkable how all the titania nanoparticles are situated in the pores of the silica nanosheets. These materials were shown to be very active photocatalysts for ambient air purification, outperforming the current commercial benchmarks.

1.1.3 Bamboo

Another example of an organic source that has a high silica content are bamboo leaves. An amount of 1 g of bamboo leaves contains 0.03 g of silica. A careful extraction is again key to extract the beautiful and fluffy silica flakes as presented in Figure 1.9.

As we zoom in closer on the silica that is extracted from the bamboo leaves, we can see nicely in Figure 1.10 how the silica is the exact negative replicate of the bamboo leaf.

1.2 Clay Minerals

1.2.1 Natural Clays

Clay minerals are yet a completely different type of porous materials [6]. They naturally occur in mud, soils, rocks, sediments, and so on. The materials are formed in the presence of water and are most of the time fine-grained. They have been used by mankind for ages, especially in early civilization, to produce ceramics, but now are also used in cosmetic and pharmaceutical applications.

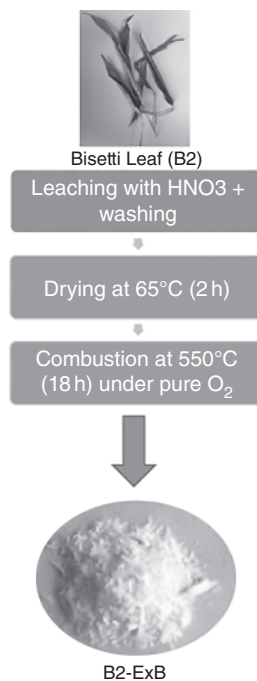


Figure 1.9
Extraction of silica out of bamboo.

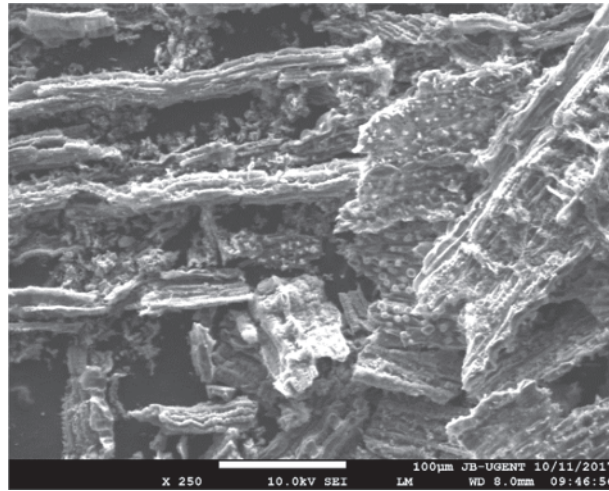


Figure 1.10
SEM picture (×250) of pure silica extracted from a bamboo leaf.

Most clay minerals are phyllosilicates or sheet silicates (Figure 1.11). They represent an entire family of silicate materials that mainly contain aluminum, silicon, and oxygen atoms. They possess a sheet-like structure with layers of corner sharing SiO_4 tetrahedra and AlO_4 octahedra (Figures 1.12 and 1.13) where the oxygen atoms

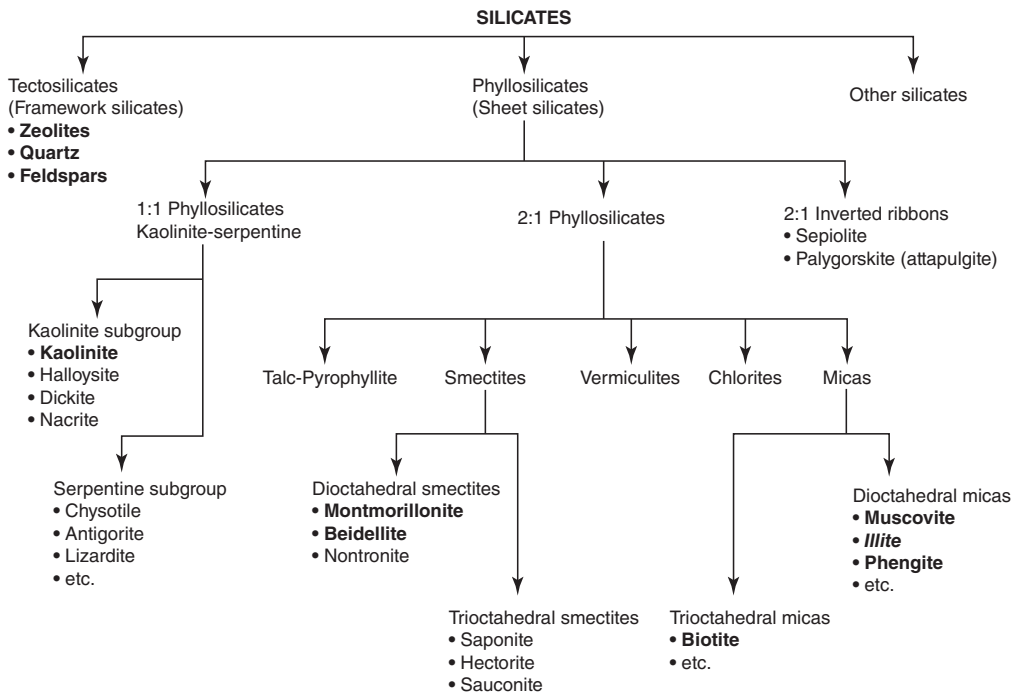
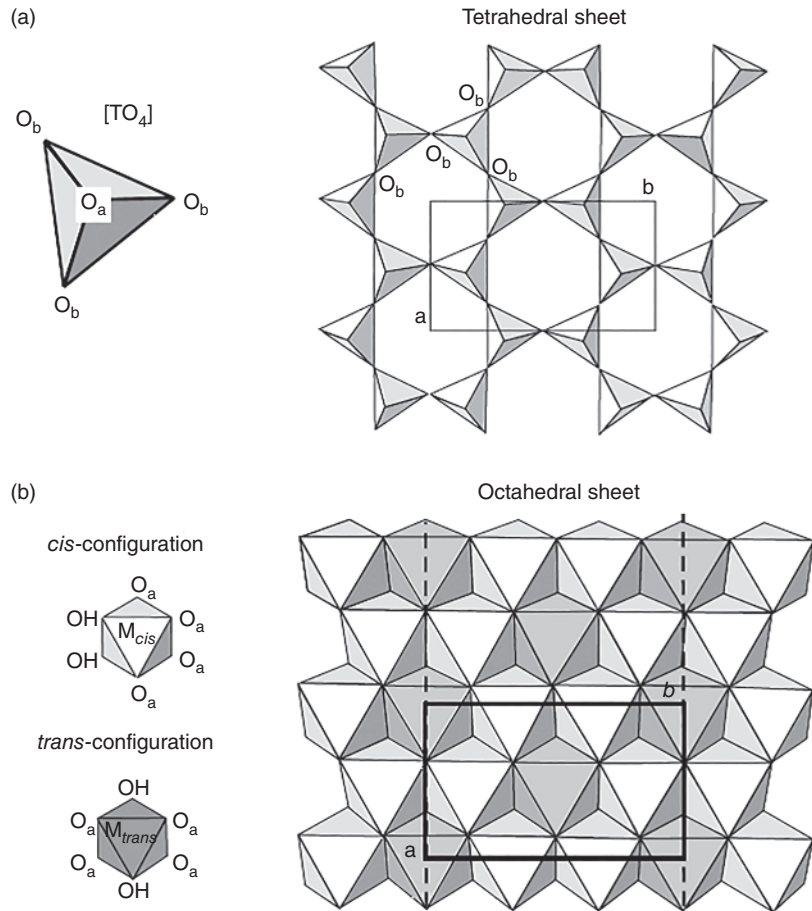


Figure 1.11
Classification of silicates. Source: Adapted from Z. Adamis et al. [7].

**Figure 1.12**

Schematic representation (a) of a tetrahedron unit and tetrahedral sheet; and (b) of an octahedron unit and octahedral sheet. Source: Adapted from G. E. Christidis et al. [6a].

are commonly used. The clay minerals are categorized according to the type of connection of the tetrahedral and octahedral layers. A 1 : 1 clay mineral consists of one tetrahedral and one octahedral group in each layer. The smectite structure, shown in Figure 1.13, is a typical example of a phyllosilicate and a 2 : 1 type of clay mineral. Here, two tetrahedral sheets are connected to each side of an octahedral sheet.

The composition of the tetrahedral and octahedral sheets will determine whether the entire layer is negatively charged or not. There are also negatively balanced clays, the Layered Doubled Hydroxides (LDH); hydrotalcites are an example. In cationic clays, a charged layer will be balanced out by small cationic species, such as Na^+ or K^+ atoms, that are present in the so-called interlayer of the clay mineral. This interlayer can also contain water (Figure 1.13).

The stacking of the different layers (containing tetrahedral and octahedral sheets), vary with the interlayer will form a crystalline phyllosilicate material. Examples of 1 : 1 clay minerals are the kaolinite and serpentine group with kaolinite (Figure 1.14a) being the most famous mineral of that group. The clay minerals of this group have a

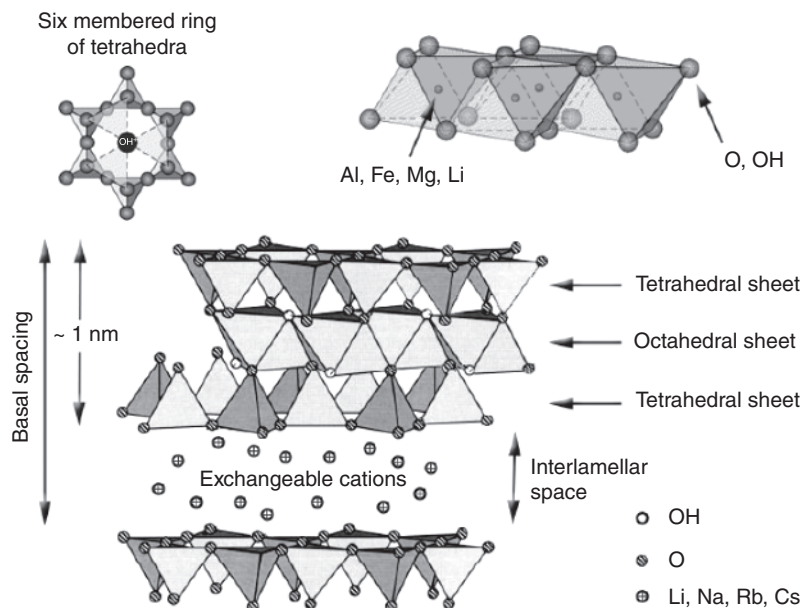


Figure 1.13

An example of a clay mineral: the Smectite structure (2 : 1 clay) with two tetrahedral sheets that sandwich one octahedral sheet within the clay-stacking pattern. Source: Reproduced with permission of the RSC. Redrawn from Ref. [8].

general formula of $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ and normally do not have any layer charge. Halloysite is the hydrated form of kaolinite and can exhibit a wide range of morphologies, such as the tubular crystals as shown in Figure 1.14b.

Due to the possibility of containing cations in the interlayer, clay minerals are highly suited to being ion exchange materials in many environmental but also industrial applications [6a]. They play an important role in, for example, catalytic cracking processes. They can act as an acid catalyst as they contain both Lewis and Brønsted acid sites on the clay mineral surface [9]. Also, biological and biomedical applications have been explored with clay minerals [8]. These materials are closely related to zeolites and zeotypes (Chapter 3).

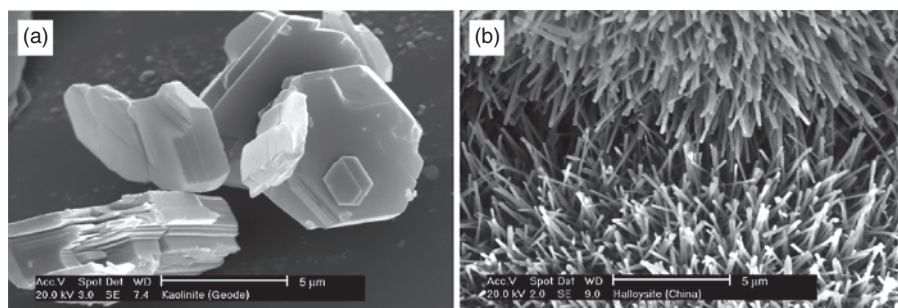


Figure 1.14

SEM images of the clay minerals (a) Kaolinite (pseudo hexagonal crystals) and (b) halloysite (tubular crystals). Source: Taken from Ref. [6a].

1.2.2 Pillared Interlayered Clays – PILCs

As ever, humans have tried to tune such clays to their specific demands. One famous example was the research into the synthesis of PILCs. This was based on the pioneering work of Richard Maling Barrer in 1955 [10]. He obtained microporous materials by replacing the interlayer exchangeable cations in the smectite montmorillonite with tetraalkylammonium ions. However, organic pillared clay minerals of this type are thermally unstable. At temperatures above 250 °C the interlayers collapse. When used below the decomposition temperature, these clays can, however, still be applied as catalysts [11] or adsorbents [12]. In the late 1970s, scientists, still in search for an answer to the need for large-pore nanoporous materials (see Chapter 5), started investigating the possibility of creating porosity in the interlayer space of layered clay hosts by inserting inorganic polymers [13]. These PILCs are prepared by exchanging the charge-compensating cations (e.g. Na^+ , K^+ , and Ca^{2+}) between the swelling phyllosilicate clay layers with larger polymeric or oligomeric hydroxy metal cations. Upon heating, these metal hydroxy cations undergo dehydration and dehydroxylation, whereby stable metal oxide clusters are formed (e.g. Al_2O_3 , TiO_2 , Fe_2O_3 , ...).

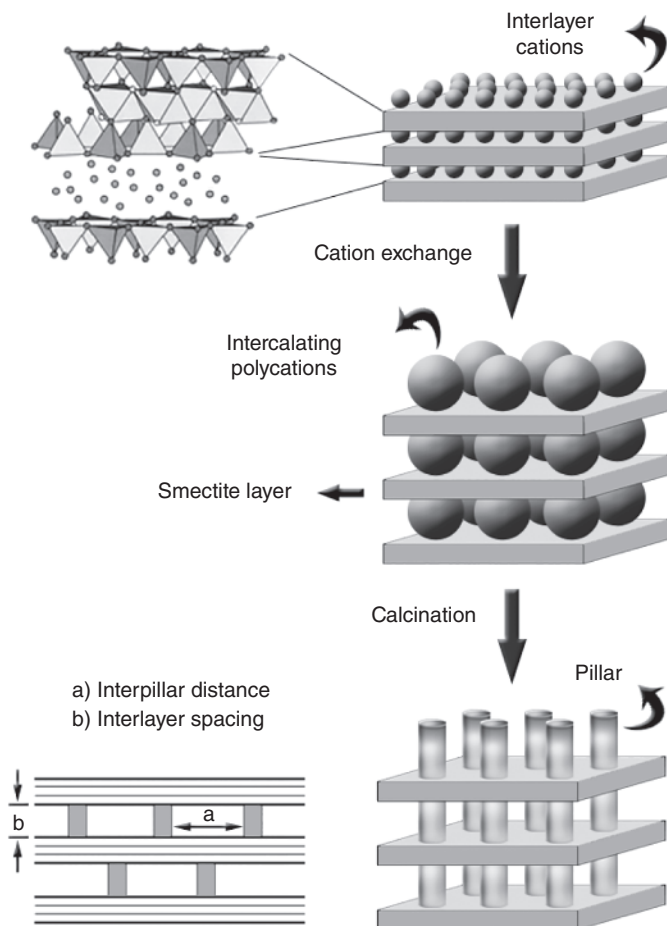


Figure 1.15

Concept of pillaring.

These metal oxide clusters act as *pillars*, keeping the silicate layers permanently separated and creating an interlayer space. In Figure 1.15 a schematic overview is given, illustrating the concept of pillaring. With these novel two-dimensional aluminosilicates, an easy method to develop materials with pores ranging from 0.5 to 2.0 nm and surface areas up to $500 \text{ m}^2 \text{ g}^{-1}$ was introduced. Moreover, clay minerals intercalated with inorganic species retain their porosity above 300°C .

Ever since the first announcement of the commercial availability of PILC in 1979 [13c] their use in petroleum cracking alone has exceeded that of other catalysts. With an acidity as strong as zeolite Y (Chapter 3), PILCs demonstrate a high activity in cracking, while displaying a selectivity for larger product molecules. However, due to their low hydrothermal stability, the original objective of using these materials as catalysts for Fluid Catalytic Cracking (Chapter 3) was not achieved [14]. Nevertheless, PILCs have proved to be very interesting acid catalysts in various organic reactions [15].

However, with the discovery of a new class of ordered mesoporous aluminosilicates in 1992, namely M41S (Chapter 5) [16], a new era in ordered porous materials commenced and much of the interest in PILCs faded away.

References

1. Elbaz, A., Lu, J., Gao, B. et al. (2017). *Polymers* 9: 386.
2. Hamm, C.E., Merkel, R., Springer, O. et al. (2003). *Nature* 421: 841–843.
3. Mann, D.G. and Droop, S.J.M. (1996). *Hydrobiologia* 336: 19–32.
4. (a) Vrieling, E.G., Beelen, T.P.M., van Santen, R.A., and Gieskes, W.W.C. (2000). *J. Phys. Chem.* 36: 146–159; (b) Vrieling, E.G., Beelen, T.P.M., Sun, Q.Y. et al. (2004). *J. Mater. Chem.* 14: 1970–1975; (c) Zhang, D.Y., Wang, Y., Zhang, W.Q. et al. (2011). *J. Mater. Science* 46: 5665–5671; (d) Gelabert, A., Pokrovsky, O.S., Schott, J. et al. (2004). *Geochim. Cosmochim. Acta* 68: 4039–4058.
5. Ouwehand, J., Van Eynde, E., De Canck, E. et al. (2018). *Appl. Catal. B-Environ.* 226: 303–310.
6. (a) Christidis, G.E. (2010). *Advances in the Characterization of Industrial Minerals* (ed. G.E. Christidis). European Mineralogical Union; (b) Kerr, P.F. (1952). *Clays Clay Miner.* 1: 19–32; (c) Theng, B.K.G. (ed.) (1979). *Clay minerals*, Ch. 1. In: *Developments in Soil Science - Formation and Properties of Clay-Polymer Complexes*, vol. 9, 3–36. Elsevier; (d) Velde, B. (1995). *Origin and Mineralogy of Clays: Clays and the Environment* (ed. B. Velde), 8–42. Berlin, Heidelberg: Springer.
7. Adamis, Z., Williams, R.B., and Fodor, J. I. L. Organisation, U. N. E. Programme, W. H. Organization, I. P. o. C. Safety, I.-O. P. f. t. S. M. o. Chemicals (2005). *Bentonite, Kaolin, and Selected Clay Minerals*. World Health Organization.
8. Ghadiri, M., Chrzanowski, W., and Rohanzadeh, R. (2015). *RSC Adv.* 5: 29467–29481.
9. Wu, L.M., Zhou, C.H., Keeling, J. et al. (2012). *Earth-Sci. Rev.* 115: 373–386.
10. Barrer, R.M. and Macleod, D.M. (1955). *Trans. Faraday Soc.* 51: 1290.
11. Vaccari, A. (1999). *Appl. Clay Sci.* 14: 161–198.
12. (a) Zhu, L.Z., Ren, X.G., and Yu, S.B. (1998). *Environ. Sci. Technol.* 32: 3374–3378; (b) Meier, L.P., Nueesch, R., and Madsen, F.T. (2001). *J. Colloid Interf. Sci.* 238: 24–32.
13. (a) Brindley, G.W. and Sempels, R.E. (1977). *Clay Miner.* 12: 229–237; (b) Lahav, N., Shani, U., and Shabtai, J. (1978). *Clays Clay Miner.* 26: 107–115; (c) D. Vaughan, R. Lussier, J. Magee, US Patent: Pillared interlayered clay materials useful as catalysts and sorbents. Number: US4176090, 1979; (d) D. Vaughan, R. Lussier, J. Magee, US Patent: Stabilized pillared interlayered clays. Number: US4248739, 1981; (e) D. Vaughan, R. Lussier, J. Magee, US Patent: Pillared interlayered clay products. Number: US 4271043, 1981.
14. Magee, J.S. and Mitchell, M.M. (1993). *Fluid Catalytic Cracking: Science and Technology*, vol. 76. Elsevier.
15. Ding, Z., Klopogge, J.T., Frost, R.L. et al. (2001). *J. Porous Mat.* 8: 273–293.
16. Beck, J.S., Vartuli, J.C., Roth, W.J. et al. (1992). *J. Am. Chem. Soc.* 114: 10834–10843.

