

MICRO- AND MESOPOROUS MINERALS PHASES

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The crystal structure of porous materials (minerals) is characterized by the presence of a framework (host structure) which is crossed by channels (pores) wide enough to allow exchange of guest chemical species. Conventionally the effective width of a channel must be larger than 3.2 Å, *i.e.* the size of a N₂ molecule. Micro- and mesoporous materials have effective channel widths in the range 3.2–20 Å and 20–500 Å, respectively; for sizes larger than 500 Å a material is classified as macroporous.

The exchange and catalytic properties connected with zeolites, also known as molecular sieves, are well known. Less known is instead that other minerals show, at least in principle, the same porous features and are thus zeolite-like mineral phases. Following an international meeting (Accademia dei Lincei, Roma, December 2004; FERRARIS, 2005) dedicated to porous mineral phases other than zeolites, a volume has been published (FERRARIS & MERLINO, 2005) which reports twelve invited contributions there presented. It turns out that porous features are shown by the crystal structures of mineral and mineral-like phases belonging, among others, to the following groups: heterophyllosilicates, palysepiolites, rhodesite-related structures, labuntsovite, several titan-, niobo-, zircono-, vanado-, stanno-, and indo-silicates, sodalite, cancrinite, davyne, tobermorite, gyrolite, manganese oxides (tunnel oxides), apatite, sulfides, selenides, chrysotile, carbon forms, and clathrates.

In several cases porous properties of the mentioned phases have been observed in Nature, but their technological exploitation is still in its infancy. A promising feature is that their framework is not only tetrahedral as in zeolites, but includes also other polyhedra: the terms heteropolyhedral and mixed octahedral-pentahedral-tetrahedral frameworks are in use. In other cases completely non-silicate frameworks occur as in sulfides and oxides. The presence of coordination polyhedra other than tetrahedral ones opens the possibility of inserting a wide variety of cations in the framework thus allowing the synthesis of porous compounds showing, *e.g.*, interesting optical and magnetic properties. Tunability of these properties can be achieved by inserting the most appropriate cation (*e.g.*, rare earth elements) and/or by using intermediate members of solid solutions. Examples of the mentioned types of porous structures will be presented at the meeting.

Of particular interest is the possibility, based on analogy with clays, of obtaining from heterophyllosilicates (*cf.* FER-

RARIS & GULA, 2005) mesoporous pillared materials (FERRARIS, 2006). According to the IUPAC nomenclature, “pillaring is the process by which a layered compound is transformed into a thermally stable micro- and/or mesoporous material with retention of the layer structure.” The structural parallelism between phyllosilicates, like micas and smectites, and heterophyllosilicates leads to speculate on the possible use of some of the latter compounds as starting material to produce structures analogous to the pillared clays. Observations in the field (KHOMYAKOV, 1995; CHUKANOV & PEKOV, 2005) and few laboratory experiments (CHELISHCHEV, 1972) suggest that research work aiming to obtain pillared heterophyllosilicates could be rewarding. In particular, there are several evidences of solid-state transformations from one to another member of the bafertsite series via leaching/substitution of the interlayer composition (*i.e.*, the *HOH* layer is preserved). In some cases, swelling becomes evident by comparing the structures of the parent and daughter phases. As summarized by KHOMYAKOV (1995), an active interaction with water, at epithermal and hypergene or even atmospheric conditions, is characteristic of many highly alkaline titanosilicates in the bafertsite-like series. For example, the following transformations lead to phases that show a (more) hydrated and, to some extent, swelled interlayer relative to the parent phases: *vuonnemite* → *epistolite*; *lomonosovite* → *murmanite*.

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