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Modular structures – the paradigmatic case of the heterophyllosilicates

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Abstract. As an example of modular structures, the layered silicates named heterophyllosilicates are reviewed with emphasis on their polysomatic, merotype, plesiotype and topologic aspects. The opportunities offered by a modular analysis of complex inorganic structures are shown via the procedure followed to model the crystal structure of nafertisite and to build various types of series. The heuristic power of the modular crystallography is also proved by successful analyses of oriented intergrowths (and twinning) in members of the bafertisite mero-plesiotype series and the consequent appearance of disorder in the crystal structures of samples affected by syntaxy, *e.g.* epistolite. Finally, the hypotheses of using, by analogy with phyllosilicates, *HOH* layers of some heterophyllosilicates to obtain hybrid layered materials are reviewed. In fact, the heterogeneous *HOH* layers of the heterophyllosilicates can formally be derived by substituting rows of disilicate groups with *X*-polyhedra (*X* mainly Ti) in the *T* sheets of a *TOT* phyllosilicate layer.

Introduction

Since the beginning of crystal chemistry, coordination polyhedra have been recognized as building units of the inorganic crystal structures to overcome the lack of molecules in these structures. Aggregations of coordination polyhedra, *e.g.* SiO_4 tetrahedra, to describe and structurally classify inorganic structures have long been recognized. In particular, series of compounds based on accretion of complex modules (*homologous series*) have been introduced about 50 years ago by Magnéli (1953), but only the successful introduction of the *polysomatic series* of biopyriboles by Thompson (1978) gave a great impulse to a new branch of crystallography named *modular crystallography*. For a wide review one can see Merlino (1997) and Ferraris *et al.* (2004) who discuss different types of modularity, including polytypism and twinning. For the purposes of this article we refer to the polysomatic series, *i.e.* to a kind of homologous series the members of which share at least two complex modules, and related *merotype* and *plesiotype series* (Makovicky, 1997).

As illustrated in the general reviews quoted above, the success of a modular analysis of complex structures is due to its usefulness under several aspects, such as: (i) predicting and modelling unknown structures which are related to known series; (ii) establishing structure-property correlations that may indicate paths to synthesize new materials; (iii) interpreting structural defects and oriented growths that may lead to an apparent structure disorder and modifications of the chemical composition; (iv) classification of structures. Aspect (ii) is an important tool in materials science; in fact, following the case of tetrahedral-octahedral-tetrahedral (*TOT*) layers of the phyllosilicates (layer silicates), which are raw material to prepare pillared clays and hybrid organoclays, several other inorganic layers are intensively investigated to synthesize hybrid materials [see, *e.g.*, Auerbach *et al.* (2004)]. Often families of layered materials form polysomatic or related series.

Reviewing the (poly)somatic features of the layered titanosilicates named *heterophyllosilicates* by Ferraris *et al.* (1996), this paper intends to provide a first approach to principles, problems and applications of the fast expanding topic of modular structures.

Polysomatic and related series

Following the definition of biopyriboles, several polysomatic series have been described; for earlier reviews one can see Veblen (1991) and Merlino (1997). Most of the known polysomatic series are based on two building modules, *A* and *B*, which often, but not necessarily, are planar; cases involving more modules can be found, *e.g.*, in the quoted reviews.

The chemical composition of the members and the parameter stacking the layers linearly depend, in the order, on the composition and the dimensions of the building modules. With reference to a two-module series, the gen-

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eral formula of a polysomatic series is formally indicated as A_mB_n; the ratio m/n fixes the chemical composition but not the sequence of modules that can be different for a pair of m, n values. Different members with the same m, n values are polytypes because their structures differ only in the stacking sequence of the same modules. Examples will be mentioned for heterophyllosilicates; nomenclature problems connected to these aspects are discussed, *e.g.*, by Armbruster (2002) for series involving the minerals högbomite, nigerite, and taffeite. The periodicities (cell parameters) that are parallel to the building layers must be approximately the same (or multiples) in all layers, otherwise the dimensional matching at the interface between two modules would be impossible.

The number of known complex modules that occur in distinct structures is increasing. Limited to oxygenated and halide compounds, the occurrence in literature of the following modules has been noticed by Ferraris *et al.* (2004): apatite, bastnäsite, brucite, corundum, epidote, fluorite, gehlinite, gibbsite, halite, huanghoite-(Ce), lomonosovite, lorenzenite, mica, nacaphite, nasonite, nolanite, palmierite, palygorskite, perovskites, pyrochlore, pyroxene, rutile, seidozerite, schafarzikite, sepiolite, silinaite, spinel, synchisite, talc, topaz and zhonghuacerite-(Ce).

Merotype (μέϱος = part) and *plesiotype* (πλησίος = near) *series* (Makovicky, 1997) are strictly related to the polysomatic series. In a merotype series, all members are based on one or more common modules alternating with modules that, instead, are typical of each member. In a plesiotype series, only the main features of the building modules and the principles of connectivity are preserved, but details of both the chemical composition and topology differ in members of the series. Merotypy and plesiotypy can occur at the same time as reported for the bafertisite series below.

Heterophyllosilicates

Analogies between layered titanosilicates and phyllosilicates have been noted by N. V. Belov and his school about forty years ago evidencing that the former are based on layers formally derived from a *TOT* mica layer by periodic substitution of Ti-polyhedra for Si-tetrahedra; for earlier Russian literature on this topic one can see Pyatenko *et al.* (1976). At that time Woodrow (1967) exploited the analogy to solve the structure of astrophyllite; later Egorov-Tismenko and Sokolova (1990) introduced the seidozerite-nacaphite series and correlated features of the interlayer content. In the meantime, Matsubara (1980) had compared the topology of "quasi-silicates sheet minerals" evidencing three types of heterogeneous sheets (*i.e.*, the *H* sheet introduced below): lamprophyllite-, lomonosovite- and astrophyllite-type.

The discovery of nafertisite, a rare titanosilicate first reported from the Khibina hyperalkaline massif (Khomyakov *et al.*, 1995), suggested to Ferraris *et al.* (1996) the correlation via a polysomatic series of the new mineral and the mentioned mica-like titanosilicates. In fact, as illustrated below, it was shown that a new type of layer occurring in nafertisite can be obtained by incrementing the mica component in the layers previously described in the seidozerite-nacaphite series and in astrophyllite. Specifically, in the members of the new series a row of Ti polyhedra (or replacing cations, *e.g.*, Nb; hereafter, only Ti is mentioned for short) periodically substitutes a row of disilicate groups in the *T* tetrahedral sheets of a *TOT* layer; the octahedral *O* sheet is instead maintained (Fig. 1). The layers thus obtained and the series based on them were named (Ferraris *et al.*, 1996) *HOH* and *polysomatic series of heterophyllosilicates*, respectively: *H* stands for *hetero* to indicate the presence of rows of 5- or 6-coordinated Ti in the *H* sheet.

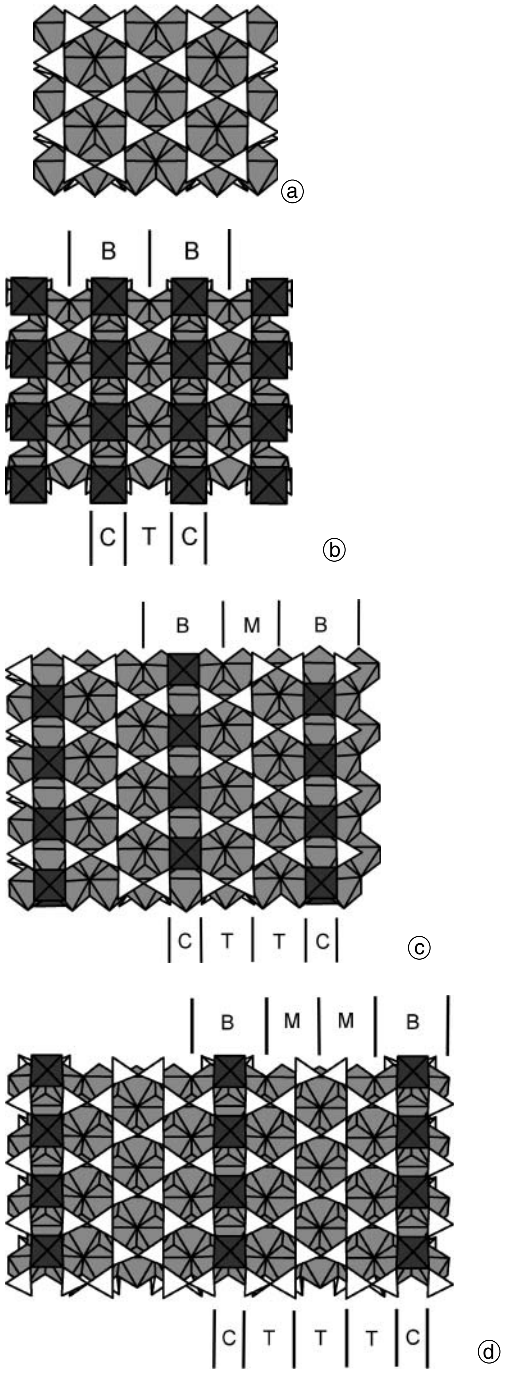

Fig. 1. From top to bottom: phyllosilicate *TOT* layer; bafertisite-type *HOH* layer; astrophyllite-type *HOH* layer; nafertisite-type *HOH* layer. The hetero polyhedra of the *H* sheet are dark grey. Modules *M* and *B* defined by Ferraris *et al.* (1996) and modules *C* and *T* defined by Christiansen *et al.* (1999) are shown.

Fundamentals of the heterophyllosilicate polysomatic series

Fundamentals of the polysomatic series of heterophyllosilicates can help to understand basic concepts of modular crystallography.

Nafertisite {*nfr*; $(Na,K,\square)_4(Fe^{2+},Fe^{3+},\square)_{10} \cdot [Ti_2O_3Si_{12}O_{34}](O,OH)_6$; $A2/m$, $a = 5.353$ Å, $b = 16.176$ Å, $c = 21.95$ Å, $\beta = 94.6°$} is fibrous and shows disorder around the fibre axis. Ferraris *et al.* (1996) collected single-crystal X-ray diffraction data from a moderately disordered fibre. The low-quality data did not allow a direct solution of the structure but could be used to validate a structure model of nafertisite (Fig. 2) built by comparing its chemical composition and cell parameters with those of bafertisite {*bft*; $Ba_2(Fe,Mn)_4[Ti_2O_2(O,OH)_2Si_4O_{14}](O,OH)_2$; $P2_1/m$, $a = 5.36$ Å, $b = 6.80$ Å, $c = 10.98$ Å, $\beta = 94°$; Pen and Shen (1963)} and astrophyllite {*ast*; $(K,Na)_3(Fe,Mn)_7 \cdot [Ti_2O_3Si_8O_{24}](O,OH)_4$; $P\bar{1}$, $a = 5.36$ Å, $b = 11.63$ Å, $c = 11.76$ Å, $\alpha = 112.1°$, $\beta = 103.1°$, $\gamma = 96.6°$; *P*, instead of the *A* cell of Woodrow (1967) is shown (*cf.* Piilonen, 2003b)} by noting the following.

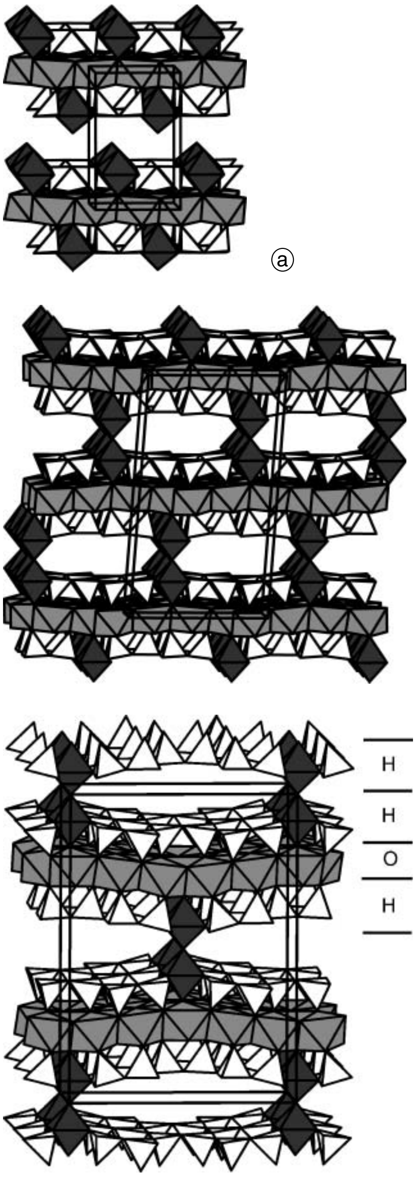

Fig. 2. From top to bottom: clinographic view along [100] of the crystal structure of bafertisite, astrophyllite and nafertisite. In the latter strcuture *H* and *O* sheets are shown. The interlayer content is not shown.

a) The difference in composition between astrophyllite and bafertisite is about $(I,\square)(Y,\square)_3[Si_4O_{10}] \cdot (OH,O)_2$ and is comparable to the composition of an *M* mica-type module (*I* and *Y* represent interlayer and octahedral cations, respectively).

b) The difference in composition between nafertisite and astrophyllite is again about $(I,\square)(Y,\square)_3 \cdot [Si_4O_{10}](OH,O)_2$ and corresponds to half the difference between the compositions of nafertisite and bafertisite.

c) Bafertisite, astrophyllite and nafertisite have a common value of $a \sim 5.4$ Å, which matches the *a* value of mica.

d) The value of the differences $(b_{ast} - b_{bft}) \sim (b_{nfr} - b_{bft})/2 \sim 4.7$ Å corresponds to the value of $b/2$ in mica.

e) $(d_{002})_{nfr} = 10.94$ Å matches the separation between the *O* sheets of two adjacent *HOH* layers in bafertisite and astrophyllite (also referred as thickness of *HOH* layer).

The conclusion was that nafertisite is reasonably based on a *HOH* layer that, at least dimensionally, can be obtained from those of astrophyllite and bafertisite by incrementing the mica component.

The investigation of a second occurrence of nafertisite (Petersen *et al.*, 1999) confirmed the chemical and crystal data given above. Recently, caryochroite $(Na,Sr)_3 \cdot (Fe^{3+},Mg)_{10}[Ti_2Si_{12}O_{37}](H_2O,O,OH)_{17}$; $a = 16.47$ Å, $b = 5.303$ Å, $c = 24.39$ Å, $\beta = 93.5°$ has been described as a second titanosilicate which, on the basis of cell parameters, chemical composition and infrared spectrum, likely is based on a nafertisite-type *HOH* layer (Kartashov *et al.*, 2006).

The polysomatic series of heterophyllosilicates

The slice of *HOH* layer containing in its *H* sheets rows of Ti polyhedra with composition $B = I_2Y_4[X_2(O,OH)_4 \cdot Si_4O_{14}](O,OH)_2$ has been called bafertisite-type module by Ferraris *et al.* (1996) and is intercalated with a mica-type module $M = IY_3[Si_4O_{10}](O,OH)_2$ to form a series B_mM_n with general formula $I_{2+n}Y_{4+3n} \cdot [X_2(O')_{2+p}Si_{4+4n}O_{14+10n}](O'')_{2+2n}$ corresponding to the *heterophyllosilicate polysomatic series* mentioned above. In the formula, atoms belonging only to the *H* sheet or shared between the *H* and *O* sheets are shown in square brackets. *I* and *Y* represent interlayer and octahedral cations, respectively; O′ (bonded to *X*) and O″ (belonging to the octahedral *O* sheet only) can be O, OH, F or H_2O; the $14 + 10n$ oxygen atoms are bonded to Si. The *X* cation (mainly Ti) is 5- or 6-coordinated according to a square pyramid or an octahedron, in the order; these polyhedra share one corner with the octahedral sheet and four corners with four Si tetrahedra of the *H* sheet (Figs. 1, 2). The value of *p* (0, 1, 2) depends on the configuration around *X*. In case of octahedral coordination, the sixth corner can be (i) unshared ($p = 2$), (ii) shared with an octahedron of the adjacent layer ($p = 1$) or (iii) with an interlayer anion ($p = 0$); $p = 0$ holds also when (iv) an edge is shared between two octahedra across the interlayer or (v) the coordination polyhedron of X is no longer an octahedron but is a squared pyramid. In the cases (ii) and (iv), the *HOH* layers are connected by strong coordination bonds and thus a "layered" heteropolyhedral framework structure is formed.

Depending on the periodicity of the Ti substitution and ignoring some topological features discussed below, the following three types of *HOH* layers (Figs. 1, 2) occur in the polysomatic series of heterophyllosilicates as defined by Ferraris *et al.* (1996).

1. $(HOH)_B$ *bafertisite-type layer*: the B bafertisite-type module alone is periodically repeated and members B_1M_0 are obtained. Structures based on this layer (Table 1) are discussed in detail below.
2. $(HOH)_A$ *astrophyllite-type layer*: a one-chain-wide mica-like module M is inserted between two B bafertisite-type modules and members B_1M_1 are obtained. Structures based on this layer are monoclinic and triclinic and differ mainly because of chemical composition (Piilonen *et al.*, 2003a, b).
3. $(HOH)_N$ *nafertisite-type layer*: two one-chain-wide mica-like modules M are inserted between two B bafertisite-type modules and members B_1M_2 are obtained.

The main features of the layer-building principles can be understood just examining the projections of the layers in Fig. 1. It must be noted, however, that actually in three dimensions (Figs. 2, 3) the modules B and M may run parallel to (011).

Alternative slicing of heterophyllosilicates and topology of the *HOH* layers

As shown by several examples reviewed by Ferraris *et al.* (2004), the way of slicing a structure for a modular description is not necessarily unique; thus, Christiansen *et al.* (1999) consider the layer *HHO* instead of *HOH* and slice it into two rod-shaped modules (Figs. 1, 2): a T module with the composition of the M module (*i.e.*, a mica composition) and a C module which consists of two corner sharing hetero-octahedra and one octahedron belonging to the O sheet. The B module defined above contains the C module and Si-tetrahedra. Christiansen *et al.* (1999) define the astrophyllite "homologous series" $I_{1+q}Y_{1+3q}X_2Si_{4q} \cdot (O,OH,F)_{7+12q}$ where I, Y and X have the same meaning as in the polysomatic series of heterophyllosilicates ($p = 1$) and $q = n + 1$.

Christiansen *et al.* (1999) note that if the topological features are considered their homologous series cannot include all the heterophyllosilicates. These authors, following the polytypic analysis of astrophyllite (Zvyagin and Vrublevskaya, 1976), interpret as polytypism the three types of *HOH* layers which replace the "bafertisite-type layer" of Ferraris *et al.* (1996) if the configuration of the attachments between the O and H sheet is taken into account. The observed topologies are (Fig. 3): (i) the O sheet is a pseudo-mirror plane for its two adjacent H sheets (linkage 1); the two H sheets show a relative displacement which is either (ii) $b/2$ (linkage 2) or (iii) a compromise between (i) and (ii). In parentheses is given the nomenclature used by Sokolova (2006) who has systematized these topological aspects actually already described in literature.

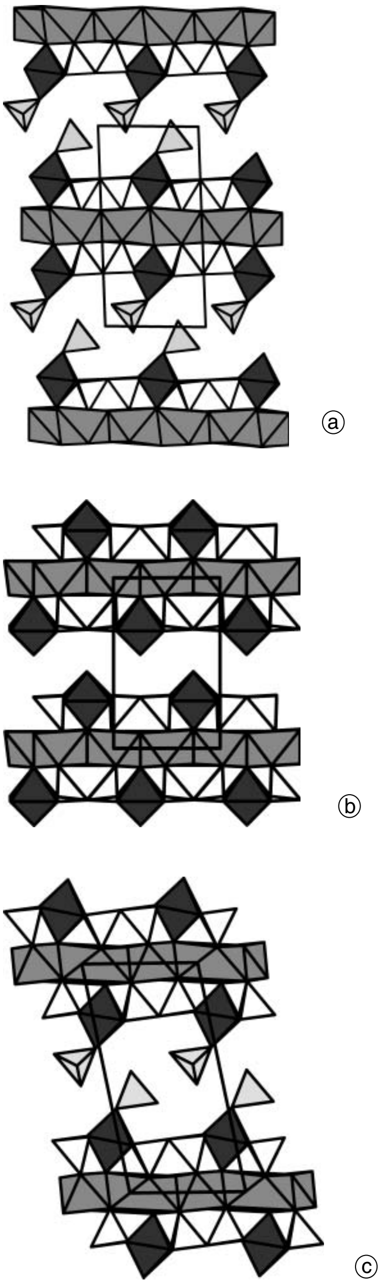

Fig. 3. From top to bottom: structure of vuonnemite, bafertisite and lomonosovite projected along [100] to show, in the order, linkages 1, 2 and 3 between H and O sheets according to Sokolova (2006). Interlayer cations are not shown.

Sokolova (2006) presents a long and detailed analysis of the heterophyllosilicates based on the three topologies illustrated by Christiansen *et al.* (1999); she uses a TS (titano-silicate) module which differs from the *HOH* module by including also a part of the "interlayer" I cations. To the TS block a general formula $A^P{}_2B^P{}_2M^H{}_2M^O{}_4 \cdot (Si^2O_7)_2Z_{4+n}$ has been assigned. The correspondence with the formula of Ferraris *et al.* (1997) is: A^P and B^P represent I cations located in front of the six- and four-

Table 1. Members of the mero-plesiotype bafertisite series for which the crystal structure is solved; they are listed in increasing order of the t (either a or c) cell parameter across the layers.

Name	Chemical formula	t^a	References^b
Murmanite^{IV}	$(Na,\square)_2\{(Na,Ti)_4[Ti_2(O,H_2O)_4Si_4O_{14}](OH,F)_2\} \cdot 2\ H_2O$	11.70	Khalilov (1989), Nèmeth *et al.* (2005)
Bafertisite^{II}	$Ba_2\{(Fe,Mn)_4[Ti_2O_2(O,OH)_2Si_4O_{14}](O,OH)_2\}$	11.73	Guan *et al.* (1963), Yang *et al.* (1999)
Hejtmanite^{II}	$Ba_2\{(Mn,Fe)_4[Ti_2(O,OH)_4Si_4O_{14}](OH,F)_2\}$	11.77	Rastsvetaeva *et al.* (1991b)
Epistolite^{III}	$(Na,\square)_2\{(Na,Ti)_4[Nb_2(O,H_2O)_4Si_4O_{14}](OH,F)_2\} \cdot 2\ H_2O$	12.14	Sokolova and Hawthorne (2004), Nèmeth *et al.* (2005)
Vuonnemite^{III}	$Na_8\{(Na,Ti)_4[Nb_2O_2Si_4O_{14}](O,OH,F)_2\}(PO_4)_2$	14.45	Ercit *et al.* (1998)
Lomonosovite^{IV}	$Na_8\{(Na,Ti)_4[Ti_2O_2Si_4O_{14}](O,OH)_2\}(PO_4)_2$	14.50	Belov *et al.* (1978)
Yoshimuraite^{II}	$Ba_{4\{Mn4}[Ti_2O_2Si_4O_{14}](OH)_2\}(PO_4)_2$	14.75	McDonald *et al.* (2000)
Innelite^{III}	$(Ba,K)_2Ba_2\{(Na,Ca,Ti)_4[Ti_2O_2Si_4O_{14}]O_2\}(SO_4)_2$	14.76	Chernov *et al.* (1971)
Bussenite^{II}	$Ba_4Na_2\{(Na,Fe,Mn)_2[Ti_2O_2Si_4O_{14}](OH)_2\}(CO_3)_2F_2 . 2\ H_2O$	16.25	Zhou *et al.* (2002)
Lamprophyllite^{III}	$(Sr,Na)_2\{(Na,Ti)_4[Ti_2O_2Si_4O_{14}](OH,F)_2\}$	19.22	Krivovichev *et al.* (2003)
Nabalamprophyllite^{III}	$Ba(Na,Ba)\{(Na,Ti,)_4[Ti_2O_2Si_4O_{14}](OH,F)_2\}$	19.74	Rastsvetaeva and Chukanov (1999)
Barytolamprophyllite^{III}	$(Ba,Na)_2\{(Na,Ti)_4[Ti_2O_2Si_4O_{14}](OH,F)_2\}$	19.83	Pen *et al.* (1984)
Orthoericssonite	$Ba_2\{Mn_4[Fe_2O_2Si_4O_{14}](OH)_2\}$	20.23	Matsubara (1980)
Quadruphite^{IV}	$Na_{13}Ca\{(Ti,Na,Mg)_4[Ti_2O_2Si_4O_{14}]O_2\}(PO_4)_4F_2$	20.36	Sokolova and Hawthorne (2001)
Surkhobite^{II}	$(Ca,Na,Ba,K)_2\{(Fe,Mn)_4[Ti_2O_2Si_4O_{14}](F,O,OH)_3\}$	20.79	Rozenberg *et al.* (2003)
Perraultite^{II}	$(Na,Ca)(Ba,K)\{(Mn,Fe)_4[(Ti,Nb)_2\ O_3Si_4O_{14}](OH,F)_2\}$	20.84	Yamnova *et al.* (1998)
Delindeite	$Ba_2\{(Na,Ti,\square)_4[Ti_2(O,OH)_4Si_4O_{14}](H_2O,OH)_2\}$	21.51	Ferraris *et al.* (2001b)[1]
Polyphite^{IV}	$Na_{14}(Ca,Mn,Mg)_5\{(Ti,Mn,Mg)_4[Ti_2O_2Si_4O_{14}]F_2\}(PO_4)_6F_4$	26.45	Sokolova *et al.* (2005)
Sobolevite^{IV}	$Na_{12}CaMg\{(Ti,Na,Mg)_4[Ti_2O_2Si_4O_{14}]O_2\}(PO_4)_4F_2$	40.62	Sokolova *et al.* (2005)

a: The unit cells given by the quoted authors have been converted to reduced cells, if the case; t corresponds to either a or c parameter.
b: Reference to the most recent structure work; if more than one work is reported, they contain complementary information.
$^{II, III, IV}$ Groups according Sokolova (2006).

membered rings of the H sheet (Fig. 1), in the order, and coordinate oxygen atoms of two HOH layers; $M^H = X$; $M^O = Y$; $Z_{4+n} = O'_{2+p} + O''_2$. Sokolova (2006) analyses then the correlation between crystal chemistry and H—O—H linkage and establishes four different types of TS blocks: group I (*e.g.*, seidozerite) where linkage 1 is realized across a larger Na-centred octahedron of the O sheet; group II (*e.g.*, bafertisite) shows linkage 2; group III (*e.g.*, vuonnemite) where linkage 1 is realized across a smaller Ti-centred octahedron of the O sheet; group IV (*e.g.*, lomonosovite) shows linkage 3. Groups I–IV are shown in Table 1 for the minerals there listed. These groups do not account for delindeite (Ferraris *et al.*, 2001b) and bornemanite (Ferraris *et al.*, 2001a); in the order, extensive vacancies in the O sheet and inadequacy of the published structure model are invoked by Sokolova (2006) to justify the two exceptions to her classification in four groups[1].

Bellezza *et al.* (2004) described the heterophyllosilicate grenmarite, $(Zr,Mn)_2(Zr,Ti)(Mn,Na)(Na,Ca)_4(Si_2O_7)_2(O,F)_4$, a new member of the götzenite-seidozerite-rosenbuschite group, using the following modules: the O sheet and a ribbon representing the content sandwiched between two O sheets. This point of view can bee justified by the compactness of the interlayer in this group, where two X-polyhedra share an edge and strictly link two adjacent HOH layers. Another variant has been adopted by Kadiyski *et al.* (2008) who describe the structure of dovyrenite, $Ca_6Zr[Si_2O_7]_2(OH)_4$, related to the götzenite-seidozerite-rosenbuschite group, splitting it in two modules: a rosenbuschite-like module, corresponding to the HOH layer of this mineral without the heterogeneous X-polyhedron, and a tobermorite-like module consisting of a sheet of sevenfold coordinated Ca. This sheet corresponds to the ribbon used in grenmarite excluding the disilicate groups. Kadiyski *et al.* (2008) give also an alternative description of dovyrenite (and rinkite) emphasizing "heterophyllosilicate" layers $H'OH'$ where the isolated heteropolyhedron of typical heterophyllosilicates is replaced by a chain of seven-coordinated Ca polyhedra otherwise belonging to the tobermorite-like module. An "interlayer" comparable to that of dovyrenite can be evidenced also in seidozerite, but here sevenfold and eightfold coordinated Ca alternate.

A sheet with the same chemical composition and topology of the H sheet occurring in the HOH bafertisite-type layer occurs in the titanosilicate jonesite (Krivovichev and Armbruster, 2004) where it concurs to build a double layer crossed by eight-membered channels similar to those described for the rhodesite series of microporous structures (*cf.* Ferraris and Gula, 2005).

The mero-plesiotype bafertisite series and modularity

Whereas a complete theory of the principles governing the stacking of layers in the polytypes has been developed,

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[1] (Added in proof) Sokolova and Cámara (2007) have refined the structure of delindeite using a cell with double a and b parameters and confirmed that the O sheet contains vacancies and eightfold coordinated cations.

particularly for OD polytypes, an equivalent theory exists neither for the general case of homologous series nor for the particular case of the polysomatic series (*cf.* Ferraris *et al.*, 2004), even if sometimes also for the latter series the combination of modules seems ruled by symmetry constrains similar to those described for polytypism (*cf.* Christiansen *et al.*, 1999; Egorov-Tismenko, 1998; Zvyagin, 1993 and 1997).

Anyway, the heuristic path illustrated for modelling the crystal structure of nafertisite looks quite powerful and has been applied to several unknown structures after their relation to known structures or, even better, to polysomatic series, has been recognized (*cf.* Ferraris *et al.*, 2004). In fact, when the structure of nafertisite was established, a systematic topological and crystal chemical analysis of the building modules, as illustrated above, was not yet available. In spite of that, chemical composition and lattice parameters alone successfully suggested the path to model the structure. According to my experience, the lattice dimensions, followed by chemical composition, are the most important clue in searching structures related to an unknown one.

Merotypy and plesiotypy

The so called bafertisite-like *HOH* layer (Figs. 1, 2) is the most versatile of the three known heterophyllosilicate layers, being able to sandwich a large variety of interlayer contents. Above we have reviewed three topological variants of this module and mentioned as several authors (Matsubara, 1980; Egorov-Tismenko and Sokolova, 1990; Egorov-Tismenko, 1998; Christiansen *et al.*, 1999; Sokolova, 2006) gathered together in different ways titanosilicates based on it. To further underline the predictive capability of modular principles, the development of the “bafertisite series” is here reported mainly following the work of the author. The titanosilicates based on a bafertisite-like layer were called seidozerite derivatives and arranged in a “merotype” series (Ferraris, 1997; Ferraris *et al.*, 1997) which represents a branching of the B_1M_0 member of the heterophyllosilicate polysomatic series. For this branching the general formula reduces to $A_2\{Y_4[X_2(O')_{2+p}Si_4O_{14}] \cdot (O'')_2\}W$. In this formula: $[X_2(O')_{2+p}Si_4O_{14}]^{\nu-}$ and $\{Y_4[X_2 \cdot (O')_{2+p}Si_4O_{14}](O'')_2\}^{\mu-}$ represent the negatively charged *H* sheet and *HOH* layer, respectively; *A* and *W* replaces *I* in the general formula to distinguish between interlayer cations (*A*) and anions plus H_2O (*W*).

The members of the bafertisite series with solved crystal structure are listed in Table 1. All these minerals are characterized by similar values of periodicities ($\sim$5.5 and $\sim$7 Å, or multiples) parallel to the *HOH* layer. As in the layer silicates, two adjacent *HOH* modules define an interlayer space that, in this case, may contain either a single cation or an entire mineral-forming module, like nacaphite, $Na_2Ca[PO_4]F$, which occurs in quadruphite (Sokolova and Hawthorne, 2001), polyphite and sobolevite (Sokolova *et al.*, 2005). The interlayer content determines the value of the stacking parameter *t* which increases both with the number *n* of *HOH* layers per unit cell and the complexity of the sandwiched module (Table 1). On its own, the *HOH* layer is about 10 Å thick, a value that actually represents the distance between two consecutive *O* sheets; when the interlayer content is simple, $t \sim n = 10$ Å. Also in view of a possible use of the *HOH* layer for technological applications discussed below, minerals of the götzenite group [group I of Sokolova (2006)] are not included in Table 1 because, as already noted by Rastsvetaeva *et al.* (1991a) and Ferraris (1997), they show actually a tight framework structure, even if the *HOH* layer can be singled out.

On the basis of Makovicky (1997) definitions and the topological analysis of Christiansen *et al.* (1999), the bafertisite series (seidozerite derivatives) was recognized as a mero-plesiotype series (Ferraris *et al.*, 2001b). In fact, a same (in first approximation) *HOH* module occurs in all members whereas a second module, namely the interlayer part ($A + W$), is peculiar for each member (merotypy). At the same time, the series has a plesiotype character because *HOH* modules modified both in their chemical composition and topology occur. As noted by Egorov-Tismenko (1998), the subgroup consisting of seidozerite, lomonosovite, “beta-lomonosovite” (not approved as mineral species), vuonnemite, quadruphite, sobolevite, polyphite and nacaphite form a polysomatic series A_nB_m where *A* and *B* are seidozerite and nacaphite modules, respectively. In this series, polytypic configurations are observed for the members AB_2 (lomonosovite, “beta-lomonosovite” and vuonnemite) and AB_4 (quadruphite and sobolevite).

Predictive power of the series

Some compounds with unknown structure (delindeite, shkatulkalite, M72, M73, M55, M74 and bornemanite) were included in the bafertisite series by Ferraris (1997) and Ferraris *et al.* (2001b) on the basis of the cell parameters and chemical data arranged according to the general formula of the series, *i.e.*, by an approach consistent with the structural application of modularity concepts. In the case of bussenite (former M74) and delindeite the structure was later determined and the prediction confirmed. Bykovaite (former M72; Khomyakov *et al.*, 2005) and M73 (IMA-code 2006-021 http://www.geo.vu.nl/~ima-cnmmn/minerals2006.pdf) have been accepted as new species belonging to the bafertisite series following characterization by transmission electro microscopy (TEM; Nèmeth, 2004). By TEM investigation, Nèmeth (2004) showed that M55 consists of at least two phases compatible with the series.[2] A structure model for bornemanite based on bafertisite-like layers (Ferraris *et al.*, 2001a) has been recently criticized by Sokolova (2006). Following the same principles, Christiansen *et al.* (1999) proposed a structure model of perraultite independently of the structure determination by Yamnova *et al.* (1998). In the same paper Christiansen *et al.* consider jinshajiangite isostructural with perraultite. Finally, phosphoinnelite (Pekov *et al.*, 2006) has been defined as a new species by analogy with innelite, a member of the series (Table 1).

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[2] M** are labels introduced by Khomyakov (1995). For bykovaite, M73 and M55 see also Table 1 in Nèmeth *et al.* (2005).

Modularity, supercells and oriented growths

The presence of a common, at least dimensionally, *HOH* module in the titanosilicates of the bafertisite series is the basis for several interesting phenomena like epitactic overgrowths (Khomyakov, 1995; Pekov and Chukanov, 2005), twinning and syntactic intergrowth discussed below.

Ferraris *et al.* (2004) noted that for most of the monoclinic and triclinic titanosilicates listed in Table 1 the values of the c parameter and β angle are such that $c \sin(\beta - 90) \sim a/n$ ($n = 3, 4, \ldots$). This relation implies that a [*uvw*] row with periodicity $c' = nc \sin\beta$ and normal to the *HOH* layer does exist. The supercell with parameters a, b and c' is (pseudo)orthorhombic if $\alpha = 90°$ (monoclinic members) and (pseudo)monoclinic (angle $\alpha_m \neq 90°$) in the triclinic members with $\gamma \sim 90°$. The presence of supercells (*i.e.*, sublattices) with symmetry other than that of the structure point group favours twinning by (pseudo)reticular merohedry. This type of twinning has been reported by Moore (1971) for ericssonite and lamprophyllite and by Watanabe *et al.* (1961) for yoshimuraite; according to Nèmeth *et al.* (2005) it likely occurs in the crystals of epistolite and murmanite they have investigated. If the same supercell is shared by different members of the series, phenomena of syntactic intergrowth can occur, as reported by Nèmeth *et al.* (2005) for murmanite and epistolite. These two minerals are secondary phases derived, in the order, from the primary minerals lomonosovite and vuonnemite by hydration and loss of PO_4 (*cf.* formulae in Table 1). According to the inheritance principle (Khomyakov, 1995), a daughter phase can share with its mother phase complex structural modules which are preserved through the transformation. Following the mentioned definition of four groups by Sokolova (2006), the preserved *HOH* layer is group IV in the pair lomonosovite-murmanite and group III in the pair vuonnemite-epistolite. The intergrowths between the two primary minerals vuonnemite and lomonosovite reported by Pekov (2000), is inherited, together with the topology of the *HOH* module, by the derived secondary minerals epistolite and murmanite (Nèmeth *et al.*, 2005).

Due to sharing of common supercells, the intergrowths between both the two mother phases (vuonnemite and lomonosovite) and the two daughter phases (epistolite and murmanite) are oriented, *i.e.*, are syntactic intergrowths as shown by Nèmeth *et al.* (2005). In particular, selected area electron diffraction (SAED) patterns showed that the observed presence of murmanite ($a = 5.387$ Å, $b = 7.079$ Å, $c = 11.74$ Å, $\alpha = 93.80°$, $\beta = 97.93°$, $\gamma = 90.00°$) within a matrix of epistolite ($a = 5.455$ Å, $b = 7.16$ Å, $c = 12.14$ Å, $\alpha = 104.01°$, $\beta = 95.89°$, $\gamma = 90.03°$) is a syntaxy based on the following supercells: $a = 5.455$ Å, $b = 7.160$ Å, $c = 93.728$ Å, $\alpha = 88.75°$, $\beta = 90.57°$, $\gamma = 90.03°$ for epistolite; $a = 5.387$ Å, $b = 7.079$ Å, $c = 92.843$ Å, $\alpha = 89.47°$, $\beta = 91.35°$, $\gamma = 90.01°$ for murmanite. The overlapping of diffractions belonging to different intergrown phases is the reason for unsatisfactory refinements obtained for epistolite, murmanite and some other minerals listed in Table 1, like hejtmanite and bafertisite discussed below, and vuonnemite. The different topology of the *HOH* layers in epistolite and murmanite helps to confirm the presence of the described syntaxy. In fact, the disorder observed in the structures of epistolite and murmanite corresponds to that expected from the overlapping of the two types of layers, group III and IV (Nèmeth *et al.*, 2005). The same authors call the attention on the syntaxy hypothesized by Rastsvetaeva *et al.* (1991b) between hejtmanite (Table 1) and a similar unidentified phase differing in their structures mainly for the position of Ba and the doubling of the a and b parameters. By analogy, Nèmeth *et al.* (2005) propose that the same type of syntaxy may occur also in bafertisite, the Fe-equivalent of hejtmanite. Consequently, the failure of properly refining the crystal structures of bafertisite and hejtmanite may be related to the presence of syntaxy.

HOH layers for nanostructured materials?

The structural parallelism, mentioned in the Introduction, between phyllosilicates and heterophyllosilicates led Ferraris (2006) to speculate on the possible use of some of the members of the bafertisite series as starting material to produce structures analogous to the pillared clays and organoclays (*cf.* Auerbach *et al.*, 2004). Observations in the field and some laboratory experiments (Khomyakov, 1995; Azarova *et al.*, 2002; Pekov and Chukanov, 2005) suggest that swelling of bafertisite-type layers, a first step towards preparing hybrid materials, is possible as indicated, *e.g.*, by the solid-state transformations lomonosovite + $H_2O \rightarrow$ murmanite + Na_3PO_4 and vuonnemite + $H_2O \rightarrow$ epistolite + Na_3PO_4 via leaching of interlayer content and hydration.

A second necessary step is the synthesis of suitable phases containing the bafertisite-type layer; in fact, the minerals listed in Table 1 are generally rare and show a complex chemical composition. The only synthetic bafertisite-type compound reported in the literature is $Na_8\{(Na,Ti)_4[Ti_2O_2Si_4O_{14}]O_2\}(VO_4)_2$ that corresponds to the phosphate lomonosovite and has been prepared by crystallization from melt (Massa *et al.*, 2000). Recently, some progress towards the preparation by hydrothermal synthesis of a layered titanosilicate with a simplified bafertisite stoichiometry has been presented (Ferraris *et al.*, 2008).

Conclusions

The complex modularity of the heterophyllosilicates offers the opportunity of illustrating different aspects of modular crystallography that, hierarchically, include merotypy, plesiotypy and homology; in all cases polytypism can occur as well [*cf.* Ferraris *et al.* (2004) for an extensive critical review of these aspects]. Misuse of nomenclature creates confusion as noted, *e.g.*, by Egorov-Tismenko (1998) who underlines that "it would be incorrect to include in [the seidozerite-nacaphite polysomatic series] rinkite, götzenite, rosenbuschite, lamprophyllite, murmanite, epistolite, bafertisite and innelite as was done in Sokolova (1997)." In fact, the listed minerals, from rinkite to innelite, do not contain a nacaphite module, thus they cannot be included in a polysomatic series built by modules of seidozerite and nacaphite. All of them could instead be included in the mero-plesiotype bafertisite series but, as mentioned in the section “Merotypy and plesiotypy”, I prefer to exclude from this series the götzenite group, group I of Sokolova (2006), because its members show actually a tight framework structure even if the *HOH* layer can be singled out.

A review of results obtained in predicting crystal structures and interpreting structure-property relations for minerals belonging to the polysomatic series of the heterophyllosilicates well shows the heuristic power of the modular crystallography to address crystallographic problems. Last, but not least, a modular analysis of complex structures may offer guidelines to researches aiming to obtain new materials, like layered hybrid compounds.

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